Chemistry of Cement

Proceedings of the
Fourth International Symposium
Washington 1960

UNITED STATES DEPARTMENT OF COMMERCE • Luther H. Hodges, *Secretary*
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ERRATA

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In printing this monograph, several paragraphs on page 200 were transposed. The reverse side of this sheet gives the correct arrangement.

Additional Corrections

Page 265, equation (6): The exponent should be 1/3 instead of 2/3. (Author's correction).

Pages 317-318. There is an error in the calculation of the r_0 values of tables 1 and 2. Correcting for this reduces the average value of r_0 from 1.01 to about 0.76, and reduces the variability of the calculated values. Otherwise the subject matter of the paper and conclusions are not affected. (Author's correction).

Roy's [19] Y-phase (C_6S_3H) comes in below 350 °C at the expense of hillebrandite. Unlike foshagite (which may occur in nature intimately intergrown with hillebrandite, e.g., see Taylor [20]), the Y-phase cannot occur in equilibrium with hillebrandite $+H_2O$ except along a univariant P–T curve. Its formation therefore probably represents a more advanced stage in the dehydration series than the development of foshagite. Phase X of Roy [19] or calcio-chondrodite (C_5S_2H or "CaC") becomes stable in this temperature region and can be in equilibrium with Y or $C_3SH_{1.5}$ depending on the exact C/S ratio. Since it has never been positively identified as coexisting with hillebrandite and the individual steps involving the incoming of Y and of CaC have not yet been differentiated they are shown as coming in together in triangle VII.

At 335 °C reyerite breaks down to xonotlite+silica$+H_2O$ (Harker [16]). As might be expected from a consideration of ΔV for the reaction, the P–T curve is nearly parallel to the pressure axis on a P–T diagram. Triangle VIII therefore represents the equilibrium assemblages after the breakdown of reyerite but before the breakdown of xonotlite.

It is convenient from now on to consider the various successive steps isobarically with rising temperature, as the saturated steam curve has no meaning above the critical point of water. The following triangles therefore apply at approximately 15,000 psi.

At 415 °C (and 15,000 psi) xonotlite decomposes to wollastonite$+H_2O$ and dehydration in the silica-rich half of the system is complete. Triangle IX shows the equilibrium assemblages between 420 °C and 515 °C with foshagite now coexisting with wollastonite.

It is noteworthy that the occurrence of wollastonite with hillebrandite has been reported (at Velardena, Mexico, Wright [21]), whereas experimental work indicates that in the CaO-SiO_2-H_2O system wollastonite+hillebrandite$+H_2O$ should not be in equilibrium, and no wollastonite-hillebrandite-H_2O compatibility triangle is seen in this series. The experimental and natural observations, however, may not really be in conflict for the following reasons: (1) It has been recently shown that natural hillebrandite and foshagite are frequently intergrown and difficult to identify separately, and that at least part of the Velardena "hillebrandite" is really foshagite (Heller and Taylor [9]). (2) At Velardena the wollastonite occurs in veins cutting the "hillebrandite" and thus may not be in equilibrium with the hydrated mineral.

The next step occurs when $C_3SH_{1.5}$ breaks down at 520 °C (at 15,000 psi), and the calcio-chondrodite-calcium hydroxide join is established, see Roy [19]. Triangle X represents the equilibrium assemblages between 525 and 630 °C.

At about 635 °C (and 15,000 psi) foshagite breaks down to wollastonite$+Z+H_2O$, but at higher pressures the product is $Y+$wollastonite$+H_2O$ (Roy, unpublished data), suggesting metastability of the Z-H_2O join which is shown as a dashed line in triangle XI as in all others containing Z. The temperature is based on data obtained using three different starting materials: the natural mineral from Crestmore, synthetic foshagite having a 4:3 $CaO:SiO_2$ ratio, and a gel having the same ratio.

Reactions in the Presence of Liquid and Further Dehydration Steps

Curves for decomposition of the following phases at successively higher temperatures were given by Roy [19]: Y-phase$\rightleftharpoons\alpha'$-$C_2S+H_2O$; Z-phase$\rightleftharpoons$rankinite; and X-phase (calcio-chondrodite, C_5S_2H, or CaC)$\rightleftharpoons\alpha' C_2S+CaO+H_2O$, and these data form part of the bases of the next four triangles. However, after Wyllie and Tuttle [4] described the phenomenon of melting of $Ca(OH)_2$ under elevated H_2O pressures it became apparent that the field of $Ca(OH)_2$ liquid must enter the ternary system, at least above 815 °C (the eutectic for the system $Ca(OH)_2$-H_2O at 15,000 psi), and additional information was necessary to more completely describe the equilibria. Preliminary data have therefore been obtained by the authors to investigate the probable extent of the liquid field in the ternary system at 800, 900 and 950 °C and the equilibria among the crystalline phases at these temperatures at 15,000 psi.

The next four triangles represent an attempt to present the data in a reasonable manner, although the data are by no means complete, as indicated by the dashed lines. Triangle XII shows the proposed stability relations at 800 °C and 15,000 psi, where both Z-phase and Y-phase persist in the presence of H_2O vapor, and Y-phase+calcio-chondrodite (CaC)$+H_2O$ are stable together. A small field of $Ca(OH)_2$+liquid exists, and the liquid field extends into the ternary system, but not as far as the CaC-H_2O join. A fairly large field where CaC is the primary phase in equilibrium with liquid is found at this temperature.

Between the temperatures of triangle XII (800°) and XIII (840 °C) three changes take place in the following order: (1) At 815 °C Y-phase decomposes to $\alpha' C_2S+H_2O$ and $\alpha' C_2S+CaC+$Vapor are probably stable together for a narrow temperature interval. (2) At 820 °C Z-phase converts to rankinite. As discussed before, Z-phase may not be truly stable, in which case wollastonite+Y-phase could be stable together above the decomposition of foshagite as shown in triangle XI, and rankinite would form at 815 °C above the decomposition of Y-phase. (3) Finally, at 835 °C $Ca(OH)_2$ is entirely melted, and the equilibria at 840 °C are probably as shown in triangle XIII.

Triangle XIV shows the proposed equilibria at 900 °C, where C_2S exists as a primary phase in equilibrium with liquid, the field becoming larger with increasing temperature largely at the expense of the CaC+L field. At 950 °C the C_2S primary phase field is even larger (triangle XV) and the CaC+L field is smaller, suggesting that CaC

Preface

Symposia on the chemistry of cements have become established through a succession of international assemblies held at irregular intervals. More than a half century ago such meetings among researchers, covering various materials including cements, were sponsored by the International Association for Testing Materials.

The first international congress dealing exclusively with the chemistry of cements and related materials seems to have been a meeting sponsored by the Faraday Society and held in London on January 14, 1918. Because of the priority of that meeting in this special field, it has come to be known as the First International Symposium on the Chemistry of Cement.

The First Symposium was designated as "A General Discussion" on "The Setting of Cements and Plasters." Ten brief papers were presented by eleven scientists from five countries. Twelve discussions followed the presentation of the papers. The Proceedings consisted of 69 pages published in the Transactions of the Faraday Society, Volume XIV, 1918–19.

The Second Symposium was sponsored by the Royal Swedish Institute for Engineering Research and the Swedish Cement Association. A three-day meeting was held in Stockholm in July of 1938 under the designation "Symposium on the Chemistry of Cements." Forty-seven persons from 13 countries participated in the presentation of 13 papers and 52 discussions. The Proceedings, consisting of 578 pages, were published in Stockholm in 1939 by the Royal Swedish Institute for Engineering Research.

The intervention of World War II delayed consideration of the next symposium. Preliminary plans for a general meeting in Washington were abandoned, but eventually arrangements were made for the Third Symposium to be held in London under the sponsorship of the Department of Scientific and Industrial Research and the Cement and Concrete Association. The five-day meeting was held in September of 1952, and was attended by 260 persons, 84 of whom participated with 23 papers and 102 discussions. The Proceedings, consisting of 870 pages, were published in London in 1954 by the Cement and Concrete Association.

Preliminary conversations on the organization of the Fourth Symposium were initiated in April 1956, at which time agreement was reached by the National Bureau of Standards and the Portland Cement Association that the Symposium would be jointly sponsored by those organizations. By the spring of 1959 a tentative program had been set up with the cooperation of leaders in cement research of several foreign countries. Later in that year the organization of the working committees was completed. The sponsors and members of committees are listed below.

Sponsors: National Bureau of Standards, Allen V. Astin, Director; Portland Cement Association, G. Donald Kennedy, President.

Executive Committee: I. C. Schoonover, and A. Allan Bates, Cochairmen; R. H. Bogue, Secretary, Robert E. Pflaumer, Douglas E. Parsons, Myron A. Swayze, W. S. Weaver, C. E. Wuerpel, and Hubert Woods.

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Arrangements Committee: J. H. Walker and Bruce Foster, Cochairmen; Clayton Davis and William Lerch.

Editorial Committee: E. T. Carlson and H. H. Steinour, Cochairmen; E. S. Newman and M. D. Catton.

Papers for presentation at the Symposium were received at the Secretary's office, beginning in January 1960, and continuing to September. After review by the Program Committee and some preliminary editing by the Editorial Committee, they were reproduced by a photoduplicating process, and copies were mailed, as they became available, to the Symposium members.

The Fourth Symposium was held at Washington, D.C., October 2–7, 1960. Invitations to membership in the Symposium were accepted by 362 persons, including 169 from the United

States and 193 from 34 other countries. The number actually in attendance was 271. All sessions of the Symposium were held at the National Bureau of Standards.

At the first session, held on Monday morning, October 3, Dr. I. C. Schoonover, Associate Director of the National Bureau of Standards, and Dr. A. Allan Bates, Vice President of the Portland Cement Association, acted as cochairmen. Dr. A. T. McPherson, Associate Director of the National Bureau of Standards, welcomed the guests on behalf of the Bureau, and Mr. G. Donald Kennedy, President of the Portland Cement Association, indicated his pleasure in cosponsoring this important gathering. Dr. Eberhard Spohn, President of the Heidelberg Cement Company, responded on behalf of the members of the Symposium.

The first formal address, given by Dr. Wallace R. Brode, formerly Science Advisor to the Secretary of State, was entitled "Some Problems Associated with the Growth of Science." This was followed by an address, given by Dr. F. M. Lea, Director of the Building Research Station of the United Kingdom, entitled "Cement Research, Retrospect and Prospect."

Succeeding sessions were devoted to technical papers, grouped under seven general topics related to the chemistry of cement.

The titles of the individual papers will not be given here, as they are listed in the table of contents. The program included the following sessions.

Session II—Chemistry of Clinker; Monday afternoon, October 3; Dr. Henri Lafuma and Dr. R. H. Bogue, presiding.

Session III—Chemistry of Hydration of Cement Compounds; Tuesday morning, October 4; Dr. Fritz Keil and Mr. Charles E. Wuerpel, presiding.

Session IV—Chemistry of Hydration of Portland Cement; Tuesday afternoon, October 4; Dr. Niko Stutterheim and Mr. Myron A. Swayze, presiding.

Session V—Properties of Cement Paste and Concrete; Thursday morning, October 6; Dr. Wolfgang Czernin and Mr. Hubert Woods, presiding.

Session VI—Destructive Processes in Concrete; Thursday afternoon, October 6; Dr. Arturo Rio and Mr. Douglas E. Parsons, presiding.

Session VII—Chemical Additions and Admixtures—was combined with Session VIII.

Session VIII—Special Cements; Friday morning, October 7; Prof. B. G. Skramtaev and Dr. A. R. Collins, presiding.

The technical communications were of three categories, as follows:

1. Principal papers by outstanding contributors to the literature of cement and concrete technology, who were invited to present their appraisal of the present state of knowledge in their assigned topics;
2. supplementary papers submitted by members of the Symposium, presenting new and original research dealing with the specific topics of the Symposium; and
3. discussion of principal and supplementary papers, presented by members of the Symposium.

Papers were presented in condensed form, but are given in full in these Proceedings. Some of the discussions were submitted prior to the Symposium, others at the time of the meetings or subsequent thereto.

After the Symposium, authors were invited to submit corrections to their papers, but did not have opportunity to read printers' proof. Readers of the Proceedings are asked to make allowance for this, as well as for the facts that some papers are the joint product of authors and translators, and that translations had sometimes to be edited without access to the original manuscripts.

Following the sessions in Washington, many of the members of the Symposium accepted a general invitation to travel to Skokie, Ill., to visit the laboratories of the Portland Cement Association and to attend a series of seminars there. A two-day expense-paid bus trip from Washington to the vicinity of the laboratories was arranged by the Portland Cement Association for foreign guests to enable them to see the countryside and to observe some typical highway systems, expressways, toll roads, and city streets in the United States.

The program at Skokie, October 10–12, included seminars on cement manufacture and on basic and applied research, as well as laboratory tours and demonstrations.

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Explanatory Notes

Abbreviations. The following symbols, which have been widely adopted by cement chemists for formulating more complex compounds, are used interchangeably with the respective oxide formulas throughout this book: $C=CaO$, $S=SiO_2$, $A=Al_2O_3$, $F=Fe_2O_3$, $M=MgO$, $N=Na_2O$, $K=K_2O$, $H=H_2O$. Less common abbreviations of this type are defined as they occur.

Commonly used abbreviations of more general nature include the following:

DTA=differential thermal analysis
FM=fineness modulus
IR=infrared
NMR=nuclear magnetic resonance
psi (or p.s.i.)=pounds per square inch
rh (or r. h.)=relative humidity
w/c (or W/C)=water-cement ratio

Identification Numbers of Papers. Each symposium paper has been assigned an identification number. Examples: Paper II–1 is the first principal paper of session II; paper II–S1 is the first supplementary paper of session II. With few exceptions, the numbers correspond to those assigned to the copies of the papers distributed in advance of the symposium.

Scale of Magnification. In micrographs, the scale of magnification frequently is indicated by a horizontal line. Where not marked, the length represents one micron.

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Proceedings of the Fourth International Symposium on the Chemistry of Cement

SESSION I. GENERAL ADDRESSES

Paper I-1. Some Problems Associated With the Growth of Science*

Wallace R. Brode

(Former Associate Director, National Bureau of Standards, and Former Science Advisor to the Department of State)

In an address [1],[1] as retiring president of the American Association for the Advancement of Science, made in Chicago last December, I stressed the need for a National Science Policy in our Government. The reactions and input to these suggestions provided the background for a presentation [2] before the American Chemical Society some four months later, in which I moved toward an international science policy and program, but still slanted toward the Governmental requirements.

Again there has been reaction, opposition and support, to the ideas which were presented, with the development of a still broader concept of the need for coordinated science planning and programing between governments, universities, industries, and research organizations, both within and between countries.

A measure of the advance of civilization of the world as a whole, and its concomitant parts, is the advance in science and technology. Advance in science and technology is at times a prestige method by which nations try to establish their influence and position. The spread of scientific and technical knowledge is a part of the program by which enlightened nations try to raise the cultural level of the world community. Much of the approximately three billion dollars of foreign aid which the USA annually provides is directed toward scientific and technological training and assistance. Yet we, and other nations who maintain a scientific and technical approach to a way of living, are beginning to realize that at the present rate of increase in our scientific production and activity, we are rapidly approaching limitations in personnel, facilities, and funds which will require establishment of priorities including their funding, location, emphasis, and support.

Predictions of the Future

Essentially there are two extremes in the kinds of events which we predict in advance. One is the event which is quite certain, and by reason of repetitive character or a limited possibility, can be estimated with reasonable accuracy. The other kind of event is that which requires a "crystal ball" and may be said to be at best an intelligent guess.

A good example of these two kinds of forecasts is to be found in an address by Harvey W. Wiley, a noted U.S. Government Chemist, who, on the occasion of the 25th anniversary of the founding of the American Chemical Society, which was celebrated in 1901, predicted that on the occasion of the 100th anniversary of the founding of the American Chemical Society, in 1976, the population of the United States would have grown from 71 to 225 million and the membership of the American Chemical Society would have grown from the then two thousand to ten thousand members. Census experts tell us that barring the unforeseen Mr. Wiley will be correct within about 3 percent on his population prediction, whereas in his prediction on the expansion of science the ACS now has 90,000 members, and we still have 16 years to go in which we can expect a further growth to about 150,000 members as compared with his underestimate of 10,000 members.

People talk of the "population explosion" of our civilization, with dire predictions of the time when there will be standing room only. It is true that

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960.

[1] Figures in brackets indicate the literature references at the end of this paper.

world populations are increasing at a logarithmic rate with an average annual world increase of 1.7 percent. This produces a doubling of the world population every 50 years and of course mathematically speaking this could lead to standing room only. By the year 2000 the earth will have about double its present population. Some areas are growing faster than the average. The United States, India, and Red China are growing at about the average rate of 1.7 percent per year. Europe is growing at a slower rate of 0.7 percent per year. Asia at 1.8 percent, Africa at 2.2 percent, and South America at 2.5 percent, are all growing slightly above the average rate of 1.7 percent per year. In contrast—for quite a number of years—the growth in number of scientists and engineers and the production of technical papers has been increasing at the rate of 10 percent per year with a doubling every 8 years, rather than doubling every 50 years as does the population.

Science Support

The U.S. National Science Foundation, in a release issued in September 1960, estimated that the total outlay in this country for research and development for this year (1960) would amount to about 13 billion dollars, of which about 1 billion would be spent for basic research. This amount of 13 billion is about double that expended four years ago for research and development. On the basis of gross national product (GNP) this is not too staggering a figure, for with a 500 billion dollar GNP this represents only about 2.5 percent of the GNP for research and development and only about 0.2 percent of the GNP for basic research. I am advised that these percentages of the gross national product devoted to research and development are roughly paralleled in a number of the leading technical nations. The actual support and use of research funds may vary from nation to nation. For example, in the United States our basic research funds are furnished to the extent of 36 percent by industry, 55 percent by the Government, and 15 percent by universities and foundations, whereas they are used for the performance of research to the extent of 17 percent by the Government, 35 percent by industry, and 48 percent by the universities and foundations.

The amount we are expending for research and development is not disturbing, but rather the rate at which these funds are being expanded each year compared with the growth of the gross national product and our population. At the present expansion rate of these funds we will, in 10 years time, be spending some 30 billion dollars a year on research and development. By that time our gross national product will have increased to about 700 billion and the percentage of the GNP devoted to research and development will have risen from 2.5 to 4 percent.

The growth of science and technology at a faster rate than our population, wealth, and facilities, implies a trend which if extended to the world at large may overload our abilities to cope with the demands and most certainly will require some form of coordinated planning between governments, universities, and industries.

In addition to the problems of size and expansion rate, there is also a problem of the relative emphasis or direction of programs. The relative emphasis may be between government, industry or universities, or it may be between various areas of science and technology such as space, oceanography, health, nuclear physics, or the chemistry of cement.

It must be obvious that, as we approach saturation limits or shortages, there must be a rational program to conserve and distribute our research and development resources. Such planning requires the establishment of national and international goals and a serious consideration of the problems, not only by those who stand to profit by future developments in science and technology, but also more especially by those who are concerned over the long range prestige and advance of science and technology.

A century from now the world population will be four times what it is today, and this does not seem to be too complex a problem to prepare for. What requires more immediate attention is the expansion of science. The President of the American Chemical Society, Dr. Albert L. Elder, in his Presidential address in September 1960, considered the problem of the population explosion as viewed from the vantage point of the food chemist. For the moment the increasing world food requirements appear to be solvable, for science and technology have demonstrated through work in crop, breeding, and production techniques that yields can be increased at a faster rate than the population increase. In fact, the number of persons engaged in agricultural production in technologically oriented countries is reducing at a faster rate than the increase in the number of scientists and technologists. Today in this country, one person on a farm, with the aid of modern technology and science, produces enough food for 20 persons whereas in the less well developed areas of the world one person feeds three on a lower level of subsistence.

The great crisis which looms ahead is science itself, a crisis which is far more imminent and threatening in the closing half of this century than the population, food, or wealth problems.

The Educational Explosion

In many of the less well developed areas of the world where educational facilities are inadequate, it is expected that in the next decade or two, in order to achieve an adequate status, educational facilities will have to be provided on a much greater scale than are now available. This is a problem in the United States, as well as many other areas of the world. Due to changes in birth rates during the past war, there will be nearly double the number of persons of college age in 1970 as are now in this age bracket. We may expect, with the general increasing percentage of persons electing to go to college that we will have somewhat more than double the number of college students in 1970 than we have today. There is also a trend to gravitate towards science as a major, so that we may also expect a higher percentage of these students to major in science. We may in fact have three or four times as many science students in 1970 as today. There is a problem in the United States as to where we will be able to obtain the essential teachers for our own schools and also for other areas which we wish to help. The teaching problem may well be answered in part by research in mechanical devices, tape recordings, motion pictures, closed television, and other facilities. Space may be created through the use of three shifts on a 24-hour day, seven day a week schedule.

Some good may always accompany overcrowding, for it may be necessary to reduce enrollment and in doing so we can be selective and retain the higher quality of student.

Chemical Abstracts as a Measurement of Scientific Growth

The membership of individual scientific societies in each nation is a reasonable measure of scientific interest in that nation, but the foreign membership in such a society is not a good measure of the interest in the field since foreign membership is often one of convenience and may be induced by the availability of publications under a membership arrangement. While the American Chemical Society has 90,000 members, only about 6,000 are foreign, and the distribution is not at all proportional to known scientific strength of some of these foreign countries.

On the other hand the well-known magazine published by the American Chemical Society, known as Chemical Abstracts, uses the nationality of the authors of papers abstracted to provide a mechanism to measure the relative scientific production of a given area. Chemical Abstracts is only concerned that all acceptable contributions to chemistry are properly abstracted and indexed.

The so-called population explosion of the world with its annual expansion of 1.7 percent per year and a doubling of the world population every 50 years, is inconsequential when compared with the 10 percent per annum growth of our scientific literature with a doubling every 8 years. As much has been published in science in the past 10 years as in the preceding time since the discovery of the printing press, and it is a well-quoted phrase that 90 percent of all the scientists who have ever existed are alive today. The growth curves do not show any sign of having reached an inflection, and in fact they may well be on the accelerating growth side rather than the decelerating growth area which must be reached eventually before we reach the time when every citizen must be a scientist and the annual production of chemical abstracts equals the weight of the earth.

Science is expanding at a faster rate than our population, yet the contributions of science and technology are not distributed in proportion to populations. There are many highly populated areas of the world that are currently providing little to our scientific advance. What will be the effect on our scientific growth if these areas are brought into a state of fertile production? The ethnologists and anthropologists advise us that the entire human race is so nearly alike intellectually that we should expect relatively the same distribution of intelligence quotient (IQ) patterns in all areas of the world, and that if the mentally competent and alert individuals are given educational opportunities we should expect from them a relative number of important discoveries and scientific papers.

We have in the United States about 0.5 percent of our population as scientists and engineers (1 million out of 180 million), and with our population increase and even greater numbers of students and the increased proportion of these in science, we can still hardly expect to maintain a 10 percent increase per year so as to maintain our proportional contribution to the 10 percent world increase which has been a reasonably constant rate for the past 50 years.

At the present time the United States produces about 30 percent of the material in Chemical Abstracts, whereas the Soviet Union produces about 16 percent but the rate of increase of the United States contributions is about 8 percent per annum whereas the Soviet increase is about 15 percent per annum. By language in Chemical Abstracts 50 percent of the world's physical science literature is in English, 16 percent in Russian, 9.5 percent in German, 6.5 percent in Japanese, 5 percent in French, 4 percent in Italian, and 1 percent in Spanish.

Yet all of us realize that these percentages are not proportional to world populations, and while each of us would probably like to see a minimum number of scientific languages, each would like to see his own language retained as one of the principal mediums of scientific communication. It must be obvious that only a limited number of languages can be effective in promoting the interchange of science, and hence many scientists choose a language of communication which is other than their native tongue but which is comprehended by a larger audience.

For example, it should be noted that the population of South America is essentially the same as that of North America, and if the ethnologists are right, and we have no reason to doubt them, we should expect that with equivalent education and opportunity, their production in science could be equivalent to our own. It is this accelerating increase of production in these less well developed areas of the world which will keep the total rate of world annual increase in science at 10 percent or higher for a long time to come.

The amount of material distributed to the registrants of this symposium in advance of this meeting should convince one of the expanding character of our scientific literature. It might be worth while to quote a few statistics so as to impress on you the enormity of this scientific explosion which we are experiencing. Chemical Abstracts published abstracts on 120,000 papers last year and will publish about 135,000 abstracts this year, and by 1975 this will be 500,000 and it will be 1 million by 1985. There is now being published a 10-year cumulative index for Chemical Abstracts, the 5th Decennial, which consists of 19 volumes of 1,500 pages each. This covers the years from 1947 to 1956 and will cost about 2.5 million dollars to edit and publish.

We will not be able to publish another decennial index on account of the size, but the next 5-year cumulative index covering the years 1957 to 1961 will be just as big as the previous 10-year index of about twenty 1,500-page volumes, and the next 5-year cumulative index for the period of 1962 to 1966 will be forty 1,500-page volumes and will cost about 8 million dollars to produce. The annual edition in 1967 will have 250,000 abstracts, will require about 40,000 pages of text and 20,000 pages of index, and to publish this will require about 500 employees in addition to several thousand abstractors. The floor space for this staff will amount to about 40,000 square feet, and the budget for operation will be about 10 million dollars.

At some time between the years 2000 and 2050, we must reach an inflection point, for by the year 2000 about 10 percent of our population will be scientists and engineers if we are to maintain the present rate of increase. More probably other areas of the world will be approaching a technological level at a more rapid rate so as to maintain the world advancing rate of 10 percent. By the year 2050, however, even these areas may be saturated or tending towards a lower growth rate. In the past, wars were quite effective in providing a retardant or moratorium on basic scientific advance. The world is changing and it seems likely that we may be in for intellectual competition, rather than armed conflict, to establish prestige and technological advantage in such areas as space, health, food, new materials, and transportation. This may well result in greater acceleration in scientific production.

The same staggering increases face us in nearly every area of science and in some of the new and popular areas, such as electronics, space, nucleonics, biophysics, and health; the acceleration rates are greater than in the chemical areas.

These increases are not the result of publishing poorer work so as to increase the volume, but rather our information is to the contrary, for with competition to obtain publishing space and backlogs in journals the rejection rate has risen, and the quality of our published material is also rising.

The limiting factors which we are approaching are the ceilings on available personnel, financial support, and facilities. It becomes increasingly important that our communication be improved so that adequate planning and priorities can be effected to conserve our capabilities to realize a maximum production for our efforts.

Just how this improvement of efficiency is to be effected is in a measure dependent on good coordination and planning within each country or state and then across the boundaries by direct exchange and communication on all levels, but with reasonable direction through coordination boards or commissions in the international unions, trade combinations, exchange agreements, symposia, and conferences such as this International Symposium on the Chemistry of Cement, where world experts can exchange ideas and information.

In part, this desired coordination is being effected through better scientific liaison between nations. Some 25 nations have scientific attaches here in Washington, and the program of scientific attaches which I promoted in the major science centers of the world has demonstrated that it is possible to accelerate the flow of information and improve our scientific contacts so as to lead to a closer scientific coordination of our research programs.

I sincerely hope that I have not left the impression that we are approaching a tower of Babel or an imponderable mass of data, for a part of our scientific research program both here and abroad is directed towards the improved methods of literature storage and retrieval. The enormous mass of data to be handled in the future does not disturb me for I have confidence that scientific research will find a method to cope with it. The early monks who prepared the hand lettered manuscripts of the past would also have been disturbed if they had thought that our present day printing demands would require the issuance of weekly magazines in color with 5 to 6 million copies for their circulation.

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Paper I-2. Cement Research: Retrospect and Prospect *

F. M. Lea

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It is most appropriate that we should meet for this International Symposium on the Chemistry of Cement in the City of Washington and at the Bureau of Standards. Here in this city, in a neighbouring laboratory, there were commenced over 50 years ago those studies on the nature of rocks, that have contributed so much also to our knowledge of the constitution of industrial silicates. The Geophysical Laboratory and the names of its earliest workers on the phase equilibria between lime, alumina, and silica—Rankin, Shepherd, Wright—are familiar to all cement chemists. We know our present meeting place, the Bureau of Standards, as the laboratory from which P. H. Bates made many of his contributions to cement chemistry, to be followed by many others from the staff of the Bureau, and where there was established in 1924 the Portland Cement Association Fellowship under the leadership of R. H. Bogue. To the many contributions that have come from this Fellowship, we have also to add those from the Portland Cement Association laboratory, first at Chicago and then at Skokie, where we are to continue our meetings next week.

The thread that runs through progress in any field of scientific endeavour is often easier to see in retrospect than in prospect. Looking at the past we can see how one step has built on another; looking at the present we can identify the obvious gaps in knowledge and form some idea of the kind of work that is needed; but looking to the future we can only foresee much more dimly where such work may lead us. At the Stockholm Symposium over twenty years ago, it was evident, for instance, that we needed to know much more about the distribution of water in set cement, but we could hardly then have foreseen how far the study of the vapour pressure of set cement was to lead us in an understanding of its physical structure and properties.

These symposia on the chemistry of cements give us an opportunity to review the advances that have been made, to evaluate and discuss the evidence, and to mark out some of the problems that need attention.

The fulfilment of these purposes is the function of the later sessions and in this opening address I can only look broadly at the state of the science and the trends that can be seen emerging, and try to suggest some cross-connections between different parts of the subject matter. If, in doing this, I fall into speculation, perhaps this is an occasion on which it may be permitted.

When we met in London in 1952 we were all impressed by the notable advances that had been made in knowledge of the structures of the cement minerals, considered as idealised chemical entities, and of the phase relations to be expected if conditions of equilibria were maintained. The basis of the constitution of portland cement, and to a rather less extent of high alumina cement, was well-established. Not a great deal that is new is now to be found on such matters but rather has attention been directed more to the deviations from ideality that occur in practice. Variability in clinker structure and the effect of impurities and crystal imperfections on the cementing properties of cement minerals are questions of important practical significance that are discussed in our papers. It is evident that minor oxides in solid solution have significant effects on the atomic arrangements, crystal form, and hydraulic properties of alite and β-dicalcium silicate. We cannot therefore perhaps attach such constant characteristics to the four main clinker minerals as has been implicitly assumed in the past. The relations that can be derived between compound content and the properties of cements are statistical in nature and we have to recognise that the deviations which arise come not merely from experimental error but also from the ignoring of some variables. But may we not expect that with greater knowledge of such matters it may be possible to adjust the production of cements more closely to particular desired ends? We may well look to the further refinement of the analyses of crystal structure and to the application of the concepts of defects and dislocations in crystals, to enhance our understanding.

As always, advances in techniques open up new possibilities. Methods of X-ray diffractometry are now offering a direct means for the quantitative determination of the compound content of portland cement, in place of calculation. We still have to improve this method, since the separation of overlapping peaks, and the discrimination of weak peaks from the background, at present requires a considerable amount of personal judgment. This problem presents itself most acutely in the determination of low amounts of tricalcium aluminate and this is of much practical importance in the further development of sulphate-resisting cement. Perhaps a theoretical study of the shape of diffraction maxima could lead to methods whereby complicated patterns could be analysed by computers. On the other hand better techniques may lead to sharper peaks and increased resolution, and human error might be reduced by improved counting methods such as pulse height

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960.

discrimination or by the use of monochromatic sources.

Perhaps the most notable feature of this Symposium compared with that held in London in 1952 is the increased proportion of papers that bear on the hydration of cements. Infrared spectroscopy, nuclear magnetic resonance, and microwave absorption are all techniques which now offer possibilities, not only for determining the way in which water is bound in set cement, but also for following the hydration process. Advantage has been taken of improvements in electron microscopy and diffraction to study further the structure of set cement, though perhaps not all the high hopes placed on this powerful instrument have yet been realised. The difficulties in interpreting results on hydrates and materials subject to phase change because of the high vacuum and the heating effect of the electron bombardment need no stressing. Sometimes these can be turned to advantage by observing dehydration and decomposition phenomena in the microscope, the changes being followed by lapsed time photography and the diffraction pattern of the selected area.

Differential thermal analysis, with improvements in technique and in methods of interpreting the results, enables hydrated compounds to be differentiated by their water loss at low temperatures, though here again we encounter the difficulty of separating overlapping peaks. This method, combined with X-ray diffraction data, is giving much information on the hydration products in set cement, as, for example, on the composition of the calcium sulphoaluminates formed and the way it changes with age.

It is questionable if any phase equilibria in aqueous systems have received so much attention as those of $CaO\text{-}Al_2O_3\text{-}H_2O$ and $CaO\text{-}SiO_2\text{-}H_2O$. The former at least we can say is now largely resolved over a wide range of temperatures and many of the gaps in knowledge of the latter have been filled. We cannot yet say, however, that full agreement has been reached on the lime-silica ratio of the tobermorite-like compounds formed in the hydration of cement and there is the curious anomaly that the hydration product of dicalcium silicate appears, according at least to some authors, to have a higher lime-silica ratio than that from tricalcium silicate. Is this perhaps linked with the idea that hydration of the tricalcium silicate is controlled by the rate of diffusion of water through overlying hydrate films, but that of the dicalcium silicate by its slow intrinsic hydration rate? We know of various quaternary hydrated calcium alumino-silicates, and have evidence for the formation of a gehlenite hydrate from the action of lime on a calcined kaolin pozzolana and from the hydration of slag glasses in the presence of lime, but we have not as yet positive evidence of its presence in set cement, and still less that of a hydrogarnet, at normal temperatures. There are many problems here still to be resolved.

Hydrothermal reactions have been much studied, both because of their practical importance and the hope that they would indicate without question the final equilibrium products in the lime-silica-water system. This hope has not been realised, for we now know that even under the severe conditions of autoclaving there are many intermediate stages and that metastable products can be formed. The variables governing these reactions are nevertheless important, since the properties of autoclaved products depend much on the constitution and crystal growth of the phases formed.

The role of carbon dioxide in the aging of cement products has now come again to the fore. There was a long period, following the first report nearly thirty years ago of the effect of carbonation on the shrinkage of set cement, during which interest remained dormant. Not only does the rate and time of carbonation affect shrinkage but it is also of importance in relation to the corrosion of reinforcement. The discovery of combined carbon dioxide in forms other than calcite in set cement is of much interest and there is scope for more work on equilibria in aqueous systems containing lime, alumina, ferric oxide, sulfur trioxide and carbon dioxide.

Pozzolanas were not considered at the 1952 Symposium but it is evident from the review on this occasion that the products formed from the reaction of their silica and alumina constituents with lime are essentially the same as those formed in the hydration of portland cement. Little is still known about the part played by iron and alkalies. Similarly, work since 1952 has given more information on the hydraulic properties of slag glasses. We are concerned here with two factors, the intrinsic reactivity of the slag glass towards water in the presence of activators and the strength-forming properties of the reaction products. The interaction of these two factors produces regions of high and low strength in slag composition with the position of the maximum varying somewhat with the type of activator. Though experiments with too many variables become very involved, it seems necessary to include as a variable the relative proportions as well as the nature of the activators used. In supersulphated cement, for example, a slag of low lime-silica ratio requires more clinker and less calcium sulphate than one of high ratio.

Knowledge of the hydration products of high alumina cement has advanced in parallel with that of the $CaO\text{-}Al_2O_3\text{-}H_2O$ system and there are suggestions for ways of inhibiting the inversion of the hexagonal plate to the cubic aluminate. If this could be prevented at the higher temperatures that can be attained in use it would have much practical importance.

Though many details remain to be clarified we have now a fair picture of the chemical and physical nature of set cement and of the chemical reactions involved in the initial hydration. Despite much work there is still much to learn of the kinetics of the initial reactions, of the part played by surface forces, and of the mechanism by which the initial framework of setting cement is developed. We still know much less about set cement at very early ages than about the more mature product.

We know that both the strength and drying shrinkage of set portland cement are influenced by the proportion of gypsum added and that the optimum content varies with the composition of the cement. Does not this suggest that the initial framework established in setting determines the way in which the subsequent structure of hydration products is set up? If this is so, then it should influence the gel-space ratio and such properties as shrinkage and strength. Again it is evident that surface forces and particle charge determine the rheological properties of a cement paste and that these can be altered by surface active agents. Is this a merely transitory influence or do such forces predetermine the subsequent development of structure? In the absence of an adequate theory there is no guide to indicate how additives might be tailored to produce specific effects. We might contrast this with the part that the theory of polymers has played in the development of plastics.

Solution followed by precipitation and topochemical solid reactions are alternative suggestions for the mechanism of the initial hydration reactions. Do these leave their own specific marks on the physical framework of the set cement or is this primarily dependent on the chemical nature of the reaction products? The rapid initial reactions are dominated by the hydration of aluminates and their combination with gypsum, but initial setting and the development of structure is often attributed primarily to the tricalcium silicate. Sulphoaluminates can produce a structural framework, as is evidenced by supersulphated cement, and false set is attributed to the reformation of gypsum from its dehydrated forms. We have also the suggestion from electron microscopy that plate crystals from the tricalcium aluminate play an active part in the formation of structure by acting as a kind of template for other structures forming in their vicinity. If this kind of concept is valid then the framework of set cement, though composed predominantly of hydrated silicates, may still have its form, and to some degree its properties, predetermined by other products. There is much in the papers presented to this Symposium bearing on this topic but, as one of our authors says, a true understanding of the mechanism of thixotropy, setting and hardening, still lies in the future.

An allied theme running through many of the papers is the nature of the cement bond and its attachment to the aggregate. Here our ideas are derived from electron microscopy, considerations of crystal structure, and of specific surface. We can recognise that the conflict between crystal and colloid theories of set cement has been replaced by a more detailed description in which the large surface area underlying colloidal behaviour and crystal bond both play their part. We still are not clear about the relative importance of surface forces and chemical bonds; we cannot say that a large surface area is a necessary condition for hydraulic properties for this does not hold for the well-crystallised products that act as the bond in cement cured in high pressure steam. The evidence on the influence of crystal shape is also more conflicting now than it appeared in 1952. There is evidence that the bond of cement to aggregate is improved by mild reaction of the aggregate surface and this may be due to some rearrangement of the lattice in the contact phase. This would seem similar in principle to the welds that Bernal suggested are formed in set cement by the intergrowth of the lattices of crystals in contact.

There are various theories of the mechanism of deformation and rupture of concrete under load, but, on the principle of economy of hypotheses, we should not be content until these can be related to the bond within the cement paste and between the paste and the aggregate. Some theories of rupture are statistical derivations from the weakest-link theory, while others depend on the analysis of stress distribution and elastic and plastic deformations before, and at, failure in idealised models. Precracking in compression is often attributed to local breakdowns in adhesion between cement and aggregate caused by local shear stresses arising at the interface, and subsequent failure either to tensile failure of the cement crystals, or of the bond between them and aggregate, in a direction perpendicular to the applied load, or to the development of inclined shear planes. Has not the nature of the cement bond a direct bearing on such conceptions? The gradual reduction in the magnitude of the wet-dry movement of concrete on successive cycles of wetting and drying, and the observation in one of our papers that the irreversible element in the first drying shrinkage disappears after prolonged wet curing may point to the gradual creation of additional valence bonds. May not this be reflected in some change in the mode of rupture? The strength of a heterogeneous material like concrete is a complex property, but there is a need to try to link the physical and engineering approaches to the problem. It is of interest to see such an attempt made in another of our papers.

In many problems we tend to seek solutions in terms of phenomena which are specific to portland cement. There are, however, many properties of cement and concrete which do not differ materially when the concrete is made from quite different cements. Strength, elasticity, shrinkage and creep, for instance, show essentially similar characteristics in concretes made from portland cement, slag cements, or high alumina cement. If the shrinkage of a test specimen made from ground calcium monoaluminate is essentially similar to that of one made from ground tricalcium silicate then we must be tempted to seek the fundamental cause of shrinkage in the physical chemistry of the pore space assembly rather than in its chemical and mineralogical character. If we press this too far it may lead us into error, for there is good evidence that shrinkage has not a single source but rather several that come into play at different stages of drying. Capillary theory, gel sorption, and changes in the interlayer water probably all play their part at different relative humidities. The difficulty is to disentangle them. More attention has been paid to changes in the capillary and adsorbed water than to the interlayer water, but we now know that not only the tobermorite-like hydrates, but also hydrated tetracalcium aluminate and calcium sulphoaluminate all show changes in lattice spacing with changes in water content. There is scope for some comparative studies on the vapour pressure-water content-shrinkage relations of various kinds of hydraulic binders and the way that these are influenced by the surface area of the set cement. The results might in turn also help to clarify the nature of the structural framework of set cement.

There is much empirical knowledge of creep in concrete and an understanding of the rheological models, combining viscous and elastic elements in series or parallel, that will give mathematical expressions for it, but it is well recognised that such models only represent the behaviour and do nothing to explain it. Thus, such models can be used as a physical representation of creep in both concrete and coal, though the mechanism of creep in the two cases is probably quite different. There is still a lack of the basic fundamental data that alone can provide a critical test of the various theories that have been advanced to explain the mechanism of creep. The data on creep in water-stored concrete seem free from ambiguity but not so for that of concrete stored in air. One reason for the lack of progress has been the common assumption that creep and shrinkage are independent and that values for the former can be deduced by subtracting from the total deformations observed the shrinkage measured contemporaneously on unloaded specimens. This may well be a valid approach for purposes of structural engineering analysis, but not for the theory of the mechanism of creep. If it is now accepted that creep and shrinkage are interdependent phenomena the implications for the kind of further experiment needed are self-evident.

The more the quality of concrete can be controlled the more disturbing become the unidentified causes of deterioration. As long as deterioration could be vaguely ascribed to poor concrete, no further remedy than to make better concrete seemed needed. The marked advances in knowledge of alkali-aggregate reaction, of dimensional change in aggregates, and of frost resistance, have enabled not only failure from these causes to be identified, but also the remedies prescribed. There still remain arguments about the theory of these actions but the general picture is clear. Though diagnosis of causes of deterioration is not always easy—map-cracking, for example, can arise either from expansive reactions or aggregate shrinkage—there are reports from various countries of deterioration believed to be due to unknown reactions between cement and aggregate. It is evident that we are still far from running out of problems.

In the papers to this Symposium attention is directed mainly to the more basic aspects of the subject, with the purpose of explaining observed phenomena. This is the first step to the control of events which is the object of technology, but between explanation and control there is often a gap to be bridged. If we look back at the matters discussed at earlier Symposia and consider later developments in cement and concrete technology we find many examples of the accomplishment of this operation. We need have little doubt that the new knowledge being discussed here will be recognised by the time of the next Symposium to have formed the basis for new advances in practice.

SESSION II. CHEMISTRY OF CLINKER

Paper II-1. Phase Equilibria and Constitution of Portland Cement Clinker*

R. W. Nurse

Synopsis

A short section on new methods of research mentions high temperature microscopy, high temperature X-ray diffraction, and X-ray absorption microspectroscopy as significant advances in technique.

New and modified phase diagrams of interest to cement chemists are then reviewed. The principal advances have been in the phase relations of the iron-containing solid solutions and in alkali-containing systems. Some interesting problems remain to be solved even in the well-studied binary and ternary systems. The effect of water and other volatile components on phase relations requires more study.

Experimental studies on the clinker components themselves have given more data on alite and β-C_2S. Studies of hydration and gain in strength show the importance of the minor oxides in solid solution in the clinker minerals. Evidence is also reviewed showing that the strength of cement may be affected by the size and shape of the crystalline components in the clinker.

Among methods for the direct estimation of clinker constitution, X-ray diffractometry is of most interest. The method is still under development but is already giving useful and interesting results. The most significant finding is that the ferrite phase is much richer in iron than would be expected from simple theory, and nevertheless exists in contact with C_3A.

In reviewing the present position the author draws attention to the frequent observation that the clinker has not reached equilibrium at the clinkering temperature and still contains free CaO. The consequences of this have been discussed earlier by Swayze, with the conclusion that liquids will be formed more saturated with CaO than predicted from the equilibrium diagram. Such liquids can crystallise to form C_3A and an iron-rich ferrite, in agreement with the X-ray findings.

Finally some suggestions for further research are made, including an exchange of carefully selected clinker samples between national laboratories.

Résumé

Un paragraphe rapide sur les nouvelles méthodes de recherche mentionne l'important progrès d'ordre technique que constituent la microscopie à température élevée, la diffraction des rayons X à température élevée et la microspectroscopie de l'absorption des rayons X.

Des diagrammes de phase nouveaux et modifiés, susceptibles d'intéresser les chimistes du ciment, sont ensuite passés en revue. C'est dans les relations de phase des solutions solides contenant du fer et des systèmes contenant de l'alcali que les progrès principaux ont été réalisés. Certains problèmes intéressants sont encore à résoudre même dans les systèmes binaires et ternaires, cependant bien étudiés. L'effet de l'eau et d'autres composants volatils sur les relations de phase nécessite une étude plus poussée.

Des études expérimentales sur les composants mêmes du *clinker* ont fourni plus de données sur l'alite et β-C_2S.

Des études de l'hydration et de la résistance accrue montrent l'importance des oxydes mineurs en solution solide dans les minéraux du *clinker*. Également passés en revue sont des témoignages qui montrent que la résistance du ciment peut être affectée par la taille et la forme des composants cristallins dans le *clinker*.

Parmi les méthodes pour l'estimation directe de la constitution du *clinker*, la diffractométrie des rayons X est des plus intéressantes. La méthode est encore à l'étude mais elle donne déjà des résultats utiles et intéressants. La découverte la plus importante est que la phase ferrite est beaucoup plus riche en fer que ne le laissait attendre la simple théorie, et n'en existe pas moins en contact avec C_3A.

Passant en revue la situation présente, l'auteur attire l'attention sur l'observation fréquente que le *clinker* n'a pas atteint sa position d'équilibre à la température à laquelle il se forme et contient encore du CaO à l'état libre. Les conséquences de ceci ont été discutées précédemment par Swayze, qui conclut que les liquides formés seront davantage saturés de CaO que le diagramme d'équilibre ne le prédisait. De tels liquides peuvent se cristalliser pour former C_3A et un ferrite riche en fer, conformément aux découvertes des rayons X.

Enfin sont faites des suggestions pour des recherches ultérieures, en particulier l'échange entre laboratoires de différents pays d'échantillons de *clinker* soigneusement sélectionnés.

Zusammenfassung

Die neuen Forschungsmethoden werden kurz besprochen, wie die Hochtemperaturmikroskopie, die Hochtemperaturröntgenstrahlenbeugung und die Mikrospektroskopie der Röntgenstrahlenabsorption, welche die bedeutsamsten Fortschritte der Technik darstellen.

Dann werden neue und modifizierte Phasendiagramme besprochen, die den Zementchemiker interessieren. Die größten Fortschritte wurden hier für die Phasenbeziehungen der eisenhaltigen festen Lösungen und der alkalienenthaltenden Systeme erzielt. Sogar in den binären und ternären Sytemen, die doch so gründlich studiert worden sind, sind immer

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Building Research Station, Department of Scientific and Industrial Research, Watford, England. (This paper was presented at the Symposium by J. H. Welch.)

noch einige interessante Probleme ungelöst geblieben. Die Wirkung des Wassers und anderer flüchtiger Komponenten auf die Phasenbeziehungen muß noch untersucht werden.

Die Experimentaluntersuchungen der Klinkerbestandteile haben neue Werte für Alit und β–C_2S geliefert. Hydratationsstudien und Messungen der Festigkeitserhöhung haben die Bedeutung der Oxyde, die nur in kleinen Mengen vorkommen, in der festen Lösung der Klinkermineralien bewiesen. Andere Untersuchungen werden auch besprochen, aus denen es sich ergibt, daß die Zementfestigkeit durch die Größe und die Gestalt der kristallinen Bestandteile im Klinker beeinflußt wird.

Von den Methoden zur direkten Bestimmung der Klinkerkonstitution ist die Messung der Röntgenstrahlenbeugung die interessanteste. Die Methode ist noch in der Entwicklung begriffen, hat aber dennoch schon nützliche und interessante Ergebnisse gezeitigt. Die größte Entdeckung war hier, daß die Ferritphase viel mehr Eisen enthält, als man es der einfachen Theorie gemäß erwarten würde, und daß sie in Berührung mit C_3A nichtsdestoweniger existiert.

In der Besprechung der modernen Kenntnisse weist der Author darauf hin, daß der Klinker sein Gleichgewicht bei seiner Brandtemperatur nicht erreicht hat, wie daß ja so oft beobachtet worden ist, daß er immer noch freies CaO enthält. Die Folgerungen, die man daraus ziehen muß, sind schon früher von Swayze besprochen worden, der nämlich gefunden hat, daß flüssige Phasen entstehen, die im Sättigungszustand mehr CaO enthalten, als vom Zustandsdiagramm vorausgesagt wird. Solche Flüssigkeiten können unter der Bildung des C_3A und eines Ferrits, der sehr viel Eisen enthält, kristallisieren, was durch die Röntgenbilder bestätigt wird.

Am Ende werden einige Vorschläge für zukünftige Untersuchungen gemacht; es wird unter anderem vorgeschlagen, daß verschiedenen Regierungslaboratorien sorgfältig ausgewählte Klinkerproben miteinander austauschen sollen.

Introduction

The purpose of this paper will be first to review briefly those phase diagrams or modified phase diagrams of interest in the field of portland cement chemistry which have appeared since the 1952 Symposium. Work on the clinker components as such will then be discussed, and then direct studies on clinker or cement. Finally an attempt will be made to assess the present situation and outlook with regard to the constitution of portland cement.

Since the last Symposium, Bogue's book [1] [1] has appeared in a new and revised form, and also a new edition of Lea and Desch [2]. The existence of these two authoritative works will considerably lighten the present author's task. Structural questions will only be dealt with in so far as they have a direct bearing on the constitution of clinker.

A very brief reference will first be made to methods and techniques.

Methods

The principal advance since Bogue's review of 1952 [3] is in the wider use of high temperature microscopy. This method has not only proved to be faster than conventional quenching, but also more reliable. Only occasionally (in order to gather more material for examination, or to avoid too rapid volatilization) is it necessary to revert to the quench method. Up to 1,800 °C. the thermocouple loop can be used, and by means of a plain iridium loop observations can be made up to 2,200 °C. Temperatures are then measured by optical pyrometry or estimated from the voltage drop across the heater [4].

When the primary phase will grow as a single crystal, it is sometimes possible to separate the crystalline matter from residual liquid and to make separate observations on each.

The same technique of holding the specimen in a thermocouple loop forms the basis of a useful and reliable method of high temperature powder X-ray diffraction [5]. With 20/40 rhodium-platinum thermocouples a temperature of 1,850 °C can be reached. The general utility of high temperature X-ray methods has been discussed by Trömel [6].

In many systems subsolidus reactions are of importance. Frequently these present considerable difficulty because of the very slow rate of reaction. It is sometimes convenient to study the equilibria at high pressures and in the presence of water, extrapolating to NTP and 'dry' conditions [7, 8]. McConnell has used a kinetic method in which the dependence of rate of reaction on temperature for both forward and reverse reactions is used to find the transition temperature [9].

Roy [10] has described a convenient method of preparing mixtures for study.

A new technique which holds out much promise for application to the problem of clinker constitution is X-ray absorption microspectroscopy. This enables an estimate to be made of the mass of an element present in an element of a thin section from 1 to 10 μ square; alternatively a microphotograph can be taken of the surface in which the blackening of the photographic image is proportional to the amount of a given element present in the original surface [11]. Such methods could be used to find the composition of liquids and of the phases in contact with them. Oxides in solid solution in crystalline phases could also be determined.

Replicas of clinker surfaces have been studied in the electron microscope [12, 13].

No outstanding advances have been reported in conventional microscopy. It does, however, appear to the present author that the point counting method developed by A. A. Glugolev has many advantages over the intercept method still employed by many workers [14].

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[1] Figures in brackets indicate the literature references at the end of this paper.

Phase Equilibria

The Calcium Silicates

That part of the system $CaO-SiO_2$ of importance to portland cement has been revised by Welch and Gutt [15]. Their diagram shows (fig. 1) that C_3S does not decompose at 1,900 °C as previously thought, but melts incongruently at 2,070 °C, forming CaO and liquid. It follows that C_3S has a small field in the binary system where it is stable in contact with liquid (fig. 2).

The metastable inversions at 923 and 980 °C (pure C_3S) and 850° (alite) found by Nurse and Welch have been confirmed and further studied by Yamaguchi, Ikegami, Shirasuka and Amano [16]. It is of some importance that the significance of these inversions should be established because of current interest in the conditions of occurrence of alite in various systems. If the original suggestion of Jeffery is correct, then the phase in contact with liquid near the melting point will in most systems be trigonal C_3S or alite and a phase field for triclinic C_3S will probably only appear at subliquidus temperatures. In studies on the solubility of impurities in C_3S it is important therefore to state the temperature at which the preparations have been processed. The solubility of oxides in C_3S and the stabilization of alite will be further discussed later.

Welch and Gutt actually observed and recorded photographically the incongruent melting of C_3S, and earlier workers had also doubted the original conclusions of Shepherd and Rankin; it appears therefore that ternary and higher order systems involving CaO and SiO_2 require revision in the higher temperature regions involving C_3S.

Yannaquis [17] has thrown some doubt on the lower decomposition point at 1,275 °C, stating that only impure C_3S is decomposed.

There have been no suggestions for revision of the thermal relationships of C_2S in the system $CaO-SiO_2$ except for unconfirmed reports of a cubic form at high temperatures [18] and a β' form at low temperatures [19].

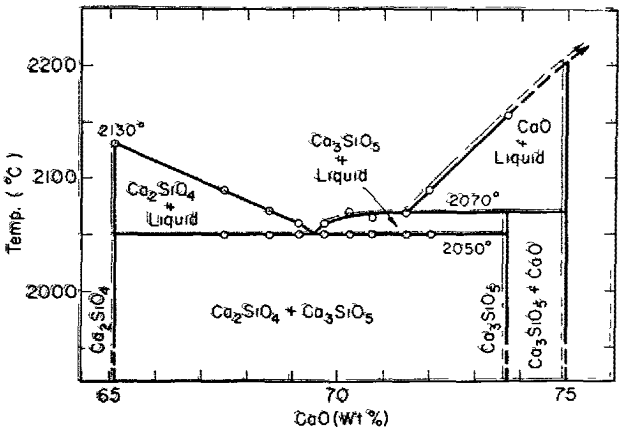

FIGURE 1. *Portion of the system* $CaO-SiO_2$.

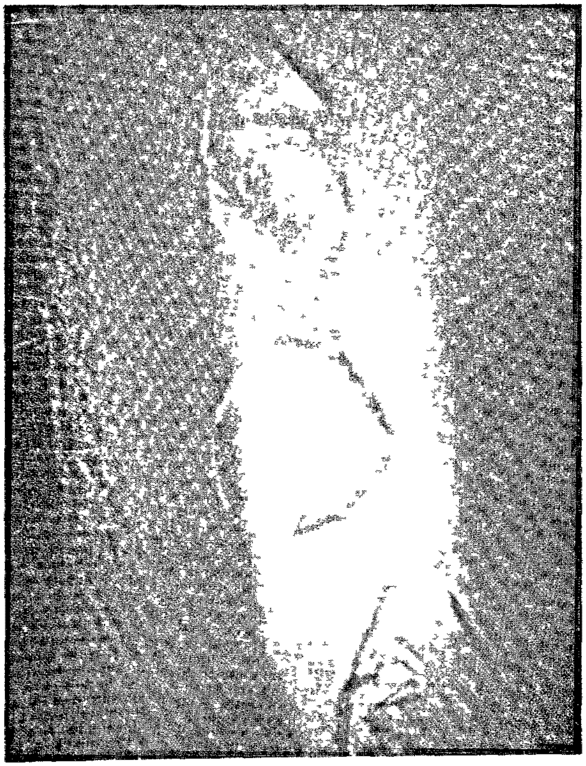

FIGURE 2. *Photograph (×170) of* C_3S *crystals stable in contact with melt in the system* $CaO-SiO_2$ *(Temperature 2,060 °C).*

The Calcium Aluminates

The painstaking optical observations on the system $CaO-Al_2O_3$ by Wright have been vindicated by the isolation of single crystals of unstable C_5A_3 enabling the parameters of the unit cell to be measured [20]. From these measurements and the determined density it would appear that the unstable mineral is truly of C_5A_3 composition in contrast to the stable form which is now agreed to be $C_{12}A_7$. Nurse and Welch [21] find the melting point of the latter can be as low as 1,391°C; the higher values which have been obtained by the quenching method are explained by the amazingly rapid growth of this compound during quenching and by the effect of furnace atmosphere. Unless special precautions are taken, the normal furnace atmosphere contains enough water to be able to influence the melting curve. In drier atmospheres the field of stability of $C_{12}A_7$ narrows, and although it has not been observed to disappear it seems likely that it may do so in the complete absence of water. At 1,000 °C $C_{12}A_7$ can take up just over 1 percent of water. Further work is required to relate this behaviour to the suggested structure.

Neither unstable C_5A_3 nor $C_{12}A_7$ has been confirmed as occurring in portland cement, and they will not be discussed further at present. Equilibria involving $C_{12}A_7$, must however, be considered as part of the cement quaternary system and further study of the binary system CaO-Al_2O_3 is therefore essential.

The Ferrites and Aluminoferrites

While it can now be considered as established without question that the browmillerite (ferrite) phase of importance in portland cement is of variable composition, there still remains some uncertainty as to the range of this composition, and more particularly as to the relationship between bulk composition, temperature and solid solution composition.

The earliest paper describing the solid solution was that of Toropov, Merkov, and Shishakov [22], and this was followed very closely by that of Yamauchi [23]. Only very recently, however, has an attempt been made to establish enough tie lines to enable a calculation of crystallization paths to be made and this only for the pseudoternary system CaO-CA-C_2F [24]. This system, as described by Newkirk and Thwaite is reproduced in figure 3, and is based in part on earlier works by Swayze, McMurdie, and Yamauchi. Figure 3 is a corrected version of the original, kindly provided by F. Ordway.

The solid solution is shown as a shaded area extending from the C_2F composition to point L. The width of this area was established by means of quantitative measurement on the X-ray spectrometer and may therefore possibly in part represent experimental error. Structural considerations [25] suggest that the series should follow a line joining C_2F to a hypothetical C_2A; such a line on figure 3 would follow closely the high CaO boundary of the shaded area.

Newkirk and Thwaite found C_3A in a devitrified C_6A_2F glass in agreement with the position of C_6A_2F as shown in the diagram. At the Building Research Station we have tried to decompose C_6A_2F to give C_3A but without success. On the contrary, a partially reacted melt containing a little C_3A absorbed it completely on annealing at 1,200 to 1,250 °C. It therefore seems likely that the solid solution line does run from C_2F towards C_2A.

Toropov and Boikova in a revision of the first author's work [26] consider the solid solution to be formed between C_4AF and the orthorhombic C_5A_3. However, in their conclusions these authors revert to the conception of a structure in the series C_2F-C_2A and round off their limiting solid solution to C_8A_3F, containing only 17 percent of Fe_2O_3 and not comprised within the system with C_5A_3.

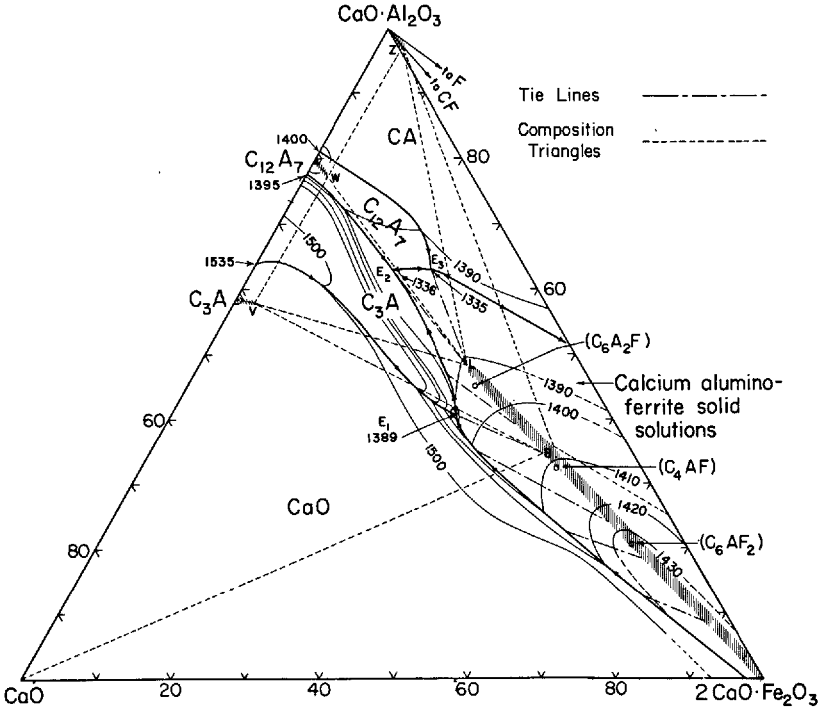

FIGURE 3. *The pseudo-ternary system* CaO–C_2F, *after Newkirk and Thwaite.*

Compatibility triangles within the pseudosystem CaO-CA-C_2F according to Newkirk and Thwaite are as follows:

$CaO+C_3A+Fss(B)$
$C_3A+C_{12}A_7+Fss(L)$
$C_{12}A_7+CA+Fss(L)$
$CA+Fss(B)+CF$
$CA+Fss(L-B)$
$C_3A+Fss(L-B)$
$CaO+Fss(B-C_2F)$
$CF+Fss(B-C_2F)$
2 solid solutions $(C_3A+C_{12}A_7)$
2 solid solutions $(C_{12}A_7+CA)$

where Fss(B) and Fss(L) represent solid solutions of compositions B and L in figure 3 respectively.

If the solid solution relations between C_2F and C_2A do not involve quaternary equilibria, the solid solutions L′ and B′ representing the compositions in solid equilibrium with C_3S, C_2S, and C_3A, and CaO, C_3S, and C_3A, respectively, should coincide with L and B in figure 3. The evidence provided by Swayze is that the solid solutions in equilibrium at the quaternary invariant points as shown by the lines 1 to 8 and 2 to 9 in figure 4 do differ in composition from points L and B. For an exact analysis of crystallization paths it will therefore be necessary to know the location of a sufficient number of tie lines within the tetrahedral volume. Some of these tie lines will undoubtedly terminate in solid solutions relatively rich in C_2F, even though the final products of crystallization do not involve C_2F–B solid solutions. The Alkemade spaces inside the larger system will be:

(1) CaO–C_2F–B–C_3S
(2) C_2S–C_2F–B–C_3S
(3) CaO–C_3A–B–C_3S
(4) C_2S–C_3A–L–C_3S
(5) C_3S–C_2S–L–B
(6) C_3S–C_3A–L–B

In this list L and B are used to represent the high and low A/F solid solutions so that the relationship to figure 3 is clear; the actual compositions may depart appreciably from those at points L and B.

Leaving aside assemblages (1) and (2) which are not true portland compositions, the composition of the ferrite phase is fixed for assemblages (3) and (4) and has the A/F ratio of the clinker for (5). Only in assemblage (6) is C_3A found in contact with a variable iron phase, and C_2S is then absent. As will be seen later, these conditions are not those found in practice.

The accepted authority for the relation in the bounding plane CaO–C_2F–CA is Burdick [28]. A C_3F compound does not appear in this system as it has hitherto only been observed as a result of solid state reaction. According to Burdese and Gallo [29] it decomposes at 800° and it is therefore unlikely that it will ever appear in the presence of liquid even in systems higher than quaternary. It may conceivably appear as a product of devitrification of glass of high iron content and in this case would be confused with C_3A in X-ray examinations (a_0 for $C_3A=15.2$A, for $C_3F=15.4$A).

It will be noted that the series Fss(B)—C_2F cannot exist in equilibrium with C_3A in completely solid preparations. Compositions which solidify containing C_3A and CaO, and are therefore potentially of interest as cement compositions, can, however, yield solid solution richer in C_2F than point B at temperatures above that of point E (1,389 °C). By interpolation of tie lines it can be seen that the solid solution richest in C_2F involved in such crystallization paths would be just beyond C_6AF_2. Under conditions of fairly rapid cooling one would therefore expect to find in contact with C_3A a zoned solid solution extending from C_6AF_2 towards point B. Similarly in the triangle C_3A—B—L rapid cooling may result in zoning from B towards L. These conclusions will not necessarily be valid however for equilibria in the presence of silicates.

The Basic Quaternary System

The most recent investigation of the quaternary system CaO–C_5A_3–C_2S–C_2F remains that of Swayze [27] (fig. 4). If we accept the revisions of the bounding planes which have already been discussed, Swayze's diagram requires amending in respect of the high temperature and of the C_3S volume and to take account of Newkirk and Thwaite's limitations to the ferrite solid solution series. However it does not seem likely that the fixing of the invariant points (1 and 2 in Swayze's terminology, T_1 and T_2 of Lea and Parker) can be very much in error, and these will probably lie as they do at present, outside their corresponding tetrahedra of compatibility, so that the iron compounds formed at the invariant points will be members of the solid solution series. Swayze identifies them as having Al_2O_3/Fe_2O_3 ratios of 0.50 and 0.85 for invariant points (1) and (2) respectively.

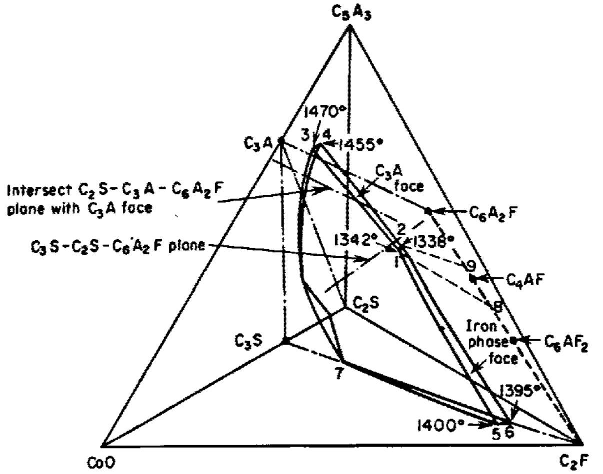

FIGURE 4. *The C_2S phase volume in system* CaO-C_5A_3-C_2F-C_2S *(after Swayze).*

Systems With Magnesia

The system CaO-C_2S-C_5A_3-C_2F as modified by 5 percent of MgO has been explored by Swayze [27], who showed that the compositions of the invariant points move in the direction of higher A/F ratio to such an extent that the plane through C_3S, C_2S and the limiting iron phase solid solution passes on the high Fe_2O_3 side of these points (in contrast to the situation in the unmodified quaternary). Since the same uncertainty as to tie lines remains in this case, all that need be noted at present is that in the presence of MgO the iron phase will be more likely to be of higher A/F ratio and of fixed composition.

Some recent work in the ternary system CaO-MgO-Al_2O_3 by Welch [30] should be mentioned, since, although it is of more interest in connection with high alumina cement, the new compounds discovered do affect the triangulation of the system. A ternary compound C_3A_2M has been found with a very small phase field in the system. It melts incongruently to form first MgO, CA and liquid, and then MgO and liquid. Invariant points are approximately as follows:

Equilibrium phases	CaO	Al_2O_3	MgO	Temperature °C	Type
CA, $C_{12}A_7$, C_3A_2M, liq	44	51	5	1344. 5	Eutectic
MgO, $C_{12}A_7$, C_3A_2M, liq	44	50	6	1346	Eutectic
MgO, CA, C_3A_2M, liq	43	51	6	1350. 5	Reaction point

Another new compound, C_7A_5M, is itself stable only below the lowest solidus temperature in the ternary system. It forms a series of solid solutions with gehlenite within the quaternary CaO-MgO-Al_2O_3-SiO_2; with increasing gehlenite content, incongruent melting is first established, to be followed by a range of congruent melting extending towards gehlenite. The "unstable C_5A_3" compound of high alumina cement tentatively identified by Parker as C_6A_4MS [31] is almost certainly associated with compositions in the C_2AS-C_7A_5M solid solution series.

The join from C_2S towards merwinite, C_3MS_2, has been studied by Gutt [33]. As merwinite is added to C_2S, the liquidus temperature falls slowly; below the liquidus separate fields of existence are found for α'-C_2S and merwinite.

Liquidus temperatures in the system CaO-MgO-Al_2O_3-SiO_2 have been studied by Osborn, de Vries, Gee, and Kraner [34] and by Prince [35]. Phase equilibria, especially in the high alumina part of the system, have been reviewed and amplified by de Vries and Osborn [36].

Alkali Systems

The systems CaO-Na_2O-Al_2O_3 and CaO-K_2O-Al_2O_3 have been studied by Brownmiller and Bogue [37] and Brownmiller [38] respectively. In the high CaO portions of interest in cement chemistry the systems differ in that no potassium compound analogous to C_8NA_3 was found. The synthesis of the potassium compound was however recently reported by Suzukawa [39]. Whereas C_8NA_3 has a smaller unit cell than C_3A, C_8KA_3 has a larger. It seems possible that a small amount of SiO_2 is necessary for the formation of C_8KA_3.

The same author has reinvestigated the compound $KC_{23}S_{12}$ and confirms the view of the present author that it is α'-C_2S stabilized by K_2O.

Thilo and Funk [40] have investigated the effect of small amounts of sodium and potassium on the stabilization of C_2S. They find that even the small amount of alkali absorbed from the furnace atmosphere can markedly affect the polymorphism of this compound.

The systems K_2O-Al_2O_3-SiO_2 and Na_2O-Al_2O_3-SiO_2 have recently been investigated by Schairer and Bowen [41, 42].

In Eubank's study of the quinary system Na_2O-CaO-Al_2O_3-Fe_2O_3-SiO_2 the quinary invariant point was located and found to be at 1,310 °C [43]. No estimate of the composition of the iron phase in equilibrium at this temperature was made. It was thought that the addition of MgO to the system would have lowered the temperature of first liquid formation to about 1,275°.

Systems of Minor Components

Phosphate as a small amount of P_2O_5 is present in the analysis of most portland cements, but in recent years has become of greater interest because of the exploitation of difficult limestone deposits, or the desire to use various trade wastes as raw material in cement manufacture. The effect of phosphate in portland cement has recently been reviewed by Steinour [44] who concluded that the rules put forward by Nurse [45] are a sufficiently accurate guide to practice. Nurse showed that the major part of the P_2O_5 is combined in solid solution with the C_2S, and that as a consequence the amount of C_3S is markedly reduced. Nurse, Welch, and Gutt have since published the phase diagram of the system C_2S-C_3P [46], showing a series of solid solutions between α-C_2S and a new high temperature form of C_3P isomorphous with α-C_2S. At subliquidus temperatures two compounds are formed, but are not likely to be met with in cement compositions.

The system CaO-C_2S-C_3P has been further studied by Gutt [33] who has explored the liquidus surface covering the temperature range 1,640 to 2,150 °C and has established the primary crystallization fields of the phases present which include C_3S. The field of C_3S extends to about 13 percent P_2O_5. Work is continuing to determine the compatibility triangles and suggests at the time of writing that a small amount of C_3P is soluble in C_3S.

In the system CaO-Al_2O_3-P_2O_5 a mixture of C_3P and C_3A appears to decompose forming C_4P, C_3A, and C_5A_3 [47]. The high lime portions of the system were not explored by Stone, Egan, and Lehr [48] but they do indicate their belief that C_3P and C_3A can exist in equilibrium together.

Fluorides are occasionally found as impurities in limestone. They may also be added deliberately as a flux or whitening agent or to offset the deleterious effect of P_2O_5.

Eitel's original studies on the systems CaO-CaF_2-$2CaO{\cdot}SiO_2$ and CaO-CaF_2-$5CaO{\cdot}3Al_2O_3$ showed that in the former there was no field for C_3S and in the latter none for C_3A. Later evidence however suggests that both C_3S and C_3A can exist in the presence of small amounts of calcium fluoride [16]. The system CaO-CaF_2-$CaO{\cdot}SiO_2$ includes a field for cuspidine, $3CaO{\cdot}2SiO_2{\cdot}CaF_2$. Cuspidine decomposes at 1,450 °C into CaF_2 and $2CaO{\cdot}SiO_2$ [49]. Toropov, Volkonskii, and Sadkov [50] confirm that C_3A is decomposed by 5 percent of calcium fluoride and show the same effect with 5 percent of sodium or potassium fluoride. When members of the ferrite solid solution series are acted upon by calcium fluoride, they decompose into $C_{12}A_7$ and a ferrite near to $6CaO{\cdot}Al_2O_3{\cdot}2Fe_2O_3$ in composition [51].

In a study of the system of reciprocal salt pairs SiF_4-SiO_2-CaO-CaF_2, the region of two liquids formation was delineated; it does not reach to probable cement compositions [52].

Experimental Studies on Individual Clinker Components

Alite

There have been several studies on the C_3S—alite relationship, but none have yet been extensive enough or sufficiently precisely controlled to establish the phase field of alite in the cement system. It can now be shown that at least one reflection due to C_3A appears in diffractometer traces of both the single crystals of alite used by Jeffery and the synthetic powder preparation $C_{54}S_{16}AM$. It appears likely therefore that the alite structure can be formed with a deficiency of Al. Another possibility is that there is slow unmixing of C_3A at low or even room temperatures. In early studies on alite the solubility of C_3A in C_3S was given as 6 to 7 percent at 1,400 °C; Naito, Ono, and Iiyama [53] report the maximum substitution of Mg and Al in the series $(Ca_{1-x-y}Mg_xAl_y)_3(Si_{1-3y}Al_{3y})O_5$ to be $x=0.025$ and $y=0.0075$, but do not state the variation with temperature; and Yamaguchi, Ikegami, Shirasuka, and Amano give details of alite containing either MgO or calcium fluoride [16]. Alite containing CaF_2 in solid solution has also been studied at the Building Research Station, and small scale strength testing on the product shows that the strength is greatly inferior to that of pure C_3S.

It is by no means obvious whether, in the work done so far on the range of composition of alite, a sufficiently clear distinction has been drawn between lattice changes in the triclinic structure of pure C_3S brought about by solid solution and the assumed transformation, triclinic $C_3S \rightleftharpoons$ monoclinic C_3S (alite). No synthetic work at all has been done on the further transformation monoclinic $\rightleftharpoons$ trigonal. Existing methods of X-ray diffraction at high temperatures would not discriminate between the three suggested forms. Films taken at 1,500 °C by Trömel for the present author show no difference in structure as compared with room temperature. Volkonskii [54] however reports an inversion in pure C_3S at 1,375°, giving an α-C_3S with d-values at 2.94, 2.78, 2.32, 2.00, and 1.47 A. Tröjer also has distinguished two forms of C_3S in the microscopic examination of clinker [55].

The practical significance of this question is of course the question of reactivity towards water. It appears possible that the reactivity may depend more on the nature of the substances in solid solution than on their effect on the crystal structure (which in any case is slight). There is some evidence too of the part played by physical characteristics. Jander [56] has stated that the reactivity of C_3S depends on (1) substances in solid solution, (2) structural defects, (3) cracks and irregularities of colloidal dimensions. Grzymek [57] believes that small and elongated crystals of alite can hydrate more rapidly, even if ground to the same specific surface as larger and more equant crystals. Both of these theories could account for the frequent observation that the strength obtained from a cement is not always a function of its C_3S content.

Dicalcium Silicate

Investigations on the polymorphism of C_2S have been very numerous, but most of them would more appropriately be discussed under the heading of "Structure." Metzger [58] has observed small quantities of α'-C_2S in cement, and it seems probable that under unusual conditions of composition such as high K_2O, or P_2O_5, combined with quick cooling, larger quantities of α' will be formed. Azelitskaya [59] finds that the strength is lowered as a consequence.

There is still some confusion as to the hydraulic properties of the forms of C_2S. At the Building Research Station we find that γ is almost inert, β hydrates at a rate depending on the kind of stabilizer, α' gives very poor strength, and α is nonhydraulic. In stabilizing α' and α, increasing quantities of $3CaO{\cdot}P_2O_5$ were used. Budnikov and Azelitskaya [60] however declare that γ-C_2S has hydraulic properties.

The evidence given by Nurse [61] to show that the strength obtained from β-C_2S depends on the nature of the stabilizer has been extended by Kukolev and Melnik [62]. The same authors show that a mixture of BaO, P_2O_5, and B_2O_3, which gave the best result in experiments with C_2S alone, is also effective in increasing the strength of a cement, provided the potential composition is high in C_2S [63].

Ferrite Phase

The ferrite phase has been studied by Midgley [64, 65, 66]; Cirilli and Brisi [67, 68]; Santarelli, Padilla and Bucchi [69]; Fratini [70]; and Fratini and Turriziani [71]. Yamaguchi and Kato [72] agree with Midgley that because of zoning effects the X-ray reflections from the ferrite are not always sharp. Sanada, Miyazawa, and Tazawa [73] quote the solubility of MgO in C_4AF as 1.5 percent and in C_2F less than 1.0 percent. Fratini uses a chemical method and Midgley magnetic separation in order to concentrate the ferrite before X-ray examination. According to Royak [74] Na_2O can enter into solid solution with C_4AF.

Tricalcium Aluminate

Tricalcium aluminate has been observed zoned by Tröjer [55]. As previously mentioned, the two alkali compounds, C_8KA_3 and C_8NA_3 will be recorded as C_3A in X-ray examinations, as will any C_3F which may be formed. No estimate of the kind of solid solution present in C_3A can be made from the *d*-values of lines which are visible in clinker X-ray diagrams. As will be shown later, it is important in quantitative work to realize that the spacings are slightly variable. Muller-Hesse and Schwiete [75] give the solubility of MgO in C_3A as 2.5 percent.

The only effects observed on heating C_3A to 1,500°C in the high temperature X-ray camera were caused by thermal expansion [54].

The Direct Determination of Constitution

Microscopy

The results obtained up to 1948 by the direct microscopic estimation of compound content have been reviewed by Lea [2]. He concluded that in general, measured C_3S contents were higher than as calculated from the Bogue formula, and those for C_2S were lower, especially for high A/F ratios. The measured C_3A and C_4AF contents are lower. Quick cooling tends to eliminate MgO; commercial clinkers are in general cooled fast enough to be intermediate between the quenched and fully crystalline conditions.

Some of the more recent papers on microscopy of cement clinker have drawn particular attention to the inhomogeneity of clinker, caused by insufficient grinding of the raw meal, by the taking up of fuel ash, and by the blending of clinkers from different periods of production or from different kilns. Tröjer [55] finds C_3S to be lower than calculated and C_2S higher, and ascribes this to coarseness of the raw meal. Schwarz [76] makes only qualitative microscopic observations, but points out the poor correlation between calculation and observation, especially with regard to glass content. In a detailed study Alègre and Terrier [77] finally conclude that for properly burnt clinker the agreement between microscopic observation of C_3S, C_2S, and interstitial matter and the Bogue calculation of C_3S, C_2S, and (C_3A+C_4AF) is very good.

Broadly it may be stated that the conclusions drawn by Lea are still valid. Many authors point out the seriousness of discrepancies in estimates of C_3A, having regard to the importance of this constituent in determining resistance to chemical attack.

X-ray Diffraction

The apparatus and technique of X-ray diffraction have been developed considerably since the early studies of Brownmiller and Bogue. It is universally agreed that for quantitative work diffractometry is essential, but photographic methods have also been greatly improved and at least one recent quantitative study [78] has employed photographic methods. Using an internal standard of NaCl and a Guinier type camera and measuring intensities by means of a photodensitometer, von Euw claims the following standard errors: alite ±2 to 3 percent, C_4AF ±1 to 1.5 percent, C_3A ±0.5 percent, C_2S ±6 to 9 percent. The author states that in general results are obtained close to those calculated from chemical analyses, but draws attention to the discrepancy with regard to C_3A. He does not consider the complications introduced by the variable composition of the ferrite phase.

H. G. Midgley [64, 65, 66] has used powder methods to determine the composition of the ferrite phase. He finds a range from about C_6A_2F to C_6AF_2 with a median composition a little higher in C_2F than C_4AF.

A chemical method was employed by Fratini and Turriziani for separating the ferrite phase from cement before X-ray examination using a diffractometer. Although unwilling to draw firm conclusions, they pointed out that although the ratio of A/F in their cements varied from 0.98 to 2.90, the A/F ratio in the ferrite phase never exceeded 1.0.

The most comprehensive study to date is that of Copeland, Brunauer, Kantro, Schulz, and Weise [79]. They employed a North American Phillips Geiger counter diffractometer with Cu Kα radiation, in an attempt to measure directly the percentages of the phases present in portland cement. Unfortunately they were forced in the long run to rely also on chemical data.

As an internal standard they used metallic silicon or potassium bromide, intimately mixed with the cement or clinker sample by pulverization in a vibratory ballmill. The difficulties they had to overcome included:

(1) The existence of C_3S in clinker as alite, including in its composition some MgO and Al_2O_3.
(2) The presence of stabilizers (concluded to be principally MgO and Al_2O_3) in C_2S.
(3) The overlapping of the most important lines in the C_3S and C_2S patterns.
(4) The variable composition of the ferrite phase.
(5) The partial overlapping of ferrite and C_3A lines.

These difficulties were dealt with by a method of calibration using synthetic mixtures of alite and β-C_2S in one case and ferrite and C_3A together with alite and C_2S in another. These mixtures were made up from the oxides and burnt to equilibrium. They were not mechanical mixtures of the individual constituents. In order to separate overlapping peaks an empirical relationship was deduced to correct for the error in C_3A caused by the ferrite peak. Before planimetering, the peaks were separated by a geometrical construction based on the symmetry of the C_5A line at 2.71 A. The composition of the ferrite phase was obtained either directly from the *d*-spacing of the 200 reflection as described by Midgley or by including in their final calculations (which were done with the aid of a computer) a determined relationship between the A/(A+F) ratio of the ferrite phase and the *d*-value. An apparent discrepancy between Midgley's data and that of American authors is caused by a drafting error on Midgley's figure (1) (reference 65) in which the left-hand ordinate should be lowered by one division (i.e., the 200 spacing for C_4AF should read 2.64).

One method the American authors used for computing the A/F ratio of the ferrite phase and the absolute contents of ferrite and C_3A in the clinker was independent of a knowledge of the chemical analysis of the clinker. A second method for obtaining the same data however required a knowledge of the Fe_2O_3 content. The alite and C_2S contents were computed by two methods, one involving a knowledge of the CaO and the other of the SiO_2 content of the original cement or clinker.

Agreement between the different methods was quite good in regard to the content of constituents; there were rather larger discrepancies between the two methods of estimating the A/F ratio of the ferrite phase.

Comparing the results obtained by diffractometry with the potential phase composition, Copeland, Brunauer, Kantro, Schulz, and Weise conclude that the median value for the molar ratio of A/F in the ferrite phase is about 1.0 and that therefore agreement with a calculation which assumes the ferrite is C_4AF should be good, provided complete crystallization has taken place. In fact the average difference between the two estimates of ferrite content was only 0.7 percent and the maximum difference 2.2 percent. For C_3A the comparison was not considered satisfactory, the determined value being lower than calculated. In part this was ascribed to the Al_2O_3 in solid solution in the silicates. For alite the mean difference between the X-ray results and calculation was negligible, although the average absolute difference between the two sets was 3.6 percent. A similar average difference was noted for C_2S, but in this case the X-ray value almost consistently exceeded the calculated value. The authors also compare their results with earlier microscopic examination of the same cements.

A Phillips counter diffractometer has also been employed at the Building Research Station to determine cement constitution. A fuller account of this work will be given in a supplementary paper [82]. Briefly, the experimental methods employed give a somewhat better resolution of the X-ray spectra than was obtained in the foregoing investigation, permitting a much simpler approach to the problem.

The radiation used was CuKα and the specimen with its KBr internal standard was milled in a vibratory rod mill to less than 5μ, as checked by microscopic examination. The composition of the ferrite phase was measured on an X-ray photograph of the magnetic fraction, using the 202 spacing. A check was made on the position of the 200 peak on the diffractometer trace. Standard calibration curves for the peaks used in measurement were prepared from mechanical mixtures of alite (Jeffery's composition, found to contain a small amount of excess C_3A), β-C_2S stabilized with B_2O_3, C_3A and various ferrites.

Where peaks overlapped, either in the calibrating runs or in the trace from a cement, it was generally possible to allow geometrically for the error involved. The peaks were assumed to be symmetrical and were drawn in, referring when necessary to the nearest peak of the same size on the calibration chart for the same constituent. Alite was estimated directly from the peak at about 29½° 2θ and β-C_2S from that at 31°. An indirect estimate of these two components was also available from the combined intensities at 32½° and 34½°. When the two independent estimates of alite and C_2S differed, the cause was investigated and the error was usually found to be due to the presence of calcium carbonate or hydrated substances. An important difference from the American method in estimating C_3A was that the 2.71 A peak of pure C_3A was found to wander over a range in various cements; the smoothing of the peak was therefore done on the trace as found and not around a hypothetical 2.71 A maximum.

Three runs were made on each cement using a newly made specimen each time, and three independent measurements of peak areas were made. As an illustration of the accuracy obtained, the following standard deviations were obtained on a typical cement; alite 60±4 percent, C_2S 18±5 percent, C_3A 11±1 percent, ferrite 6.5±2 percent.

Particularly for low A/F cements, the C_3A tended to be higher than as calculated from the Bogue formula, the reverse of the results found by the American workers.

Assessment of Results and of Future Needs

Even the earliest workers in the field of portland cement constitution arrived at a fairly accurate assessment; namely that four mineral constituents C_3S, C_2S, C_3A, and C_4AF, with possibly some glass, constitute the major part of cement and that the relative amounts of these govern such properties as strength and durability. Since that time the emphasis in research has been to try to replace tedious and inaccurate microscopic examination by sets of rules, deduced with the aid of the phase rule, connecting constitution with bulk chemical composition.

More recent work, some of which is summarized in the foregoing sections, has tended to challenge the basic assumptions on which this approach is founded. In the first place it has been shown that the four constituents enter into solid solutions, not only between each other but also with the minor constituents or impurities of the cement. For the ferrite phase the range of composition is considerable, and the relative success of the earlier estimates of constitution must be explained by the fact that the average composition turns out to be very near to C_4AF. Secondly, calculations based on the phase rule must necessarily start with the assumption that equilibrium is obtained at clinkering temperature and maintained thereafter. This conception has been challenged for some time and has led to modified versions of the Bogue calculation such as those of Lea and Parker or Dahl.

At the present stage improvements in microscopic technique and the development of X-ray diffractometry offer hope of more exact direct determination of constitution. For control and specification purposes, however, it will always be desirable to avoid as far as possible determinations requiring expensive apparatus and highly skilled operators.

A further difficulty appears with the suggestion that the properties which the various constituents confer on the cement as a whole may vary with the detailed nature of those constituents.

It seems that both C_3S and C_2S exist in definite polymorphic forms in cement, but may be stabilized by varying amounts of varying kinds of impurity. There is good evidence that these stabilizers affect the cementing power of C_2S and some evidence that this is the case with C_3S also. It has also been shown that crystal habit and size may affect the reactivity of the anhydrous components.

The regulation of the tricalcium aluminate content of cement is now considered vital in producing sulfate-resisting portland cement. For specification purposes it is highly desirable that the accuracy of predicting or determining C_3A content should be improved. Unfortunately the discrepancies between different methods of estimation are greater for C_3A than for other components. The question of C_3A is linked closely with that of the ferrite phase, and this has led to methods involving either (a) some arbitrary assumption of a composition for the ferrite phase or (b) an independent determination of the ferrite composition.

Using Midgley's method for obtaining the composition of the ferrite phase, the compound composition can be worked out using the same principles as for the Bogue method, but first calculating all Fe_2O_3 as C_2F. From the experimentally determined ratio of C_2F/C_2A in the ferrite phase the total quantity of ferrite can be found, and also the CaO and Al_2O_3 combined as ferrite. The rest of the calculation then follows Bogue. In this way estimates of C_3A have been obtained at the Building Research Station more in agreement with the results of diffractometry (table 1).

TABLE 1.—*Data of H. G. Midgley comparing Bogue (B), modified Bogue (M.B., see text) and diffractometer estimates of* C_3A *and ferrite contents*

Sample		540	539	AS	AF	A40
C_3A	B.	0.9	0.7	15.4	2.5	9.9
	M.B.	3.4	3.0	13.6	2.3	13.3
	Diff.	4.5	4.8	13.5	3.7	11.5
Ferrite	B.	19.3	18.8	10.2	18.0	9.2
	M.B.	17.4	16.9	12.2	18.3	7.9
	Diff.	16.5	17.5	10.5	17.5	8.5

The list of phase assemblages previously given shows that cements containing C_3S and C_2S should either crystallize ferrite of the composition at the invariant point or of the same A/F ratio as the clinker. While relatively few results have yet been published, it is clear that in practice the A/F ratio of the ferrite phase is not simply related to the A/F ratio of the cement and that the distribution of A/F ratio is not that expected. (See for instance the histogram given by Midgley [65].)

This fact needs to be considered in conjunction with the observation that C_3A is found in contact with ferrites of A/F ratios lower than that of C_6AF_2. Cirilli and Brisi [67, 68] with laboratory clinkers found that C_3A disappeared at A/F=1.0 when MgO was absent and at A/F=1.2 when MgO was present. The evidence therefore seems to point to lack of equilibrium as an explanation of the facts. Astreeva [80] states that the composition of the ferrite phase depends on rate of cooling, a slowly cooled clinker having *lower* C_3A because more aluminate is dissoved in the aluminoferrite phase.

Consideration of the cooling conditions brings us to the question of glass. It is here that the results of X-ray methods conflict most with the older assumptions. Glass in quantity should be detectable by X-ray methods either by the increase of diffuse scattering in certain bands or by low totals for the other constituents. On either count, the indication is that the glass content must be very low. Devitrified glass might well give an X-ray pattern when optical examination fails to resolve any structure. It is possible that the heat content of such a finely crystalline mass might be appreciably higher than that of material in the fully crystalline condition and would give anomalous values for glass determined by heat of solution methods.

The independent crystallization of glass has of course been considered earlier by Lea and Parker. If the liquid from which the glass was formed were in equilibrium with the solid phases, the iron compound formed would however be in equilibrium with $C_{12}A_7$ and therefore of a high A/F ratio.

It seems that more consideration needs to be given to a suggestion of Swayze. He showed [27] that the crystallization of liquids saturated with regard to CaO would differ from that of liquids in equilibrium with C_3S and C_2S. Saturation with CaO could arise because of oversaturation of the cement composition with regard to CaO, or because there had been insufficient time for all free CaO to be completely reacted. Swayze showed that such liquids would crystallize to give some C_3A and an iron phase lower in A/F ratio than C_4AF. Such a theory seems to fit the facts as yet available very closely.

This review has been written at a time when X-ray diffractometry is only just being applied to the problem of cement constitution. It offers great possibilities but as yet results are scanty and in some respects contradictory. It seems clear however that greater attention must be paid to the question of homogeneity and equilibrium in clinker. The microscopic method necessarily reveals these defects if enough samples are examined, while the careful blending of specimen and standardizing substance required in diffractometry conceals them. Hitherto we have thought of lack of equilibrium in terms of the attainment of equilibrium at the clinkering temperature and departure therefrom during cooling. Swayze's work and the results of X-ray determination of the ferrite phase reveal the importance of the fact that in most clinkers equilibrium has never been attained.

I would like to conclude by offering for discussion certain problems and methods of study.

(1) Obtaining more data on constitution and the possible errors involved in computing it

It would be desirable to organize the exchange between cooperating laboratories of one or two carefully taken samples of clinker from each country. The clinker should be sampled from the kiln discharge so that no blending of clinker representing differing kiln conditions takes place. Each laboratory would examine the clinkers by whatever methods they choose to employ and circulate the results to the other laboratories.

(2) More research on minor components and solid solutions

I have indicated in this paper how small amounts of oxides such as P_2O_5, K_2O, BaO, and fluorides such as CaF_2 can influence cement properties. Many other minor constituents have not yet been considered. Important among these are sulphur as SO_3 and sulphide, and FeO. The interaction between SO_3 and alkalies has been adequately studied [81], but there is evidence that not only does SO_3 go into solid solution with the silicates, but it strongly influences the solubility of other groups at the same time. The method of X-ray absorption microanalysis seems promising for work of this kind.

(3) Experiments in the heat treatment of clinker

If the explanation given for the unexpected results on the C_3A and ferrite content of clinker is correct, then it should be possible by the laboratory heat treatment of both real and synthetic clinkers to bring about true equilibrium, and a more "normal" distribution of the interstitial phases.

These subjects are by no means academic ones. As Swayze has already pointed out, many specifications contain restrictions on the A/F ratio which are no longer realistic. The current demand for cements of low C_3A content makes consideration of this question urgent. At the moment C_3A is regulated in specifications by the Bogue calculation. Can a better method be found? Let us hope that these questions will find an answer by the time of the next Symposium.

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Discussion

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The following contribution is of interest in connection with the problem of the stability of dicalcium silicate.

It was established [1] [1] in 1955 that dicalcium silicate prepared synthetically from products of analytical purity may be obtained in its β-modification without a trace of γ, and will be indefinitely stable; the synthesis is accomplished by repeated heating in the range of α' stability (for example, 1,100 to 1,200 °C).

We have, on one hand, confirmed that the pure β-modification is not due to an excess of CaO in the solid solution, because one obtains without difficulty the γ-modification containing 0.5 percent of this oxide; on the other hand, we established that impurities such as Na_2O and K_2O, normally present in the initial products, have no effect on the β-γ inversion [2, 3]. The study of powder diagrams of the α', α, β and γ forms, obtained at temperatures at which these forms are stable, carried out either on Geiger-Müller counter diffractometer recordings or through microphotometry on photographic diffraction patterns, reveals a decisive effect of the fineness of the crystalline grains as a stability factor.

The α' phase always becomes transformed during cooling into the β phase at 675 to 650 °C. If the β grains are smaller than a certain critical size of the order of $(5\mu)^3$, the probability that such a grain contains a γ nucleus is very slight; thus the metastable phase can be preserved at ordinary temperature. On the other hand, when the grains are large (for example, $>(30\mu)^3$), a nucleus of γ is always present in the grain and grows as the temperature decreases sufficiently below the point of the α'-β inversion, producing a transformation of the entire β grain into γ. Among the experimental facts which confirm this interpretation, the most outstanding is the following: two identical specimens of β-dicalcium silicate are brought to a temperature definitely above the point of the α'-α inversion (about 1,460 °C), such as 1,550 °C; one of these is quickly quenched while the other is permitted to cool slowly to below the point of this inversion, or 1,400 °C for example, before it too is quenched in the same manner. In the first case one obtains 90 percent β-C_2S; in the second 95 percent γ-C_2S. In the first case the α' crystals, not having had time to grow, have yielded the β modification consisting of small crystals which have remained stable, while in the second case the α' crystals have had time to grow during the α-α' inversion, so that—in spite of quenching—the β-γ inversion is almost complete.

The nature of the stability of the β modification can now be defined more precisely, thanks to the results of a recent investigation based on the effect

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[1] Figures in brackets indicate the literature references at the end of this paper.

of pressure on the β-γ inversion. Pellets of β-C_2S powder agglomerated into disks with a thickness of 2 mm were subjected to percussion (drop of a mass corresponding to the energy of several tens of kilogram-meters) or to crushing between the platens of a hydraulic press operating with a maximum pressure of 10,000 kg/cm^2. We have observed that under these conditions it is possible to produce a partial β-γ inversion in the cold.

Percussion (shocks, blows), producing work of about 40-kg-m on a pellet of uniform density, results in a transformation at a low rate, which can attain 30 percent if the percussion is repeated several times. The proportion of β transformed by crushing in a hydraulic press is an increasing function, especially of the pressure, of the number of cycles of pulverization-compression, and of the fineness of the crystalline grains. It increases very fast as a function of the duration of applied load during the first 10 min and only slightly beyond this time; it is independent of the rate of pressure increase. In contrast, if the β powder is subjected to *hydrostatic pressure* (in an oil-filled compression chamber) which can even be very high (9,600 kg/cm^2), no transformation is produced.

We have compared the effect of pressure on silicates of different compositions.

In the case of *pure silicate*, for a given granulometric range (of the order of 0.5 to 10 μ) and a given pressure, the maximum proportion of transformed crystals increases with the number of pressure applications, tending, however, towards a limit of the order of 50 percent; this limit decreases rapidly with the proportion of larger grains greater than the critical volume defined above, which is of the order of $(5\mu)^3$; if the largest grains remain above this figure, the proportion transformed drops to 25 percent.

In the case of silicates containing additions, the results permit us to define three types of behavior:

(1) Transformation as if *the addition had no effect*. This is the case of the oxides Na_2O and K_2O at a concentration of 0.3 percent.

(2) *No transformation*. This is the case with silicate synthesized with B_2O_3 (even only 0.5 percent), with natural silicate [4], and with belite in clinker. These different products have a crystalline lattice which is different from that of pure β-silicate or the silicates mentioned in the preceding paragraph. The displacements of the lines, measured on Debye-Scherrer diagrams are very weak, but measurable. The lattice has a monoclinic cell which is slightly different from that of β. It should be noted that the D.-S. diagrams of β-C_2S + 0.5 percent B_2O_3 and of larnite show the same modifications and that that of belite is similar to the diagram of β-C_2S + 2 percent B_2O_3.

(3) Transformation *in greater proportion than* for pure silicate. This is the effect of an addition of 1 percent of P_2O_5 in the form of $CaNaPO_4$ [6]. The product obtained with this admixture, the D.-S. diagram of which does not differ from that of the pure silicate, becomes transformed to the extent of 85 percent.

Numerous examples are known of allotropic transformations produced by compression of the unstable phase. Thus Burns and Bredig [9] have observed the transformation of calcite into aragonite with prolonged grinding. In our case, the γ phase is less dense than the initial β phase. An increase in pressure can not favor this transformation, and this is exactly what we have observed in our experiments with hydrostatic pressure [10].

The transformation is actually produced by *deformation* of the crystal under the influence of the compression. The transition from the β to the more stable phase is always thermodynamically possible. But this transformation does not begin unless nuclei are present; these nuclei are formed during shearing of the crystal during the percussion or the crushing of the crystal in a press.

The effectiveness of compression in producing the transformation depends on a number of factors. First among these is the size of the powder grains. It is natural to think that the fine grains will have more chance to resist the pressure without shearing. Moreover, each nucleus which is produced in a small isolated grain can transform only this grain, thus only a very small volume.

Our experiments also shed light on the effect of so-called stabilizing admixtures. The only admixtures that have a stabilizing action are those which modify the lattice of pure silicate. Alkaline oxides that do not change the lattice have no effect, and the oxide P_2O_5 even favors the β-γ inversion. It seems that addition of phosphorus has the effect of making the β-crystals more deformable, a fact which would explain the higher proportion of transformed crystals. This idea is suggested by the observation that γ-crystals mixed with β-crystals before application of pressure, and initially rather coarse, are crushed and reduced into very small crystals following application of pressure. This does not happen with other silicates. One could imagine that—on the contrary—silicates with modified lattices (as by addition of B_2O_3, etc.) become less deformed, decreasing the number of possible sites for the nuclei, or that the formation of a nucleus is less easy in a modified lattice than in a lattice of pure silicate; indeed the two effects could be additive.

These different effects could be related to the modifications in the redistribution of interionic fields which are due to the introduction of anionic groups more electronegative, $(BO_4)^{5-}$, or less electronegative, $(PO_4)^{3-}$, than $(SiO_4)^{4-}$; or groups of different kinds such as $(AlO_4)^{5-}$ and $(FeO_4)^{5-}$, associated with cations having a more highly polarizing effect than Ca^{2+} or Mg^{2+}. This is the case of larnite, and possibly of belite in clinker [8].

The effect of B_2O_3 must also be due to the fact that the $(BO_4)^{5-}$ groups, being less voluminous but having a higher valence than $(SiO_4)^{4-}$, cause formation of vacancies through maintenance of electric neutrality in the lattice by elimination of Si^{4+} ions, probably in the form of silica. At 0.5 percent B_2O_3 we would have a missing Si for 160 molecules of C_2S, or for 40 unit cells of β; the existence of such vacancies is easier to accept than the insertion of supplementary Ca atoms into as compact a lattice as that of β.

A mechanism based on the same principle, but apparently more complex, could be responsible for the behavior of larnite which contains Al_2O_3, Fe_2O_3, and MgO [4]. Nevertheless, systematic studies are needed to reveal the various effects of cations and anions in variable concentrations.

Although industrial grinding is largely a percussion process, it is not improbable that shearing forces might be applied several times to a given crystal and might provoke a limited transformation in insufficiently homogeneous clinkers containing grains with an excess of silica or phosphorus.

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Discussion

A. J. Majumdar and Deane K. Smith

This discussion of Dr. Nurse's paper will be restricted mainly to brief descriptions of our recent work in the areas of polymorphism of dicalcium silicate, stability or metastability of pentacalcium trialuminate, and compositional variations in the iron phase crystallizing in the quaternary system $C_2S—C_3S—C_3A—Fss$. (Fss=calcium aluminoferrite solid solution.)

Polymorphism in Dicalcium Silicate

The presently accepted picture of the thermal transformations in the dicalcium silicate phase is due to Bredig [1950] and was reviewed by Nurse in the 1952 Symposium. An alternative interpretation of changes taking place when Ca_2SiO_4 is heated to and cooled from clinkering temperatures has been put forth by Toropov et al. [1957]. Figure 1 shows both interpretations. They differ significantly both in the sequence of appearance of phases and in the temperatures of the phase changes. In addition to suggesting a new phase, β', Toropov claims that the β phase has a stable field at atmospheric pressure.

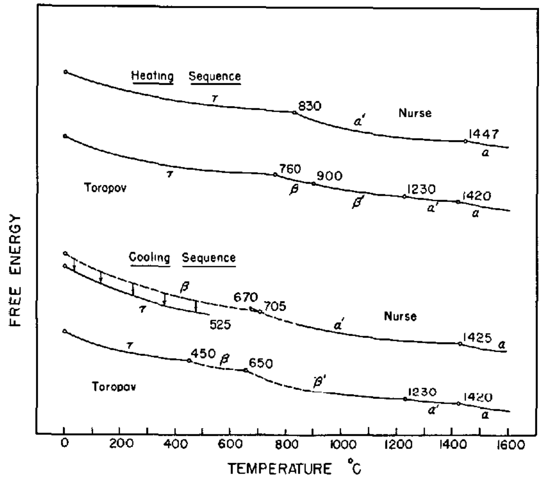

FIGURE 1. *Schematic free energy-temperature curves after Nurse (1952) and constructed from Toropov's (1957) data.*

The dashed portions on the cooling curves indicate regions where the phase is not the same as on heating.

In our recent paper (soon to be published in the Journal of the American Ceramic Society) we have neither confirmed the existence of Toropov's β' phase nor verified a stable field for the β modification. Instead, our work indicates that Bredig's diagram more nearly represents the true relations in this one-component system. If our interpretation of the dependence of the $\beta\rightarrow\gamma$ transformation on the thermal history of the sample is correct, the system is complicated by the presence of heretofore unreported metastable (?) phases as diagrammatically shown in figure 2.

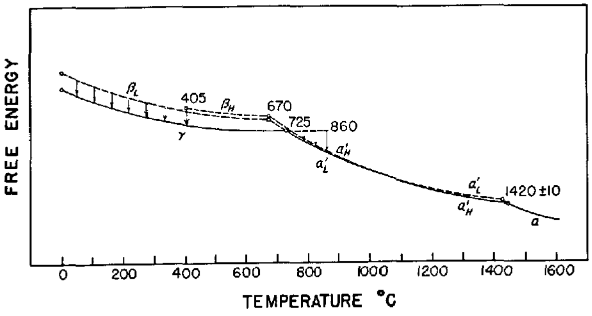

FIGURE 2. *Hypothetical schematic free energy-temperature curves for the phases of* Ca_2SiO_4.

Solid lines indicate stable phases; dashed lines, metastable phases.

We used samples of Ca_2SiO_4 prepared by three different methods; the $CaO:SiO_2$ ratio was very close to 2:1 in all samples. Some samples had additives up to 0.1 wt percent representing common impurities in clinkers. High-temperature powder diffractometry and differential thermal analysis were the principal techniques used in the investigation. The important results of this work are as follows:

(1) A critical heating temperature of $1{,}420 \pm 10$ °C was found which had a marked effect on the $\beta \rightarrow \gamma$ transformation on cooling. Samples cooled from above this temperature "dusted" and converted completely to the γ form, whereas samples cooled from below this temperature showed only partial conversion of β to the γ form and no dusting. Guinier and Yannaquis [1957, 1959] have observed that samples cooled from 1,500 °C produced the pure γ modification while samples cooled from 1,100 °C produced a mixture of β and γ forms. They suggested that growth of larger crystals at the higher temperatures resulted in an increase in lattice strain energy on cooling, thus promoting complete inversion to the room-temperature stable γ form. Our work indicates that, although grain-size effects may be present, they are minor for particles larger than 40μ, and the effect of thermal history on the completeness of $\beta \rightarrow \gamma$ inversion is much more complex.

The critical heating temperature of 1,420° coincides with the α'–α inversion temperature. Apparently if the α phase forms during the heating of a Ca_2SiO_4 sample, the room-temperature product is all in the γ form. The X-ray patterns of the α' phase formed on cooling from a Ca_2SiO_4 sample below 1,420° show slight differences when compared with the patterns of the α' phase formed on heating. Although these differences may be due to the shifting and growth of grains at the elevated temperature, structural differences may be indicated. The phase formed from α has been designated α'_H in figure 2. Yamaguchi [1957] has shown that the X-ray pattern of the β form can be completely indexed only if the a axis is multiplied by four and the c axis by three. Perhaps this superlattice is reflected in α'_H, although our high-temperature X-ray patterns have not been sharp enough to verify the hypothesis.

The β_H phase formed from α'_H–Ca_2SiO_4 likewise indicates some structural differences. If the $\beta_H \rightarrow \gamma$ transformation has a lower activation energy barrier than the $\beta_L \rightarrow \gamma$ inversion, the dependence of this transformation on the α–α' transformation can be explained.

(2) The sluggishness of the γ–α' inversion on heating does not appear to be due completely to reaction rates. A range of over 100 °C has been found where both forms appear to coexist. If a sample starting as all γ is heated to 725 °C, some α' appears in the first 15 min, but a 20-hr heat treatment does not promote continued conversion to α'. Even at a temperature of 850 °C extended heating does not increase the $\alpha':\gamma$ ratio over that formed in the first 15 min. These observations are contrary to the effects expected if the sluggishness of the transformation is due to slow reaction rates.

The presence of two phases of the same composition over a range of temperatures violates the phase rule unless the compositions shift slightly from the single-phase compositions. No evidence for a mixed-crystal phase in this region of coexistence was found in the X-ray patterns. The presence of impurities, which did not stabilize the β form, did not affect the β–γ transformation in any marked manner.

The "C_5A_3" Phase

We have attempted to establish the field of stability for the "C_5A_3" compound reported by Aruja [1957], but so far our experiments have not yielded any positive evidence for the existence of such a field. Five mixtures ranging in composition from 100 percent C_5A_3 to 100 percent $C_{12}A_7$ were prepared. The C_5A_3 and $C_{12}A_7$ starting mixes were synthesized by coprecipitating calculated amounts of $Al(OH)_3$ and $CaCO_3$ from solutions, followed by ignition at an elevated temperature. Chemical analysis shows 51.53 percent Al_2O_3 and 48.47 percent CaO for the $C_{12}A_7$ preparation (theoretical—51.47 percent Al_2O_3, 48.53 percent CaO) and 52.30 percent Al_2O_3 and 47.70 percent CaO for the C_5A_3 preparation (theoretical—52.17 percent Al_2O_3 and 47.83 percent CaO). Thus, the compositions of the mixtures correspond within experimental error to the desired values and are distinguishable as two separate compositions. Both X-ray and optical examination revealed the presence of a trace of CA in the C_5A_3 mixture whereas the $C_{12}A_7$ was found to be homogenous.

The mixtures were placed in platinum capsules which were then sealed and subsequently heated above 1,500 °C in a furnace. It was assumed that complete melting had taken place in all the samples at this temperature. The charges were then cooled slowly at a rate of 50 °C per day to 1,000 °C whence they were quenched. X-ray and optical examination of these quenched samples failed to show the presence of the "C_5A_3" compound of Aruja. Compositions other than $C_{12}A_7$ yielded CA in addition to the cubic $C_{12}A_7$, the former being more abundant in C_5A_3-rich mixtures. Therefore it does not seem likely that "C_5A_3" and $C_{12}A_7$ are compatible phases.

The experiments of Welch with the hot-wire apparatus as reported by Aruja have been recently repeated at the Fellowship Laboratory with success. There is very little doubt that a phase with the optical and X-ray diffraction characteristics almost identical with those of "C_5A_3" can be grown reproducibly following the procedures described by Aruja [1957]. In our experiments we have not yet succeeded in growing "C_5A_3" alone. In all our runs other crystalline phases, mainly CA and $C_{12}A_7$, were found to be present in conjunction with "C_5A_3" and glass. In addition we have not yet been able to grow this orthorhombic phase from the C_5A_3 composition. Thus, the phase relationships at or near the liquidus temperature also cannot be successfully explained on the basis of our present data.

The possibility that "orthorhombic C_5A_3" is a high-temperature modification of $C_{12}A_7$ has also been explored. Thermal analyses of $C_{12}A_7$ have not shown any evidence of change in heat content of the sample below its melting point. High-temperature powder diffraction has also failed to indicate that any rapid polymorphic inversion exists in $C_{12}A_7$ up to 1,375 °C. On the other hand, "C_5A_3" has been grown from a $C_{12}A_7$ melt. Thus the original assumption of Rankin and Wright [1915] that "C_5A_3" is a metastable phase seems to be supported by the recent work.

The Fss Phase

The most recent work on the composition of the Fss phase in quaternary equilibrium with C_2S, C_3S, and C_3A is due to Swayze [1946]. By directly estimating the proportions of the siliceous phases in the equilibrium four-phase assemblage, Swayze calculated the composition of the Fss phase using a knowledge of the chemical composition of the mixture investigated. This method, although theoretically valid, can yield only approximate results for two reasons. First, the accuracy of estimating the amount of a phase by microscopic method in the system under consideration is not too good. Second and more significant, the three phases, C_2S, C_3S, and C_3A, are not "pure" compounds but rather contain marked amounts of the other components in solid solution.

When one speaks of the compatibility tetrahedron as having C_2S, C_3S, C_3A, and C_4AF at the apices, one assumes that the compositions of the phases are stoichiometric. Actually the true tetrahedron has its corners displaced a significant amount from the hypothetical positions, and the question whether the invariant point is inside or outside the true tetrahedron requires not only locating the invariant point but locating the true apices as well. On the basis of their experimental data Lea and Parker [1934], in their classic study, were still uncertain about the location of the invariant point. It remains doubtful even today whether one has definitely established that the invariant point lies outside the tetrahedron of compatibility as stated by Nurse in the present Symposium paper. As a matter of fact, this question cannot be solved until precise data on the chemical compositions of the compatible phases at the invariant point are available; the presently accepted equations due to Dahl [1939] for calculating the amounts of potential compounds have to be modified in the light of the true compositions of "impure" compounds that make up the corners of the compatibility tetrahedron. The composition of the Fss phase at the invariant point can be definitely established only when compositions of the other phases coexisting with it are more accurately known.

The exact nature of the invariant point is important in any discussion of the paths of crystallization of a mixture from above the invariant point temperature. If the invariant point happens to be a eutectic, the compositions of the final products of crystallization below the invariant temperature will be identical, at each temperature, for all mixtures within the compatibility tetrahedron. If equilibrium is maintained throughout the cooling cycle, no phase would show zoning. In the crystallization of the ternary Fss phase, we have not detected any evidence of zoning, even in deliberate attempts to develop zoned crystals by rapid cooling from the melt. Zoning might occur in the quaternary system if the presence of silica increases the viscosity of the melt and appreciably affects the diffusion rates of the mobile ions. Evidence of zoning in the Fss phase in actual clinkers cannot be taken as positive proof for zoning occurring in a true four-component system. Aside from the presence of many minor impurities whose effects are not well established, a clinker rarely reaches equilibrium due to temperature inhomogeniety in the kiln and compositional variations in the raw materials. These variations may account for the range of reported compositions for the Fss phase in clinkers.

If the invariant point is a peritectic, most mixtures having the proper bulk composition will complete crystallization at the invariant point under equilibrium conditions, and the final liquid to crystallize would have the composition of the invariant point. However, for some mixtures the liquid will be used up before the peritectic point is reached on cooling, and the Fss phase from such mixtures might show zoning because it would be different compositionally from the phase that would crystallize at the invariant point. Thus, it can be seen that the composition of the equilibrium Fss phase may depend on the nature of the invariant relationship in the system.

In the Fellowship Laboratory we are attempting to establish the unique compositions of the four compatible phases at one temperature below the liquidus. Seven quaternary mixtures were equilibrated at 1,275±5 °C for a period of 72 hr. The work is far from completion at this stage, but careful X-ray diffractometry measurements by interval counting at 1/50th of a degree 2θ indicate that in each sample the Fss phase has interplaner spacings almost identical to those of C_4AF. This identification agrees well with the observations of Copeland and coworkers [1959]. It is not yet established how much silica is dissolved in the Fss phase, but apparently not enough is taken into the structure to change the unit cell dimensions appreciably.

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Discussion

N. Yannaquis and A. Guinier

The interpretation of Majumdar and Smith rests entirely on the existence of two crystalline forms of α'-C_2S. As the authors, in their contribution, did not specify their experimental evidence, it is difficult to discuss their conclusions.

(1) We wish to make it known that we have sought long and carefully to show the existence of an abnormal form of the α' phase, and that we have finally had to admit that all the differences apparent in the diagrams obtained with the diffractometer could be explained by a variable granulometry *of a single crystalline phase.* The difficulty in the diffractometer study of the phases formed within the apparatus at high temperature results from the inability to give to the specimen the grain fineness indispensable for good registry. When the crystals are too large, it is known that the individual diffraction spots are never all aligned on the center of the line given by the fine powder. If the number of spots registered by the counter is small, the line observed may be displaced. In addition, the measured intensities are subject to fluctuations, considerable and not always erratic, if there is a preferential orientation of growth of the crystals. For this reason it is not possible to establish the existence on the diagram of an α' phase of slightly different structure.

We therefore believe that one must hold to the hypothesis, pointed out as well by the authors themselves, that the differences observed are due to the form of the grains. The correlation found between the aspect of the diagrams and the production of the β or the γ phase arises from the fact that the two phenomena are influenced by the same factor: the form of the grains of the α' phase.

(2) It is not exactly correct that when the silicate has been heated above the point of transformation $\alpha' \rightarrow \alpha$, the product obtained on cooling is *always* the γ phase. One can obtain the pure β phase if the silicate is quenched rather than slowly cooled.

(3) It is possible to index all the lines of the β phase [1] on the basis of a monoclinic lattice very close to that given by C. M. Midgley [2]. The difference between the values of d, calculated and observed, is at most a few thousandths of an angstrom unit.

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Discussion

Myron A. Swayze

The following remarks are on two sections of Dr. Nurse's excellent report: one concerning the influence of other clinker minerals on the composition of the series of aluminoferrite solid solutions; the other some practical suggestions to govern the selection of clinker samples for use by a group of laboratories in further studies of clinker constitution.

The 1959 report by Newkirk and Thwaite [1][1] on the ternary system $CaO—CA—C_2F$ and the 1946 report by Swayze [2] on the system $CaO—C_5A_3—C_2F$ differ in some details that concern the series of ferrite solid solutions. Where Swayze pictured this series as a single straight line running from C_2F to C_6A_2F, the Newkirk-Thwaite report considers the series to be a band of compositions including the compounds C_2F, C_6AF_2, and C_4AF, but on the low lime side of C_6A_2F and running beyond it towards $C_{12}A_7$ to an assumed point L, in relative agreement with previous reports by Yamauchi [3] and Malquori and Cirilli [4]. This assumed endpoint composition was not tested by Newkirk and Thwaite, nor is there any clear evidence that previous authors made similar checks of their assumed endpoints of their lines or bands. It is therefore interesting to note that while Newkirk and Thwaite found the composition C_6A_2F to contain C_3A in addition to the ferrite phase, Nurse in his present paper finds it to be a homogeneous compound.

The principal and serious difference between these two reports on the ternary system is in the location of the correct $CaO—C_3A—Fss$

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[1] **Figures in brackets indicate the literature references at the end of this paper.**

invariant point composition, and in the composition of the ferrite phase crystallizing at this point. Swayze reported an A/F ratio of 0.50 for the ferrite phase at this point, while Newkirk and Thwaite show an A/F ratio of 0.77. While to the operating cement chemist this difference may seem academic, it becomes of practical significance if the same alumina-iron oxide relations carry through into the more complex systems approaching commercial portland cement compositions. The only evidence we have [2] is that these conditions do prevail. Therefore this present inconsistency in available data on compositions in the ternary system should be resolved by a more careful and thorough study. Nurse's present remarks to the effect that crystallization of a ferrite phase with an A/F ratio of less than 0.64 in the presence of free CaO "seems to fit the facts as yet available very closely" indicate that such a restudy is badly needed. In this connection I would recommend that mixtures of raw materials be held down to a maximum of 1.5 g ignited basis and that homogeneity of the final mix preparations be checked thoroughly. Also, more reliance should be placed on petrographic and X-ray examinations of quenched burns at critical temperatures on closely spaced mixtures than on differential thermal analysis readings, which can show similar responses for several different compositions in small critical areas. This is brought out clearly by Toropov, in his paper on solid solutions of the clinker minerals [5].

It is evident that presence of free CaO as a primary phase in liquids of the ternary system shrinks the length of the ferrite line or band down to a range from 0.00 to 0.50 A/F ratios, or if preferred to the range from 0.00 to 0.77. It should be equally evident that in such a case the band of ferrite compositions will shrink to a line over these A/F ranges, since the low limed portions of the band should not be compatible with liquids saturated with CaO. Similarly, in the CaO-C_5A_3–C_2F–C_2S system, the full range of ferrite compositions is impossible, since the principal invariant points are outside the phase volume in which C_6A_2F is stable. The top limit on A/F ratio in this case appears to be about 0.85 when CaO is absent. The presence of solid C_3S in the cooling liquids of this system should again reduce the band of stable ferrite phases to a line, since C_3S is reduced to C_2S during cooling by liquids unsaturated with CaO. While the modification of this quaternary system with MgO shifts the principal invariant points towards the CaO-C_5A_3 boundary far enough to make C_6A_2F crystallization possible, it is still doubtful if a band of ferrite phases can exist in the presence of solid C_3S, or if the line of ferrite phases can extend past the composition C_6A_2F any appreciable distance. The further addition of alkali oxides to the system should make such an extension possible, although the band of ferrite phases would still be doubtful.

The other section in Nurse's report on which practical comment should be made concerns the selection of commercial clinker samples for tests on constitution by an international group of cooperating laboratories. Clinker composition from interior to exterior can be affected materially by contamination from coal ash on clinker surfaces which have come through the kiln in nodular form. It is therefore suggested that selection of these important samples should be limited to kilns using oil or gas for fuel.

Another point on selection of clinker samples is with regard to differences in the silica/(alumina + iron oxide) ratio that exist between large and small clinkers from the same lot. Our research laboratory has been aware of this for some years, although it has not been noted in the literature. This segregation is evidently due to the very low silica content of the clinker liquid and to differential rates of clinker cooling after leaving the burning zone of the kiln. Since small sized clinkers lose their temperature more rapidly to the relatively cool secondary combustion air on leaving the kiln hot zone, their liquid content shrinks during its crystallization and leaves solid C_3S crystals out in relief on the surface. This faster cooling of small clinkers permits them to have a blotting action on larger hot clinkers whose liquid is still at the surface due to slower cooling. The result is a reduction of the silica ratio in the fine clinkers and an increase of it in coarse clinker, due to this transfer of the low silica liquid. It should therefore be advisable in sampling clinker for this important research that all laboratories be supplied with the same size of clinkers, preferably in the intermediate range of diameters.

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Discussion

H.-G. Smolczyk

At the end of his excellent paper Dr. Nurse suggests that some laboratories in different countries should carry out X-ray investigations of the same clinkers. I am very optimistic and should like to add to this broadminded proposal another further suggestion to be put forward for consideration. In this discussion I also want to address all those who at the Symposium showed X-ray diagrams of any

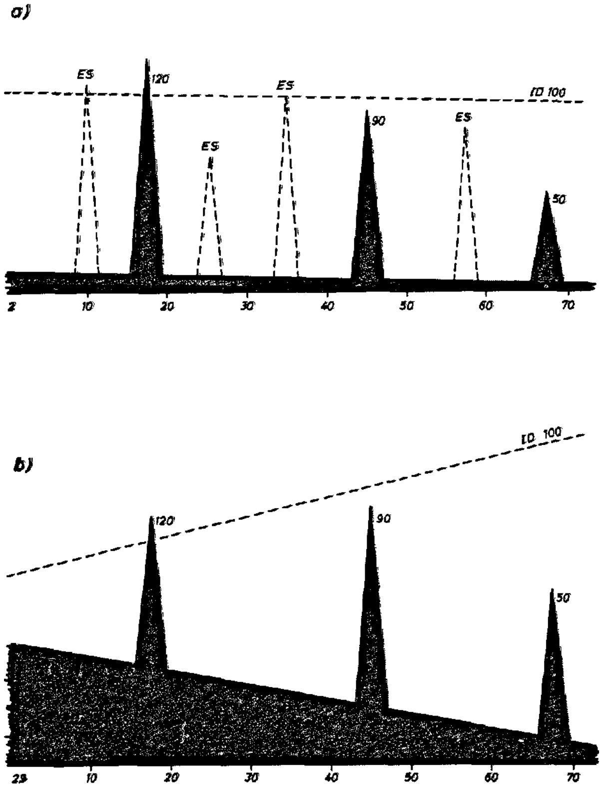

FIGURE 1. *Two examples of different intensity distribution (ID) in X-ray diagrams.*

kind. (As done by the workers of the Portland Cement Association, the Building Research Station, and by H. E. Schwiete, G. Malquori, H. zur Strassen, J. H. P. van Aardt, R. Turriziani, F. W. Locher, Y. Suzukawa, N. A. Toropov, and myself.)

Many of those diagrams were in perfect accordance with one another, others seemed to differ. Much trouble could be saved and many a misunderstanding could be avoided if we could compare qualitative X-ray diagrams or even rough sketches or X-ray intensity tables of different laboratories by a simple method and in a nearly quantitative way. But to this very moment we have not found a standardized reference system. The complicated method using internal standards would not serve this purpose, for it demands a different standard or a different concentration of the standard for every new case, and if for instance the complete diagram of a partly hydrated clinker is to be described, one single diagram with only one internal standard would be of no help.

Now I simply want to describe how, for about two years, we have tried to overcome this difficulty. Beforehand I want to say that at our institute two X-ray diffractometers are continuously busy producing diagrams of different minerals, slags, pastes, mortars, and concretes. Every time the X-ray tubes are changed or some repair is done, some new adjustment must be performed. But often we do not have the time to adjust both diffractometers so that afterwards they will show exactly the same intensities and the same intensity distributions. Especially in the course of long-time studies with fixed testing periods there has been little time available, and our adjusting procedure has then been limited to the exact peak position and to the maximum intensity of each of the diffractometers. To be able to compare each of the 6,000 diagrams already produced with all the others, in spite of all the above mentioned impediments, I have developed the following method:

Each peak height of a diagram is expressed as percentage of an "Intensity Distribution 100," that has been fixed experimentally. This "ID 100," is measured anew and in accordance with the entire diagram of an "External Standard" after every change made on the diffractometer. Afterwards this "ID 100" is subject only to daily investigations of one single peak.

Figure 1 shows one normal (a) and one much exaggerated (b) possibility for the "ID 100" and also a way in which one and the same diagram could possibly change. One can clearly see that in spite of the different looking patterns the relative intensities have maintained the same values. For our purposes we have fixed as "External Standard" the following peak heights of α-Al_2O_3:

h_1: (102), $d=3.479$ A, ES-Int.$=65.6$
h_2: (014), $d=2.552$ A, ES-Int.$=100.0$
h_3: (116), $d=1.601$ A, ES-Int.$=83.9$

This α-Al_2O_3 has some advantages that serve this special purpose: It can be ground for hours without any change of intensities. Its X-ray diagrams are absolutely reproducible. The intensities are not too high. It is insoluble. It is available everywhere. For clinker and quartz analysis α-Al_2O_3 can also be used as an internal standard.

The three peaks of the external standard are to be seen in figure 1a. The peak h_4 at 10° is of a silicate used to fix the low-angle region of "ID 100." (For this special section of the diagram another substance should be found to serve as "Low-Angle External Standard.")

To obtain the "ID 100" of a certain X-ray diffractometer with a certain adjustment, it is only necessary to take an X-ray diagram showing these 4 lines, multiply their heights by $\frac{100}{h_{1-4}}$ and connect these 4 points. Every diagram produced by this diffractometer can be expressed in percentage of this newly constructed "ID 100," and can easily be compared with diagrams obtained for instance a year earlier.

As long as the adjustment of the equipment has not changed, i.e., as long as the shape of the new "ID 100" has remained the same, for daily checking it is only necessary to measure the height of one peak out of the α-Al_2O_3 diagram. For this purpose we measure the peak at 35° three times a day.

If the chemical composition of the substance that has been recorded in such a way is known, the diagram can also be used for a quantitative determination by applying the well-known theoretical equation

$$x=\frac{I_x}{I_0}\cdot\frac{\mu_G}{\mu_x}$$

x=the amount of the mineral in the compound; I_0=the intensity of 100 percent of the mineral; μ_x= the mass absorption coefficient of the mineral; μ_G= the mass absorption coefficient of the entire compound,
or better with the exact equation of Leroux, Lennox, and Kay [1]

$$x=\frac{I_x}{I_0}\cdot\left(\frac{\mu_G}{\mu_x}\right)^{-c}$$

wherein the constant c has to be fixed experimentally.

Now my opinion is this:

I should appreciate very much if we could do something similar on an international basis. That is, if, after thorough consideration, we could come to an agreement on an "International Standard" with entirely fixed intensities as "ID 100," we could express all our diffractometer diagrams in percentage of this "ID 100," and we should be able to compare all our intensities, no matter where they came from.

I thank Dr. R. H. Bogue, Dr. S. Brunauer, Dr. L. E. Copeland, and Dr. D. L. Kantro for valuable discussions on this subject.

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Discussion

Levi S. Brown

It is said that superlatives have no place in science, or that science has no place for superlatives. Exception surely should be taken with respect to hot wire microscopy, referred to in this paper, and to which this discussion is limited.

The merit of the exception can be best appreciated by those experienced in investigations of high-temperature phase equilibrium. To give this some sort of quantitative expression, consider the ternary diagram of the lime-alumina-silica system. More than 15 years of intensive research went into the building of this diagram. The eventual comprehensive report notes that the investigation comprised ". . . some 7,000 heat treatments . . . ." Realization that each one takes up at least a half a day brings some concept of the enormity of the accomplishment.

But then some concept of the enormous facility that could be conferred by the hot wire microscope is gained by realization that with it the same investigation could have been carried out with one-seventh to one-tenth of the 7,000 heat treatments, and probably better. Each one could take care of 7 to 10 quenches, at the same time directly establishing critical or invariant temperatures, with less time lost in assurance of equilibrium conditions. These original investigators surely would have looked upon this apparatus as superlative.

Of course the hot wire microscope is not all-sufficient in itself. From the very nature of the application, close working distances and high magnifications are proscribed. In the mapping of a new system, detailed determination and description of specific optical properties of new compounds must be worked out by more orthodox petrographic methods.

That however becomes a relatively slight insufficiency in the realization that it only has to be done once. That serves to point up further the practical utility of the instrument in present day industrial technology or control, in many and varied high temperature processes, as in glass making, and smelting operations. The capabilities and facilities offered are great.

Discussion

Rustum Roy

Dr. Nurse in his paper mentioned very briefly the new techniques which have been brought to bear on some of the problems of the structure of the individual clinker components. This discussion reports some of our work with high-temperature diffractometry, hydrothermal catalysis, and very high uniaxial pressures. In spite of the application of these and other new tools the understanding of the polymorphism of dicalcium silicate still leaves much to be desired.

The $\beta\rightleftharpoons\alpha'$ *Transition.* The *relative* ease of reversibility of this transition has been known from differential-thermal-analysis data for a long time. However, such data do not indicate much about the actual sequence of reaction, nor of the extent of conversion. In the high-temperature X-ray study by D. Roy [1],[1] a temperature of 670 °C has been assigned to the inversion. In the up-temperature direction 10 min at 680 °C is sufficient to convert most of the β to α' and the amount of α' increases normally with time. On cooling, holding for even 2½ hr at 640 °C fails to convert the α' to β while 30 min at 610 °C yields a larger percentage of β. One may, therefore, say that we obtain on our samples [1] a temperature of—very roughly—675 °C in the up-direction and 625 °C in the down-direction. Such a "hysteresis" is quite analogous to the similar anomaly in cristobalite studied by Hill and Roy [2], in which case in the well-ordered phase the

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[1] Figures in brackets indicate the literature references at the end of this paper.

up-temperature conversion is at 268 °C and the down-temperature one is at 225 °C. The reconciliation of these anomalies with phase rule necessitates some new hypotheses. Such a proposal is discussed later. *The $\gamma \rightarrow \alpha'$ transition* was located by D. Roy [1] at 675 °C at 2,000 psi (H_2O) pressure and was extrapolated back by calculation to 725 °C at atmospheric pressure. All investigators are agreed that the starting material determines the temperature at which the reaction proceeds fast enough to be detected. In the sample studied [1] the reaction runs rapidly only above 840 °C. While there is a tendency for the γ- phase to persist even 100 °C above the equilibrium temperature (as shown by high-temperature X-rays), this persistence probably does not require a special explanation. The kinetics of a reconstructive silicate transformation with a large volume change cannot be expected to be very different at such low temperatures. In the down-temperature direction, of course, the reaction $\alpha' \rightarrow \gamma$ has never been carried out, although one can cool the sample to nearly 500 °C for several hours before the alternative transition to β is accomplished.

The $\beta \rightleftharpoons \gamma$ Transition. This is, of course—according to present general agreement—the only really monotropic transition, since β is always less stable than γ in the temperature range of its existence *at atmospheric pressure.* Calculations by D. Roy [1] using available thermochemical data (Gronow and Schwiete [3]) show that the β—phase should be stable even at room temperature (see fig. 1) at about 2,000 atm.

The common failure of pure β—C_2S (i.e., omitting cases due to equilibrium stabilization by solid solution) to invert to γ may, in general, be ascribed only to the sluggishness of a rather complex reaction involving breaking nearly all Ca—O bonds and some Si—O bonds at such low temperatures ($<<670$ °C). Our data here reflect the remarkable stability of β—C_2S (prepared hydrothermally) since runs of 2 to 5 weeks near 400 °C failed to cause inversion to γ. Moreover, the data on the stability of "large crystals" of hydrothermally made β-crystals do not agree with those reported by Yannaquis and Guinier [4]. Crystals of the β-phase which have an estimated volume of 1000 A^3 appear to be quite stable—indeed, they survive inversion better than the smaller crystals. Furthermore, the phase made dry by heating gels at temperatures between 1,475 and 1,300 °C all inverted to γ with no change in behavior at the $\alpha \rightarrow \alpha'$ transition point.

The most recent of our data are those obtained under very high pressures. Dachille and Roy [5] have pointed out that, in many cases, so-called "grinding" in very simple laboratory devices such as mortars and pestles and Wig-L-Bug shakers can cause the attainment of pressures of 15-20,000 bars. In a later study, by the introduction of a simple apparatus which provided the means of applying shearing stresses superimposable upon quasi-hydrostatic pressures of up to 90,000 atm, Dachille and Roy [6] were able to separate clearly the effects of pressure alone, and the catalytic effect of shearing stresses which exceeded the strength of the material and caused fracture.

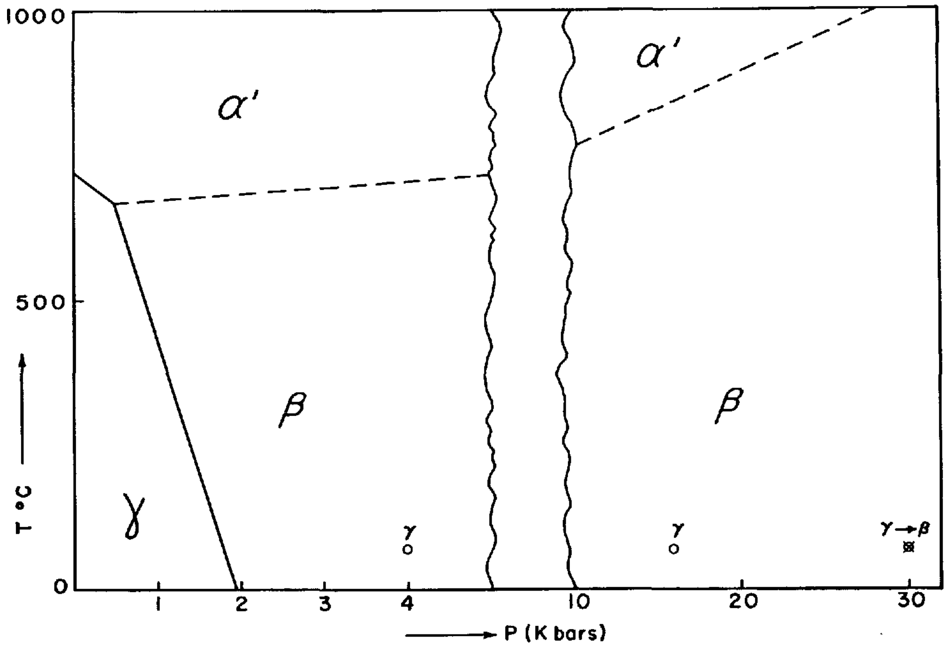

FIGURE 1. *Phase relation of C_2S as affected by temperature and pressure.*

Applying this same "displacive shearing" apparatus it is possible to convert γ to β at room temperature at 30,000 bars in 1 hr.[2] D. Roy was unable to convert γ to β at 17,000 bars without the shearing. Moreover, not only will a Wig-L-Bug type mixer convert β partly to γ (also described by Yannaquis and Guinier with a "percussion" of a different type) but it will also convert γ partly to β. The situation here is exactly analogous to that described by White, Dachille and Roy [7] for the PbO case which also has a negative *p-t* slope. The pressure + catalysis of bond breakage converts the γ to β, whereas the catalytic effect alone in those grains which are not necessarily at a high pressure causes them to invert from β to the γ phase *which is more stable at low pressures.*

Discussion—New Hypotheses on Transitions. The principle of parsimony demands restraint in the creation of new hypotheses to explain apparent anomalies. The apparent violation of the phase rule in the $ZrO_{2\,\mathrm{mono}} \rightleftarrows ZrO_{2\,\mathrm{tet}}$ transition, due to the coexistence of the two forms over a 150 °C range (see, for example, Mumpton and Roy [8]), and the high-low cristobalite transition [2] is so well established experimentally by many different workers that an explanation is necessary.

When a small volume element of the less dense phase forms inside a crystal of the more dense form, the larger element of the latter containing it is, of course, also placed in compression. The simplest hypothesis is to assume that the transition is suppressed in such cases due to a pure pressure effect on the transition temperature. If we disregard for the moment the anisotropy inherent in the shape factor or that dependent on the mutual crystallographic relationship, one can easily see that the transition temperature of the phase under compressive stress is now altered by an amount determined by the Clapeyron relationship. Since the $\gamma \rightarrow \alpha'$ and $\beta \rightarrow \gamma$ changes involve large volume changes one can expect a substantial change of inversion temperature with pressure. In the latter case it has been calculated to be 350 °C per 1,000 atm. And, since the strength of such crystals is probably in the order of 10,000 atm the effect of the *pressure alone* may be quite enough to suppress the transition from proceeding further. This type of effect *can* account for the abnormal sluggishness of certain reactions and the apparent coexistence of two phases of the same composition over a temperature range, since the volume element of the matrix surrounding the less dense phase may be under sufficient pressure to actually be stable till the matrix crystals fracture.

A great deal has been written on the influence of "strain" in altering the mutual stability relations between two phases, while no clear cut experiments are at hand to demonstrate that it is strain and not "hydrostatic" pressure which is effective. If it is implied, for example, in a one-component system that Phase B will invert to Phase A at temperature T', this situation can be treated very simply by regarding the strained A as another polymorph A* with different free energy. On this basis hysteresis would be explained as being caused by the inversion, let us say, of A→B on the up-cycle at T °C and on the down-cycle of B→A* at a *necessarily lower* temperature, with subsequent change of A* to A. Hence, there is no question of pressure or coexistence of two phases, but merely the failure to distinguish between A* and A. This explanation may be applied to the high-low cristobalite case and possibly to the $\beta \rightarrow \alpha'$ case in Ca_2SiO_4.

In the case of the $\alpha' \rightarrow \gamma$ transition the failure to invert at all on cooling may be due to the pressure stabilization of matrix α' caused by pressure due to formation of γ within the α'. The sluggishness on heating has previously been ascribed to the usual difficulty of reconstructive transitions, but some apparent coexistence may be realized by having some α' crystals forming within γ crystals and requiring a *higher* temperature for the transformation of the resulting strained γ.

The $\beta \rightleftarrows \gamma$ transition now appears to be qualitatively straightforward while anomalies may be found when the curve under pressure is determined quantitatively. While β is "very nearly" a stable phase at atmospheric pressure, it requires only quite low pressures ($\sim$2,000 bars) to stabilize it even at room temperature. γ can be converted to β even at room temperature but expectedly requires a bond breakage mechanism over and above the requisite hydrostatic pressure (to move γ into the β stability field). Likewise, the transformation of $\beta \rightarrow \gamma$ at atmospheric pressures requires mainly the formation of nuclei which can be provided by shearing stresses *which cause fracture.* It is as yet difficult to say whether or not the total strain energy which can be stored in such phases is sufficient to significantly alter the activation energy for nucleation.

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Discussion

H. Krämer and H. zur Strassen

Our recent investigations on the influence of minor components on clinker composition showed some surprising results. The influence of MgO and Na_2SO_4 is greater than that expected and indicated by the phase diagrams.

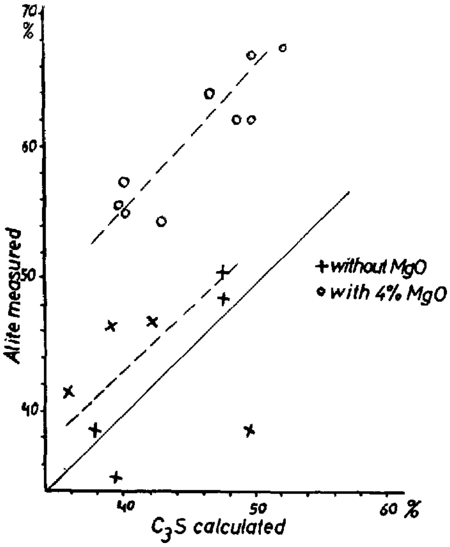

FIGURE 1. *Comparison between C_3S content calculated and alite content measured by microscope.*

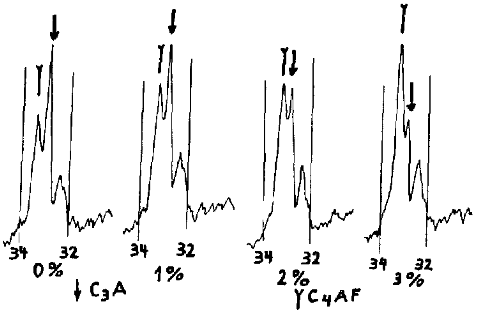

FIGURE 2. *Interstitial phase of clinkers burned with increasing MgO content.*

MgO influences the relation between all the four components and C_3S, and especially the iron phase. Figure 1 shows a comparison between the C_3S content calculated according to Bogue (on the abscissa) and the actual alite content (on the ordinate) which has been measured by microscope in polished sections (point counting method). The straight line would show the alite content if the Bogue formula gave the correct result. It may be seen that in clinkers without MgO the values calculated and measured coincide approximately. For clinkers with 4 percent MgO the average alite content is about 14 percent higher than calculated.

The X-ray diffraction patterns in figure 2 show the interstitial phase of clinkers burned with increasing MgO content. The silicates had been destroyed by ammonium chloride. The relation between the iron phase ($d \sim 2.64$) and the C_3A phase ($d \sim 2.69$) shows that the content of the iron phase with growing MgO content increases, whereas the C_3A phase decreases. These findings confirm both Swayze's melting diagrams and the observations of Cirilli and Brisi [1],[1] to the effect that the iron phase can take up more alumina in presence than in absence of magnesia. If the alumina content increases, the lattice dimensions should shrink [2]. But according to our measurements (table 1), based on the (200) reflection, the contrary is found.

TABLE 1.—*Spacings and intensities (I/sec) of C_3A and iron phase (according to figure 2)*

MgO content:	0%		1%		2%		3%	
	d	*I*	*d*	*I*	*d*	*I*	*d*	*I*
C_3A	2.6922	115	2.6882	104	2.6882	93	2.6859	80
C_4AF	2 6367	57	2 6420	73	2.6481	80	2.6458	91

The increase in the alite content (fig. 1) is the result of all the phenomena which cause a reduced lime requirement of the clinker phase in the presence of MgO: the smaller lime content of the equilibrium melt as shown by the diagrams of Hansen and Swayze; the reduced C_3A content as confirmed by these studies; the substitution of CaO by MgO in the alite itself as shown by Locher [3].

The influence of alkali oxides and alkali sulfates is shown in figure 3. In these diagrams characteristic lines of CaO and alite are marked. It may be seen that the diagram of the clinker containing K_2SO_4 is very similar to that of the clinker without any addition, showing that K_2SO_4 does not influence the distribution of the other components. Very much in contrast to these diagrams is that one with sodium sulfate and you can see that the clinker has suffered a radical change. The alite peak has disappeared whereas the peak of the free lime has grown. This is similar to the effect obtained by adding potassium oxide to the clinker.

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[1] Figures in brackets indicate the literature references at the end of this paper.

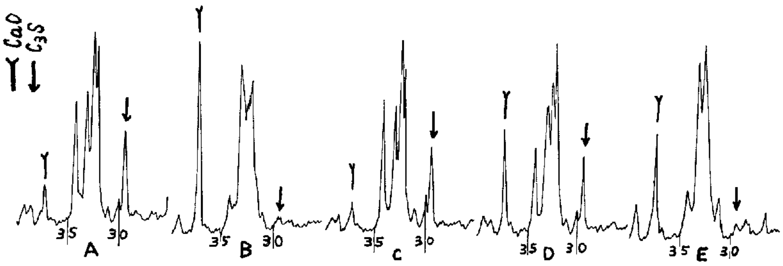

FIGURE 3. *The influence of alkali oxides and alkali sulfates on the clinker composition:*

A—without addition
B—2% K_2O
C—2% K_2SO_4
D—2% Na_2O
E—2% Na_2SO_4

In order to corroborate this statement a photograph of a polished section of this clinker is shown in figure 4. There are grains of C_2S with twin stripes together with plain grains of free lime, thus showing that in this case C_2S and free lime are stable without the formation of alite.

It is our opinion that the sodium sulfate is taken up by C_2S in solid solution, because the ionic radius from sodium and calcium is nearly the same and the SiO_4-group has nearly the same space requirement as the SO_4-group. This solid solution should prevent the formation of alite, in the same way as $KC_{23}S_{12}$ does.

These findings show the important influence of minor components on the phase equilibria of clinker, and the difficulty of drawing quantitative conclusions in particular from X-ray diagrams.

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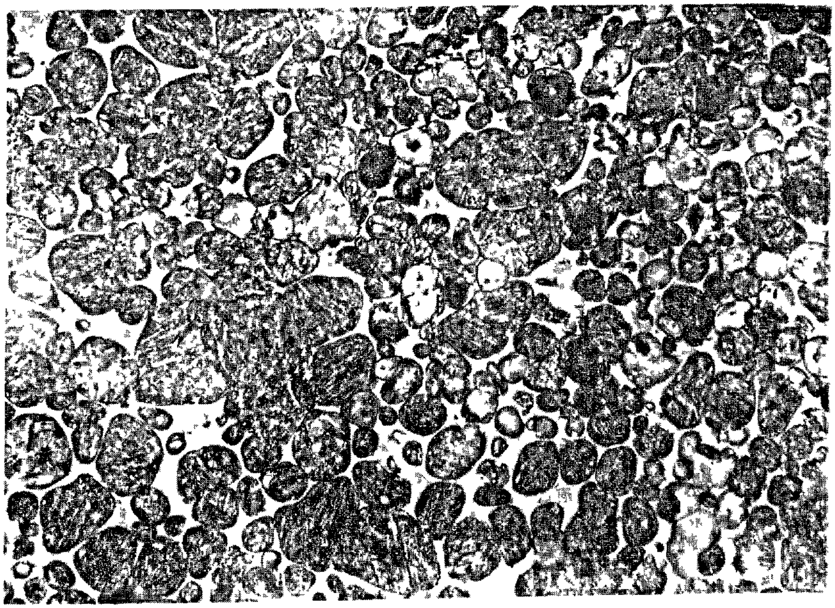

FIGURE 4. *Polished section of a clinker containing 2% Na_2SO_4.*

Discussion

Katharine Mather

Nurse [1] [1] has reported that at the Building Research Station it had been observed that "the 2.71–A peak of pure C_3A was found to wander over a range in various cements." The range was not cited in the paper by Nurse or the supplementary paper by Midgley, Rosaman, and Fletcher [2.] Midgley et al., report that they used the "2.699–A" peak to identify C_3A. The Index to the Powder Data File [3] shows 2.70 A as the strongest line of pure C_3A. With copper radiation, the line falls at 33.14 deg 2θ.

In diffractometer charts made here of portland cements and clinkers, the location of the intense spacing of C_3A has ranged from 33.10 deg 2θ (2.704 A) to 33.20 deg 2θ (2.696 A), in charts where the position of the alite spacing indexed as (20·2) [4] fell in the range 29.90 to 30.04 deg 2θ (2.986 to 2.972 A). The reproducibility of this alite spacing from chart to chart was taken as indication that the specimen surfaces were flat and accurately positioned. It is difficult to attach meaning to discussion of the change in position of spacings unless some criteria are provided of the reproduction of flat specimens with their front surfaces in the same plane.

Nurse, and Midgley and his collaborators, also reported that the latter found C_3A contents by X-ray diffractometry in cements of low A/F ratio that were higher than those calculated according to the Bogue formulas—the reverse of the situation reported by Copeland [5], Brunauer [6], and their collaborators. The A/F ratios of the cements in which Midgley and his collaborators obtained these results were not reported. The finding is also the reverse of that reported by Insley [7], by Ward [8], and by Brown [9] from quantitative determinations of clinker compositions by light microscopy.

It seems possible that both the reported wandering of the location of the most intense C_3A spacing, and the reported finding of C_3A contents above those indicated by the Bogue calculations in cements of low A/F ratio, may arise from the presence of a constituent (or constituents) detected here that gives rise to a spacing at slightly lower diffraction angle than the 2.70–A spacing of C_3A, a spacing which easily may be misinterpreted as C_3A. The best evidence that this spacing (or spacings) at slightly lower diffraction angle (32.84 to 33.00 deg 2θ with copper radiation) is not tricalcium aluminate in a substituted form, lies in the fact that cements whose diffraction charts show this peak do not produce calcium sulfoaluminate in quantities to support this interpretation when the cements are hydrated with excess SO_3. We have found this spacing in cements meeting the requirements of type I and type II of Federal Specification SS–C–192b; the spacing has been much more frequently found in type II cements. We have not examined enough cements of type III and type V to form an opinion on how often this spacing occurs in X-ray diffraction charts of those types.

While we have several pieces of information about this spacing, we have not made a coordinated study of it. We first recognized it in a review of data in which we plotted the spacings of the most intense aluminoferrite peaks and what we took to be the most intense C_3A peak, against the A/F ratio of the cement or clinker for 49 samples. The positions of the (20·2) alite spacing and the combined silicate peaks at about 34.3 deg 2θ with copper radiation were also plotted against A/F ratio as controls of the planeness and position of the specimen surface.

The means and standard deviations of each kind of spacing in each range of A/F ratio were also computed, and the following surprising results for the "C_3A" spacing emerged:

A/F by weight	Mean position of C_3A	Standard deviation	Number of observations
	A		
3.10–2.40	2.7010	0.0030	11
2.40–1.70	2.7018	.0041	12
1.70–1.00	2.7080	.0083	17
<1.00	2.7002	.0042	4

It was reasonable to separate the group containing 17 values into two subgroups, one of 9 values ranging from 2.696 to 2.704, with a mean of 2.7018 and standard deviation of 0.0030, and a second of 8 values ranging from 2.707 to 2.725, with a mean of 2.7150 and a standard deviation of 0.0075. A fifth value of 2.715 in the group with A/F ratio below 1.00 was rejected. We then interpreted these results as showing that the C_3A spacing was 2.700±0.004 A, and that the spacing at approximately 2.715 A arose from some other constituent. We later found that spacings at 2.707 to 2.712 can be resolved by manual scaling into pairs of spacings at 2.700 and at 2.715 or 2.720 A respectively. We did not interpret the 2.715± as the second most intense peak of the aluminoferrite, because of the intensity relations in the charts.

Later, eight type II cements were examined [10] on the diffractometer and also tested according to the ASTM method of test for potential sulfate resistance of portland cement [11]. In studying the diffractometer charts C_3A was regarded as present when some or all of the following features appeared: a spacing at 2.70±0.004 A; presence of any of the less intense spacings of C_3A that are not interfered with in portland cement, especially those of 4.24 and 4.08 A or at 1.558 A. By these criteria, small amounts of C_3A were found in five of the cements. Four had a line that fell in two instances at 2.72 A (32.90 deg 2θ) and in the others at 2.725 A (32.84 deg 2θ).

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[1] Figures in brackets indicate the literature references at the end of this paper.

In the ASTM test for potential sulfate resistance of portland cement, the expansion of mortar bars, containing added calcium sulfate to bring the total SO_3 content by weight of cement to 7.0 percent, is measured at various ages after water storage of the bars. In this particular group of tests, all of the cements appeared to be potentially sulfate resistant, since the expansions were essentially negligible at the usual end point, 28 days, were still small at one year, and were more clearly related to the magnesia content of the cements, as determined by X-ray diffraction or chemical analysis, than to any other feature of the cement composition. When the bars were one year old the test was discontinued and one bar from each set was examined. Only very minor amounts of calcium sulfoaluminate could be found in any of the bars; the relative amounts did not agree with the hypothesis that the 2.720 or 2.725-A, constituent was contributing to the production of calcium sulfoaluminate; therefore it was concluded that the 2.720- or 2.725-A constituent was not a substituted form of C_3A. It appeared probable that it was a modification of one of the calcium silicates.

It is therefore suggested that the most definite way of establishing whether the tricalcium aluminate spacing wanders is, first, to establish reference spacings in the diffraction patterns, by setting tolerances for certain silicate spacings or by adding a substance with precisely known spacings. Second, if the tricalcium aluminate spacing then apparently departs from the value for the pure substance, some of the cement should be hydrated with an excess of sulfate to determine whether the amounts of calcium sulfoaluminate produced are compatible with the amount that should be produced if the wandering spacing arose from a substituted tricalcium aluminate.

It is quite possible that more than one substance may produce a spacing or spacings confusible with that of C_3A. Suzukawa [12] reports that C_3A containing either sodium or potassium can occur in clinker under some circumstances; he agreed with Greene and Bogue [13] that NC_8A_3 had a longer spacing of its most intense line than C_3A. Brownmiller and Bogue [14] on the other hand, found a shorter spacing for NC_8A_3 than for C_3A. Potassium-substituted C_2S or $KC_{23}S_{12}$, the stabilized α' form of C_2S, can exist in portland cement [15]. The cements in which we have found the spacing or spacings confusible with C_3A have generally been cements with more K_2O than Na_2O, but this is the case with most cements made in the United States; they have not been the cements of higher alkali content in the groups in which we have found them.

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Closure

R. W. Nurse

In replying to the discussion it will be easier to deal with specific subjects than to analyze each contribution separately.

At the time of drafting my paper I had not seen the recently published work of Yamaguchi and Miyabe [1][1] which identifies the reactions at 920 and 970 °C in pure C_3S and 830 °C in alite, reactions which were discovered at the Building Research Station and reported by Jeffery at the 1952 Symposium. This work shows quite clearly that preparations processed at such temperatures as 1,500 °C will take up impurities to an extent dictated by the solubility in the trigonal phase; these solubility limits cannot therefore give any quantitative information on the unit cell contents of alite (the monoclinic form). Since the transition temperature of $C_{54}S_{16}$-AM was lower than that of pure C_3S, MgO and Al_2O_3 are presumably more soluble in the trigonal

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[1] Figures in brackets indicate the literature references at the end of this paper.

form than in alite. Differences in heat treatment can therefore readily account for the different results obtained by the author and by Locher, Krämer, and others. The practical importance of pursuing this line of research is brought out by Welch and Gutt.

The important contributions concerned with effects of ash and reducing conditions and with reaction velocities (Heilmann, Kondo, Longuet, Suzukawa, Woermann) raise the question of the low temperature decomposition of C_3S. This reaction is normally very sluggish, but it is suggested that various impurities will catalyze the reaction until it becomes a serious problem to the cement chemist. This may well be so, and the possibility was considered by many of the earlier authors who studied the problem. I wish however to draw attention to the fact that secondary free lime can form from the decomposition of C_3S by other processes. In the first place, where the impurity oxide has more than one possible valency, the metal may change from an anionic to a cationic role and so displace a certain amount of CaO. In the second place, if the impurity forms a high temperature solid solution with C_2S, as so many do, then the phase assemblage C_3S–CaO–C_2S solid solution may become stable. If rates of reaction were fast enough all the free lime would be present as primary crystals, but in many cases long processing at high temperature is necessary to form the solid solution; in such mixes the C_3S forms first and later decomposes, giving secondary free CaO. Thus many impurities such as barium and strontium silicates (Toropov) sodium sulphate (Krämer and zur Strassen) will behave in a manner analogous to that of P_2O_5 as described in the studies of the present author and his colleagues. FeO, as Woermann shows, decomposes C_3S, and this must in part be caused by the fact that fayalite goes into solid solution with C_2S as established by Bowen, Schairer, and Posnjak [2].

The discussion on C_2S shows that we still are not able to control all the variables affecting the transformations of this phase. Thus Yannaquis finds that alkalies do not stabilize the β-γ inversion, but many other workers disagree; he very correctly draws attention to the importance of nucleation and crystal size.

Majumdar and Smith point out the range of coexistence of γ and α' and suggest that this implies a differing chemical composition for the two phases. I think this is an additional reason to suspect solid solution with CaO necessarily present as one of the reactants from which the C_2S is formed. For instance de Keyser's reaction (Symposium 1952) at 900 °C could be interpreted as exsolution of CaO from part of the γ-C_2S with a corresponding rise in the γ-α' inversion temperature. This is confirmed by his observation of increased free CaO in the X-ray pattern. Material prepared hydrothermally or by dehydration will tend to contain free CaO because the lime/silica ratio in any hydrate formed is likely to be less than 2.0. As with alite, we must be careful to determine the solubility of impurities by heat treatment within the range of stability of the polymorph under study. The enlargement of the β-C_2S unit cell suggested by Majumdar and Smith is confirmed by work in progress at Cambridge [3] and this suggests that the anomalous X-ray patterns for β-C_2S recorded by Toropov and also by Majumdar and Smith may arise from ordering reactions taking place during cooling.

I was very glad to read the contribution from R. Roy, since it repeats and confirms so many observations in my paper on C_2S, presented to the 1952 Symposium. The temperatures given at that time are all somewhat higher than those of Roy; this may be due to the kinetic nature of the DTA results, but may also be caused by the difficulty of maintaining a known and uniform temperature in a diffractometer specimen. Roy's figure confirms part of my figure 6, but he is able to put a calculated scale on the ordinates; his first hypothesis of the effect of pressure on the C_2S inversions is also described in my 1952 paper (pp. 67–8). The second part of his hypothesis is very interesting and it may be that the small and as yet unexplained breaks found in some DTA curves of C_2S can be attributed to "strained" phases, or what is almost the same thing, order-disorder changes.

Most of the hysteresis in phase changes can, I am sure, be explained by nucleation theory.

The aluminates $C_{12}A_7$ and C_5A_3 have been mentioned by Suzukawa and by Majumdar and Smith. I would like to reaffirm the importance of atmospheric water in experiments on these compounds. At the Building Research Station we have been trying to finalize the phase diagram for CaO-Al_2O_3 over the last 10 years or so. It was not until we recognized that the ternary behavior of this system was caused by atmospheric water that some consistency was obtained. Even now, we do not feel able to publish all the results, but since they conplement some data given later in this volume by Roy (paper III–S9) some details observed by Welch will be given.

$C_{12}A_7$ prepared by crystallization in bulk from the liquid on cooling from 1,450 °C in air was found to have the following properties: density 2.68; refractive index 1.61 (Na light). During subsequent reheating in air of the pulverized material a gradual gain in weight took place which reached a maximum of about 1.3 percent at 1000 °C. This reheated material was then cooled quickly and on further examination by microscopy and X-ray diffraction was found to have an increased refractive index of 1.62 and reduction of the unit cell volume amounting to 0.3 percent; the density had also increased to 2.73. It was shown conclusively that water had been taken into the structure, by reheating this material in a dry oxygen-free nitrogen atmosphere. In these circumstances a sample heated to 1,450 °C lost 1.33 percent in weight, of which 1.20 percent was recovered by absorption in $Mg(ClO_4)_2$. The sample was maintained in the same atmosphere during cooling and crystallized essentially as orthorhombic C_5A_3. The presence of water vapor in the atmosphere in which $C_{12}A_7$ is heated has a marked effect on the melting point. In moist air the $C_{12}A_7$ liquidus temperature is at 1,391.5 °C whereas in dry argon $C_{12}A_7$ melts incongruently to CA + liquid at 1,374 °C. Since C_5A_3 melts incongruently at 1,361 °C in air and at 1,352° in dry argon it must necessarily be regarded as a phase which is metastable with respect to $C_{12}A_7$ at temperatures close to its melting point.

The question of the ferrite phase is so closely linked with the general question of cement constitution that I will deal with both together. It follows from the published work of Swayze, Newkirk, and Thwaite that the quaternary cement system must be subdivided into the phase assemblages I have listed in my main paper. Some important conclusions follow. For instance a cement may be formulated for high sulfate resistance, with a low A/F ratio. If the lime saturation factor is not too high, it will fall within the assembly C_3S–C_2S–ferrite solid solution and contain no C_3A; a rise in the L.S.F. can however throw the composition into the assembly C_3S–C_3A–ferrite solid solution,[2] when the sulfate resistance will presumably be lessened. In order to judge adequately the importance of such calculations we need to know with confidence the values of the limiting ferrite solid solutions. Krämer and zur Strassen in their contribution reaffirm the opinion of earlier workers that these compositions will be altered by the presence of minor components. It is to be hoped that it can be shown that the compositions will be essentially constant for all normal portland clinkers, but they must be determined on clinker, as well as of course for various pure oxide systems. The experimental approach outlined by Majumdar and Smith seems very promising for this study.

The ferrite system is so difficult experimentally that it should be attacked by all the methods available. I agree with Toropov and Swayze that the microscopic method should not be neglected, but the results should be checked and compared with X-ray determinations. On the theoretical side it seems unnecessarily restrictive to insist on stoichiometric end members for the series; if Toropov is correct in saying there is a series from C_2F towards C_5A_3 as well as "C_2A", then there are ternary solutions which cannot comply with the structural formula. Single crystal X-ray work would throw some light on this.

It is difficult to believe that the assemblage C_3S–C_3A–ferrite solid solution occurs in real clinker, since it implies the disappearance of C_2S in favor of C_3A, and it is very rare not to find C_2S in a clinker. However, most clinker contains free CaO, and potentially therefore, if equilibrium were achieved, the C_2S could disappear. The basic question is the composition of the liquid at clinkering point; will this correspond to an invariant point with CaO and C_3S or C_3S and C_2S? Provided none of the phases are "protected" as described by Swayze, I would suggest that the composition of the liquid will be determined by the ratios of anions and cations and will not be materially affected by the fact that full combination between CaO and SiO_2 has not yet been reached for the solid matter. If this is so, in clinker where uncombined CaO is still present, the assembly C_3S–C_3A–ferrite will be replaced by CaO–C_2S–C_3S–C_3A ferrite, which is frequently observed.

Since the conclusion from our discussion can only be that much more remains to be done, it would be appropriate to conclude by discussing techniques. However, the method of X-ray diffractometry has been thoroughly discussed at many points in the program, so that I will only thank those experts who have contributed to this question. The standardizing procedure suggested by Smolczyk seems attractive. I would also agree with Mrs. Mather concerning the need to look for substances interfering with C_3A. I have found in certain clinkers substantial quantities of α'-C_2S, and in such cases the C_3A peak at 32.9° 2θ is confused. I am glad to say that the suggestion to exchange standard clinker samples has been well received and we may all hope that the studies of the next few years will solve many of our problems.

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Paper II-2. Crystal Structures of Clinker Constituents*

Fred Ordway

Synopsis

The concepts of a phase, a compound, and a solid solution, based on the mathematical abstraction of a continuum bounded by discontinuities of infinitesimal width, are discussed in relation to the known characteristics of the structures of real solids. Present knowledge of the structures of clinker constituents, as revealed by the literature, is outlined.

Résumé

Les concepts de phase, composé, et de solution solide, basés sur l'abstraction mathématique d'un continu limité par des discontinuités de largeur infinitésimale, sont discutés par rapport aux caractéristiques connues des structures de solides véritables. La connaissance actuelle des structures des constituants du clinker, telle que la révèle la littérature, est brièvement exposée.

Zusammenfassung

Die Begriffe einer Phase, einer Verbindung und einer festen Lösung, wie sie durch die mathematische Abstrahierung eines Kontinuums, welches durch Diskontinuitäten unendlicher kleiner Weite begrenzt wird, hervorgebracht werden, werden in ihren Beziehungen zu den bekannten Merkmalen der Strukturen wahrer fester Körper besprochen. Die heutige Kenntnis der Strukturen der Klinkerbestandteile, wie man sie in der modernen Literatur findet, wird klargestellt.

Introduction

In the study of matter, its structure and its behavior are inseparable. Dr. Nurse probably found it difficult to exclude structural considerations from his paper on phase equilibria and clinker constitution, and the availability of his paper was almost a prerequisite to avoid duplication in preparing this one. Rather than ignore this close relationship, we should emphasize it. Accordingly, I take the liberty of repeating fundamentals well known to the student of phase equilibria, and others well known to the structural chemist, in order to depict a fundamental philosophy accommodating both.

Fundamental Concepts

The phase equilibria of the clinker constituents, their formulas, and their structures are all merely different aspects of the same phenomenon. We might describe this phenomenon from the viewpoint of statistical thermodynamics as the equilibrium behavior of a system of atoms of O, Ca, Si, Al, Fe, Mg, K, Na, etc., in a given range of temperatures, of compositions, and perhaps of pressures. The complete theory would contain both the chemistry of cement clinker, as embodied in the equilibria between phases, and the structures of all the phases. We cannot actually derive the phase equilibrium relations from fundamentals, but our observations of them must be interpreted in the light of theoretical concepts. To discuss the relation between our concepts of phase equilibria and structure we begin with the former.

Determinacy

The basic premise of a thermodynamic discussion is the assumption that any system to be discussed can have but one equilibrium state under any specified conditions. Whether this state is a result of inherent determination in all of nature, or of averaging the somewhat uncertain individual behaviors of very many atoms, is not initially important; modern statistical theories and the classical ideas of earlier days both justify the expectation of highly precise determinacy in macroscopic samples under most conditions.

The single "true" equilibrium is thought of as a state to which the system eventually returns, after any change in conditions, when restored to the original conditions. The equilibrium is called metastable if certain changes, such as high temperature or pressure, make accessible a new equilibrium state which the system assumes preferentially. The identification of any equilibrium as "true" rather than metastable must be regarded as provisional, limited by convenience and by the range of experimental conditions that has been explored at the time. We often discuss "true" equilibrium states in chemistry which, from the viewpoint of nuclear physics, are clearly metastable.

In the present discussion, we take equilibrium states to be definable in practice by allowing adequate time or choosing an appropriate sequence

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of conditions, so that confusion with possible metastable states is obviated. We assume in principle that every sample of specified composition, temperature, and pressure will attain in finite time a state that differs by less than experimental error from a true equilibrium, and that this true equilibrium depends only on the specified conditions, not on previous temperature, pressure, or compositions of materials from which the sample was synthesized.

Continuity and Discontinuity

The entire thermodynamic theory of phase equilibria is based on the fundamental assumption that we can distinguish between continuity and discontinuity in the intensive scalar properties (those properties independent of the quantity of material and the spatial orientation) of a sample of matter at equilibrium. The distinction is applied in two ways—firstly to the variations in properties with position within the sample, and secondly to the variations in properties with changing composition, temperature, or pressure.

Continuity With Position

We may examine a sample of matter by various experimental methods. Any such examination is basically a comparison of a property of the sample, or part of it, with the same property of another sample, or another part of the same sample. If the comparison is made with a standard that is related to some accepted units of measurement, and it yields a quantitative result, we say that property of the sample has been measured rather than merely compared. Intensive scalar properties are, of course, the only significant ones because we may take a sample of any desired size, within the limits of the experimental technique, and the comparison of properties must be independent of orientation.

From the given sample at equilibrium, we may select small portions of matter at various positions and examine these separately. Such examinations, in principle, form the basis for all statements as to the continuity or discontinuity of properties. Thus, any such statement must always represent definite limitations in the variety of properties compared, the sensitivity of comparisons, the smallness of the portions of the sample taken for examination, and the closeness of successive points at which they are taken.

Phases at Equilibrium

If there is no discontinuity in the variations of intensive scalar properties from point to point, the sample is said to be homogeneous, and to consist of a single phase. We suppose that composition, temperature, and pressure of the sample are the only significant variables, there being no gradients of magnetic, electric, or gravitational fields, for example; then the intensive properties of a single phase at equilibrium are not only continuous but constant throughout. The phase may be identified and distinguished from other phases by the precise values of these constants at stated conditions of composition, temperature, and pressure. If more than one phase is present, each is separated from the others by a surface across which at least one intensive property exhibits a discontinuity.

Arbitrariness of Distinguishing Phases

The intensive properties whose values and continuity identify a phase include, in principle, all the ordinarily measured properties such as density, refractive index, conductivity, specific heat, vapor pressure, lattice constants, etc. Moreover, they include all derivatives, of whatever type and order, of such properties with respect to the independent variables of composition, temperature, and pressure.

Clearly the choice of an experimental basis for deciding whether two portions of a given sample are the same phase must be fundamentally arbitrary. We examine the sample by certain methods and make those distinctions which seem profitable. Identity of microscopic appearance and X-ray diffraction pattern, for example, are common criteria by which two homogeneous portions of a sample may be identified as the same phase.

We must always understand that study by other methods may later reveal significant differences in physical properties. If there are significant differences in behavior in any process of interest to us, then the two phases must be distinguished, however difficult that may be. Fortunately we can usually expect significant differences in energy, which cause significant chemical differences, to produce significant differences in physical properties as well. Systems which can form several distinguishable structures of approximately equal energy may be far more difficult to elucidate than those forming a few widely different structures.

A second element of arbitrariness is spatial resolution of the experimental technique. Clearly the structure of a sample cannot be said to change discontinuously on an atomic scale at phase boundaries, any more than it does within a phase. The spatial resolution of our examination of the sample therefore must be coarse enough that we do actually recognize discontinuities at the phase boundaries; the resolution may be submicroscopic, but not atomic. Even with this restriction the results of differing techniques may disagree. A sample that is microscopically homogeneous, for example, may be revealed by the electron microscope as a matrix of one phase containing droplets [Sastry and Hummel, 1959; Krogh-Moe, 1959] or crystallites [Hsiao, 1958] of another.

The status of matter within the region of transition between phases is often ambiguous when details of structure are considered. We regard a polycrystalline sample as homogeneous if properties are identical within all grains, and we may treat the twin planes of a twinned crystal as the grain boundaries of a polycrystalline sample. We are assuming that any grain boundaries and imperfections (such as are described below in the section on "Real Crystals") not in equilibrium have negligible effects on the properties investigated. Whether this idealization is valid depends upon the phenomena and materials under discussion.

For example, we may find it profitable to identify two samples as β-dicalcium silicate even though the microscope reveals one to be very finely twinned, and the other not [Insley, 1936; Insley et al., 1938]. Two crystals of a metal which are identical in appearance, on the other hand, may be sharply distinguished for other purposes because one has many dislocations in its structure, and the other not.

Existence Regions

For each different phase capable of existence at equilibrium there is a volume in the $(N+1)$-dimensional space, corresponding to the range of conditions under which the phase is present in a mixture. We may call this entire volume the existence region for that phase. Clearly a part of the existence region must correspond to the presence of that phase alone; for if the phase is present in any proportion in a mixture corresponding to a given point in the $(N+1)$-dimensional space we can arrive at its solitary-existence region by moving the mixture point along those lines of constant temperature and pressure which correspond to removal of the other phases present. The N-dimensional boundaries of the solitary-existence region correspond to the phase changes that take place with various changes in the composition, temperature, and/or pressure of the homogeneous sample. The mixture point, in crossing one of these boundaries, may move directly into an adjoining solitary-existence region, corresponding to the complete transformation of the entire sample into a new phase; or it may move into a region where another existence region overlaps the first, corresponding to the appearance of a second phase without disappearance of the first.

Adjoining Existence Regions

When the mixture point crosses a phase boundary where two existence regions adjoin but do not overlap, the new phase has the same composition as the original phase. Such a situation may occur in a polymorphic transformation or the congruent melting of a solid.

Overlapping Existence Regions

If the phase change is appearance of a second phase without disappearance of the first, the principle of determinacy requires that the second phase must have a different composition from the first. Each phase is represented by a point in the $(N+1)$-dimensional space, and all possible mixtures of them correspond to the line segment joining these two points. Mixtures at different points along this line segment are in the same state, having the same temperature and pressure, and differing as to composition only in the proportions of the two phases. A family of such line segments, called tie lines, defines all the possible equilibria involving coexistence of the two phases.

Continuity With External Conditions

Our sample may also be examined by measuring its properties between successive changes in the externally imposed conditions of composition, temperature, and pressure, rather than at various points of the sample under fixed conditions. If each measurement represents equilibrium state, the series of measurements indicates the manner in which the equilibrium properties change with the external conditions. The relationships ascertained in this way are definitely limited in the variety of properties measured, the precision of measurement, and the smallness of the changes in conditions between measurements.

Phase Changes

When the composition, temperature, or pressure of a homogeneous sample is changed, we identify the sample as that same phase always, and only, if it remains homogeneous and its intensive properties exhibit no discontinuities. A discontinuity in any property with changing external conditions thus corresponds to a phase change.

Arbitrariness of Distinguishing Phase Changes

In recording any experimental study of phase changes we must always admit that future investigation, through more precise or more sensitive experiments, may detect a phase change where none had been thought to exist. Conversely, it may happen that a phase change already known may represent such slight departures from continuity, in all properties of importance to a given problem, that it can safely be ignored.

Geometrical Description of Phase Equilibria

Much of the power of phase-equilibrium theory resides in the development of geometrical ideas that are suggested by the foregoing discussion. The $N-1$ independent composition variables, together with temperature and pressure, form the $N+1$ coordinates of a space in which each point represents a unique choice of external conditions for a mixture of N components. The principle of determinacy requires that there be a single equilibrium state corresponding to each point. In that equilibrium state, the sample may be either homogeneous or heterogeneous; we identify the state by characterizing the one or more phases present. The totality of phase equilibria may be defined by prescribing, either from theory or from experiment, the region in the $(N+1)$-dimensional space corresponding to the existence of each phase that can exist.

Similarly, any coexistence region defined by the overlapping of two or more existence regions must be characterized by ties of constant temperature and pressure connecting the coexisting compositions. With the usual sets of composition coordinates, each tie is a line segment, a scalene triangle, an irregular tetrahedron, or a simplex [see Sommerville, 1958] in a higher-order space. Whatever its order, the tie represents a region within which the mixture point may move without a change in state.

The state is completely specified by the specification of any one of the coexisting phases. Thus any displacement of a mixture point that corresponds to a real change in state, within the same coexistence region, corresponds to a displacement of the point for each coexisting phase. The number of independent variables that can effect such a change must be the same as the dimensions of the boundary between the coexistence region and any adjoining solitary-existence region, since each of the individual phase points joined by a tie lies on such a boundary.

The Phase Rule

The number of independent variables determining the position of a mixture point in the $(N+1)$-dimensional space is $(N+1)$, but there are $(P-1)$ independent variables, corresponding to the subspace which is the tie for the P coexisting phases, that do not affect the state. Therefore the variance or number of independent variables affecting the state, in any region is $V=(N+1)-(P-1)=N-P+2$. This is the Phase Rule of Gibbs [1876–8] [Butler, 1936].

Phase Diagrams for Condensed Systems

The multidimensional space with a delimited region for existence of each possible phase constitutes the complete phase diagram of the system. Any intensive scalar property of a sample is continuous along any path that does not cross a boundary of one of the existence regions. Conversely, a discontinuity in even one intensive scalar property along any path in the phase diagram determines a point where that path crosses a phase boundary.

This fact is the fundamental basis for constructing phase diagrams. If the diagram is being constructed from theory, the boundaries are located where discontinuities occur in the calculated properties. If the diagram is determined by experiment, the boundaries of existence regions are located by detecting the discontinuties in the laboratory.

Instead of the full pressure-temperature-composition diagram, a section through it at a constant pressure value of 1 atm is ordinarily considered in clinker chemistry and many other fields. Strictly speaking, the clinker systems usually studied contain no vapor phase at atmospheric pressure. Any possible interactions with a gaseous phase must be considered carefully in the interpretation of experimental results. For example, the vaporization of an oxide constituent in sufficient amount to alter significantly the composition of a solid or liquid requires that the vapor phase be counted in determining P, and sufficient dissociation of an oxide to affect its composition requires that oxygen be counted in determining N.

If the idealization ignoring vaporization is satisfactory, we may restrict the discussion to condensed systems; the remainder of this paper is so restricted. The Phase Rule, with pressure fixed, becomes $V=N-P+1$.

A chosen mixture, at high enough temperatures, will be entirely liquid. For our purposes the liquid is taken to be a single phase, there being no immiscibility reported for the silicate liquids occurring in cement clinker. The liquid phase exists alone down to the upper limiting temperature for coexistence of a solid phase. This limiting temperature, or freezing point, is a function of composition. The boundary of the solid-phase existence region, defined by this function, is called the liquidus.

At a low enough temperature the mixture is entirely solid. As temperture rises from this point, melting begins at the low-temperature limit of the liquid-phase existence region. This limiting temperature, or freezing point, is also a function of composition. The boundary defined by this function is called the solidus. The most significant aspect of most of our phase diagrams, with respect to the character of the solid phase, is the relationship between the liquidus and the solidus.

Solids of Definite Composition

In cement clinker chemistry, as in most chemical studies of a prescribed realm of materials, we give first attention to the compositions that seem most important because they represent phases that are often found in the mixtures observed. That is, we are interested first in those phases whose existence regions are relatively large, but whose solitary-existence regions are comparatively small.

Of course the extent of these regions in composition is a function of the temperature. Above the highest melting point, for instance, the liquid phase has a solitary-existence region extending throughout composition space, and no coexistence regions. In this situation, no one composition can be considered more important than another.

At a eutectic temperature, on the other hand, the liquid's solitary-existence region is but a single point while its coexistence regions may range through almost the entire composition space. The eutectic point is one vertex of a tie that covers a sizable region of composition space, and thus has significance to a correspondingly sizable range of mixtures. Such liquid compositions, representing liquids present at the beginning of melting or the end of crystallization, have rightly been emphasized in Dahl's [1955] discussion of burnability and in studies of multi-component systems such as $CaO-5CaO\cdot3Al_2O_3-2CaO\cdot Fe_2O_3-2CaO\cdot SiO_2$ [Swayze, 1946] and $Na_2O-CaO-Al_2O_3-Fe_2O_3-SiO_2$ [Eubank, 1950].

As with liquids, the solids may be rated in importance according to the range of conditions under which each is observed to be present in clinker. That is, a given solid might be considered *important in proportion to the size of its existence* region in composition space and, *ceteris paribus*, to the range of temperatures over which it can exist. Such a consideration would clearly emphasize the ideal conception of a chemical compound—a crystalline phase of unvarying composition, capable of existing in equilibrium with solutions (i.e., melts) of widely varying composition and temperature.

Compounds

The ideal compound, if it melts congruently, would necessarily be a composition at which the solidus and liquidus coincide. The shape of the liquidus temperature surface as a function of composition around the melting point of a compound has been argued extensively by many authors. A distinction has often been made between a "dissociating" compound and one that is completely stable. Gibbs [1876–8] showed that the chemical potential of a given component in a mixture must be negatively infinite if that component is entirely absent from the mixture, and finite if the component is present. As Wilson [1944] has reemphasized, the junction of liquidus and solidus at a congruent melting point must be a horizontal tangency, except where the chemical potential exhibits a singularity because a component disappears. Thus the liquidus maximum for an intermediate compound can be sharp only if the compound has an infinitely negative free energy of formation (i.e., infinite stability).

The assumptions we have stated regarding the attainability of equilibrium must rule out the presence of infinitely stable compounds and thus, in principle, the existence of sharp maximums in the liquidus. A compound of relatively high stability is not forbidden, however, and may in principle have a liquidus maximum of great curvature which appears sharp within experimental error. The shape of the maximum has been interpreted in terms of the "degree of dissociation" of the compound on melting [Kremann, 1904; Kendall and Booze, 1925; Bennett and Wain, 1936].

Different authors treat in different ways the experimental observations of apparently sharp liquidus maximums reported in the literature. Zernike [1955] speaks of the system of two substances that form a perfectly stable compound as "a simple combination of the systems of each of the substances with the compound . . . obtained by just placing side by side the corresponding diagrams of the two systems," and cites phase diagrams from the literature that appear to represent such relations. Ricci [1951], on the other hand, emphasizes the reversibility of formation of the compound, and says the completely stable compound "is not a binary compound in the phase rule sense. . . . It is merely a third substance . . . giving rise to two independent binary systems."

This view is consonant with the fundamental development of Gibbs [1876–8], and seems to avoid an inherent contradiction in Zernike's viewpoint. Discussing phase equilibria in any system involves the basic assumption of equilibrium in any mixture of the specified components—but there is no mechanism for equilibrium between a component in the perfectly stable compound and the same component elsewhere in the sample. One could scarcely treat the system H_2-H_2O-O_2 or H_2-H_2O-H_2O_2-O_2 as a binary system, for example, at such low temperatures that equilibria requiring molecular changes are inaccessible.

The basic rule of continuity that defines a phase, which we have discussed under "Continuity and Discontinuity" argues for the viewpoint of Ricci [1951] rather than that of Zernike [1955]. The free energy per unit mass and its derivatives, being intensive properties, must be continuous functions of composition, temperature, and pressure for a single phase. The geometrical derivation of the liquidus from the free energy surfaces [Gibbs, 1876–8; Butler, 1936] must lead to a liquidus temperature that is similarly continuous in value and slope. In principle, a sharp maximum in the liquidus temperature for a solid phase of unchanging composition would have to correspond to a discontinuity in the liquid phase. The binary solutions between the perfectly stable compound and its separate constituent substances must therefore be considered different phases. This appearance of a phase change as composition varies in the liquid (or even in the gas phase, for a sublimation curve with a sharp maximum) would be quite reasonable because the presence of the perfectly stable compound must lead to definite discontinuities in value or slope of certain properties of the fluid phase.

The compounds related to cement clinker chemistry do not approach perfection, as we have used the term with reference to stability. They are considerably, if not completely, dissociated in the high-temperature liquids. They may, however, approach ideality in our sense of the word—having an unvarying composition in the solid phase.

For such an ideal compound, the liquidus temperature must be continuous in value and slope, and pass through a maximum at a congruent melting point. The solidus, on the other hand, must be quite discontinuous. If our compound forms a eutectic with other ideal compounds, for example, the solidus temperature is equal to the eutectic temperature everywhere within the composition simplex joining the compounds, but at each vertex it rises abruptly to coincide with the liquidus at the melting point of the corresponding compound. At all the boundaries of the composition simplex it rises abruptly to coincide with the eutectic temperatures of the boundary systems.

For such an ideal compound, the well-known methods of purification (by crystallization from the solution), characterization (by the melting point), testing for purity (by sharpness of melting), and confirming identity (by mixed melting with a known sample) are applicable without reservation. Healthy skepticism as to the universal applicability of any idealization and the physical reality of the discontinuous solidus impels us to expect, however, that every solid phase will deviate from ideal behavior to some extent. If the deviations are insignificant, we may speak of "the small composition range called a compound" [Searcy, Williams, and Schissel, 1960]. If the deviations of the solid from fixed composition are significant, we must apply the more general term "solid solution."

Solid Solutions

Taking the more general viewpoint, we may regard every solid phase as stable over some finite range of composition. If the range is small, we may term the phase a compound and ignore its variability of composition—it is always observed to have the same identifying properties, within experimental error. If the range is larger, on the other hand, the variability of properties may render even identification difficult.

We refer to solid phases of variable composition as solid solutions without implying that their solitary existence regions necessarily have any particular shape or extension in composition space. The designation of "components" of the solid solution may often be profitless, or even misleading if it suggests unsound analogies to the properties of liquid solutions.

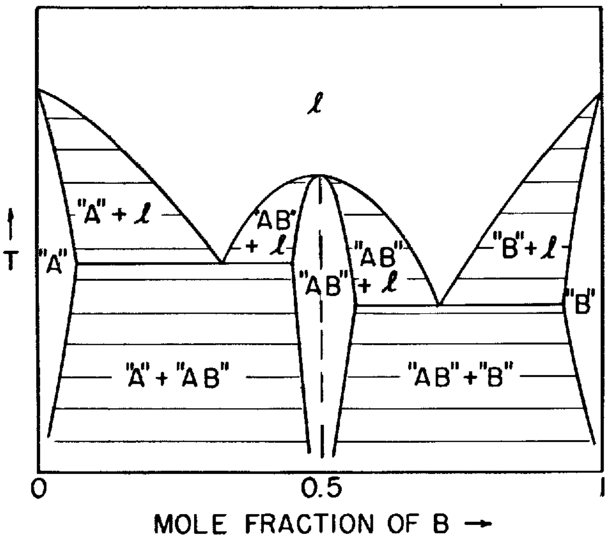

FIGURE 1. *Phase diagram for a hypothetical binary condensed system A–B, with tie lines in two-phase regions.*

A given solid phase might be called a solution "between" or "among" any set of linearly independent compositions that lie within its solitary existence region, but this usage is misleading if the same phase can have compositions outside the tie so defined.

Conversely, the solid phase of variable composition is sometimes called "a solution of *the solutes* in *the solvent*." The solutes may be any set of compositions defining a tie that encloses the solitary existence region, and the solvent may be any composition within the solitary existence region. In such a description, there is no particular basis in chemical data for naming any set of solutes other than the ultimate components of the system, but the unique composition of the solid solution that melts without decomposition might possibly be named as the solvent.

The idea that every solid phase has a solitary existence region of finite extent in composition is a satisfactory generalization because it includes the ideal compound as a limit. For example, the phase diagram in figure 1 for a hypothetical binary system A–B has finite solid-solution regions around the pure components A and B. Any of these regions might be broadened, or might be shrunk to infinitesimal width, without qualitatively changing the phase-equilibrium relationships. Any one that was reduced in width to a vertical line would represent an ideal compound. The phase could then be indicated by its formula without quotation marks.

The situation near the melting point of "AB" is shown more clearly in figure 2. A mixture point in the coexistence region ("AB" + l) below the melting point T_M can move along its tie line, as indicated under "Overlapping Existence Regions," without altering the state of the mixture. Only a change in temperature, moving it to a new tie line, produces a change in state. This being a two-phase binary equilibrium, the phase rule for condensed systems requires that the number of variables affecting the state be $V=P-N+1=2-2+1=1$.

At the melting point, the liquid and solid have the same composition. The phase rule requires

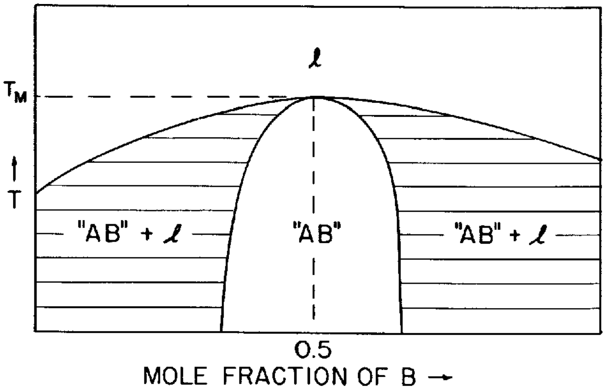

FIGURE 2. *The system A–B in the neighborhood of the melting point of "B," showing smooth maximum in liquidus and solidus.*

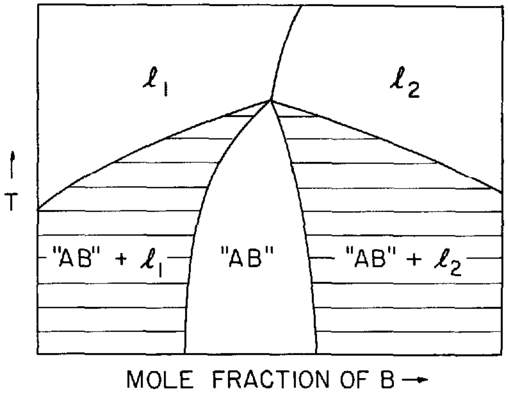

FIGURE 3. *Hypothetical phase relations for a sharp maximum in the liquidus of "AB": discontinuous liquid phase.*

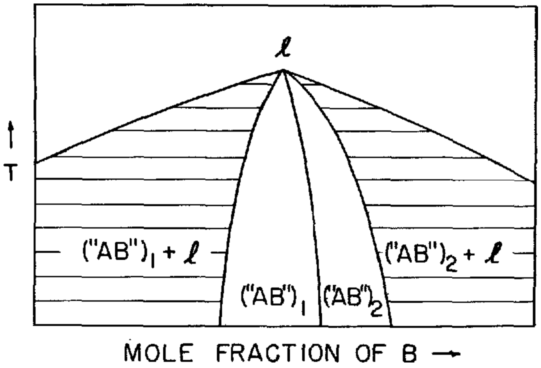

FIGURE 4. *Hypothetical phase relations for a sharp maximum in the liquidus of "AB": discontinuous solid phase.*

the same variance, since there are still two phases, but the principle of determinacy requires that one of the two phases disappear upon any infinitesimal change in temperature. Thus the coexistence region at T_M must be a single line of zero slope—the limiting tie line—and the liquidus and solidus must have smooth maxima which are tangent at the melting point.

The diagram would approach that for an ideal compound as the "AB" region narrowed, and the solidus increased in curvature at its maximum.

The existence of a sharp maximum in the liquidus of a congruently melting solid phase, as described by Zernike [1955], corresponds to a variance of zero at the melting point because there is no smooth curve passing through that point and lying in the solid-liquid coexistence region. The phase rule requires $0=N-P+1=3-P$. Thus the point must be one at which three phases coexist. Any such point must correspond to a discontinuity in either the liquid phase, as in figure 3, or the solid phase, as in figure 4.

The discontinuity in properties of liquid or solid with the composition that is associated with an observably sharp liquidus maximum would in general have to be found by experiment, but for systems of interest in clinker chemistry we expect the liquids to show no discontinuities, and therefore expect that any such phenomenon would be due to a discontinuity in properties of the solid solution. The origin of the unique compositions we think of as compounds, and the nature of the changes in solid solutions with composition, will have to be discussed in terms of the concepts of structural chemistry rather than the more abstract considerations of thermodynamics.

The Structural Basis of Definite Compositions

The traditional introduction to chemistry, for pedagogical simplicity, is a Daltonesque picture of a universe made of compounds in which the chemical elements are combined in definite, simple, and integral ratios of their atomic weights. The expectation of definite, simple, and integral chemical formulas has been of tremendous value in the understanding of chemical entities. In organic chemistry, hundreds of thousands of individual compounds have been characterized in these terms.

Although the ratios of the more complex organic compounds may no longer be simple, they remain definite and integral. The great success of research in this field is due in large degree to the existence of stable units of structure which can pass without destruction through solid and liquid (and also frequently gaseous) states. These units are called the molecules.

Molecular Structures

The hypothetical perfectly stable compound we have discussed as a limiting case is by definition a molecular compound, since its complete stability extends through the gaseous as well as the solid and liquid states. Many of the usual illustrations in introductory chemistry are molecular compounds approximating this limiting case, because the structural basis of their compositions is simplest and was therefore historically first to be elucidated.

The molecular compound consists of aggregates of relatively few atoms having relatively great stability. The forces between atoms in these aggregates (covalent bonds) are strong, specific, and directional. A unique configuration of atoms that saturates these forces is bound together far more strongly than any pair of already saturated aggregates that may happen to be adjacent. The deformation or melting of a molecular solid, or the flow or vaporizing of a molecular liquid, separates adjoining molecules without destroying them as entities.

The molecules of all substances, to the extent that they behave as independent, rigid masses, make equal contributions to the pressure in the gaseous phase and have equal effects on the well-known colligative properties of the liquid phase. From these properties the total mass of a single molecule can be established. The number of atoms of each type in a molecule is, by definition, an integer. Therefore the proportions in the formula of the molecular compound must be definite and integral. Those molecules which are easily studied in the gaseous phase have formulas that are also comparatively simple. The study of the simpler molecules has revealed the principles of bonding by which we understand the far larger molecules, whose proportions are by no means simple and whose study in the vapor phase may be impossible.

As molecules become larger the possibilities increase for relatively slight differences in molecular structure and concomitantly in energy. In crystallization, one type of molecule may be capable of replacing another without great differences in energy; solid solutions may form. Moreover, as molecular size increases the energy required for vaporization may become so large that many molecules decompose under the impacts of their neighbors rather than passing unchanged into the vapor. Ultimately, even for molecular compounds, the definition of the compound may depend on an aggregate of atoms that is stable only in condensed phases—perhaps only in the solid.

The smallest formula unit of an ionic structure may consist of a very few atoms in a simple ratio, such as CaO in calcium oxide. On the other hand the unit cell may contain a large number of atoms with complex ratios such as $Ca_2Mg_5Si_8O_{22}(OH)_2$ in tremolite [Zussman, 1959]. Such complexity often results from comparatively stable and specific bonding within certain groups of atoms, termed complex ions.

In discussing the formula of an ionic compound we rely implicitly on the idealized crystal structure, whose unit cell and space group must always be considered provisional. The size of the unit cell established by research correctly done in the past may be increased by more sensitive observations in the future, but never decreased; and the space group symmetry may be reduced, but never raised. In the case of many compounds in the perovskite family, for instance, the originally accepted cubic unit cell containing the formula unit ABX_3 is only an approximation to the presently accepted larger unit cells of lower symmetry [Wood, 1951]. Even $CaTiO_3$, after which the "perovskite structure" was named, does not actually have that simple a structure [Náray-Szabó, 1943].

The ideal crystal is described as a static array of atoms in assigned positions, but even the determination of the ideal structure has usually required the abandonment of that picture. Almost invariably the calculation of theoretical intensities in X-ray crystal structure analysis applies a "temperature factor" to the scattering power of each atom, to correct approximately for the thermal vibrations that distort the structure and smear out the time-averaged electron density distribution. The departures from ideal structures are even more important in many phenomena that concern us. We must base any quantitative interpretations of polymorphism, phase transitions, and solid solution in a clinker mineral, for instance, on the structure of the real crystal.

Thus the simplicity, definiteness, and permanence of composition decreases as the state of union or independence between each individual atom and its neighbors becomes less distinct, even in molecular compounds. In the materials that concern us, many of the interactions between atoms are not covalent at all, but ionic. Ionic and metallic bonding form stable structures in which a given atom is surrounded by a proper number of others of suitable type, the exact identity of the surrounding atoms being secondary to their size and electric charge. The numbers of positive and negative ions must of course be such as to yield zero net charge in the macroscopic crystal.

The tendency to form a complete coordination shell around each atom leads geometrically to aggregates that are indefinitely large in all three dimensions, rigid, and periodic in structure. Such an aggregate is not a molecule, but a crystal. Furthermore, the nonspecificity of the interactions between atoms permits the displacement, removal, or replacement of a small fraction of the atoms of a given element, with correspondingly small fractional change in the energy of the aggregate. Such a process changes the "pure" crystal to a solid solution.

Crystal Structures

A compound that is not defined by a molecular structure is in fact rather poorly defined. The preceding sketch of the transition from small covalent molecules to large ionic aggregates suggests that the formulas of ionic compounds, to represent properly the corresponding aggregates of atoms, should contain extremely large numbers. The simple formulas we actually use are justified by an idealization of the crystal structure.

The ideal crystal is conceived as a repetition, through the translations of a three-dimensional lattice, of a single aggregate of atoms. Whether this aggregate is a molecule, or simply the contents of a geometrical unit cell in a purely ionic structure, its formula is the formula of the substance. Moreover, this ideal structure may have a space group whose symmetry elements prescribe certain equivalences between groups of atoms within the unit cell. The asymmetric unit, from which the space-group symmetry generates the entire structure, may be an even smaller aggregate of atoms whose formula represents the substance. This smallest aggregate must contain equal positive and negative ionic charges, but may be only conceptual. The mistake of assuming it to be a physical entity is well expressed by Sir Lawrence Bragg [1960]: "Having found that the numbers of ladies and gentlemen at dinner parties is generally equal, we had falsely concluded they were all necessarily married couples, instead of realizing that it was because each lady liked to have a gentleman on either side, and vice versa."

Real Crystals

In real crystals there are many types of departures from the ideal infinite structure of atoms, related by the exact translations of the lattice and other symmetry elements of the space group. One of the most evident departures from the ideal is finiteness of size, which affects the Fourier transform representing the diffraction properties of the crystal [Hosemann and Bagchi, 1953]. Other departures, such as mosaic structure and thermal vibration, are usually considered in crystal structure analysis because of their effects on the diffracted intensity [James, 1954]. The discussions of these effects treat the structure itself as a continuum, and may apply to any crystal. We are more interested, however, in the interactions of particular atoms in specific structures that affect the phase equilibria, transition rates, growth, and thermal, mechanical, and electrical properties of the crystals so powerfully. The success of solid-state physics with the study of certain materials, in which these properties are crucial, indicates that our understanding of the behavior of cement clinker minerals will be greatly enhanced by future research, as our understanding of their composition has already been strengthened by structure investigations in the past.

Dislocations

Of the various types of imperfections in crystals, the most ubiquitous are dislocations. These are loci at which the arrangement of atoms is different from that in the ideal structure because two parts of the structure separated by a half-plane (a plane that slices into, but not through the crystal) are displaced relative to one another.

Screw Dislocations

When the displacement is parallel to the boundary of the half-plane, as in figure 5, a screw dislocation results. Such screw dislocations have been shown to exist in a great many crystals [Verma, 1953] and probably form the mechanism of most crystal growth from fluid phases. Estimates of the relative energies of deposition on a perfect crystal face and on a stepped face [Stranski, 1949; Frank, 1949; Verma, 1953], indicate that the former process cannot lead to a significant rate of growth under most ordinary conditions, but the latter can. If the step is due to a screw dislocation, as in figure 5, further deposition perpetuates it as growth proceeds around the screw, through any number of successive layers. Experimental evidence seems to favor this mechanism for many instances of crystal growth [e.g., Albon and Dunning, 1960].

If the displacement that forms the step height is only one layer of atoms, or one unit cell of the ideal structure, then we may expect the crystal to resemble the ideal structure except for the minute fraction of the atoms lying at the locus of the screw dislocation. On the other hand, if the displacement is more than one unit of the structure, the structural relationship within the layer of atoms deposited at the step may be different from that between the new layer and its predecessor. There may be, for instance, a difference in the manner in which planes of atoms are stacked on one another—a stacking fault—between successively deposited layers. Being regularly repeated, this difference constitutes a change in the repetitive pattern of the ideal crystal. Depending on the importance we attach to the new arrangement as an individual structure, we might call it a superlattice, a polytype, or a polymorph.

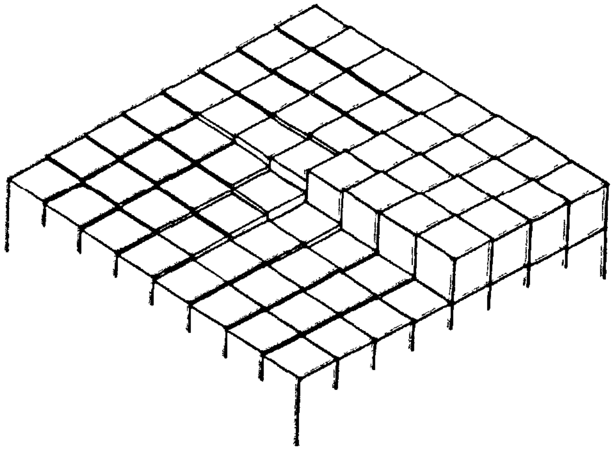

FIGURE 5. *A screw dislocation with a step height of one unit cell (Frank, 1949).*

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Structures that develop by the stacking of close-packed layers of atoms [Pauling, 1942] are affected comparatively little in energy by an error in the placement of one layer relative to its predecessors, as the relations between nearest neighbors are unchanged. Many structures which are geometrically related to close packing, such as those of zinc sulfide, silica, ice, and silicon carbide, can accommodate random or regular changes in the stacking pattern. In the case of silicon carbide [Ramsdell and Kohn, 1952] more than sixteen different polymorphs have been identified, and in a number of these the lattice period has been correlated with the measured step height of screw dislocations in the crystals [Verma, 1951; Frank, 1951]. Bernal [1954] mentioned in the preceding Symposium the possibility that the large unit cells of certain clinker minerals may originate as the step height in a screw dislocation through which growth of the crystal takes place.

Edge Dislocations

If the relative displacement of the two parts of the structure is perpendicular to the edge of the half-plane separating them, rather than parallel as for a screw dislocation, the result is called an edge dislocation. A section through such a structure is beautifully represented in photographs of bubble models by Bragg and Nye [1947]. A simple diagram representing a series of edge dislocations is shown in figure 6. This figure suggests the manner in which an array of dislocations may represent a grain boundary in a mosaic crystal or a polycrystalline single-phase specimen. The geometry and properties of such boundaries in comparatively simple structures have been thoroughly reviewed by Amelinckx and Dekeyser [1959]. Dislocations at grain boundaries and within nearly perfect crystals are strikingly displayed by the elegant X-ray diffraction technique of Lang [1959], which even yields stereoscopic "photographs" of their distribution.

Observation of the bubble models suggests that an edge dislocation in a ductile material should move through the crystal rather easily. The theory of the energies and motions of dislocations [Fisher et al., 1957; Atwater, 1959; Amelinckx and Dekeyser, 1959] appears indispensable for understanding such phenomena as creep, recrystallization, and diffusion in metals.

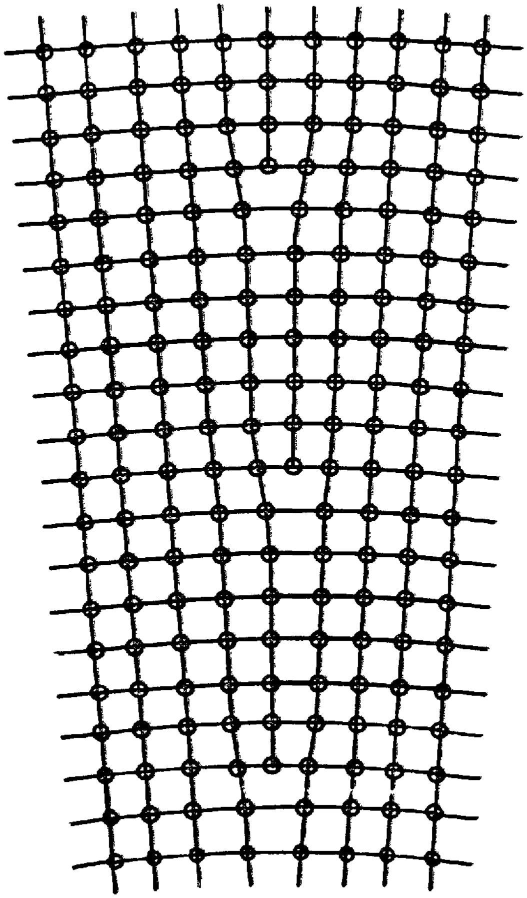

FIGURE 6 *A series of edge dislocations forming the grain boundary between two single crystals of slightly different orientation (Amelinckx and Dekeyser, 1959).*

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The more complex, rigid, and brittle structures of the cement clinker minerals permit comparatively little movement of dislocations at room temperature, but at elevated temperatures such processes may occur rather freely. Certainly many ordinarily brittle materials raised to high temperatures, such as sapphire above 1,000 °C [Wachtman and Lam, 1959], readily undergo plastic deformation.

Point Defects

The presence of dislocations in the crystal structure implies a departure from the ideal arrangement of atoms but not any particular departure from the ideal composition of the crystal. Departures from the ideal composition may exist, however, and in three possible ways: (1) by the substitution of an atom of a different element for one that is present in the ideal structure; (2) by the removal of an atom from the ideal structure to leave a vacancy; (3) by the incorporation of an interstitial atom in the space between atoms of the ideal structure. In each case, the unit involved can also be more than one atom—a complex ion or a molecule.

There is bound to be a finite equilibrium concentration of each possible type of defect in any crystal [Frenkel, 1946]. We discuss the behavior of individual impurity atoms or vacancies, and their interactions, treating their concentration as a continuous variable. If all possible sites are saturated, or a definite fraction in an ordered manner, the result is a new ideal structure. Thus the equilibrium concentration of randomly distributed defects would represent the equilibrium solid solution in the terms of the discussion of "Solid Solutions," and an ordered array of identical defects would constitute a definite compound in the terms indicated under "Crystal structures."

We might expect our clinker "compounds" to be Daltonides—fixed in composition—if their crystallization and subsequent passage through all phase transitions has been very slow. We expect that they may be Berthollides—variable in composition—if held above the temperature at which ordering of defects occurs, or if cooled too rapidly for the ordering process.

When a phase change requires diffusion of atoms to new sites (as in a transition between order and disorder of point defects) or realignment of unit cells (as in the formation or removal of stacking faults) it may not take place rapidly or completely. Such effects are well known in cement clinker (see, for example, the discussion of dicalcium silicate by Nurse [1954] in the previous Symposium), and have been even more intensively studied in some other silicates. Megaw [1959] has described the structural relations among the felspars, in which the distribution of silicon and aluminum atoms among their sites is ordered at low temperatures and becomes disordered on heating through the transition to a high temperature form, but cannot be reordered by cooling or further treatment. Other cases of sluggish transformation are discussed by Buerger [1951]. Clearly we may expect the crystals in clinker to have equilibria that are inaccessible under some conditions.

Thus a clinker constituent may vary in composition at the high temperatures of burning, and may vary in structure as well after cooling. The precise determination of these variations in all details is beyond the power of our present physical and chemical methods, except perhaps for sizable single crystals. The X-ray diffraction pattern of a microcrystalline sample leaves in doubt not only its surface chemistry but also much about its internal structure that has chemical significance.

Oscillation and Rotation

The ordering of defects may constitute a phase change as discussed under "Continuity With External Conditions," even though the energy involved is very small. This kind of process has been intensively studied in metallic structures such as the copper-gold alloy Cu_3Au and β-brass CuZn [Siegel, 1951].

There are, however, other kinds of disorder that may also be responsible for phase changes. Whenever certain atoms in the unit cell may rest in one of two or more positions of approximately equal energy separated by a potential barrier, there is a possibility of disorder without change in the unit cell contents.

The possibility of rotatory oscillation of certain groups such as NH_4 [Marshall, Staveley, and Hart, 1956] or SiO_4 [Bredig, 1943; see Nurse, 1954, and Douglas, 1954] or the oscillation of an ion [Megaw, 1954], may provide a mechanism for an order-disorder transition. In ferroelectric and ferromagnetic substances the spontaneous electric or magnetic polarization results from ordering of dipoles; it disappears at the Curie temperature, above which the dipole orientations are disordered. Some iron-containing phases of interest to the clinker chemist may well show transitions of this kind.

Clinker Structures

The models that have developed in the vigorous growth of solid-state physics are already helpful for understanding in general certain aspects of the behavior of clinker mixtures, but many detailed interpretations will require further study or experimental data. We shall review only the knowledge of clinker structure revealed by the literature since the previous Symposium.

A general result of considerable interest from recent X-ray powder work on clinker is the conclusion, which Nurse has already mentioned, that the glass content is vanishingly small. This must be not only reasonable, but self-evident to anyone who has watched the rapid final crystallization of clinker melts under the microscope, as investigators have often done at the Building Research Station and the Portland Cement Association Fellowship, and probably in other laboratories as well. The presence of glass as an explanation for abnormal heats of solution may be freely replaced by the existence of disorder, dislocations, and other regions of imperfection in an aggregate of submicroscopic crystals, the difference between the two pictures being more in degree than in kind. If the X-ray and electron diffraction properties and other characteristics of the "glass" alone are measured, however, we may be led to a more detailed description that eliminates one of the alternatives. Until there is an operational distinction between them [Bridgman, 1927] economy of hypotheses dictates that we make no distinction. These two opposing views, like the crystallization and colloid theories of setting [reviewed by Bogue, 1955] and many others through the history of science, may be resolved by a more detailed description of the phenomenon, which replaces both earlier descriptions without confirming either.

The major clinker constituents appear in several cases to be superstructures, in which the true unit cell is extremely large but can be approximated by the repetition of a considerably simpler pseudostructure. Such a relationship is to be expected when the X-ray diffraction patterns of a crystal show a great many absent reflections distributed with noticeable regularity. The expectation was mentioned in the previous Symposium, for instance by Jeffery, and in fact much of the discussion at that time dealt with pseudostructures rather than the actual structures themselves.

The full unit cells of the complex clinker structures are still at the outer limits of the crystallographer's mastery, but considerable progress has been made in the interpretation of pseudostructure relationships in crystals. Reference has been made to the possible role of screw dislocations in producing layer superstructures. There are more complicated ways in which slightly unsymmetrical small units may arrange themselves so that the true large unit cell approximates a repetition of symmetrical small units. The relationship may be thought of as twinning in which the domains are only one or a few unit cells in size, rather than macroscopic. The effect of periodic structural distortion on the diffraction pattern has been discussed by Jeffery [1951]. More recently there have been notable successes in the unraveling of unit-cell twinning in a number of mineral families, such as the sulfide solid solutions whose end members are bornite Cu_5FeS_4 and digenite Cu_9S_5 [Donnay, Donnay, and Kullerud, 1958; Morimoto and Kullerud, 1959]. These minerals show transformations from twinned to simple structures at a few hundred degrees very similar to the transformations of tricalcium silicate at higher temperatures. A recent determination of a felspar structure [Newnham and Megaw, 1960] was actually carried out in two steps: first, the determination of the "average structure" and, second, of the "difference structure." It is the second step that remains, in the case of some clinker minerals.

The crystal chemistry of clinker constituents is generally surveyed through the eyes of a mineralogist, and may therefore often be interpreted in the light of well-established generalizations about the structural configurations found in minerals. To avoid being misled by extensive knowledge of stable mineral structures, we must remember that the important clinker constituents are highly unstable configurations by geological standards. They have a lower average cation charge than many minerals, and may have lower or less regular coordinations for large cations and smaller or unusually constituted complex anions. Although the cementitious properties of these substances suggest a quantitatively different environment for the reactive atoms, it is not certain that a qualitatively different picture, such as the "one-sided" coordination of calcium proposed by Büssem [1939] for tricalcium aluminate, would be justified by the energy of reaction.

The general structural relationships among the clinker constituents and other minerals have been ably reviewed by Büssem [1939] and O'Daniel [1957]. The latter concludes with a sentiment to which we heartily subscribe: "Wir müssen noch viel arbeiten!"

Calcium Silicates

Tricalcium Silicate

The pre-eminent authority on the structure of tricalcium silicate is still the work of Jeffery [1950, 1952], which was reported in the previous Symposium [Jeffery, 1954]. The alternative structure proposed by O'Daniel and Hellner [1950] has been abandoned because it disagrees with Patterson-Harker syntheses calculated from single-crystal X-ray diffraction intensities [O'Daniel, Hahn, and Müller, 1953].

The pseudostructure has been described, and shown in stereoscopic photographs [Jeffery, 1954]. It has a rhombohedral cell containing three formula units $3CaO{\cdot}SiO_2$ but is usually referred to the corresponding hexagonal cell containing nine formula units, with approximate dimensions $a=7.0$ A, $c=25.0$ A. The structure was confirmed by comparing observed and calculated intensities for 189 X-ray reflections.

Jeffery [1950, 1952] derived for alite a C-centered monoclinic lattice. In vector notation [see Buerger, 1942] this is defined in terms of the hexagonal unit-cell vectors $\mathbf{a}_H$, $\mathbf{b}_H$, $\mathbf{c}_H$ ($\gamma_H=120°$) by the equations

$$\mathbf{a}_M=\frac{1}{3}\,(14\mathbf{a}_H+7\mathbf{b}_H+2\mathbf{c}_H)$$

$$\mathbf{b}_M=\mathbf{b}_H$$

$$\mathbf{c}_M=\frac{2}{3}\,(2\mathbf{a}_H+\mathbf{b}_H-\mathbf{c}_H)$$

The expressions with fractional coefficients correspond to integral lattice translations because the hexagonal cell is triply primitive, being related to the vectors of the primitive rhombohedral cell by the usual equations [International Tables, 1952]:

$$\mathbf{a}_R=\frac{1}{3}\,(\mathbf{a}_H-\mathbf{b}_H+\mathbf{c}_H)$$

$$\mathbf{b}_R=\frac{1}{3}\,(\mathbf{a}_H+2\mathbf{b}_H+\mathbf{c}_H)$$

$$\mathbf{c}_R=\frac{1}{3}\,(-2\mathbf{a}_H-\mathbf{b}_H+\mathbf{c}_H)$$

This use of the subscript R for the rhombohedral cell should not be confused with Jeffery's [1950, 1952] notation, in which certain vectors corresponding to the hexagonal cell have that subscript. Jeffery [1952] gave the monoclinic lattice parameters as $a=33.08$ A, $b=7.07$ A, $c=18.56$ A, $\beta=94°10'$. His monoclinic cell departs from convention [Donnay and Nowacki, 1954] in having a left-handed set of axes, but this does not affect the relationships that have been discussed.

The monoclinic cell has twelve times the volume of the rhombohedral cell, and thus contains 36 formula units $3CaO{\cdot}SiO_2$, $108CaO{\cdot}36SiO_2$, or a total of 324 atoms. This large a number represents considerable difficulty to the structure analyst. It is noteworthy, however, that one axis of the large cell is simply a doubling of an elementary rhombohedral lattice translation [Jeffery, 1952]. Jeffery [1950] tentatively proposed a structure corresponding to the formula $108CaO{\cdot}32SiO_2{\cdot}2[(Al_2O_3)_x,(Fe_2O_3)_{1-x}]{\cdot}2[(MgO)_y,(FeO)_{1-y}]$, in which the two added divalent cations and the four trivalent cations substituted for silicon per unit cell play an essential structural role. He mentioned the availability of further data requiring a large-scale computer for analysis, and we hope that this work has been, or will be, carried through. The chemical uniqueness of the suggested composition for $x=y=1$ (i.e., that it is a compound rather than a solid solution) would require very careful phase-equilibrium studies or critical examination of many "natural" samples for complete confirmation, but is not essential for usefulness of the formula. Copeland et al., [1959] report that the specified composition formed two phases, and similar results have been obtained at the Portland Cement Association Fellowship [unpublished work, 1957]; but compositions only slightly different produced one phase under the same conditions, and the extent in composition of the solitary existence region may vary significantly with temperature.

The work reported by Jeffery [1950] on tricalcium silicate crystals produced by evaporating a calcium chloride flux (the procedure of Nurse, 1948, described also by Lea and Nurse, 1949) indicates that their unknown triclinic unit cell is another slightly distorted multiple of the primitive rhombohedral pseudocell. The fact that the true repetitive unit of the structure is a multiple of the pseudocell leads to "satellite" reflections in the single-crystal diffraction patterns in the following manner.

The true structure corresponds to a modulation of the pseudostructure by a three-dimensionally periodic function of comparatively long wavelength. In the diffraction patterns the Fourier transforms of the electron density distributions become visible, the pattern of the true structure being a convolution [vide Lipson and Taylor, 1958] of the transform of the pseudostructure with that of the modulating function. Distances in the transform are proportional to the frequencies of periodicities in the structure, and thus the transform of the low frequency modulating function has closely-spaced maxima.

To obtain the convolution, the widely spaced peaks in the transform of the pseudostructure (corresponding to the diffraction pattern of the rhombohedral structure) are repeatedly superimposed. Each of the superimposed repetitions of the array of widely-spaced pseudostructure peaks corresponds in position and weighting to one of the closely-spaced maximums in the transform of the modulating function. The total (corresponding to the diffraction pattern of the monoclinic structure) has strong, widely-spaced peaks like the pseudostructure, with closely-spaced peaks nearby whose intensity declines rapidly with distance from the main peaks.

A departure of the true structure from the simpler pseudostructure of rhombohedral symmetry may produce satellite reflections in this way, and may also displace the original pseudostructure reflections. The former effect is most vivid in single-crystal diffraction patterns but tends to be obscured by the powder method, which is relatively insensitive to weak reflections. The latter effect, which Jeffery [1950] detected in the single-crystal patterns by careful examination for splitting of certain spots, is detectable in well-resolved powder patterns.

The splitting of certain lines in the powder pattern has been interpreted in terms of specific distortions of the rhombohedral lattice by Yamaguchi and Miyabe [1960]. They have assumed that the unit cells for both monoclinic alite and triclinic tricalcium silicate may be approximated by the orthogonal cell whose defining vectors are

$$\mathbf{a}_Y = -\mathbf{a}_H + \mathbf{b}_H$$
$$\mathbf{b}_Y = \mathbf{a}_H + \mathbf{b}_H$$
$$\mathbf{c}_Y = \mathbf{c}_H$$

They have confirmed by high-temperature X-ray powder diffraction that the splitting of the lines changes with temperature in a manner that corresponds to the expected transitions to higher symmetry on heating: monoclinic→rhombohedral at 830 °C for alite; triclinic→monoclinic at 920° and monoclinic→rhombohedral at 970° for tricalcium silicate.

They measured the positions of peaks in the powder patterns of the low-temperature forms precisely by the internal standard method. They assigned indices to the components of the split powder lines by comparing their relative intensities with the multiplicities of the components theoretically produced by slightly distorting the orthohexagonal unit cell $\mathbf{a}_Y\mathbf{b}_Y\mathbf{c}_Y$ to monoclinic and triclinic symmetry.

Their unit-cell calculations were based on the interplanar spacings (d values) between 3.06 and 1.45 A, but in both of the patterns there were some parts of this region that could not be clearly indexed. The monoclinic unit cell was based on 24 indexed lines in the ranges 3.04–2.30 A, 1.83–1.53 A, and 1.487–1.459 A, and the triclinic unit cell was based on 25 indexed lines in the ranges 3.06–3.02 A, 2.79–2.31 A, 1.78–1.54 A, and 1.48–1.45 A. They found the dimensions of the monoclinic unit cell to be $a=12.246$ A, $b=7.045$ A, $c=24.985$ A, $\beta=90°04'$, and those of the triclinic cell, $a=12.195$ A, $b=7.104$ A, $c=25.096$ A, $\alpha=90°$, $\beta=89°44'$, $\gamma=89°44'$.

A calculation by the writer, using a least-squares program for the IBM 704 computer which minimizes the quantity $\Sigma(1/d^2)^2$, gave for the monoclinic cell $a=12.248$ A, $b=7.045$ A, $c=24.972$ A, $\beta=90°06'$, and for the triclinic cell $a=12.196$ A, $b=7.103$ A, $c=25.094$ A, $\alpha=89°57'$, $\beta=89°43'$, $\gamma=89°44'$. Either of the two sets of lattice parameters gives agreement between observed and calculated spacings within 0.003 A. (average discrepancy less than 0.0009 A) for the monoclinic pattern and within 0.004 A (average discrepancy less than 0.0007 A) for the triclinic pattern.

The relations between the various unit-cell vectors are indicated in figure 7. Yamaguchi and Miyabe [1960] state that their monoclinic cell corresponds to the following dimensions for Jeffery's monoclinic cell: $a=33.091$ A, $b=7.045$ A, $c=18.546$ A, $\beta=94°08'$. Their unit cells are justified by utility for indexing of the powder patterns, but do not have structural significance. A structural unit cannot properly be defined, with our present information, for the triclinic crystals, nor any but that of Jeffery for the monoclinic crystals.

The powder data of Yamaguchi and Miyabe [1960] are probably the most precise available within the range they have covered, although the tabulation by Heller and Taylor [1956] indicates

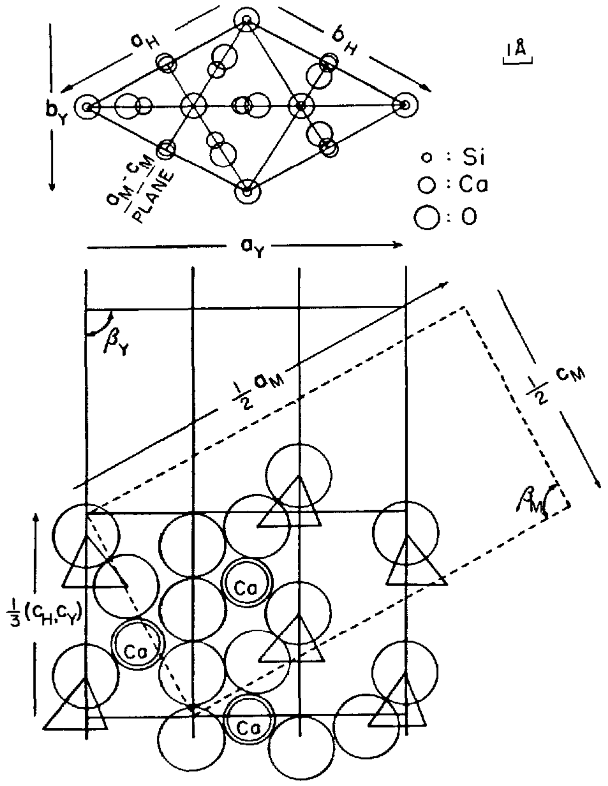

FIGURE 7. *Diagram of unit-cell relationships for tricalcium silicate.*

Subscripts indicate the definer of each set of vectors: H and M, the hexagonal and monoclinic cells of Jeffery (1950, 1952); Y, the monoclinic and triclinic cells of Yamaguchi and Miyabe (1960), from whom the diagram is adapted. (Used by permission, Am. Ceram. Soc.)

additional lines at larger and smaller interplanar spacings.

Dicalcium Silicate

No extensive structure investigations of pure dicalcium silicate or belite have appeared in the literature since the review in the previous Symposium by Nurse [1954]. His paper quotes in detail the X-ray powder data, lists the available unit-cell data from single-crystal measurements, and shows the structure found for β-dicalcium silicate by Midgley [1952a]. Extensive data on the powder patterns have been given by Yannaquis [1955]. A later review of the powder data, with indexing where possible, has been given by Heller and Taylor [1956].

The α Form

Mrs. Douglas [1952] detected a trigonal phase in crystals of bredigite from vugs in a slag, which was identified with α-dicalcium silicate. Mrs. Midgley [1952b] studied nagelschmidtite, a slag mineral containing $3CaO{\cdot}P_2O_5$ and $2CaO{\cdot}SiO_2$ in the ratio of 1:2 or 1:3, and found that its unit cell is a multiple of that determined by Mrs Douglas. These results were discussed by Nurse [1954] in the previous Symposium.

The α′ Form

Mrs. Douglas [1952] has reported preliminary studies of bredigite, a naturally occurring calcium orthosilicate of the composition $(Ca_{1.59}Ba_{0.08}Mg_{0.31}Mn_{0.09})SiO_4$. This material gives a significantly different powder pattern from pure α′-Ca_2SiO_4, but probably is closely related in structure. The analogy with β-K_2SO_4 [Bredig, 1950] may be approximately but not exactly true.

The β Form

The determination of the structure of β-dicalcium silicate (B_2O_3-stabilized) by Mrs. Midgley [1952a] makes this the most carefully investigated of the several polymorphs. The determination was based on 200 measured X-ray diffraction intensities—73 *h0l*, 100 *0kl*, and 27 *hk0*. The structure amplitudes calculated from the final atomic coordinates agree with observed values to an average discrepancy of 19 percent. This is reasonable confirmation of the basic structure, although the use of additional data on *hkl* reflections in more elaborate calculations might permit refinement of the atomic positions to higher precision.

The γ Form

Nurse [1954] reported that there were no single-crystal data on γ-dicalcium silicate. The reason for this lack is the fact that the crystals are obtainable only by dusting of the β form, and these are extremely small. Recently D. K. Smith of the Portland Cement Association Fellowship has been able to isolate usable single crystals of the γ form, however. He has been able to collect complete X-ray intensity data on this polymorph, confirm that it has the olivine structure as proposed by O'Daniel and Tscheischwili [1942], and determine the atomic positions with good precision. This work will be reported separately.

Calcium Aluminates

Tricalcium Aluminate

The paper on this phase in the previous Symposium [Ordway, 1954] was mainly a discussion of the pseudostructure proposed still earlier by Professor Büssem [1938]. The unit cell and space group (T_h^6-Pa3) of the true structure were given, but not a complete structure determination. Other activities have prevented us from applying the large-scale computation facilities now available to the X-ray intensity data on tricalcium aluminate, which were gathered some time ago, but it is hoped that this work can be carried through in the near future.

The X-ray powder pattern of tricalcium aluminate was given in detail in the previous Symposium by Yannaquis [1954], and even more high-angle lines were reported by Swanson, Gilfrich, and Ugrinic [1955]. The latter authors report the lattice constant as $a=15.262$A at 25 °C.

$12CaO \cdot 7Al_2O_3$ and $5CaO \cdot 3Al_2O_3$

The literature on "12:7" or "5:3" calcium aluminates is a striking example of the uncertainties in ascribing formulas to ionic compounds that form at high temperatures. Shepherd, Rankin, and Wright [1909] reported stable and unstable 5:3 compounds. Koyanagi [1931] thought there might also be a 3:2 compound. Büssem and Eitel [1936] found a crystal structure for the stable cubic compound corresponding to the 12:7 ratio. Lagerquist, Wallmark, and Westgren [1937] proposed a 9:5 formula. Aruja [1957] determined the unit cell and space group for orthorhombic crystals grown with a hot wire device by J. H. Welch. These apparently correspond to the "unstable 5:3" phase originally reported, and actually do have the 5:3 ratio.

At this stage, the formula must derive from a knowledge of the chemical composition, the unit cell, and the density. It is necessarily assumed that there are no defects in the structure. The manner in which these data determine the formula is best shown in a graph such as figure 8. Its coordinates are the numbers of formula units (CaO and Al_2O_3 respectively) in the unit cell. For any calcium aluminate of given unit-cell volume V and density ρ the possible compositions are represented by a line of negative slope, whose intercepts are ($NV\rho \div$formula weight of CaO) and ($NV\rho \div$formula weight of Al_2O_3) where N is Avagadro's number, or 0.01074 $V\rho$ formula units of CaO and 0.00591 $V\rho$ formula units of Al_2O_3 where V is in A^3 and ρ is in g/cm^3. Results of a chemical analysis are indicated by a line through the origin with a slope that corresponds to the molar ratio found. The line from the crystal data and that from the analytical data should intersect at a point whose coordinates are the integers x and y in the formula $xCaO \cdot yAl_2O_3$ for the unit-cell contents.

Inspection of the figure shows that the intersections are indeed closer to the points $24CaO \cdot 14Al_2O_3$ and $20CaO \cdot 12Al_2O_3$ than to the other possible points nearby. It also shows how slight an error in chemical composition, unit-cell size, or density would be required to change the indicated formula.

The structure proposed for $12CaO \cdot 7Al_2O_3$ by Büssem and Eitel [1936] is based on 51 estimated X-ray intensities. It does not account for two of the oxygen atoms, which were taken to be statistically distributed over a number of possible positions in the unit cell. Definite positions for these atoms were felt to be unlikely because the unit cells of lower symmetry that were tried did not give satisfactory calculated intensities, and no superlattice lines were seen in the powder pattern. This structure seems worthy of further study with the more powerful experimental and computational techniques now available to crystallographers, but the validity of the 12:7 formula is independent of the structure determination, as figure 8 shows.

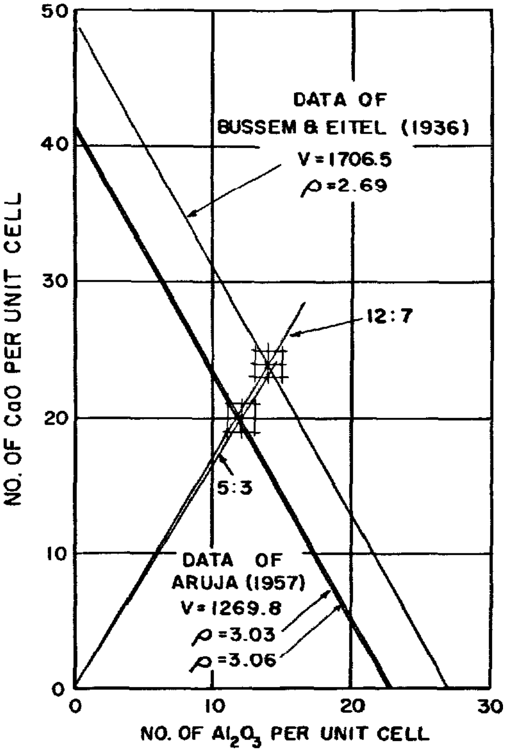

FIGURE 8. *Unit-cell contents of calcium aluminates based on unit-cell volume V (A^3), density $\rho(g/cm^3)$, and molar ratio* $CaO{:}Al_2O_3$.

Aruja [1957] has noted an analogy between $5CaO \cdot 3Al_2O_3$ and gehlenite, $2CaO \cdot Al_2O_3 \cdot SiO_2$, which may be a useful starting point in determining the 5:3 structure.

Ferrites

Nurse's paper in this Symposium reviews the phase-equilibrium studies on the ferrite solid-solution series. The continuous variation in positions of the X-ray powder lines with the parameter p ($0 \leq p \leq 0.69$) in the general formula $2CaO \cdot (Fe_{1-p}Al_p)_2O_3$ was used by Midgley (1958) for characterizing the ferrite phases in clinker samples, and by Newkirk and Thwaite [1958] for determining the tie lines representing equilibria, in the ternary system C–A–F at various temperatures, between ferrite, liquid, and either lime, C_3A, or $C_{12}A_7$. The apparent tendency of the solid solution toward lower lime content with increasing p, reported by Newkirk and Thwaite [1958,] might be taken to suggest replacement of some lime by FeO, but the phase-equilibrium study of Phillips and Muan [1958] argues against such an explanation. Studies of the structure have concentrated on the variation of p and ignored any possibility of other departures from the formula mentioned above.

It was Büssem [1937, 1939] who found for $2CaO \cdot (Al_{0.5}Fe_{0.5})_2O_3$ the probable space group *Imma*—D_{2h}^{28} [International Tables, 1952] and proposed the structure of layers of RO_6 octahedra separated by calcium ions from alternating layers of RO_4 tetrahedra. He took the cations R to be aluminum in the octahedra and iron in the tetrahedra. Cirilli and Burdese [1951] and Malquori and Cirilli [1954] accepted the space group *Imma* for the entire solid-solution series, but believed the aluminum to be distributed randomly over both tetrahedral and octahedral sites. Bertaut, Blum, and Sagnières [1957a, 1957b, 1959] investigated $2CaO \cdot Fe_2O_3$ and found the space group to be $Pnma$–D_{2h}^{16}. (Their unit cell has the *a* and *c* axes interchanged from the choice of Büssem. Thus their paper states the space group as $Pcmn$—D_{2h}^{16}, and the *h* and *l* indices of X-ray reflections in their tables must be interchanged for comparison of tabulated intensities.) The determination of the atomic positions for $2CaO \cdot Fe_2O_3$ [Bertaut, Blum, and Sagnières, 1959] has been done with considerable precision, although the rather large corrections for absorption applied to the measured X-ray intensities were estimated empirically. The final average relative discrepancy between measured and calculated structure amplitudes of the 252 reflections they observed was 14.7 percent.

The series has been further investigated by D. K. Smith [1960]. He obtained X-ray precession patterns from carefully annealed single crystals with seven different values of p covering the possible range, and found that there is actually a definite change of symmetry. As p increases from zero to 0.33, certain X-ray reflections of considerable intensity permitted by the space group *Pnma* decrease steadily to zero. The added extinctions correspond to the higher symmetry of the space group *Imma*.

Smith's interpretation of this symmetry change is shown by stereoscopic drawings in figure 9, superimposed on the structure found by Bertaut, Blum, and Sagnières [1959]. As the figure shows, the increased symmetry corresponds to a slight rotation of the tetrahedral groups.

In conjunction with the change of symmetry there is a change in the slopes of certain interplanar spacing curves as a function of composition. This nonlinearity was noted by Newkirk and Thwaite [1958], and is visible in the curves published by Malquori and Cirilli [1954] and Midgley [1954, 1958]. Like the change in symmetry, it suggests that the substitution of aluminum for iron atoms with increasing p does not take place in the same manner throughout the composition range.

Smith studied the ionic packing affecting the symmetry change, and compared the intensity variations of the sensitive X-ray reflections with those calculated for various distributions of the aluminum atoms. He concluded that the aluminum substitutes only for iron in the tetrahedral positions at first, but when p reaches 0.25–0.3 the substitution in octahedral positions appears to become equally probable. The phase change is a so-called "higher-order" transition. Further details on these changes will be available at the completion of a full three-dimensional structure refinement based on integrating Weissenberg data, which is being carried out.

It is interesting to note that none of Smith's single crystals, grown from the melt by lowering the furnace temperature 1 °C per day, showed detectable elongation of diffraction spots which would be expected if compositional zoning caused variations of p by 0.05 or more within the crystal. Swayze [1946] has repeatedly emphasized the likelihood of zoning as a persistent phenomenon because of nonequilibrium crystallization around a protected phase. Midgley [1958], in surveying the powder patterns of numerous cements, found

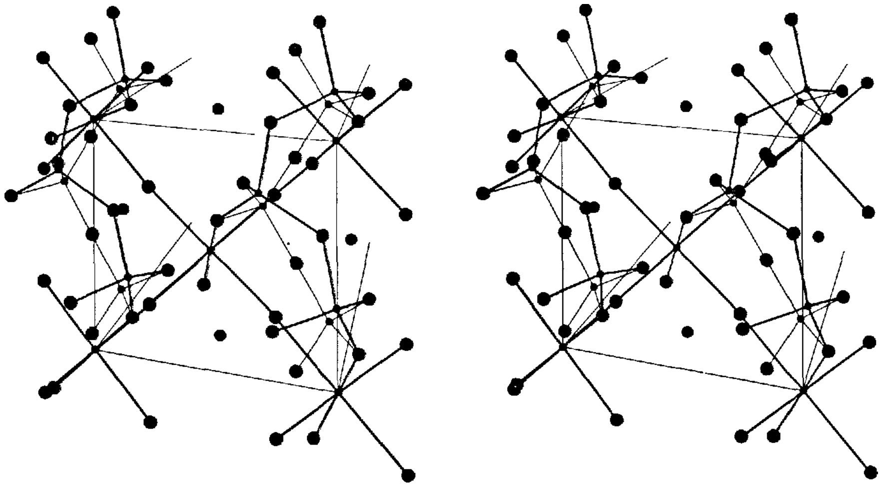

FIGURE 9. *Stereoscopic pair showing half of the unit cell of* $2CaO \cdot Fe_2O_3$. *(Smith, 1960.)*

The full unit cell contains four formula units. The *a* axis is vertical, the *b* axis points away from the observer, and the *c* axis is approximately horizontal and parallel to the page. The atoms connected by lighter lines indicate the proposed structure of higher symmetry corresponding to $p \geq 0.03$.

(To view in three dimensions, hold the figure about 10 cm from the eyes and rotate slowly until the blurred images merge. Then move it away without rotation until the merged images focus. A stereoscope can be used instead, if desired.)

in many cases a considerable line broadening ascribed to zoning. The aluminum and iron atoms apparently have a sufficiently high diffusion coefficient at the higher temperature to approach equilibrium in some clinkers but not in others. The dependence of this diffusion rate on temperature and composition should be studied quantitatively for better understanding of clinker. Even if the dependence is simple, however, its use by the chemical engineer to predict the results of given processing conditions will be a far more difficult statistical problem.

Techniques

The long-range goal of structure studies for clinker chemistry may be to determine atomic configurations that will guide the refinement of statistical models, in the theoretical approach mentioned at the start of the section on "Fundamental Concepts". The more immediately visible short-range goal, however, is the characterization of phases and transitions. For this purpose the crystallographer has continuously striven to examine real equilibrium structures, rather than "quenched" or metastable ones. The development of high-temperature microscopy, mentioned in Nurse's paper in this Symposium, is one result of this tendency.

For structure investigations, the most important developments are naturally improvements in high-temperature X-ray diffraction techniques. Powder diffraction cameras for high-temperature work have long been available, and much of the progress in studies of high-temperature polymorphism has come from their use. High-temperature microscopy has been reviewed by Brenden, Newkirk, and Bates [1960]. The hot-wire technique developed years ago for high-temperature microscopy has been used with the X-ray powder camera at the Building Research Station [Aruja, Welch, and Gutt, 1959], and we have tried similar experiments at the Portland Cement Association Fellowship. The apparatus has the advantage of being easily set up, adjusting quickly to a desired temperature, and requiring only small samples, but for our purposes these were not major considerations and many of the published designs for conventional high-temperature powder cameras seemed to have more important advantages. Since the counter diffractometer appears to promise better sensitivity for detecting weak powder lines and resolving complex patterns, we have been rather more interested in high-temperature diffractometer equipment. Several papers have described furnace attachments for use with the diffractometer [Chiotti, 1954; Mauer and Bolz, 1955; Perri, Banks, and Post, 1957], but they have either required a vacuum or special atmosphere or been incapable of routine operation over the entire temperature range (to 1,650 °C) in which we are interested. Further development of such apparatus will be extremely helpful to clinker chemists.

For the structure worker, an even more potent tool is the technique of high-temperature single-crystal X-ray diffraction. Development of that technique was the prime object of the improved version of the original hot-wire apparatus [Ordway, 1954], constructed at the Portland Cement Association Fellowship about the time of the previous Symposium [Ordway, 1955]. This unit, having automatic temperature control (fig. 10) and a suitable physical design, is intended for growing crystals under the misroscope and then transferring them, without further cooling, to the precession camera for X-ray diffraction. Similar use could undoubtedly be made of the apparatus developed by Aruja, Welch, and Gutt [1959]. Other devices for single-crystal X-ray work at elevated temperatures [Dent and Taylor, 1956; McKeown, 1956; Katz and Kay, 1957; Smith and Brown, 1959] either do not approach the highest temperatures we require or do not provide conveniently for microscopy, although some may give better uniformity of temperature across the sample.

Even the hot-wire apparatus, seemingly best for the intended manipulations, has shown certain remaining difficulties in our few preliminary tests. The removal of superfluous liquid from the crystal, and its firm attachment to the wire in order to maintain fixed orientation, are now extremely painstaking operations. The technique will have to be improved for routine use, but such a development seems inescapable. To obtain full structural information the original high-temperature clinker constituents must be examined, since they undergo so many changes when cooled.

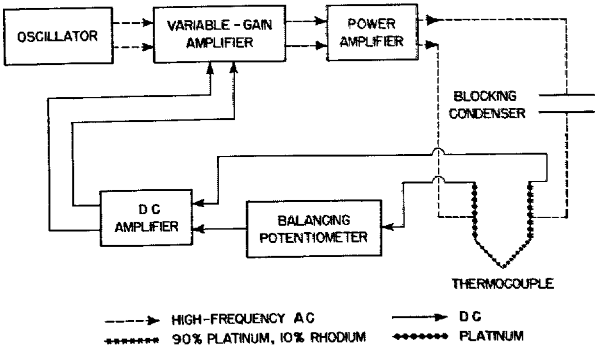

FIGURE 10. *Basic circuit of hot-wire apparatus with automatic temperature control.*

Conclusion

Further development of specialized high-temperature techniques and of the more generally used methods of structure analysis, and more intensive use of the methods already available, will undoubtedly reveal much about the structures of clinker minerals. The full benefit of this knowledge cannot be obtained, however, unless we apply it widely. The phenomena observed qualitatively in phase-equilibrium studies on clinker, or quantitatively in thermodynamic measurements, must be fundamentally interpreted in terms of structure. The results of our engineering processes of clinker burning and cooling must be interpreted in terms of microstructure and the reaction kinetics within small particles, which must be further interpreted in terms of the arrangements and motions of atoms. Regardless of the possible economic benefits, I am confident that our understanding of these processes will grow. It is sure to progress as long as it can enlist the talents of as many practitioners of insatiable human curiosity's highest development—modern science—as the present Symposium represents.

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Paper II-S1. The Effect of Minor Components on the Hydraulicity of the Calcium Silicates *

J. H. Welch and W. Gutt

Synopsis

Early studies on the constitution of cement clinker sought to interpret cement properties in terms of potential compound formation, because an overall chemical analysis of cement clinker was not in itself sufficiently indicative of the behaviour of the material.

Model phase equilibrium studies are necessarily restrictive in relation to the number of components studied, and we have become accustomed to interpreting cement performance in terms of the potential calcium silicate, aluminate, and aluminoferrite formation from the available CaO, SiO_2, Al_2O_3, and Fe_2O_3. As these oxides comprise the bulk of the clinker, the minor components have tended to assume a correspondingly minor significance.

This paper emphasises the importance of minor components in modifying the properties of the major clinker phases, a role in which their influence is far greater than their quantitative representation in the clinker might suggest. The separate effects of phosphate and fluorine additions to C_2S and C_3S have been studied in relation to the formation, polymorphic stabilization, decomposition, and hydraulicity of the calcium silicates. The effect of fluorine additions to a phosphatic clinker has also been investigated, and the results obtained underline the importance of not relying too much on subjective estimates of cement quality, based on microscopic examination of the phases present in the clinker.

It is concluded that a knowledge of the chemical composition of the major phases is insufficient to define their qualities, and that atomic arrangement as influenced by minor components plays an extremely important part in determining their potential hydraulicity.

Résumé

Les premières études sur la constitution du clinker de ciment cherchaient à interpréter les propriétés du ciment en fonction de formation potentielle des composées, parce qu'une analyse chimique complète du clinker de ciment n'était pas en soi une indication suffisante du comportement du matériau.

Les études modèles sur l'équilibre des phases sont nécessairement restrictives par rapport au nombre de composants étudiés, et nous avons pris l'habitude d'interpréter le comportement du ciment en fonction de la formation potentielle du silicate, aluminate, et de l'aluminoferrite de calcium à partir des CaO, SiO_2, Al_2O_3, et Fe_2O_3 disponibles. Comme ces oxydes comprennent la plupart du clinker, on a eu tendance à accorder aux composants mineurs une importance également mineure.

Cet exposé souligne l'importance des composants mineurs en ce qu'ils modifient les propriétés des phases majeures du clinker, et dans ce rôle leur influence est bien plus forte que ne le suggère leur représentation quantitative dans le clinker. Les effets séparés des additions de phosphate et de fluor aux C_2S et C_3S ont été étudiés par rapport à la formation, la stabilisation polymorphique, la décomposition, et l'hydraulicité des silicates de calcium. L'influence d'additions de fluor à un clinker phosphaté a également été examiné, et les résultats obtenus soulignent le fait qu'il est important de ne pas se fier trop aux évaluations subjectives de la qualité du ciment, basées sur l'examen au microscope des phases présentes dans le clinker.

On en conclut que la connaissance de la composition chimique des phases majeures ne suffit pas pour déterminer leurs qualités, et que la disposition atomique, en tant qu'elle est influencée par des composants mineurs, joue un rôle extrêmement important dans la détermination de leur hydraulicité potentielle.

Zusammenfassung

Die früheren Untersuchungen betreffend der Konstitution der Zementklinker haben immer versucht, die Zementeigenschaften als verursacht durch die Bildung dieser oder jener Verbindung auszudrücken, weil doch die quantitative chemische Analyse der Zementklinker keine genügende Aufschlüsse über das Verhalten des Materials gibt.

Modelle Phasengleichgewichtsstudien sind in ihrer Natur beschränkt, da man nie eine genügende Zahl der Komponenten studieren kann, und daher hat man sich angewöhnt, das Verhalten eines Zements in der Form der möglichen Kalziumsilikat-, Aluminat- und Aluminoferritbildung aus den vorhandenen CaO, SiO_2, Al_2O_3 und Fe_2O_3 zu erklären. Da diese Oxyde die Hauptbestandteile des Klinkers sind, hat man immer angenommen, daß alle anderen Bestandteile die nur in kleiner Menge vorhanden sind, auch nur die Eigenschaften in untergeordneter Weise beeinflussen.

Die Untersuchung zeigt, daß man großen Nachdruck auf die Bedeutung der Komponenten, die nur in kleinen Mengen vorkommen, legen muß, daß diese die Eigenschaften der Hauptphasen der Klinker sehr beeinflussen, daß sie dort wirklich eine Rolle, die in keinem Verhältnis zu dem Mengenverhältnis in dem sie vorkommen, spielen. Die Einzeleffekte der Phosphat- und Fluoridzugaben wurden für C_2S und C_3S in ihrer Beziehung zur Bildung,

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zur polymorphen Stabilisierung, Zersetzung und hydraulischen Eigenschaften des Kalziumsilikats studiert. Auch der Einfluß einer Fluoridzugabe in einem phosphathaltigen Klinker wurde untersucht, und die Ergebnisse zeigen, daß es falsch ist, sich zu sehr auf die subjektive Abschätzung der Zementqualität, wie sie auf der mikroskopischen Betrachtung der im Klinker existierenden Phasen aufgebaut ist, zu verlassen.

Es ist daher so, daß die Kenntnis der chemischen Zusammensetzung der Hauptphasen für die Qualitätsbestimmung ungenügend ist, and daß der Atomaufbau, der sehr durch Spurenelemente beeinflußt wird, eine große Rolle in der Bestimmung des voraussichtlichen hydraulischen Verhaltens spielt.

Introduction

It has long been asserted that the presence of phosphate in cement is detrimental to its quality, and for this reason phosphatic limestone has normally been avoided in cement manufacture. In Uganda no other limestone is readily available, and a cement industry was established there using phosphatic limestone as the basic raw material. In connection with this project, Nurse [1][1] studied the phosphate problem and his work formed the basis for the manufacturing process used. Nurse found that the presence of phosphate hindered the formation of C_3S, and that the phosphate combined to form a particular solid solution with C_2S. He recommended a limit for the phosphate content which would permit the attainment of satisfactory strength in the cement, and he devised a process of ignition, hydration, and elutriation for the limestone which would separate in the elutriation stage the phosphate exceeding this limit. As experience was gained it became known that the effect of P_2O_5 was less deleterious than had been forecast from the original laboratory work. This fact, combined with a fluorspar addition to the raw meal, has ensured the production of a cement of excellent quality.

Since the inception of the cement industry in Uganda, its material and products have been regularly examined at the Building Research Station. The present research program includes also the examination of laboratory-prepared clinkers containing phosphate alone, or phosphate and fluorine, by chemical and X-ray analysis, and by microscopy. Considerable evidence has been obtained in the course of this work that subjective estimates of cement quality, based on microscopic examination of the phases present in the clinker, can be wholly unreliable. This observation applies particularly to the presence of phosphate and fluorine, which are capable of causing profound structural modification of C_2S and C_3S, but it could clearly apply to certain other minor components as well. It appears essential to establish the precise properties of the phases present, and in particular their latent hydraulicity. Several recent papers [2–4] on the effect of minor components on cement quality contain no reference to actual strength determinations, and the conclusions drawn solely from mineralogical examination may well be misleading. In order to understand the phosphatic cement process more clearly, high-temperature phase equilibria in the system $CaO\text{-}SiO_2\text{-}P_2O_5$ have been studied, together with the separate effects of phosphate and fluorine on C_2S and C_3S. The results of these studies will now be discussed because although seemingly related to one manufacturing problem they appear to have a much wider implication.

Dicalcium Silicate

Effect of Phosphate

The dicalcium silicate phase was fully discussed by Nurse [5] in the previous Symposium. Since then, new techniques of high-temperature microscopy and X-ray analysis [6–8] have been developed which enabled Nurse, Welch, and Gutt [9] to examine the phase equilibria in the system $C_2S\text{-}C_3P$. This work revealed that not only $\beta\text{-}C_2S$ but also the α' and α polymorphs could be stabilized by appropriate additions of phosphate. The hydraulicity of these polymorphs and also of $\gamma\text{-}C_2S$ has now been determined.

Experimental Procedure

The mixes were prepared from crushed quartz (99.95% pure), $CaCO_3$ (99.9% pure), and C_2P ($\nless$99.9% pure) prepared from AnalaR phosphoric acid and $CaCO_3$. The powdered materials, which had been screened through a 100-mesh sieve, were mixed dry and ignited in platinum trays at 1,000° and subsequently at 1,550° in an electric furnace for 20 hr. The phases present were identified by means of a Guinier-type focusing camera, 114 mm. diam., with CuKα radiation. After grinding to a fineness of 4,000 cm^2/gm. with 4 percent of added gypsum, hydraulicity was determined by compressive-strength tests on half-inch 1:3 mortar cubes, which had been cured in moist air for one day and in water thereafter. The composition of the mixes and the strength results are shown in figure 1.

The quantities of material available for test necessitated the adoption of small-scale specimens. Although the strength results obtained on half-inch cubes enable a direct comparison to be made of different materials, the absolute strength figures cannot be directly compared with those obtained by the B.S. test on 2.78-in. mortar cubes. A number of portland cements were tested using the two different specimen sizes, and in this instance an approximate correlation was obtained from the expression:

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[1] Figures in brackets indicate the literature references at the end of this paper.

Strength (2.78-in. cube)=2.2×strength (½-in. cube)+1,200 lb/in.^{2}

Discussion

It is clear that only β-C_2S is substantially hydraulic under the conditions of the test. In view of this, the assessment of the effect of any minor component on the quality of portland cement must take into account the possible stabilizing action on C_2S, and in this respect Nurse [5] has drawn attention to the enhanced hydraulicity of P_2O_5-stabilized β-C_2S. However, the detrimental action of P_2O_5 on cement quality, attributed by Nurse [1] to the elimination of C_3S, may additionally be due in some circumstances to the stabilization of α'-C_2S. A laboratory-produced clinker, made from a plant cement raw meal containing 1.97 percent P_2O_5 and 2.0 percent K_2O (ignition loss 30.5 percent), contained α'-C_2S as the main phase provided the clinker was cooled rapidly after ignition. The compressive strength of this cement was found to be correspondingly low. α'-C_2S has also been identified in a plant-produced cement of recent manufacture. It is possible that one of the beneficial effects of fluorspar addition to phosphatic cement raw meal as practiced in Uganda consists in reducing the content of "active" phosphate below the limit for α'-C_2S stabilization. The situation is of course complicated in practice by the simultaneous presence of several minor components.

Effect of Fluorine

The addition of fluorine as fluorspar to C_2S was ineffective in stabilizing α' or α-C_2S, the products in presence of 0.81 percent or 1.7 percent fluorine being a mixture of β and γ-C_2S. This was in contrast to the behavior of C_2S in the presence of C_3S and fluorine together, as described subsequently.

Supplementary Studies

Attempts to prepare α'-C_2S by addition of K_2O, aiming at the composition $KC_{23}S_{12}$, were unsuccessful. Only β-C_2S was obtained in these experiments in contrast to the results obtained by Suzukawa [10].

Toropov, Volkonsky, and Sadkov [11] have claimed that a β' form of C_2S exists in addition to the established γ, β, α' and α forms, and this has also been investigated. Heating for 65 days at 600° failed to produce any change in γ-C_2S. X-ray analysis at ascending temperatures as shown in table 1 gave no indication of a new polymorph.

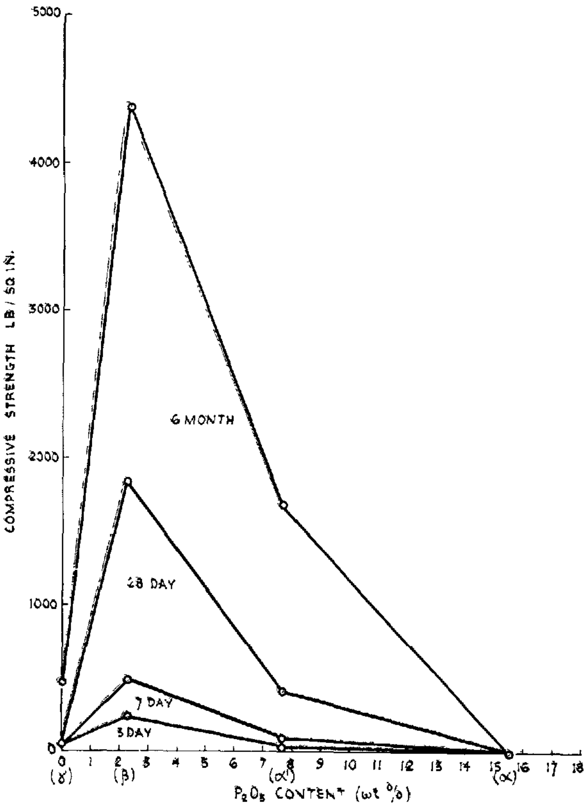

FIGURE 1. *Compressive strength (on 1/2″ 1:3 mortar cubes) of preparations on the join* C_2S-C_3P, *showing effect of* C_2S *polymorphism.*

TABLE 1. *Results of high-temperature X-ray analysis of* C_2S

Temperature	X-ray identification
Room temp.	γ
°*C*	
800	γ
900	γ+trace α'
1000	α'
1100	α'
1200	α'
1300	α'
1400	α'
1500	α

Tricalcium Silicate

Effect of Phosphate

Phase equilibria in the system CaO-SiO_2-P_2O_5 are being studied by Gutt [12], and this work provided compositions for the experiment. The compositions chosen lie on a hypothetical join C_3S—($24.1C_3P$–$75.9C_2S$), the latter being the composition (wt percent) at the maximum on the liquidus curve in the system C_2S-C_3P [9].

Experimental Procedure

The preparation of the mixes followed the description given earlier for the phosphatic C_2S preparations, except that the ignition time was extended to 60 hr and samples were pelleted and steamed during the heat treatment. The samples were then submitted to strength tests as described for phosphatic C_2S, to free lime analysis, and to X-ray examination.

Results and Discussion

The composition, free lime content, and phases identified in the X-ray diffraction patterns of the mixes are given in table 2, and the compressive strengths in figure 2. The X-ray diffraction pattern in mixes with 2, 3, and 4 percent of P_2O_5 was characterized by an overall increase in the line spacings, denoting a decrease in the unit cell volume as compared with C_3S. The line shift was observable at 1 percent P_2O_5 and was at a maximum at 2 percent P_2O_5, no further shift being detectable in mixes of higher P_2O_5 content. At 1 percent P_2O_5, α'-C_2S was also present and it grew in quantity as the proportion of P_2O_5 increased. Figure 6 gives the X-ray diffraction pattern of the composition containing 2 percent P_2O_5 side by side with the pattern given by a mixture of 85 percent pure C_3S and 15 percent (wt) α'-C_2S. The α'-C_2S, stabilized by P_2O_5, was added to serve as a quantitative standard for this phase in the experimental mixes. The fixed position of the α' pattern in the two films also emphasizes the relative shift in the C_3S lines.

As phosphate is added to pure C_3S, compressive strength at first falls, but as the addition continues it again rises at the composition 71.7 CaO, 26.3 SiO_2, 2 P_2O_5 (weight percent), giving by a small margin the highest strength in the series at 3, 7, and 28 days. Further addition of up to 4 percent P_2O_5 is detrimental to strength.

TABLE 2. *Effect of phosphate on* C_3S: *composition of mixes studied and phases present: (duplicated preparation enclosed in brackets)*

Composition			X-ray identification	Analytical [a] free CaO
P_2O_5	CaO	SiO_2		
	wt. %	*wt. %*		*wt. %*
1	72.7	26.3	$C_3S+\alpha'$ C_2S	nil
[1	72.7	26.3]	$C_3S+\alpha'$ C_2S	nil
2	71.7	26.3	$C_3S+\alpha'$ C_2S	0.1
[2	71.7	26.3]	$C_3S+\alpha'$ C_2S	.1
3	70.6	26.4	$C_3S+\alpha'$ C_2S	not det'd
4	69.6	26.4	C_3S+much-α'-C_2S	not det'd

[a] Glycerol alcohol method, W. Lerch and R. H. Bogue, Ind. Eng. Chem. Anal. Ed. 2, 296–8 (1930).

In interpreting these results, allowance must be made for the increasing amount of α'-C_2S occurring in mixes of increasing P_2O_5 content. In the 2 percent P_2O_5 mix, for example, the α'-C_2S content can be estimated to be about 30 percent by weight of the total. So far it has not proved possible to isolate the individual P_2O_5-containing C_3S phase (or phases) for study, and it has therefore been necessary to use mixes containing one additional phase and draw deductions accordingly. Since the α'-C_2S is comparatively inert hydraulically, the fall in strength in the mixes progressing from 2 to 4 percent P_2O_5 can be accounted for by the increasing dilution of the C_3S phase with almost nonhydraulic material. The 2 percent P_2O_5 mix, although diluted with some 30 percent of α'-C_2S, gives strengths comparable to pure C_3S, so that the form of C_3S present in this mix can be considered to possess enhanced hydraulic value. Between this form of C_3S and pure C_3S, however, an intermediate state occurs in the 1 percent P_2O_5 mix resulting in decreased hydraulicity.

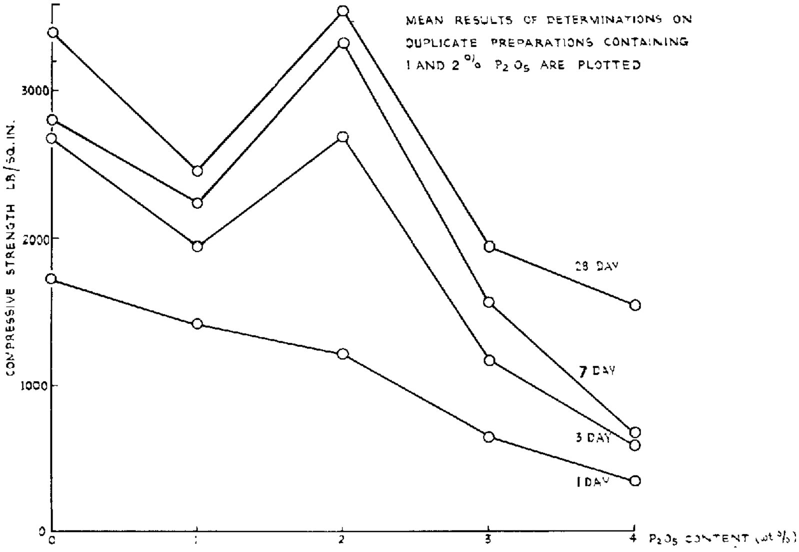

FIGURE 2. *Compressive strength (on 1/2″ 1:3 mortar cubes) of preparations on the join* C_3S–(24.1 C_3P, 75.9 C_2S wt %) *in the system* CaO-SiO_2-P_2O_5.

From the experimental work conducted to date it seems most probable that C_3S can take up a maximum of about 1 percent P_2O_5 in solid solution, but the results could also be interpreted on the basis of a 3 to 4 percent solubility of CaO in C_3S. The strength results may be explainable when further mixes in this region of composition have been examined. In this instance it seems that the increased reactivity of C_3S may be due to lattice distortion rather than true polymorphism.

Effect of Fluorine

Experimental Procedure

As in the preparation of phosphatic C_2S, the finely ground components, $CaCO_3$, crushed quartz, and fluorspar (99 percent pure), were mixed and pelleted, the components being proportioned to give a weight percentage composition between C_3S and fluorine. The heat treatment, however, was conducted in a closed tubular furnace designed to minimise the loss of volatile components. As expected from earlier work, a proportion of fluorine was lost during ignition, as indicated in table 3. The ignited products were analysed for free lime and fluorine content, and submitted to X-ray examination. Strength tests were determined as for the phosphatic C_2S preparations.

TABLE 3. *Effect of fluorine on* C_3S: *analytical fluorine and free lime in mixes studied*

Nominal composition		Actual fluorine content [a] (±0.02)	Free CaO
C_3S	F		
wt %	*wt %*	*wt %*	*wt %*
99.75	0.25	0.22	1.8
99.5	.5	.38	Nil
99.4	.6	.51	0.3
99.25	0.75	.74	.5
99.0	1.0	.88	Nil
98.0	2.0	1.73	0.1

[a] Method based on those of H. H. Willard and O. B. Winter. Ind. Eng. Chem. Anal. Ed. **5**, 7 (1933), and W. F. Hillebrand and G. E. F. Lundell, Applied Inorganic Analysis, 2d Ed., 744, Chapman and Hall, London, (1953).

Results and Discussion

The analytical results are given in table 3, and the strength results in figure 3. It was found that fluorine greatly accelerates the formation of C_3S. Whereas for complete reaction pure C_3S requires heating at 1,550 °C for about 60 hours, a fluorine content of 0.2 percent reduces the heating period to 2 hours or less. As fluorine content increases there is a progressive change in the X-ray diffraction pattern from that of C_3S towards that of alite. Triplets and doublets in the characteristic triclinic C_3S pattern tend towards single lines associated with the alite pattern. The greatest change from a pure C_3S-type to an alite-type pattern occurred in the interval between 0.38–0.51 percent fluorine, and the pattern at 0.74 percent fluorine is the nearest to that of alite found in this series (fig. 7). With still higher fluorine content, α'-C_2S and α-C_2S patterns appeared. Stabilisation of α'- and α-C_2S by fluorine alone has not been previously reported, and attempts to stabilise these forms with fluorine in the absence of C_3S were unsuccessful, resulting only in the formation of a mixture of γ and β-C_2S. It has been suggested [5] that C_2S is stabilised by CaO, and if the C_3S is regarded as a source of excess CaO the fluorspar may well be acting as a flux to aid the incorporation of excess CaO in the C_2S lattice. The composition given for the alite of normal portland cement by Jeffery [13] is $(CaO)_{54}(SiO_2)_{16}Al_2O_3MgO$, and the production of a material containing neither Al_2O_3 or MgO which gives an X-ray diffraction pattern somewhat similar to that of alite is therefore noteworthy.

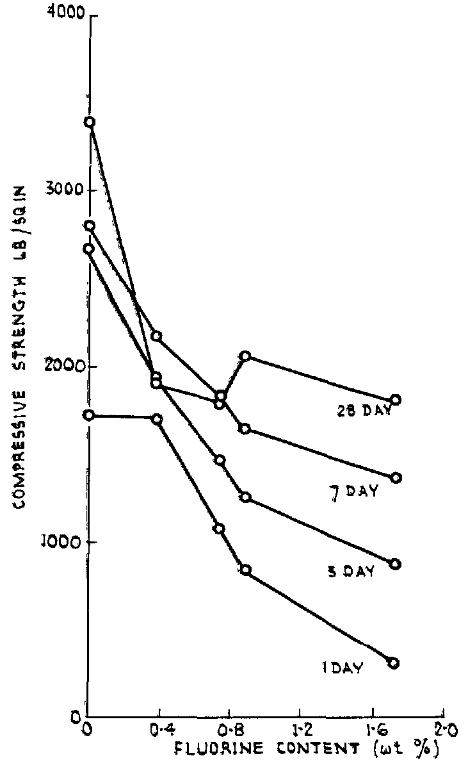

FIGURE 3. *Compressive strength (on 1/2" 1:3 mortar cubes) of* C_3S *preparations with different fluorine content.*

Apart from some anomalies in the 28-day results which have so far not been accounted for, the compressive strength results given in figure 3 show that as fluorine content increases the compressive strength of C_3S decreases. Although some α'- and possibly α-C_2S, as detected in mixes of fluorine content above 0.74 percent, must contribute to the overall fall in strength, the major effects are thought to be associated with the polymorphism of C_3S. The present results indicate that the effect of fluorine is not merely that of a flux, but that structural changes are produced which have considerable influence on hydraulicity.

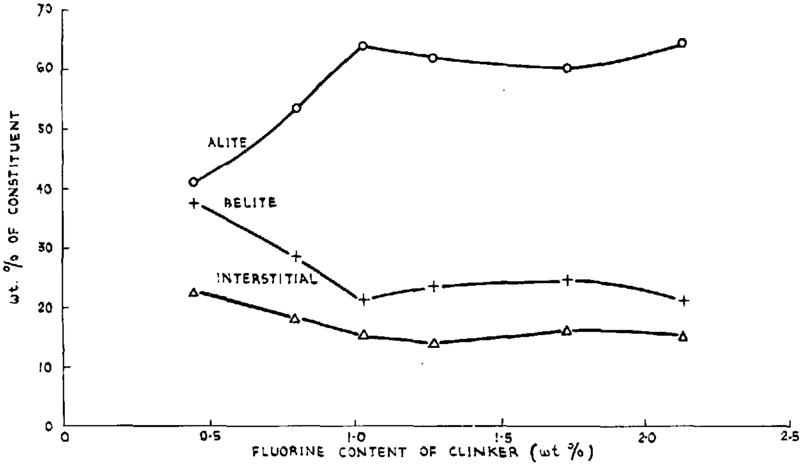

FIGURE 4. *Mineral composition of clinkers containing fluorine as determined by microscopic point counts.*

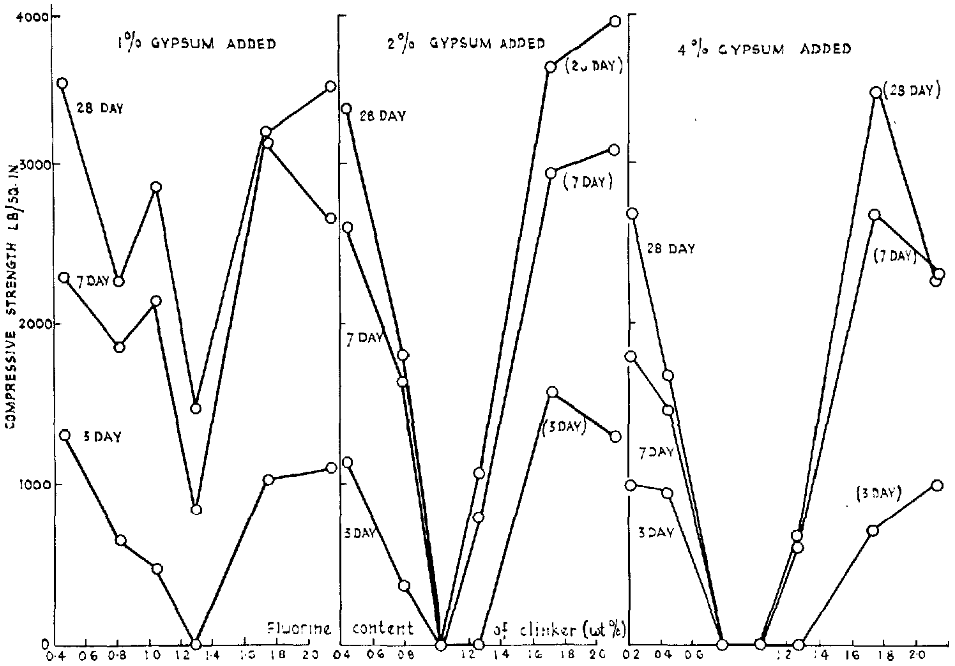

FIGURE 5. *Compressive strength (on 1/2'' 1:3 mortar cubes) of cements with different fluorine content.*

It had been previously observed in laboratory experiments on the addition of fluorspar to phosphatic clinkers that compressive strength did not rise proportionately to "C_3S" content. This is illustrated by figures 4 and 5. Figure 4 shows the mineralogical composition of the clinkers as determined by microscopic point counting, and figure 5 gives the corresponding strength results with various gypsum additions. The raw meal analysis from which this series of fluorinated clinkers was prepared is given in table 4. The lack of correlation between "C_3S" content and strength finds a partial explanation in the experimental results of fluorine addition to pure C_3S. Thus fluorine facilitates the formation of C_3S, but the fluorinated phase becomes less hydraulic, and the net effect of fluorine addition to clinker is beneficial only if the advantage of greater quantity outweighs the loss in quality.

In figure 5 two features are remarkable. First, the strength of the cement falls to a minimum in the region of 0.8–1.27 percent fluorine content, and then rises again at higher fluorine levels. This behaviour suggests that optimum performance of the cement could be achieved, at least under laboratory conditions, by careful control of the phosphate and fluorine content, and equally that considerable falls in strength might occur through unsuitable proportioning of these components. The second feature in figure 5 is the marked effect that the gypsum addition has on strength development. It can be seen that the minimum strength region referred to above is particularly accentuated by increased gypsum addition, although the reasons for this are obscure. The results do, however, emphasise the importance of the minor components in modifying the behaviour of an actual cement composition through their effect on the principal constituents.

TABLE 4. *Fluorinated clinker series: analysis of cement raw meal*

	%
SiO_2	12.52
Fe_2O_3	4.03
Al_2O_3	2.79
TiO_2	0.22
Mn_2O_3	.23
CaO	42.94
MgO	0.89
Na_2O	.65
K_2O	1.72
P_2O_5	1.62
F	0.27
Total S	49
Sulfate (SO_3)	.34
Sulfide (S)	.07
Loss on ignition	31.31
CO_2	28.88
Loss at 110 °C	0.70

Decomposition of C_3S

Until recently C_3S occupied a unique position in silicate chemistry. Early investigators claimed that the pure compound is formed only in a solid-state reaction between CaO and C_2S at temperatures above 1,250 and below 1,900 °C, at which temperature it again dissociates in the solid state into CaO and C_2S. It has since been established by Welch and Gutt [7] that C_3S does not decompose at 1,900°, but that it melts incongruently at 2,070° to form CaO and liquid. In fact the C_3S primary phase field in the system CaO–SiO_2 extends from the eutectic with C_2S at 2,050 °C, 69.5 wt percent CaO, to the incongruent boundary with CaO at 2,070 °C, 71.5 wt percent CaO. These results are supported by new work on the system CaO-C_2S-C_3P, in the course of which Gutt [12] has explored the liquidus surface and found that the primary crystallization field of C_3S extends to about 13 percent P_2O_5.

The lower temperature limit of C_3S stability has been regarded [14] as 1,250°, but this has been questioned by Yannaquis [15] and by Yamaguchi and Miyabe [16]. The former author maintains that only impure C_3S is decomposed at low temperature, and the latter authors state that they were able to cool C_3S slowly from 1,550 to 1,000 °C without decomposition. It must be remembered, however, that the actual rate of decomposition is very slow, and can only be detected by analysing the small quantities of free lime liberated over a period of many hours. In the present work the separate effects of phosphate and fluorine on the stability of C_3S in the region of 1,250 °C have been studied, and in both instances decomposition has been observed.

Effect of Phosphate

The composition 71.1CaO,26.9SiO_2,2P_2O_5 (wt percent) was heated for about 100 hr in turn at descending and then at ascending temperatures, free lime determinations being made between ignitions. Decomposition occurred between 1,160 (no free lime) and 1,050 °C (appearance of 1.4 percent free lime). On reheating, a reduction of 0.2 percent free lime occurred between 1,160 and 1,210 °C, thereby locating the decomposition temperature at approximately 1,160 °C. The stability range of C_3S therefore would appear to be slightly prolonged by the incorporation of phosphate.

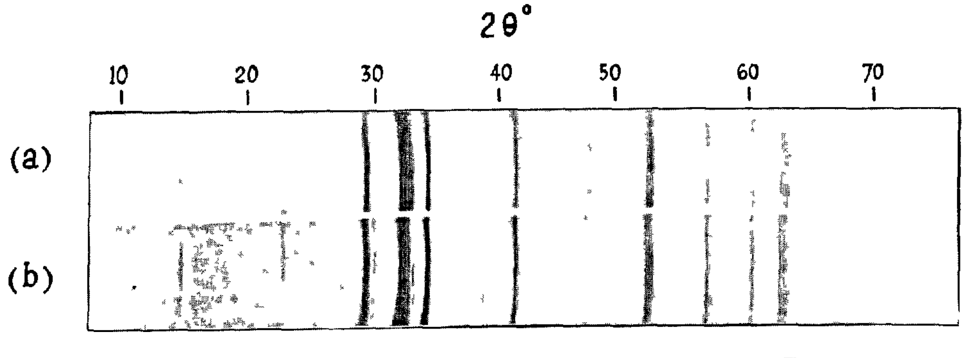

FIGURE 6. *X-ray photographs obtained in Guinier type focusing camera,* CuKα *radiation, showing shift in* C_3S *pattern due to phosphate.*

(a) Composition $2P_2O_5$, 71.7 CaO, 26.3 SiO_2, Wt. %.
(b) Mixture of pure C_3S (85%) and α'-C_2S (15%).

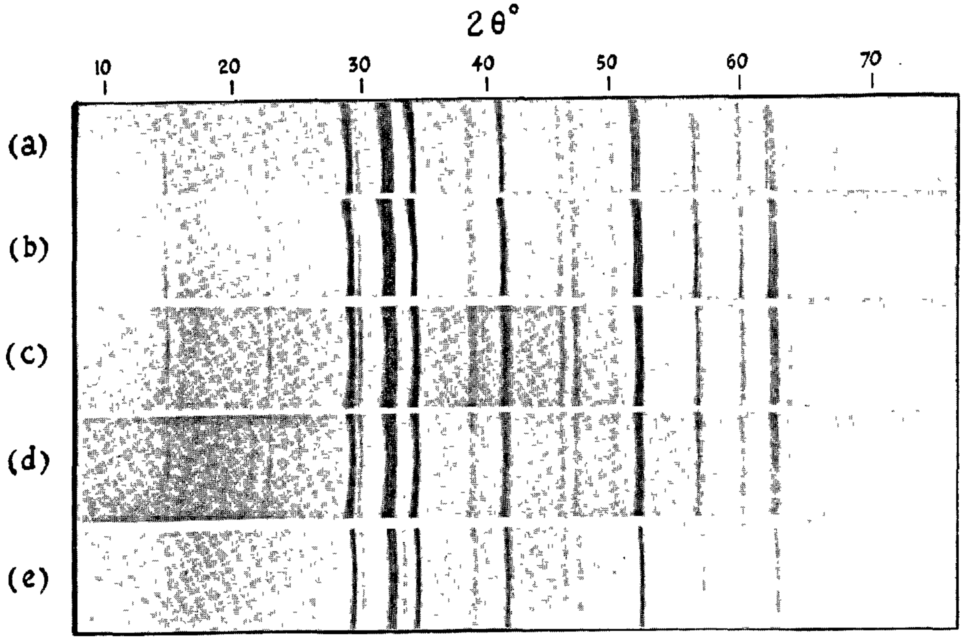

FIGURE 7. *X-ray photographs obtained in Guinier type focusing camera,* CuKα *radiation, showing change towards alite in* (C_3S+*fluorine*) *Wt% compositions.*

(a) C_3S (Pure).
(b) C_3S (0.38 F content).
(c) C_3S (0.51 F content).
(d) C_3S (0.74 F content).
(e) Alite ($C_{54}S_{16}AM$).

Effect of Fluorine

For C_3S containing 0.75 percent fluorine, decomposition was first observed at 1,230 °C and occurred readily at 1,170 °C. At the latter temperature 3.9 percent free lime was liberated after 1 hr during which the fluorine content had become reduced to 0.64 percent. The free lime had risen to 16 percent and the fluorine level dropped to only 0.06 percent after a period of 16 hr at 1,170 °C. Clearly fluorine greatly accelerates the rate of decomposition below the stability limit just as it promotes rapid combination above, and this point should be considered as one of practical importance in relation to slowly cooled fluorinated clinkers.

Conclusions

Early studies of cement constitution emphasised that gross chemical composition could only be related to cement performance by discovering the actual cement compounds produced in the clinker, and then evaluating their separate contributions to the overall behaviour. Of necessity the complexity of phase equilibrium studies has concentrated attention on the four basic components CaO, Al_2O_3, SiO_2, Fe_2O_3, and the four major phases produced by their combination in clinker compositions. In this way perhaps there has grown up a tendency to regard the four major phases as possessing rather rigid characteristics, only influenced to a minor degree by the presence of the lessor components in the raw material.

We have now progressed to the stage where we can recognise that a knowledge of the chemical composition of the major phases is not sufficient to define their qualities, and that atomic arrangement plays an extremely important part in determining the way in which water will enter into the crystal lattice and develop hydraulicity. It is in this role of modifying the crystal lattice that the minor components play such an important part, one which is quite out of proportion to their quantitative representation in the clinker.

If the significance of the minor components in cement clinker has been underestimated in the past, it is hoped that this contribution will help to underline their importance. It may also disabuse us of any idea that the constitution of clinker in terms of four major compounds gives us anything like a complete picture of predictable cement behaviour. Rather does it provide a working sketch from which we have still to fill in much of the detail.

The investigations which have been described were undertaken with the cooperation and financial support of Uganda Cement Industry Ltd.

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Discussion

C. A. White

This paper draws attention to a particular field of great importance on which there has been little previous published work. The authors have stated a very special case largely connected with the combination of the effects of both phosphate and fluoride. Ershov [1][1] has already published some unusual results on the additions of phosphate to cement raw materials. So far no mechanism for the increased hydraulicity has been proposed. The two main possibilities would appear to be, increased free surface energy of the mineral crystal faces due to the deformation of the crystal lattice by interstitial emplacement of the minor components, alternatively an effect whereby nucleation or crystal growth is controlled to give smaller crystals [2]. It would be of interest to know if the authors have noted any effect on the crystal size during their microscopic examinations.

Graphs are given showing the influence of fluorine on phosphate-containing clinkers in relation to gypsum addition and compressive strength. No evidence is given for any effects on setting times of these cements. The use of fluorine as an additive to raw meal has been variously recommended and condemned, and included in certain patents for many years. Its use in shaft kilns has been studied over the past six years and it has been found that 0.2 to 0.3 percent of fluorine results in twenty to twenty-five percent higher compressive strengths for cement compositions from sulfate resistant to 13 percent alumina content. However, it has been noted that fluorinated clinkers of this composition show different setting times when ground hot or cold, in direct relationship to the compressive strengths. Laboratory cold ground clinkers having a final setting time of 1½ hr will give 25 percent more compressive strength and yield a final setting time of approximately 5 hr when milled under normal production conditions. Heating of the cold ground cement produces a similar change. Temperature studies indicate that this is connected with formation of hemihydrate, but in the presence of fluorine no false setting or change of consistency is noted. This connection of fluorine and setting suggests that apart from effects reported by Toropov et al., [3] the fluoride ion may be complexing with aluminum and acting as a carrier in its aqueous reactions.

The general effects of such small amounts of certain minor components, there being evidence for others than phosphate and fluorine, and their influence on compressive strengths, heats of hydration and other properties are of extreme interest when it is considered that such quantities freely occur in many cement raw materials at present in use. Much further work on these lines is obviously required.

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[1] Figures in brackets indicate the literature references at the end of this paper.

Closure

J. H. Welch

We would like to take this opportunity of replying to the comments made by Mr. White on this paper. Our object in presenting the strength results obtained on fluorinated clinkers was principally to emphasise the danger of assessing cement quality solely by mineralogical examination without also checking on the actual strengths obtained. We realised that in so doing we were presenting data which to say the least appeared unusual, and for which we have not so far been able to find a satisfactory explanation. We felt, however, that the results were so interesting that they should be presented with the object of stimulating interest and discussion. On the points specifically mentioned by Mr. White we can give little help because no observations on setting time were made, except that it was observed that no set appeared to take place in the samples for which zero strength at all ages was reported. The mineralogical point counts revealed no outstanding differences in crystal development within the series as a whole, and this in turn appeared quite normal when compared with the appearance of typical factory produced clinkers.

Mr. White's observations on strength and setting time relationships, and in turn their relation to grinding temperature, must lead us to a more careful examination of these factors. It is somewhat disconcerting to find that an apparently well-burnt clinker might be very largely influenced in its cementing behaviour by the manner of the gypsum addition. Our view is that the gypsum addition during the grinding of cement clinker tends to be made somewhat empirically in normal circumstances, and that for fluorinated clinkers the optimum performance of the cement requires a much more rigorous appraisal of the problem than has hitherto been attempted.

Paper II–S2. X-Ray Diffraction Examination of Portland Cement Clinker*

H. G. Midgley, D. Rosaman, and K. E. Fletcher

Synopsis

Two methods of determining the mineral composition of portland cement clinker are discussed, both of which depend on X-ray diffraction analysis. The first is a modified method of compound calculation from the oxide chemical analysis, knowing the composition of the ferrite phase from an X-ray diffraction analysis. The second is compound analysis by direct X-ray powder diffraction using a counter spectrometer.

A comparison between the modified calculation, direct diffractometry and the more usual Bogue method shows that there is a better agreement between the first two than between the latter and either of the first two.

The greatest errors in the Bogue method appear in those cements with the lowest C_3A. In these cements the ferrite appears to be richest in C_2F which makes the Bogue estimate of C_3A too low. In these cases the direct diffractometry is not yet entirely satisfactory, owing to interference.

Résumé

Cet exposé présente la discussion de deux méthodes pour déterminer la composition minérale du clinker de ciment Portland; toutes deux dépendent de l'analyse à l'aide de la diffraction des rayons X. La première est une méthode modifiée du calcul des composés à partir de l'analyse chimique des oxydes lorsque la composition de la phase ferrite est connue grâce à une analyse à l'aide de la diffraction des rayons X. La seconde, qui utilise un spectromètre à compteur Geiger, est une analyse des composés par diffraction directe des rayons X par la méthode à poudre.

Une comparaison entre le calcul modifié, la diffractométrie directe et la méthode de Bogue plus habituelle, montre qu'il y a du meilleur accord entre les deux premières qu'entre cette dernière et l'une ou l'autre des deux premières.

Dans la méthode de Bogue les plus grandes erreurs se montrent avec les ciments de moindre teneur en C_3A. C'est dans ces ciments que le ferrite semble être le plus riche en C_2F, ce qui rend trop basse l'évaluation de Bogue. Dans ces cas-ci la diffractométrie directe n'est pas encore complètement satisfaisante à cause d'interférence.

Zusammenfassung

Zwei Methoden für die Bestimmung der Mineralzusammensetzung der Portlandzementklinker, die beide auf einer Analyse der Röntgenstrahlenbeugung beruhen, werden erörtert. Die erste Methode ist eine Spezialberechnungsmethode, die man anwenden kann, wenn man die chemische Oxydanalyse und die Zusammensetzung der Ferritphase von einem Röntgenstrahlenbeugungsdiagramm kennt. Die zweite Methode ist eine Verbindungsanalyse durch eine direkte Herstellung eines Röntgenpulverdiagramms, in der man ein Spektrometer mit Zähler benutzt.

Ein Vergleich zwischen der modifizierten Berechnung, der direkten Beugungsmessung und der gewöhnlich angewandten Bogue Methode zeigt, daß die ersten beiden Methoden besser miteinander übereinstimmen, als mit der Bogue Methode.

Die größten Fehler treten in der Bogue Methode bei Zementen mit kleinsten C_3A-Gehalten auf. In diesen Zementen ist der Ferrit augenscheinlich im C_2F angereichert, und das bringt hervor, daß die Bogue Abschätzung zu klein ausfällt. In diesen Fällen ist die direkte Beugungsmessung noch nicht ganz zufriedenstellend, da Interferenz auftritt.

Introduction

The normal Bogue [1][1] method of calculating the compound content of a cement assumes that there is complete combination between raw materials at maximum temperature in the kiln, and that the clinker formed is cooled slowly so that chemical equilibrium is maintained. The formulae for the Bogue system show the four constituents to be linear mathematical functions of the chemical analysis. As a result, if some property such as strength is to be related statistically to composition, it follows from the mathematics that an analysis in terms of the Bogue constitution is no more informative than one in terms of the simple oxide analysis but it gives a more enlightened picture of the function of chemical composition in cement technology.

As a result of the study of the quaternary system CaO-SiO_2-Al_2O_3-Fe_2O_3 by Lea and Parker [2] it became possible to correct the Bogue treatment for possible deviations from equilibrium which might result from rapid cooling or separate crystallisation of that part of the clinker which had been liquid at the burning temperature.

In drawing up formulae for calculating compound composition it is assumed that the minerals

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Building Research Station, Department of Scientific and Industrial Research, Watford, England.

[1] Figures in brackets indicate the literature references at the end of this paper.

identified in cement clinker are exactly the same as those found in phase rule studies using pure chemicals. This leads to two sources of error. Firstly, in real cement there are present the so-called minor constituents such as alkalis, FeO, MnO, and SO_3; these alter the relationship between the main cement compounds and, by entering into solid solutions with them, alter their nature as well as the amount present. Secondly, even in pure mixtures the cement compounds dissolve in each other to some extent.

Examples of the first kind are given by Welch and Gutt [3]. The best known example of the second is shown by the fact that the iron compound is not necessarily C_4AF, but a member of a solid solution series of variable composition [4–7].

To overcome these difficulties, either the composition of the ferrite must be determined before calculation, or a direct method of estimating the cement minerals must be employed. The only suitable way available for either ferrite composition determination or direct compound determination is X-ray powder diffraction. Midgley [8, 9] has shown that the ferrite composition may be determined by reference to the parameters of the ferrite solid solutions; Von Euw [10] and Copeland et al., [11] have shown that X-ray diffraction methods may be used to determine the phase composition. When the ferrite composition is known the oxide chemical analysis may be used to calculate the phase composition in the modified Bogue method as follows. First the composition of the ferrite phase is determined from powder X-ray data; all the Fe_2O_3 in the chemical analysis is assigned to $2CaO{\cdot}Fe_2O_3$ with which the appropriate amount of CaO and Al_2O_3 are then combined to give the ferrite composition determined. The remaining Al_2O_3 is assigned to C_3A; then the remaining CaO and SiO_2 are combined in the normal Bogue manner to form $3CaO{\cdot}SiO_2$ and $2CaO{\cdot}SiO_2$.

This paper will present investigations by X-ray methods into the two important questions, determination of ferrite composition and direct measurement of phase composition by X-ray powder diffractometry.

Measurement of Ferrite Composition

It is usually accepted that the ferrite phase in portland cement lies in the solid solution range C_6AF_2-C_6A_2F. The determination of the composition of this phase is not possible by chemical analysis for it is impossible to separate the ferrite from the other cement phases. It is therefore necessary to use an indirect physical measurement as an indication of the composition. Three possible physical properties that might be used are refractive index, magnetic susceptibility and X-ray diffraction. Parker and Ryder [12] used the refractive index method to determine the composition of ferrites in high-alumina cement clinkers, but unpublished data of Midgley and Ryder [13] did not give reliable results for portland cement clinker. Magnetic susceptibility measurements have not been used on portland cement clinker, for although Malquori and Cirilli [6] showed that there was a direct relationship between ferrite composition and magnetic susceptibility, the measurement of susceptibility of a cement would not give a measure of composition without knowing how much of the constituent was present. In the case of portland cement clinker both composition and quantity are equally unknown. There remains the X-ray diffraction method. It was shown by Midgley [8] that the composition of the ferrite phase could be determined from the lattice parameters measured in the powder X-ray diffraction pattern.

Three methods of measuring these parameters have been suggested: firstly on a magnetically separated fraction [8, 9] by measuring the 202 reflection at 1.94 A; secondly on the normal cement clinker by measuring the 141 reflection at 2.63 A [11, 14]; or thirdly, on a chemically separated fraction [15].

Nothing more need be said about the first two methods but the third method due to Fratini and Turriziani has been further investigated and the results are given below.

Fratini and Turriziani described a reagent consisting of 25 cm^3 water, 65 cm^3 ammonia, and 10 g ammonium citrate which preferentially dissolves the silicates from portland cement, leaving a residue consisting mainly of C_3A and ferrite. They used the method in order to obtain better X-ray powder diffraction patterns of the ferrite phase than was possible from the original cement.

The treatment they describe consists of shaking 1 g of the sample of cement with 100 cm^3 of the reagent for 12 hr. The solution is decanted from the residue and the residue shaken with a further 100 cm^3 of reagent for a further 12 hr. The residue is filtered off on a sintered glass crucible, washed rapidly with ammonia and dried at 110 °C. Their residue varied between 34 and 38.7 percent.

Keil and Gille [16] have pointed out that the aluminates are more sensitive to attack than the aluminoferrites, while Fratini and Turriziani [15] indicate that the aluminoferrites become less sensitive to attack with increasing iron content. The latter authors found that brownmillerite, ground just to pass a 178 mesh sieve, dissolved up to a maximum of 6 percent in 12 hr and that the X-ray pattern of the residue was similar to that of the original sample.

Data for the solubility of three ferrites, C_6AF_2, C_4AF and C_6A_2F, have been redetermined and the results are given in figure 1. The rate of solubility for C_3A is even greater than for C_6A_2F. Despite this, the method does give a concentration of the ferrite and C_3A phases in portland cements. Fratini and Turriziani suggest that the ferrites in

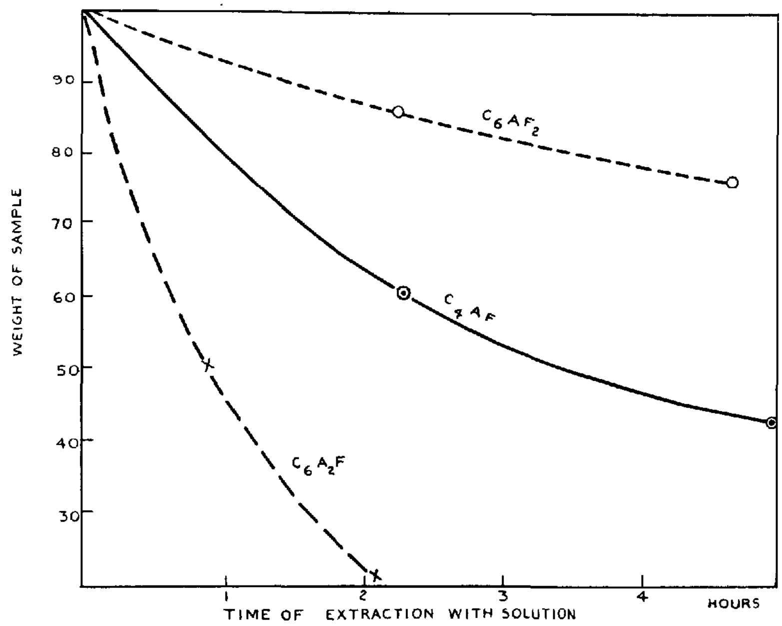

FIGURE 1. *Comparative rates of solution of ferrites (1g solid/100 cm^3).*

TABLE 1. *Weight percent of C_2F in 15 clinkers, determined by three methods*

Clinker	Camera; magnetic fraction (1958)	Direct X-ray diffraction	X-ray diffraction after Fratini and Turriziani extraction	
	202 reflection	141 reflection	141 reflection	202 reflection [a]
A. 9	56	54	52	48
A. 10	65 39 (52)	56 47 (51)	60 54 (57)	50 42 (46)
A. 20	66	60 48 (54)	61 51 (56)	No distinct peak.
A. 35	71 39 (55)	57	58 53 (55)	50
A. 36	74 39 (57)	56 48 (52)	50	48
A. 37	66	63 47 (55)	56	46 35 (40)
A. 39	66	50	54 50 (52)	49 41 (45)
A. 40	66	63 52 (57)	56	46
A. 143	65 39 (52)	59 50 (55)	56 48 (52)	48 42 (45)
A. F	56	73 59 (66)	64	62
A. 141	65 39 (52)	62 50 (56)	63 55 (59)	45
A. 7	54 39 (47)	64 46 (55)	62 52 (57)	No distinct peak.
A. 5	54 39 (47)	62 54 (58)	54	48
A. 33	71 39 (55)	68 51 (59)	63 57 (60)	37 33 (35)
A. 113	------------	70 54 (62)	70 46 (58)	66 46 (56)

[a] The use of the 202 reflection is not very satisfactory for the diffractometric techniques of using KBr or Si as an internal standard. Both KBr and Si give peaks close to the ferrite 202 region; i.e., ferrites (46.6–47.5)° 2θ; KBr 45.60°2θ, 47.74°2θ; Si 47.30°2θ.

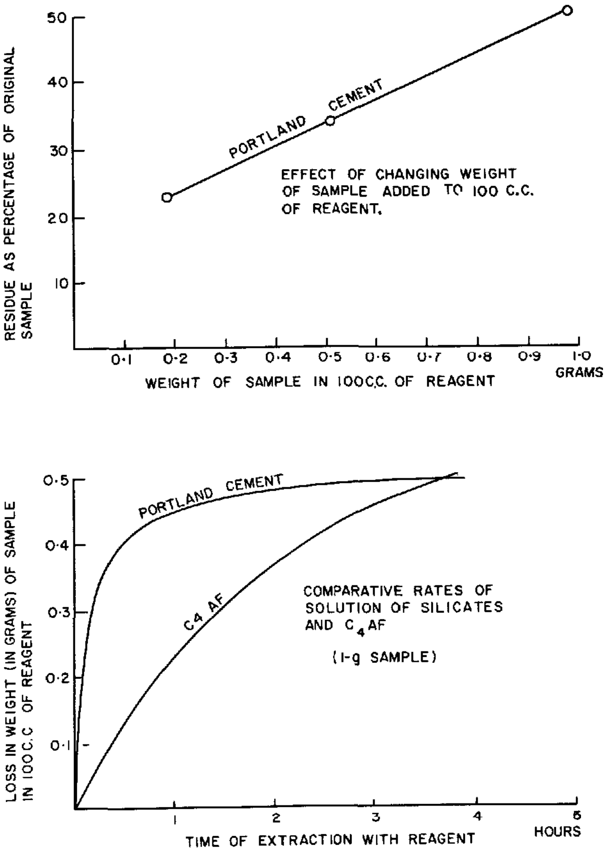

FIGURE 2. *Comparative rates of solution of silicates and* C_4AF.

portland cement are protected from attack by the silicate phases. We would suggest the much more rapid dissolution of the silicate phase can effectively deactivate the reagent before solution of the other phases has proceeded to any extent.

Further work on the chemical method has been carried out, and we have found that a single extraction carried on for about three hours can leave a residue of about 22 percent whose X-ray diffraction pattern indicates the complete removal of crystalline silicate phases. This is effected by reducing the initial concentration of the sample in 100 cm^3 of reagent to about 0.2 g (fig. 2).

The three methods outlined above have been tried on 15 of the cements originally investigated by Midgley [8] and the results are given in table 1. The experimental error in the composition is about ±3 percent C_2F.

The results given by magnetic separation, by direct diffractometry, and those given by the 141 reflection after chemical separation agree reasonably, but the results given by measurement of the 141 and 202 reflection on the same sample disagree badly. This discrepancy may be due to solid solution with some other component such as MgO.

Direct Determination of Cement Composition by X-ray Diffractometry

The method used for the quantitative estimation of cement compounds is based on the fact that the integrated intensity of a reflection produced by X-ray powder diffraction is directly proportional to the amount of the substance producing it [17, 18].

In the method reported here the integrated intensity of the diffracted beam is recorded by a ratemeter using a Geiger-Müller tube. The different diffracted beams are recorded on a ratemeter recorder plotting intensity against 2θ; thus the integrated intensity can be measured as the area under the peak produced. The apparatus used is the commercial Dutch Philips Diffractometer. To obtain a reasonably small standard deviation of the integrated intensity the powder sample for the diffractometer must be ground to less than 5μ. Various methods are available to carry out the grinding; agate pestle and mortar, ball mills, or vibratory mills, but experience has shown that all these methods either take too long or require too large a sample. To overcome these difficulties a miniature vibratory rod mill (fig. 3) has been designed and built at the Building Research Station, which will grind 0.3 g of sample in isopropyl alcohol to less than 5μ in 2 hr.

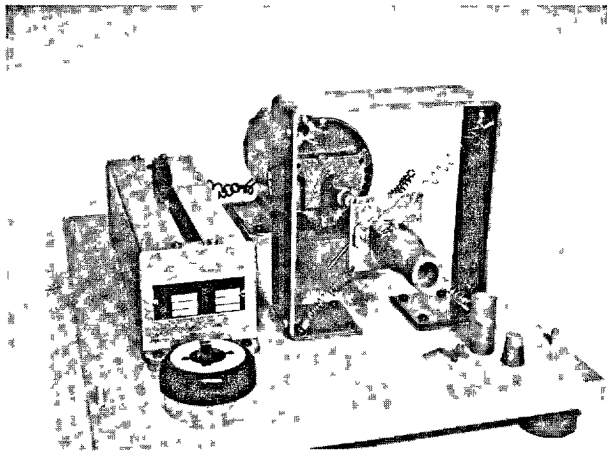

Figure 3. *Vibratory micro-rod mill.*

It is usual to compare all intensities with that produced by a fixed proportion of a suitable internal standard. This eliminates differences which might arise from sample to sample due to the method of preparation. It was found that a 12 to 1 weight ratio of sample to potassium bromide was satisfactory. In only one case has potassium bromide proved unsatisfactory as an internal standard, namely, for a cement containing calcium chloride. It is for such cases that silicon as an internal standard would be preferable. Silicon is much more difficult to grind than potassium bromide and if the sample is not equally ground, segregation may occur and there will be discrepancies in the diffraction intensities produced. The micro rod mill will adequately handle silicon mixes.

The samples were prepared by a loose packing method in a standard sample holder to avoid preferred orientation.

Mechanical mixtures of the four main cement minerals, alite, β-dicalcium silicate, tricalcium aluminate, and ferrite were made. After repeated diffractometer traces, the average integrated intensity of the compound (I_C) divided by the integrated intensity of the potassium bromide peak (I_{KBr}) was plotted against the percentage of the compound present; these were the calibration graphs.

In preparing the calibration graphs sixteen mixtures were used, eight containing alite, C_2S, C_3A, and C_4AF, four containing C_3A and C_3S, one containing alite, β-C_2S, and C_3A and three containing alite and C_3A. The standardization was complicated by the presence of C_3A in the alite used. In work on the ferrite phase it was found that, as a first approximation, the calibration for C_4AF could be used for ferrites of slightly different composition. The calibration was extended to the range C_6AF_2–C_6A_2F. The calibration constant for a composition within the range can be found by interpolation.

The peaks used for the particular compounds were as follows:

CuKα radiation,

Alite 29.4° $2\theta = 3.04$ A
Alite 30.0° $2\theta = 2.98$ A
β-C_2S 31.1° $2\theta = 2.87$ A
C_3A 33.2° $2\theta = 2.699$ A
C_4AF 33.5°–33.85° $2\theta = 2.67$A.

The calibration graphs obtained were all straight line plots passing through the origin.

Any interference due to adjacent peaks was allowed for in the graphical interpretation of the resulting pattern. In interpreting the patterns produced by cements, frequent reference is made to the original standard patterns, and also to superimposed patterns of the four main cement compounds.

The peak due to C_2S at 31.1° 2θ is weak and we have attempted a different treatment for estimating C_2S. At 32.6° 2θ and 34.4° 2θ peaks occur which are due to C_2S and alite. The total intensity is the sum of the individual intensities. Standard graphs were prepared relating I/I_{KBr} and percent alite for these two peaks in the absence of C_2S, and standard graphs relating I/I_{KBr} and percent C_2S for these two peaks in the absence of alite. The latter was checked by examining standard patterns in which both alite and C_2S were present and subtracting the contribution due to alite alone.

The method used for cements would be to estimate alite from the peaks at 29.4° 2θ, and 30.1° 2θ, and to subtract the intensity due to alite alone from the total intensity at 32.6° 2θ and 34.4° 2θ. The amount of C_2S is determined from the residual intensity. We do not always get good agreement between the three results obtained for C_2S and at the moment our data for the peak at 34.4° 2θ are suspect. Two simultaneous equations can be written for the interfering peaks and solved for alite and C_2S. These results are not always in good agreement with results obtained on the other peaks, and have only been used in interpreting patterns obtained from set portland cement mortars when the line due to alite at 29.4° 2θ can be obscured by calcite whose main peak occurs at the same position.

At the moment there is some difficulty in determining low C_3A contents in the presence of high ferrite content since severe ferrite and β-C_2S interference means that no definite C_3A peak need be apparent, and at the time of writing this has not been solved to our complete satisfaction.

Using the methods outlined in this note and scanning each sample three times the following coefficients of variation of the mean were obtained:

Alite, 5 percent
β-C_2S, 11 percent
C_3A, 3 percent
Ferrite, 6 percent

The methods outlined have been used on two series of cements, one of old cements (some more than 25 years old) used by Midgley [8] in his work on ferrites, and a second series of modern British portland cements of various kinds.

Result of X-Ray Examination of Cements

The results given by the three methods of compound determination are given in tables 2 and 3.

TABLE 2. *Compound composition of old cement clinkers*

Compounds \ Cement No.		A.40	P. 893	A.5	539 S. R. P. C.	540 S. R. P. C.	520	512	Dg
Alite	Diff[a]	65	58	59	56	39	59	53	50
	Mod		68		52	31			
	Bogue	70	66	61	56	34.5	46	53	36
β-C_2S	Diff	13	16	11	17	32	16	21	30
	Mod		7		20	41			
	Bogue	7	8	9.1	17	38.3	29	22	37
C_3A	Diff	11.5	3.7	13.5	4.8	4.5	11	12.1	14
	Mod		5.8		3.0	4.7			
	Bogue	9.5	2.5	15.4	0.7	0.9	9.6	10.7	15
Ferrite	Diff	8.5	17.5	10.5	17.5	16.5	6.4	8.8	9
	Mod		15.2		17	16.6			
	Bogue	9.2	18	10.2	19	19.3	6.2	6.3	10
Ferrite comp., wt % C_2F by diffractometer 141 reflection		57	66	54	62	67	56	56	56

(N.B. Where the C_2F content is nearly equal to C_4AF no modified calculation is shown as it would be the same as by the Bogue calculation.)

[a] Diff =by Diffractometer
Mod =by *Modified Bogue calculation*
Bogue=by Bogue calculation

TABLE 3. *Compound composition of modern British cement clinkers*

Cement No. / Compounds		(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
		572 O.P.C.[a]	625 O.P.C.	580 R.H.P.C.	615 O.P.C.	561 O.P.C.	569 O.P.C.	597 L.H.P.C.	592 O.P.C.	A. S. R. S.R.P.C.
Alite	Diff	53	54	49	53	43	60	35	53	55
	Mod		42.5			42.5			56	50
	Bogue	47	42	44	48	42	48	26	55	53
β-C_2S	Diff	24	24	27	23	30	27	45	23	17
	Mod		25			29			21.5	20
	Bogue	28	26	32	23	30	29	49	22	18
C_3A	Diff	9.3	12.8	8.3	14.5	9.8	9.7	8.8	9.7	3.6
	Mod		12.1			10.0			9.1	4.0
	Bogue	8.4	12.9	8.8	13.1	10.9	9.5	9.2	9.7	0.9
Ferrite	Diff	9.5	11.0	6.2	9.0	12.5	7.6	6.9	7.5	17.5
	Mod		9.9			9.7			6.1	17.1
	Bogue	9.2	9.2	6.6	7.3	9.0	6.3	6.6	5.6	19.6
Ferrite comp., wt % C_2F		56	52	56	56	52	56	56	51	64

[a] O.P.C. = Ordinary portland cement
R.H.P.C. = Rapid hardening portland cement
L.H.P.C. = Low heat portland cement
S.R.P.C. = Sulfate resisting portland cement

Conclusions

Although all three methods of estimating the compound composition of portland cement clinker are still subject to errors, there appears to be a better agreement between the modified method of calculation from chemical analysis and direct diffractometry, than between the Bogue method and either of the other two.

The great errors in the Bogue method appear in those cements with the lowest C_3A. In these cements the ferrite appears to be rich in C_2F, making the Bogue estimate of C_3A too low.

The diffractometry measurement of C_3A in these cases (539, 540, A.S.R.) is not yet satisfactory but the modified calculation shows agreement with the diffractometer estimate.

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Discussion*

D. L. Kantro, L. E. Copeland, and Stephen Brunauer

Quantative Analysis of Portland Cements by X-rays

Over the past few years, experimental work has been performed at a number of laboratories throughout the world in an effort to apply the method of X-ray quantitative analysis to portland cement. Much of this work has already been discussed by Dr. Nurse. However, at the time of his writing, Dr. Nurse did not have at his disposal our paper on an extension of our previously published quantitative method combining X-ray and chemical data [1][1] to the pure X-ray method [2]. We should like to discuss the results of this latter work, including data heretofore unpublished, on a recently analyzed group of cements. In addition, we should like to present a few sidelights arising from our investigations in this field.

Experimental Problems in X-ray Cement Analysis

The X-ray diffraction pattern of a portland cement involves many complexities. A portion of a pattern of a normal portland cement is reproduced in figure 1. A number of strong lines are evident, one of which, at 2.71 A $(33^{\circ}2\theta)$ represents tricalcium aluminate, and one, in the vicinity of 2.67 A $(33.7^{\circ}2\theta)$ represents the calcium aluminoferrite solid solution phase.[2] The ferrite and aluminate lines overlap, so that the area designated as "tricalcium aluminate peak" in figure 1 contains a considerable contribution from the ferrite phase. In spite of this serious overlap problem, we had to use these lines, because we were unable to find other lines of either of these materials sufficiently strong and sufficiently unhampered as to be useful for quantitative analysis.

The ferrite-aluminate overlap problem is complicated by the fact that the amount of overlap depends upon the composition of the ferrite solid solution phase. This composition can be expressed in terms of the A/F ratio of the phase. The *d*-spacings of the ferrite phase lines are dependent on the A/F ratio, and may be used for the evaluation of this quantity. For the whole cement, only the line at 2.67 A may be used, but if the cement is fractionated, either chemically [3,4] or magnetically [3], other lines may be used. However, there is always the possibility of a disproportionation in a separation procedure, if the ferrite phase is not homogeneous. The A/F ratio may also be evaluated from combined X-ray intensity and chemical data [1]. In a pure X-ray method, however, a *d*-spacing determination must be used.

The other strong lines in the pattern shown in figure 1, besides the silicon line, are due to the calcium silicates. Actually, each of these strong lines contains a contribution from each of the silicates: only a weak line, at $31^{\circ}2\theta$, is due to but one of the silicates, β-dicalcium silicate. Thus, a serious overlap problem exists for the silicates as well. However, because of the relatively numerous strong lines of these constituents of portland cement, some selection of lines is possible.

Thus, there are three basic experimental problems associated with the X-ray quantitative analysis of portland cement. These are: (1) resolution of the C_3A and ferrite phase lines, (2) precise determination of the *d*-spacing of a ferrite line, and (3) selection of suitable silicate lines. It would seem that the differences in results reported by various investigators are based on the different attacks on these three basic problems.

There is a fourth problem, though not as serious as those enumerated above, the selection of a suitable internal standard. Von Euw [5] used the 2.81 A line of NaCl; Midgley, Rosaman, and Fletcher [3] used the 3.30 A line of KBr. During the first year of our investigations we also used the latter as the internal standard, but we discarded it later in favor of the 3.14 A line of silicon. Because of the height of the KBr peak relative to the heights of the cement compound peaks, a weight ratio of 0.05 g of KBr/g of cement was used; when we substituted silicon, we could use twice as much internal standard. This has resulted in a larger area for the silicon line, and

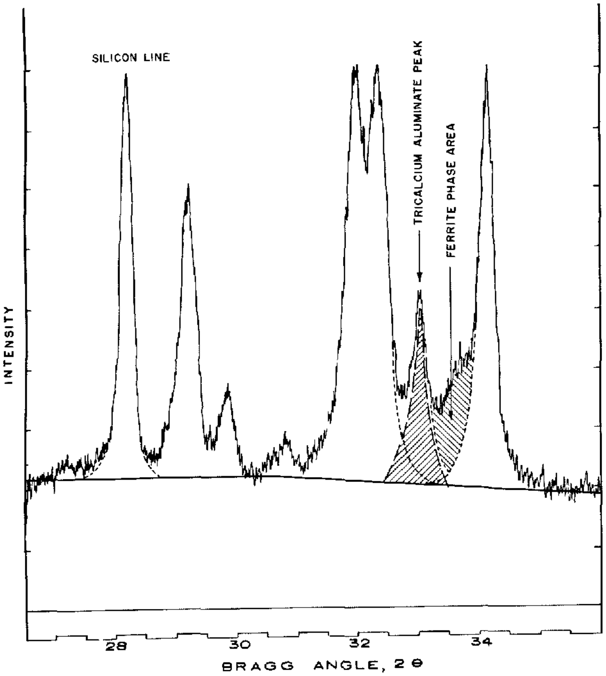

Figure 1. *X-ray diffraction pattern of a portland cement.*

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* This discussion discusses papers II-1, "Phase Equilibria and Constitution of Portland Cement Clinker" by R. W. Nurse, and II-S2, "X-Ray Diffraction Pattern of Portland Cement Clinker" by H. G. Midgley, D. Rosaman, and K. E. Fletcher.

[1] Figures in brackets indicate the literature references at the end of this paper.

[2] All angles refer to locations of reflections obtained with CuKα radiation.

in an improved precision of the data. In addition, it was not infrequent that we obtained anomalously high peaks with KBr, perhaps because of concentration of KBr in the surface layer of the mixture. Whatever the cause, this difficulty has not bothered us since we use silicon with the technique described earlier [2].

Calibration With the Internal Standard

In general, the calibration procedure is to observe intensity ratios for known weight ratios of cement compound to standard. However, it is equally important that the characteristics of the patterns from which the calibration data are obtained are as nearly like those of cement patterns as is possible. This is necessary not only because of the overlap between ferrite and C_3A lines, but also, as will be seen later, because we could not obtain linear relationships between relative intensities of lines and weight ratios of the silicates. Thus, one cannot simply make binary mixtures of each cement compound with internal standard and get usable data. Von Euw [5], Midgley and his coworkers [3] and ourselves [1] have all calibrated from mixtures of the cement compounds in proportions such as occur in portland cement.

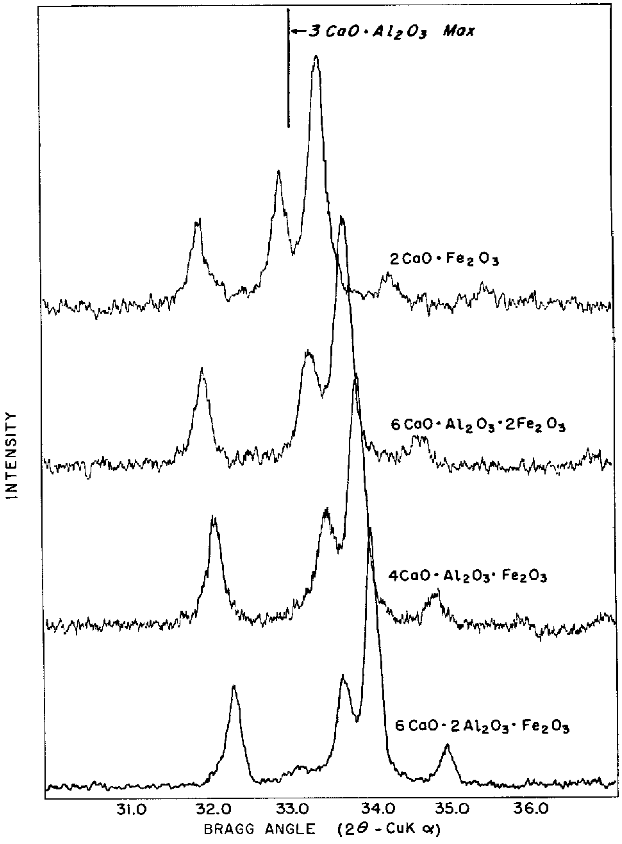

FIGURE 2. *X-ray diffraction patterns of calcium aluminoferrites.*

1. The calibration of the ferrites and aluminates requires, as was pointed out above, a consideration of the complex overlap situation that exists. As a first approximation, one may consider that the overlap correction may be obtained by a simple graphical procedure such as is illustrated in figure 1. Such a graphical procedure was used by Midgley, Rosaman, and Fletcher [3]. If this is the case, the calibration equations would take the form

$$\frac{P_F}{P_0}=\mu\frac{I_F}{I_0}=\mu R_F \tag{1}$$

where P_F/P_0 is the weight ratio of ferrite to internal standard, μ is a proportionality constant, and R_F is the intensity ratio of the ferrite line to the standard line.

On the other hand, the fact of the matter is that the ferrite region, actually composed of two ferrite lines, may strongly overlap the C_3A line and extend to even lower angles than that at which the C_3A peak occurs, as can be seen from figure 2. Thus, there may be an intensity contribution to the apparent C_3A peak which cannot easily be corrected graphically. As a second approximation, then, some equation may be set up to account for this phenomenon. We have adopted an empirical form

$$\frac{P_F}{P_0}=\mu[R_F+g(\nu)R_A] \tag{2}$$

where $g(\nu)$ is a function of ν, the molar A/F ratio, and R_A is the intensity ratio of the C_3A line to standard line.

Midgley, Rosaman, and Fletcher [3] found it expedient in their calibration to use C_4AF to represent all of the ferrites. As a first approximation, over a narrow molar A/F ratio range about unity, this is a simple and straightforward approximation, represented by eq (1) with μ independent of A/F ratio. Over the entire range of A/F values from 0 to 2, however, μ is not independent of A/F. Smith [6] has shown that there are A/F-ratio dependent intensity variations in ferrite diffraction lines, these variations being the results of crystallographic changes in symmetry caused by the substitution of aluminum for iron in C_2F. The dependence of μ on A/F ratio is of course a result of this phenomenon, and is illustrated in figure 3, the data for which were obtained from binary mixtures of C_2F, C_6AF_2, C_4AF and C_6A_2F with silicon. With the dependence of μ on A/F ratio taken into consideration, eq (2) becomes

$$\frac{P_F}{P_0}=g_1(\nu)[R_F+g_2(\nu)R_A] \tag{3}$$

where $g_1(\nu)$ and $g_2(\nu)$ are both empirical functions of ν, the A/F ratio. The use of such an equation avoids introduction of a systematic error proportional to the deviation of the A/F ratio from unity, which would result from the assumption of a μ value independent of the A/F ratio.

A similar expression may be set up for C_3A, wherein, however, the quantity μ' is independent of A/F ratio. Thus

$$\frac{P_A}{P_0}=\mu'[R_A-f(\nu)R_F] \qquad (4)$$

where P_A/P_0 is the weight ratio of C_3A to internal standard and $f(\nu)$ is some empirical function of the A/F ratio. In this equation R_A is corrected for the overlapping ferrite line in such a way that systematically high C_3A results are avoided in low overall A/F ratio cements.

2. The calibration of the silicates presents a different problem. As was stated before, all of the strong lines of either silicate coincide with lines of the other.

There is a reasonably strong line at 29°2θ, which is predominantly a C_3S line, though C_2S also makes a contribution to it. For equal weights of C_3S and C_2S, the contribution of C_3S to the intensity of the line is about 8 times that of C_2S. Midgley, Rosaman, and Fletcher [3], as well as Von Euw [5], have used this line for their determinations of C_3S. Neglect of the β-C_2S contribution to this line by Von Euw introduces only a small error for cements high in C_3S, but somewhat more significant errors for low C_3S cements (type IV).

At the beginning of our investigations we also used the same line, though we always considered the contributions of both C_3S and C_2S to the line. We discarded the line later because we found that calcium sulfate hemihydrate and gypsum, with strong lines at 2.98 A and 3.06 A, respectively, made significant contributions to the intensity of the line [7]. At the suggestion of Katharine Mather, we adopted the line at 51°2θ, instead.

There is a rather weak line at 31°2θ, which is a pure C_2S line. Midgley, Rosaman, and Fletcher, as well as Von Euw, have used this line for their determination of C_2S. We also tried this line, but found it unsatisfactory. Von Euw found it so unsatisfactory that he did not report any C_2S results in his paper. Midgley and his coworkers used the 32 and 34°2θ C_3S-C_2S lines, in addition to the 31°2θ line, to evaluate C_2S. The three results did not always agree well, and they especially suspected the 34°2θ results. In our early work, we tried both the 32 and 34°2θ lines, and we did not find either line satisfactory.

In our final work, we have adopted the 41°2θ C_3S-C_2S line and the already mentioned 51°2θ line for the quantitative determination of C_3S and C_2S. The use of two lines permits the simultaneous solution of two equations of the type

$$\frac{I_1}{I_0}=\alpha_1\frac{w_1}{w_0}+\alpha_2\frac{w_2}{w_0} \qquad (5)$$

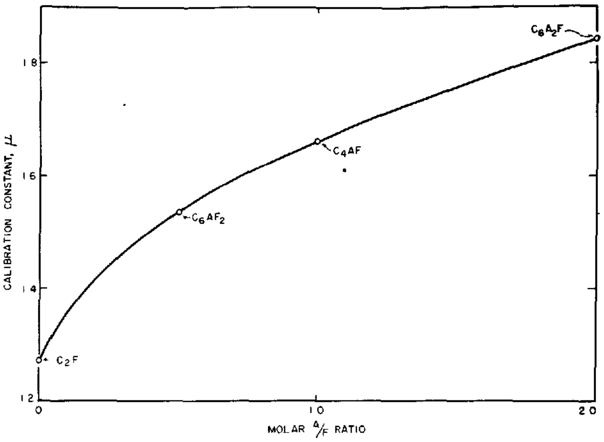

FIGURE 3. *Dependence of ferrite calibration constant on molar A/F ratio.*

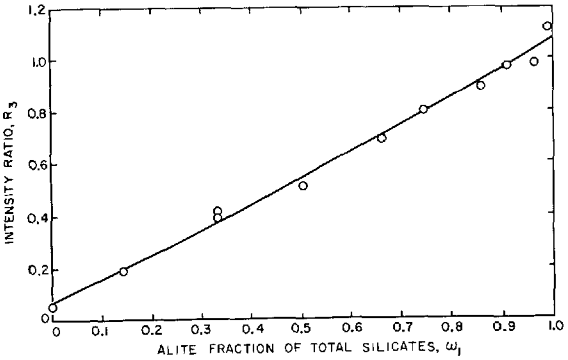

FIGURE 4. *Dependence of ratio of intensities of 51° 2θ line to 41° 2θ line on relative amounts of alite and belite in silicate calibration mixtures.*

$$\frac{I_2}{I_0}=\beta_1\frac{w_1}{w_0}+\beta_2\frac{w_2}{w_0} \qquad (6)$$

where I_1, I_2 and I_0 are the intensities of the two selected lines and the standard line, respectively. α_1, α_2, β_1, and β_2 are proportionality constants, and w_1/w_0 and w_2/w_0 are the weight ratios of C_3S and C_2S to standard, respectively. In our work. I_1 is the intensity of the line at 51.6°2θ, and I_2 that of the line at 41.1°2θ. I_0 is the intensity of the (111) silicon line (28.4°2θ).

Even though suitable lines are found from which interpretable X-ray data can be obtained, certain calibration problems still exist. It is not certain that the alite form of C_3S found in one cement is identical with that found in another cement; the same is true of the belite (C_2S) phase. That differences do exist is clearly shown by the results obtained when the calibration is carried out on preparations designed to give certain alite/belite ratios upon burning. These preparations were described previously [1]. On the basis of eqs (5) and (6) it can be shown that I_1/I_2, the ratio of the 52°2θ line to the 41°2θ line should be a linear function of w_1, the alite fraction of the total silicates. A plot of I_1/I_2 ($=R_3$) against w_1 is shown in figure 4. It can be seen that a curvilinear plot is obtained. This deviation from expectation indicates that there is a structural variation of either alite or belite or both as a function of composition. This was accounted for by the modification of eq (5) which we described in detail in an earlier publication [1]. Experimental evidence shows that the curvature of R_3 is caused by a curvature in I_1. Within experimental error, I_2 varies with composition in a linear manner.

The alite used for this work had the approximate composition $52C_3S{\cdot}C_6AM$, as contrasted to the composition $16C_3S{\cdot}C_6AM$ reported by Jeffery at the last symposium [8]. However, his results, and the results of other investigators, including ourselves, who have attempted to make alite of this composition indicated the presence of a significant amount of C_3A. We have prepared materials with overall A/S ratios of 1/52 ($52C_3S{\cdot}C_6AM$) which, while still demonstrating the alite diffraction pattern, contain negligible amounts of C_3A. These results are in quantitative agreement with those reported by Von Euw [5].

We have prepared alite using ferric oxide and magnesia instead of alumina and magnesia. The F/S ratio was 1/52. So far we have not investigated the iron stabilized alite, but it is clear that the presence of ferric oxide in alite may cause further complications.

Because of the possible variations in alite and belite structures due to the solution of different impurities, the calibration curves obtained for the silicates are not strictly applicable to the determination of alite and belite in portland cements. A somewhat better approximation is described in our second paper [2], in which the alite-belite results obtained for 20 portland cements by the combined X-ray and chemical analysis method were used for calibration purposes.

Analysis of Cements

Composition of the Ferrite Phase

The X-ray quantitative analysis of a cement is carried out in two steps: (1) determination of the composition of the ferrite phase and (2) determination of the amounts of the four major phases.

The results of the determinations of A/F ratio for 36 cements are given in table 1. The results are expressed in this table as molar A/F ratio, designated ν (columns 2, 3, and 4) and as mole percent C_2F, designated n (columns 5, 6, and 7). Values were obtained in two ways: (1) by determination of the d-spacing of the (141) ferrite line (ν_d and n_d, columns 2 and 5, respectively), and (2) by calculation from the intensity of this line and the total iron in the cement, as was described previously [1] (ν_1 and n_1, columns 3 and 6, respectively). The average values from these two methods, ν_{avg} and n_{avg} are given in columns 4 and 7, respectively. The determination of ν_1 involves the solution of a quadratic equation. In a few cases, a real solution could not be obtained because of the occurrence of a negative discriminant. In such cases, no value for ν_1 is given.

TABLE 1. *Ferrite phase compositions in portland cements*

1	2	3	4	5	6	7
Cement	ν_d	ν_1	ν_{avg}	n_d %	n_1 %	n_{avg} %
LTS-11	0.733	1.362	1.047	57.7	42.3	48.9
LTS-12	1.000	1.000	1.000	50.0	50.0	50.0
LTS-13	1.212	--------	1.212	45.2	--------	45.2
LTS-14	0.980	--------	0.980	50.5	--------	50.5
LTS-15	1.150	0.738	.944	46.5	57.5	51.4
LTS-16	0.949	1.180	1.064	51.3	45.9	48.4
LTS-17	.764	0.928	0.846	56.7	51.9	54.2
LTS-18	1.445	1.129	1.287	40.9	47.0	43.7
LTS-19C	0.862	0.983	0.922	53.7	50.4	52.0
LTS-21	1.096	1.058	1.077	47.7	48.6	48.1
LTS-22	0.815	1.178	0.997	55.1	45.9	50.1
LTS-23	.740	0.641	.690	57.5	60.9	59.2
LTS-24	.984	.966	.975	50.4	50.9	50.6
LTS-25	.805	.765	.785	55.4	56.7	56.0
LTS-31	1.170	1.014	1.092	46.1	49.7	47.8
LTS-33	0.920	1.254	1.087	52.1	44.4	47.9
LTS-34	.838	1.214	1.026	54.4	45.2	49.4
LTS-41	.865	0.939	0.902	53.6	51.6	52.6
LTS-42	1.150	--------	1.150	46.5	--------	46.5
LTS-43	0.815	.979	0.897	55.1	50.5	52.7
LTS-43A	.923	1.122	1.023	52.0	47.1	49.4
LTS-51	.764	0.923	0.844	56.7	52.0	54.2
SBR-15754	1.440	--------	1.440	41.0	--------	41.0
SBR-15698	0.742	.450	0.596	57.4	69.0	62.7
SBR-15622	.709	.920	.814	58.5	52.1	55.1
SBR-15497	.897	.842	.869	52.7	54.3	53.5
SBR-15669	1.217	.974	1.096	45.1	50.7	47.7
LS-1	0.300	.452	0.376	76.9	68.9	72.7
LS-2	.300	.442	.371	76.9	69.3	72.9
B-H	.835	.651	.743	54.5	60.6	57.4
B-L	1.070	.830	.950	48.3	54.6	51.3
BR-A	0.880	1.156	1.018	53.2	46.4	49.6
BR-B	.894	1.050	0.972	52.8	48.8	50.7
BR-C	1.008	0.970	.990	49.8	50.8	50.3
BR-D	0.613	.659	.636	62.0	60.3	61.1
BR-E	.783	--------	.783	56.1	--------	56.1

The median value of ν_d for the first 27 cements listed in table 1 is 0.96; that for ν_1 (23 of the first 27 cements) is 0.98. The median of the average values for the first 27 cements is 1.00, while the average of the average values is 0.99. In terms of mole percent, the average values of n_d, n_1 and n_{avg} are 51.4, 51.1, and 50.7 percent. These n values correspond to ν values of 0.95, 0.96, and 0.97, respectively. The mean deviation from the average is 2.7 percent.

Because there is only one ferrite diffraction line in the cement pattern amenable to d-spacing determination, and because even this determination can become quite uncertain when only a small amount of ferrite phase is present, other investigators have developed methods for separating a cement fraction containing a high percentage of ferrite. Thus, there is the chemical separation method of Fratini and Turriziani [4] and the magnetic separation method of Midgley [9]. These methods permit unencumbered observation of weaker diffraction lines.

Midgley, Rosaman, and Fletcher [3] have employed the chemical separation method, the magnetic separation method, and observations on the whole cement to determine the ferrite compositions for a group of 15 cements. They considered that their results by the magnetic separation method contained a bias on the C_2F side compared with results by the other techniques. This would indicate an inhomogeneous ferrite phase. Certainly a few cements are of this type as can be ascertained from the lack of sharpness of the (141) peak, as was pointed out by both Midgley [9] and ourselves [1]. Midgley, Rosaman, and Fletcher also observe, however, that their chemical separation results are in good agreement with the results from observation of the whole cement. At the same time they point out that the rate of solution of ferrite phase in the chemical medium used to dissolve away the silicates depends on the A/F ratio of the ferrite. On the basis of these two facts it would appear that the ferrite phase is homogeneous. Thus one may draw two conflicting conclusions from the results.

In spite of the claim of the C_2F bias of the results by the magnetic separation technique, only 7 of the 14 values reported indicate higher C_2F contents than the corresponding direct observation values, and 7 indicate lower C_2F contents. The molar A/F ratios corresponding to the mean weight percentages of C_2F for the 14 cements, obtained by magnetic separation, chemical separation and direct observation are 0.97, 1.00 and 1.00, respectively. These values are in excellent agreement with each other and are also in excellent agreement with our results.

One may, therefore, conclude that at least in the great majority of portland cements the ferrite phase is homogeneous. Because, however, there may be some cements in which the ferrite phase is not uniform [1, 9], it is safest to use the method of direct observation on the whole cement.

The constancy of A/F ratio after chemical extraction of the silicates, during which time a part of the ferrite phase is also dissolved, is consistent with the evidence presented by Copeland, Kantro, and Verbeck [10], showing that the A/F ratios of unhydrated residues of partly hydrated cement pastes are the same as those of the original cements.

The Quantities of the Four Major Phases

Analyses of 36 cements have been obtained by the combined chemical and X-ray method (CCX) [1] and by the method utilizing only X-ray data [2]. The primary calibration was that published by us originally [1], and the secondary calibration was that based on 20 of the 36 cements and published by us recently [2]. The results are given in table 2.

The conclusions based on the results from 36 cements are unchanged from those previously published. The CCX silicate data, given in columns 6 and 8 are those obtained by the total silica calculation described previously [1]. A comparison of the X-ray with the CCX results shows that the systematic errors of the pure X-ray ferrite, C_3A, C_3S, and C_2S values relative to the CCX values are +0.5, +0.1, +0.3, and +0.5 percent, respectively. The mean deviations are 0.9, 0.3, 2.5, and 1.4 percent, respectively, and the root mean square deviations (standard deviations) are 1.1, 0.4, 3.3, and 1.9 percent, respectively. Because of the nature of the calculations, the ratio of C_3S error to C_2S error is the same as the C_3S/C_2S ratio.

TABLE 2. *Compositions of portland cements*

1	2	3	4	5	6	7	8	9
Cement	Ferrite, percent		C_3A, percent		C_3S, percent		C_2S, percent	
	CCX	X-ray	CCX	X-ray	CCX	X-ray	CCX	X-ray
LTS-11	7.5	9.2	8.4	7.6	57.3	60.0	19.0	19.9
LTS-12	7.3	7.3	7.9	7.9	51.0	48.3	27.4	26.0
LTS-13	7.0	8.3	6.8	6.8	50.2	53.8	27.6	29.7
LTS-14	9.0	11.1	3.2	3.2	57.1	55.2	26.0	25.1
LTS-15	7.4	6.0	9.9	10.4	60.9	63.5	12.5	13.0
LTS-16	11.0	11.7	4.3	3.9	54.5	58.7	22.8	24.5
LTS-17	8.8	9.6	7.6	7.3	58.6	53.4	20.2	18.5
LTS-18	7.9	7.6	7.4	7.6	52.5	53.2	26.5	26.9
LTS-19C	8.5	9.0	6.2	6.0	57.7	54.1	20.8	19.6
LTS-21	10.1	10.0	3.6	3.6	45.7	49.6	35.6	38.6
LTS-22	11.8	13.4	3.1	2.3	49.4	50.2	29.9	30.4
LTS-23	14.2	13.3	2.2	2.6	55.6	55.5	23.2	23.2
LTS-24	14.4	14.4	2.1	2.2	48.8	50.3	26.4	27.2
LTS-25	13.5	13.2	0.2	0.3	38.7	37.6	43.0	41.8
LTS-31	6.6	6.3	7.6	7.7	57.7	56.7	17.1	16.8
LTS-33	7.9	8.7	7.4	7.0	55.8	58.7	17.6	18.5
LTS-34	10.2	11.4	3.6	3.0	61.3	62.8	13.6	13.9
LTS-41	14.6	15.0	0.2	0.0	25.4	25.6	52.4	52.8
LTS-42	8.8	10.0	1.3	1.3	31.6	33.2	52.4	55.0
LTS-43	13.1	14.1	3.0	2.5	30.2	33.9	47.9	53.7
LTS-43A	9.5	10.1	1.6	1.2	29.9	30.2	53.6	54.1
LTS-51	9.4	10.1	0.6	0.2	49.7	48.2	36.4	35.2
SBR-15754	8.0	10.0	7.1	7.1	52.0	52.3	25.2	25.3
SBR-15698	6.2	5.0	8.3	8.7	65.0	54.2	16.4	13.6
SBR-15622	11.7	13.1	0.0	0.0	52.6	51.9	30.6	30.3
SBR-15497	7.5	7.2	8.9	9.0	55.6	59.2	16.2	17.3
SBR-15669	6.0	5.7	0.7	0.9	29.7	30.4	57.8	59.1
LS-1	11.5	13.1	.0	.0	65.3	66.8	17.9	18.3
LS-2	10.8	12.2	.0	.0	70.0	63.9	12.3	11.2
B-H	13.2	11.8	6.4	7.0	56.6	55.2	23.8	23.3
B-L	8.6	7.7	9.0	9.3	51.8	56.4	28.6	31.2
BR-A	6.8	7.6	11.8	11.5	44.1	42.9	26.8	26.2
BR-B	6.3	6.8	9.3	9.2	41.5	46.6	32.0	36.0
BR-C	8.5	8.4	7.1	7.2	39.5	43.8	35.9	39.8
BR-D	15.3	15.6	0.0	0.0	43.4	42.8	34.6	34.0
BR-E	0.8	2.3	6.4	6.4	59.0	56.8	31.1	29.9

The C_3A contents determined for these cements are in every case lower than the values obtained by the Bogue potential compound calculation. Midgley, Rosaman, and Fletcher [3] reported C_3A values higher than the potential values for cements with low overall A/F ratios. However, one would expect that the C_3A would be the lowest in these very cements because of the tendency of low A/F ratio ferrites to take up additional alumina. As was stated before, the ferrite line may overlap the C_3A line in such a way as to be unresolvable graphically. As can be seen from figure 2, this would be the case all the more if the ferrite has a low A/F ratio. Hence, the Midgley, Rosaman, and Fletcher result appears to be a manifestation of an increasing high systematic error in C_3A content with decreasing ferrite A/F ratio.

TABLE 3. *Sums of oxides and major phases in portland cements*

Cement	Oxide sum	CCX sum	X-ray sum
	Percent	*Percent*	*Percent*
LTS-11	92.3	92.2	96.7
LTS-12	93.6	93.6	89.6
LTS-13	93.0	91.6	98.5
LTS-14	94.0	95.4	94.6
LTS-15	94.5	90.8	92.9
LTS-16	93.3	92.5	98.8
LTS-17	94.9	95.2	88.7
LTS-18	93.6	94.3	95.3
LTS-19C	92.2	93.3	88.7
LTS-21	95.5	95.0	101.8
LTS-22	93.9	94.3	96.2
LTS-23	95.7	95.3	94.6
LTS-24	91.8	91.8	94.0
LTS-25	94.2	95.4	92.9
LTS-31	90.3	89.0	87.6
LTS-33	91.5	88.7	92.9
LTS-34	90.9	88.6	91.1
LTS-41	92.6	92.5	93.4
LTS-42	94.4	94.1	99.4
LTS-43	94.1	94.2	104.3
LTS-43A	95.0	94.5	95.6
LTS-51	94.8	96.0	93.7
SBR-15754	92.0	92.2	94.7
SBR-15698	93.1	95.9	81.6
SBR-15622	94.6	95.0	95.3
SBR-15497	90.9	88.2	92.8
SBR-15669	94.4	94.3	96.1

The combined chemical and X-ray method has the advantage of restricting the error in the system somewhat by the limitations imposed by the oxide analysis. There are, however, a number of minor oxides in portland cement which may be dissolved in one or more of the four major phases. The CCX method does not take these into account. On the other hand, the X-ray method, not limited by the oxide analysis, measures the total amount of each of the major phases, regardless of the presence of minor oxides. Thus, a comparison of the sum of the major and minor oxides, corrected for substances known not to occur in the major phases [2], with the sums of the major phases obtained by the CCX and X-ray methods is useful in illustrating the overall accuracy of the methods. These sums are given in table 3. The CCX sums are on the average 0.3 percent smaller than the oxide sums, while the X-ray sums are on the average 0.8 percent greater. This implies that at least some of the minor oxides in the cement are dissolved in the four major phases. The mean deviations of the CCX and X-ray sums from the oxide sums are 1.0 and 2.6 percent, respectively, and the root mean square deviations (standard deviations) are 1.5 and 4.4 percent, respectively. It is to be expected that the CCX deviations would be smaller than the X-ray deviations because of the restrictions imposed on the system by the method.

Finally, the oxide results indicate that there is no significant amount of amorphous material in cement. The material designated as glass or glassy phase is actually microcrystalline, and hence detectable by X-rays.

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Discussion

H.-G. Smolczyk

Methods of X-ray investigation were the subject of several discussions at the Symposium. Although I discussed the matter several times with different gentlemen I shall try to combine some of these different discussions about preparation methods in one contribution. I should like to offer this discussion as a supplement to the very interesting paper of the Building Research Station.

At the Forschungsinstitut für Hochofenschlacke at Rheinhausen we fully agree to the opinion that the technique of preparing the samples is one of the most important parts of a quantitative X-ray diffraction analysis, and that wet grinding has important advantages.

Therefore, I want to report about the good experience we have had—for about 4 years—with a very simple wet grinding method for X-ray powder samples.

We use an ordinary small closed agate ball mill with a volume of 100 ml. In it, 1 cm^3 of the coarsely ground material together with 30 cm^3 of benzene (C_6H_6) are ground for 40 min. Then the benzene is removed and the very fine powder (2–6μ) dried quickly in a flow of dry air or in a vacuum. Afterwards the powder is placed in an ordinary sample holder with a rectangular window and is densely compacted. Careful precautions are taken to obtain an entirely even surface.

Some smaller advantages of this method are the short grinding time, the easy separation of the powder, with its higher density, from the lower density benzene, and the chemical inactivity of the benzene which excludes any reaction with the cements or with their hydration products.

The two main advantages will be described in detail:

(1) By carefully using this preparation technique a high degree of reproducibility is obtained. Moreover, the preferred orientations of some hydrates—e.g., calcium hydroxide or ettringite—are reproducible, too, and diagrams obtained with these substances can be used even for quantitative analysis. Care must be taken, however, that the X-ray pattern of the mineral used for comparison shows the same degree of preferred orientation.

To give an impression of the accuracy that can be obtained by this method, two examples from our practice are given. Each sample was prepared four times, and the intensity of the $Ca(OH)_2$ peak at $2\theta=18°$ ($CuK\alpha$) of each of the 8 specimens obtained was measured. The results were as follows (in percent of $Ca(OH)_2$):

Sample A: 21.8; 20.1; 18.8; 19.4; average, 20.0 ±0.7

Sample B: 0.9; 1.3; 1.5; 1.2; average, 1.2 ±0.2

$$\left(\text{Error calculated by } E=\pm\sqrt{\frac{\Sigma\Delta^2}{n(n-1)}}\right).$$

It must be mentioned here that the 18° peaks showed intensities which were approximately five times higher than normal, due to the effect of preferred orientation. The determination of 1.2 percent of $Ca(OH)_2$ was possible, however, only by using this orientation effect. Otherwise the low peak would have been disturbed too much by the high statistical background.

(2) In spite of the material being ground to an extremely fine powder, this method is nondestructive, and even the hydrates are not destroyed. Ettringite ($32H_2O$), which was nearly destroyed by 1 hr of dry grinding, did not change its intensities after having been ground in benzene for 10 hr (fig. 1a, 1b, and 1c). In order to detect a possible change of the diagram with time of exposure, the intense X-ray beam ($CuK\alpha$; 30 kv) was directed on the surface of the sample for 12 hr. Even then, however, the X-ray diagram did not change at all.

It should be added that after the Symposium it was learned that for the last two years, a similar method of wet grinding has been used in the laboratories of the Portland Cement Association at Skokie, Illinois (cf. L. E. Copeland, and R. H. Bragg, ASTM Bull. No. 228, Feb. 1958, pp. 56–60).

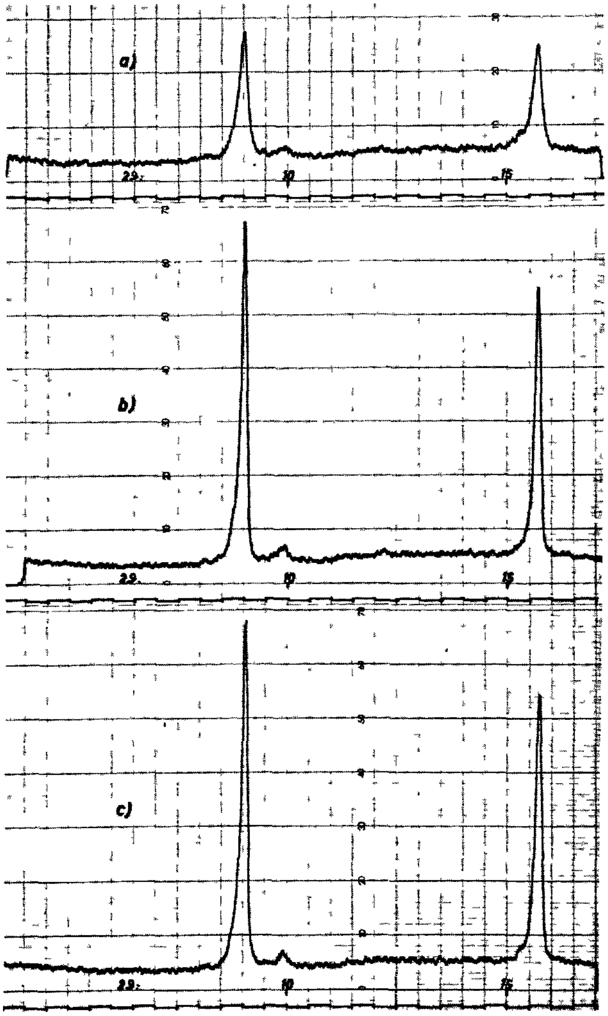

FIGURE 1. *Ettringite (X-ray diagrams).*

(a) 1 hr dry grinding
(b) 40 min grinding in benzene
(c) 10 hr grinding in benzene

Paper II-S3. Influence of Reducing Atmosphere on the Constitution of Clinker*

Y. Suzukawa and T. Sasaki

Synopsis

The influence of FeO on the β-γ inversion of C_2S stabilized with various kinds and amounts of agents and on the dusting of synthetic clinkers of the system C—A—F—S—M—N was studied.

It was found that the β-γ inversion due to the presence of FeO is related to the ionic radius of stabilizers and that the amount of FeO required for dusting the clinker decreases with the increase in the content of Na_2O.

Furthermore, commercial shaft kiln clinker, which is partially reduced, was studied, and the presence of $C_{12}A_7$ (or unstable C_5A_3) was shown.

Based on the results obtained, it is clear that C_2S forms solid solutions with FeO more predominantly than with alkalis.

Résumé

Cet exposé étudie l'influence de FeO sur l'inversion β—γ de C_2S stabilisée par différentes sortes et quantités d'agents, et sur la pulvérisation spontanée de clinkers synthétiques du système C—A—F—S—M—N.

L'étude révèle que l'inversion β—γ due à la présence de FeO est en relation avec le rayon ionique des stabiliseurs, et que la quantité de FeO requise pour pulvériser spontanément le clinker décroît avec l'augmentation de la teneur en Na_2O.

On étudie également le clinker commercial de four à cuve, qui est partiellement réduit, et la présence de $C_{12}A_7$ (ou C_5A_3 instable) est indiquée.

Les résultats obtenus montrent nettement que C_2S forme des solutions solides avec FeO d'une façon plus prédominante qu'avec les alcalis.

Zusammenfassung

Der Einfluß des FeO auf die β—γ-Inversion des C_2S, nachdem es mit verschiedenen Verbindungen und durch verschiedene Mengen dieser Verbindungen stabilisiert wurde, wurde für synthetische Klinker des C—A—F—S—M—N Systems studiert, und die Staubentwicklung der Klinker wurde unter den gleichen Bedingungen untersucht.

Es wurde gefunden, daß die durch FeO hervorgebrachte β—γ-Inversion zu dem Ionenradius der Stabilisatoren in einem gewissen Verhältnis steht, und daß die Menge des FeO, welche nötig ist, einen zerrieselnden Klinker hervorzubringen, nimmt ab, wenn der Gehalt an Na_2O zunimmt.

Auch Klinker, welche in einem Drehrohrofen einer Fabrik erzeugt wurden, wo sie teilweise reduziert werden, wurden untersucht, und es wurde gefunden, daß $C_{12}A_7$ (oder unstabiler C_5A_3) anwesend ist.

Die Ergebnisse zeigen, daß C_2S vorzugsweise mit dem FeO feste Lösungen bildet; dieses wird den Alkalien vorgezogen.

Inversion of C_2S

There has been little information on the influence of FeO on the β-γ inversion of C_2S except for reports of Bowen, Schairer, and Posnjak [1-4].[1]

The β-C_2S stabilized with various kinds and amounts of agents, such as B_2O_3, P_2O_5, Na_2O, K_2O, BaO, Cr_2O_3, MnO_2, or their combinations, was prepared from pure γ-C_2S, and mixtures of the system β-C_2S-$2FeO{\cdot}SiO_2$ were heated in a pure N_2 atmosphere at 1,220 °C for 20 min by the same method as reported by Bowen and Schairer [1].

Chemical and X-ray analysis of the preparations showed that in the β-C_2S stabilized with Na_2O, K_2O, BaO, Cr_2O_3, or MnO_2 (substituting groups for Si^{4+}), the β-γ inversion occured when 0.4–0.5 percent FeO was added, but in the β-C_2S stabilized with B_2O_3 or P_2O_5, no β-γ inversion occurred when 4 percent FeO was added [5, 6]. As has already been reported by Dietzel and Tscheischwili [7] and Glasser and Osborn [8], the β—γ inversion of the preparations containing Cr_2O_3 or MnO_2 is due to the reduction of stabilizers during heat-treatment. The β-C_2S stabilized with both B_2O_3 and Na_2O showed similar behavior to that stabilized with B_2O_3.

As an example, X-ray diffraction results on β-C_2S stabilized with 0.28 percent Na_2O are shown in figure 1.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Central Research Institute, Ube Industries, Ltd., Ube-Shi, Yamaguchi-Ken, Japan. (A summary of this paper was read at the Symposium by R. H. Bogue.)

[1] Figures in brackets indicate the literature references at the end of this paper.

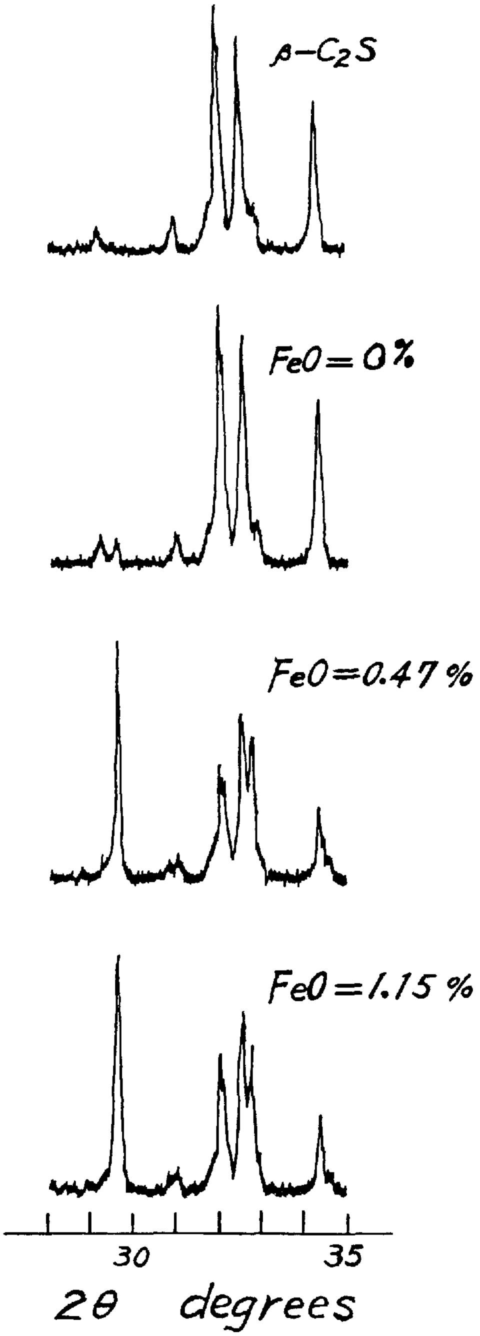

FIGURE 1. *Geiger-counter diffractometer tracings.*

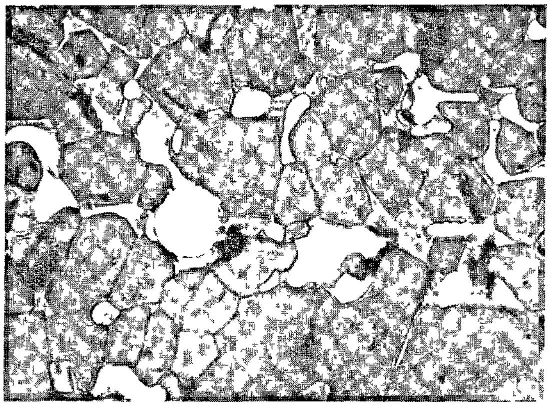

FIGURE 2. *Partially reduced shaft-kiln clinker etched with 0.5 percent alcoholic solution of* HNO_3. × *250.*

Dusting of Clinker

A series of clinkers of the system C–A–F–S–M–N having constant major oxide components except for Na_2O were prepared from pure chemical reagents. Chemical compositions of the original clinker of the system C–A–F–S–M are: S=25.0, A=6.4, F=3.0, C=64.6, and M=1.2 percent.

After pulverizing, the clinkers were mixed with various amounts of ferrous oxalate and reheated in a pure N_2 atmosphere at 1,350 °C, and then cooled slowly or quickly near the bottom of the furnace. The amount of FeO required for dusting the clinker, which was determined by the method of trial and error, is shown in table 1 [5].

The decrease in the amount of FeO with the increase in the content of Na_2O is due perhaps to the lowering of the inversion temperature of C_2S as reported by Newman and Wells [9] and to the change in the chemical compositions of clinker as reported by Suzukawa [10].

TABLE 1. *Amount of* FeO *required for dusting*

Sample No.	Method of cooling	Na_2O (Residual)	FeO
		Percent	*Percent*
A	Cooled slowly from 1,350 to 1,200 °C for 30 min	0.00	2.36
B		.13	1.71
C		.40	1.10
A′	Cooled quickly at 1,350 °C	.00	2.81
B′		.14	2.69
C′		.36	2.48

Similar experiments were also made on the synthetic clinkers of the system C–A–F–S–M–K, but owing to the volatilization of K_2O, no apparent results were obtained on the relation between the amount of K_2O and that of FeO.

A comparative test was made on the strength of mortar (1×1×6 cm; water : cement : sand =0.65 : 1 : 2) containing synthetic normal and dusted clinkers of the system C–A–F–S–M–N. It was found that the dusting due to the presence of FeO (1.76 percent) decreased the strength by 20 to 30 percent.

Shaft-Kiln Clinker

In shaft kilns, partially reduced clinker is sometimes produced, and the Fe_2O_3 is reduced to FeO or on rare occasions to metallic iron. A typical microscopic photograph is shown in figure 2. No ferrite phase is observed, and the presence of $C_{12}A_7$ (or unstable C_5A_3) and metallic iron is shown. X-ray analysis of the clinker showed patterns (d=4.90; 2.975 A) corresponding to those of ($C_{12}A_7$ [11].

Furthermore, partially dusted clinkers were sieved into two fractions. Chemical analysis of each fraction showed that in the fraction <1.2 mm, the content of SiO_2 and FeO was greater and that of Al_2O_3, CaO, and MgO smaller, respectively, than in the fraction >1.2 mm.

On the basis of the preceding discussions, the dusting of shaft-kiln clinker is partially ascribed to the formation of solid solution of C_2S with FeO

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Paper II–S4. Reactions of Coal Ash With Portland Cement Clinker During the Burning Process*

T. Heilmann

Synopsis

When using fuel of high ash content for burning portland cement clinker in a rotary kiln, a certain part of the ash will be precipitated onto the raw materials during their passage through the kiln, forming an integral component of the clinker produced.

The various components of the raw mix are introduced into the kiln as a more or less homogeneous mixture; however, the ash from the fuel, or at least part of it, is precipitated onto the surface of the nodules or clinker during their heating, calcination, and sintering in the burning zone, thereby causing a degree of heterogeneity. The nature and the extent of the reaction between ash and clinker is, naturally, of great importance to the operation of the kiln as well as to the general quality of the clinker.

Results are given of laboratory test burnings made in order to investigate the way in which the ash reacts with the clinker minerals and the components resulting from these reactions. The molten ash has a very pronounced "wetting action" in relation to the surface of the clinker minerals. Therefore, only a small part of the ash will remain on the outer surface, the rest penetrating very quickly into pores and cracks to initiate reactions with the clinker minerals.

The speed of the reactions has been investigated together with its dependence on the burning temperature as well as on the composition of the clinker. In particular, the important part which the movement of CaO plays in the formation of the clinker minerals has been demonstrated. The results are illustrated by a number of photographs of polished clinker sections.

Résumé

Lorsqu'un combustible de forte teneur en cendres est utilisé pour la cuisson de clinkers de ciment Portland dans un four rotatif, une certaine partie des cendres se dépose sur les matières premières pendant leur passage à travers le four, formant un composant intégral des clinkers produits.

Les différents composants du mélange cru sont introduits dans le four sous forme d'un mélange plus ou moins homogène; cependant, les cendres provenant du combustible, ou au moins une partie de celles-ci, se déposent sur la surface des nodules ou des clinkers pendant la chauffe, la calcination et le frittage de ceux-ci dans la zone de cuisson, provoquant ainsi un degré d'héterogénéité. La nature de la réaction des cendres sur les clinkers et la mesure dans laquelle s'opère cette réaction sont, bien entendu, de grande importance pour le fonctionnement du four aussi bien que, d'une façon générale, pour la qualité des clinkers.

L'exposé contient des résultats de cuissons d'essai faites aux laboratoires en vue d'une étude de la façon dont réagissent les cendres avec les minéreaux des clinkers et les composants résultant de ces réactions. Les cendres fondues ont un "effet humidificateur" très prononcé sur la surface des minéraux des clinkers. En conséquence, seule une faible partie des cendres reste à la surface tandis que la partie restante pénètre très rapidement dans les pores et les fissures en amorçant des réactions avec les minéraux des clinkers.

La vitesse des réactions a été étudiée en fonction de la température de cuisson ainsi que de la composition des clinkers. Tout particulièrement, on a relevé le rôle important que joue le mouvement du CaO pour la formation de minéraux de clinkers. Les résultats sont illustrés au moyen de photos de sections polies des clinkers.

Zusammenfassung

Bei Benutzung von Brennstoff mit großem Aschengehalt zum Brennen von Portlandzementklinker in einem Drehofen wird ein Teil der Asche sich beim Durchgang der Rohmaterialien durch den Ofen auf denselben niederschlagen und einen integrierenden Bestandteil des erzeugten Klinkers bilden.

Die verschiedenen Bestandteile der Rohmischung werden dem Ofen als eine mehr oder weniger homogene Mischung zugeführt; die Asche des Brennstoffes, oder wenigstens ein Teil davon, schlägt sich indessen auf der Oberfläche der Granalien oder Klinker nieder, während diese im Ofen erhitzt, kalziniert und gesintert werden, und verursacht dadurch eine gewisse Heterogenität. Beschaffenheit und Umfang der Reaktion der Asche mit dem Klinker sind natürlich für den Betrieb des Ofens als auch für die allgemeine Qualität des Klinkers von großer Bedeutung.

Es liegen Resultate von Laborbrennversuchen vor, die unternommen wurden, um die Weise, in der die Asche mit den Klinkermineralen reagiert, und die durch diese Reaktionen entstehenden Bestandteile zu untersuchen. Die geschmolzene Asche hat eine sehr ausgesprochene "benetzende Wirkung" auf die Oberfläche der Klinkerminerale. Daher wird nur ein geringer Teil der Asche an der äußeren Oberfläche verbleiben, während der Rest sehr schnell in Poren und Risse eindringen wird, um Reaktionen mit den Klinkermineralen einzuleiten.

Man hat die Reaktionsgeschwindigkeit und auch ihre Abhängigkeit von der Brenntemperatur und der Zusammensetzung des Klinkers untersucht. Besonders ist nachgewiesen worden, welch bedeutende Rolle die CaO-Wanderung bei der Bildung der Klinkerminerale spielt. Die Ergebnisse sind durch einige Fotos von Klinkerschliffen veranschaulicht.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the laboratories of F. L. Smidth and Company, Copenhagen, Denmark.

Introduction

During the burning of portland cement clinker with coal in a rotary kiln, the ash, introduced as part of the fuel, will for the greater part react with and become an integral part of the clinker.

The amount of ash in relation to clinker may vary within a wide range and in the first instance will naturally depend on the ash content of the fuel, as well as on the heat economy of the kiln. Furthermore the type of heat-transmitting elements used will influence the amount of ash which is absorbed by the raw materials during the contact with the smoke gas.

The possible dust-absorbing elements installed and the extent to which the dust is recycled to the rotary kiln will also be of influence. In the case where a highly effective filter is installed, the total dust which is absorbed being returned to the kiln, the ash enters completely into the clinker as an integral component.

In general the coal ash will have a chemical composition which differs widely from that of the desired clinker and from the composition of the raw mix which is introduced into the kiln.

By suitable fine grinding and homogenization of the raw mix it is possible to insure that complete reaction between the individual components of the raw mix takes place during the burning process. The coal ash, however, will on account of its deviating composition and the way in which it is absorbed by the material in the kiln cause a certain amount of inhomogeneity in the clinker produced. Consequently the clinker will be a heterogeneous mixture of:

a. Clinker minerals formed by the original components of the raw mix, and,
b. Products resulting from the reaction between the ash and the clinker minerals.

The nature and the extent of this reaction, which is naturally of great importance to the general quality of the clinker, have been examined by a number of laboratory test burnings. The speed has also been investigated to discover its dependence on the burning temperature as well as the composition of the clinker.

General Remarks on the Absorption of Ash in a Rotary Kiln

Generally a coal ash will have a composition varying within the following limits:

	Average	Usual limits of variation
	Percent	*Percent*
SiO_2	46	35–60
Al_2O_3	26	15–35
Fe_2O_3	13	5–20
CaO	5	0–10

MgO, sulfur, and alkalies will also be present in varying amounts. In special cases a coal ash may have a composition outside the above-mentioned limits.

The melting range of coal ash will generally be within 1,050 to 1,250 °C; thus the ash in the coal flame will be in a completely molten state. However, during the further passage of the smoke gas through the kiln, the molten particles of ash will be cooled and thus gradually solidify.

In most kilns about half of the ash will be absorbed by the raw materials in the calcining and the burning zones, where the greater part of the raw materials is usually present in the form of nodules. In this part of the kiln the ash will be precipitated onto the surface of the nodules to initiate the reaction with the clinker minerals.

In the wet process the ash absorbed in the chain system part of the kiln will for the greater part be mixed homogeneously with the raw mix and behave as any of the other components.

The amount of ash which is introduced into a kiln will, as already mentioned, depend both on the ash content of the fuel and on the kiln's heat economy. In table 1 some figures are given, showing the amount of ash in relation to clinker calculated for different ash contents, (15 to 35 percent), and different heat economies, (800 to 1,600 kcal/kg clinker).

TABLE 1. *Ash content of clinker, in percent. Heat value of ash-free fuel, 7,800 cal/g*

% Ash in coal	Calories per kilogram clinker				
	800	1000	1200	1400	1600
15	1.8	2.2	2.6	3.1	3.5
20	2.6	3.2	3.8	4.5	5.1
25	3.5	4.3	5.2	6.0	6.9
30	4.4	5.5	6.6	7.7	8.8
35	5.5	6.9	8.3	9.6	11.0

From the table it can be seen that in the case of, for instance, a wet kiln with an average heat economy of 1,400 kcal/kg clinker and fired with coal containing 20 percent of ash, 4.5 percent of ash in relation to the clinker will be introduced into the kiln. If the ash is completely absorbed by the raw materials, the ash will lower the lime saturation of the clinker by about 10 percent. If for instance a lime saturation in the clinker of about 95 percent is desired, then the raw mix should have a composition corresponding to a lime saturation of 105 percent. Thus the raw mix will contain an amount of CaO which is a surplus when compared with the amount which could normally react with the SiO_2, Al_2O_3, and Fe_2O_3 of the raw mix.

If portland cement clinker, burnt with a fuel of moderately high ash content, is examined microscopically, a certain inhomogeneity in the clinker is usually found. Sometimes an outer shell of comparatively low lime content is seen, clearly originating from the ash precipitated onto the surface of the clinker or nodules. Often, however, the clinker surface will show to a limited extent only signs which could be traced to the precipitation of coal ash. Thus the ash must have a pronounced tendency to react effectively with the ordinary components of the raw mix, even if a considerable amount of the ash is precipitated onto the surface of nodules or clinker during their passage through the kiln.

Before describing in detail the method of testing, it would be of interest to estimate the amount of ash which would, under conditions normally prevailing in a coal-fired rotary kiln, be available per unit contact area between ash and clinker.

The amount of ash per unit area expressed in grams per square centimeter (a) will depend on:

a. The amount of ash in relation to clinker (A percent), and

b. The specific surface of the clinker (o cm^2/g) as expressed by the following equation:

$$a=\frac{A}{100\ o}. \tag{1}$$

If the size of the clinker nodules is measured by the diameter d cm, and the apparent specific gravity of the clinker is s g/cm^3, the specific surface would be given by

$$o=\frac{6}{ds},$$

and the amount of ash per unit area could also be expressed as

$$a=\frac{Ads}{600}. \tag{2}$$

Table 2 shows the variation of ash per unit area (mg/cm^2) with the total amount of ash in relation to the clinker weight and the average size or the specific surface of the clinker. An apparent clinker specific gravity (s) of 2.8 g/cm^3 is assumed, which corresponds to about 10 percent by volume of pores.

Table 2. *Average amount of ash per unit area (mg/cm^2) of the clinker surface, calculated for an apparent specific gravity of the clinker, $s=2.8$ g/cm^3*

Average diameter of clinker..........mm..	1	2	5	10	20
Specific surface of clinker..........cm^2/g..	21	9.3	4.3	2.1	1.1
Ash in relation to clinker weight:					
2..........%..	0.9	1.9	4.7	9.4	19
5..........%..	2.3	4.7	12	23	47
10..........%..	4.7	9.4	23	47	94
20..........%..	9.4	19	47	94	190

Character and Extent of the Reactions Between Ash and Clinker

The tests have shown that two factors influence the character and the extent of the ash absorption:

a. The tendency of the molten ash to spread out over the surface of the clinker substance, and

b. the direct reactions, where the layer of ash is in contact with the clinker substance.

The molten ash has a very pronounced "wetting action" in relation to the clinker minerals, giving rise to a very small angle of contact between them. This means that the ash will be able to penetrate very quickly from the outer surface into cracks and openings in the clinker substance, thereby greatly increasing the area for reaction.

By the direct reactions through the contact areas, lime is gradually (although initially very rapidly) transferred from the clinker into the ash This leads to the formation of C_2S crystals in the original layer of ash and a corresponding transformation of C_3S into C_2S in the clinker. Furthermore, free CaO is also transferred from the clinker to the ash.

The above-mentioned two factors were investigated separately by two series of tests (A and B).

Test Series A

The Spreading of the Molten Ash Over the Clinker Surface

The tendency of the molten ash to spread out over the surface of the clinker minerals is shown quite clearly by some of the tests in series B, in particular in cases where small amounts of ash per unit area have been used. Furthermore, this tendency was also investigated by some special tests carried out in the following way:

The raw mix to be used for the tests was first calcined for one hour at 1,000 °C and then compressed into a briquet 1.5 cm diam with a pressure of about 5 tons, corresponding to 2.8 t/cm^2. The surface was then drilled to form a spherical depression having a total surface of about 1 cm^2, for receiving the ash. In the bottom of the depression a small hole of 1 mm diam was drilled and filled with *uncalcined* raw mix. The briquet was then burnt for 30 min at 1,500 °C.

During this burning the sintering of the uncalcined raw mix would cause one or more cracks, whereas the rest of the surface area of the depression would be free from cracks. The crack or cracks formed in the small hole would lie in one plane, making it possible, by a later cutting and polishing, to obtain the whole of this "artificial" crack in the polished section of the clinker.

The briquet was then heated to 1,500 °C. A small amount of molten ash was heated separately in a small loop formed at the end of a platinum wire and then dropped into the spherical depression in the briquet's surface. The temperature was maintained for a further period of 10 sec, when the briquet was removed from the furnace and cooled rapidly in about 15 sec to a temperature below 1,000 °C.

After this treatment the briquet was cut, polished, and etched with nitric acid in order to show the dicalcium and tricalcium silicates. For this test series A, clinker C1 and ash A1 were used (for compositions see table 3).

From the photographs, figures 1, 2, and 3, it can be seen that the molten ash has been able to penetrate momentarily down into the crack, when the reaction between the ash and the clinker minerals has started in the usual way through the surface of contact. It will also be seen that the width of the crack is only about 0.35 mm.

At the bottom of the hole characteristic zones of reaction have already developed and can be seen. These will be described in greater detail later in connection with the contact reaction. Dendritic crystals of C_2S appear in the original layer of ash and in the clinker a layer of C_2S crystals can be seen, having been formed by the removal of CaO from the original C_3S crystals. Outside this layer the clinker substance is in its original state.

By comparing the reactions seen in these photos with corresponding photos from test series B, (for instance fig. 4), where the molten ash has been in contact with a clinker substance free from cracks but with the same reaction time of 10 sec, it can be seen that the thickness of the reaction layers and the degree of reaction is very nearly the same in the two cases, indicating that the molten ash has penetrated into the crack almost instantaneously. If this was not the case, reactions so far progressed would not have been observed at the bottom of the hole.

Test Series B1 and B2

Description of Test Procedure

In order to study the direct contact reactions between ash and clinker minerals, it was necessary to prepare a contact area which was, as far as possible, free from any kind of cracks into which the ash could penetrate and thus obliterate the picture.

The preliminary steps in the preparation of the test specimens were the same as those outlined for test series A (see page 89), a small briquet of calcined raw mix being made and the surface drilled to form a spherical depression, 1 cm^2 in surface area. The spherical shape was chosen in order to insure an even distribution of the molten ash over the clinker surface. A cylindrical depression would, owing to the low contact angle between the molten ash and the clinker substance, give an uneven distribution of the ash over the surface.

Two series of test burnings were carried out. The first, *test series B1*, when the briquet of calcined raw mix was prepared in the abovementioned way, was heated with the desired amount of ash to the required burning temperature in a period of about 2 hr. This temperature was then maintained for a definite time, which varied from 20 min to 6 hr, and the test piece was then cooled at moderate speed over a period of about 20 min.

These tests would to some extent imitate the heating taking place in industry. This is especially so in the case of a wet process kiln, when ash is precipitated onto the surface of nodules from the time they leave the chain system. The amount of ash used in these tests was varied from 2.4–200 mg/cm^2, and the long burning time of 6 hr. was chosen in order to study the ultimate state of reaction between the ash and the clinker.

Another series of test burnings *test series B2* were carried out in order to imitate the conditions prevailing in the burning zone of a kiln when the molten ash would be precipitated directly onto the surface of the nodules. By these tests the speed of the reaction between the ash and the clinker minerals was investigated and the various steps in the chemical reactions were studied.

In order to fix the original surface of the clinker substance exactly a small hole of 0.5 mm diam was drilled in the briquet and a platinum wire of the same diameter was placed into the hole. The briquet was then burnt (without any ash) at a temperature of 1,500 °C for half an hour and the depression was reground in such a way that the end of the platinum wire was flush with the surface of the clinker.

The briquet was then heated in an electrical furnace to the temperature at which the reactions were to be investigated and the desired amount of ash was heated separately as explained previously on pages 89–90. When the desired temperature was reached the molten ash was dropped into the depression on the briquet's surface and the temperature maintained for the desired test period. After this the briquet was removed from the furnace and cooled rapidly in about 15 sec to a temperature below 1,000 °C. This rate of cooling was chosen in order to prevent the test pieces from developing cracks and to prevent any phenomena of dusting.

The amount of ash used was maintained at a constant value of 150 mg/cm^2, as this rather high amount would insure a continual surplus of ash, available to react with the clinker, throughout the

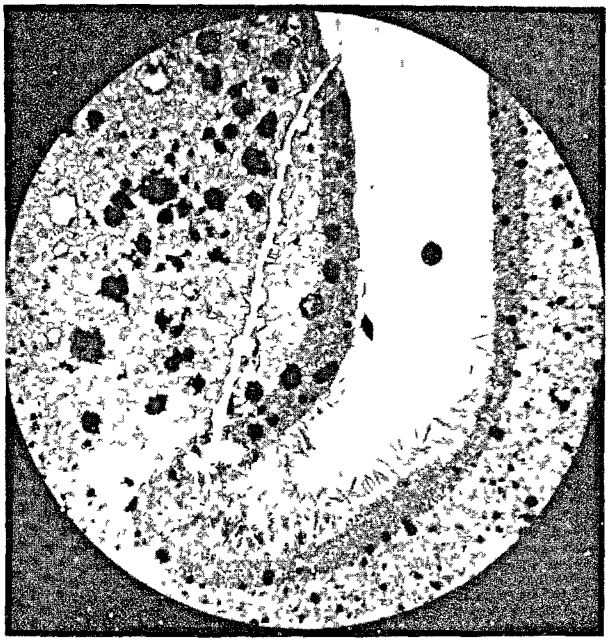

FIGURE 1. × *50. Test series A. Clinker C1.*
Ash A1.—1,500 °C—10 sec.

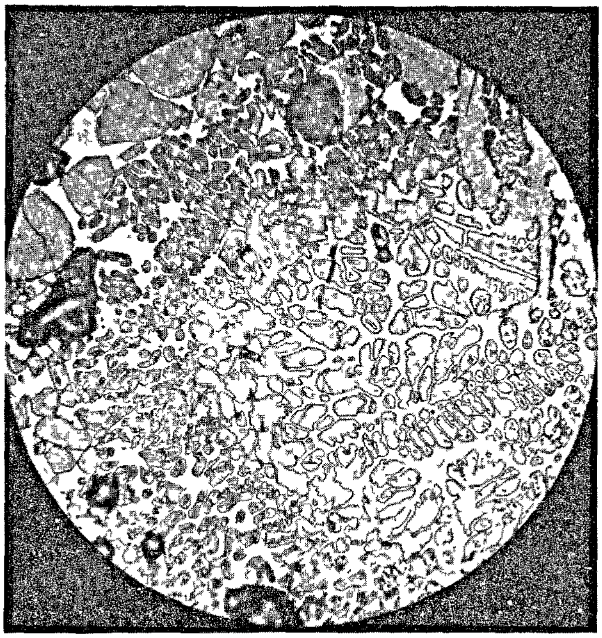

FIGURE 3. × *350. Test series A. Clinker C1.*
Ash A1.—1,500 °C—10 sec.

FIGURE 2. × *125. Test series A. Clinker C1.*
Ash A1.—1,500 °C—10 sec.

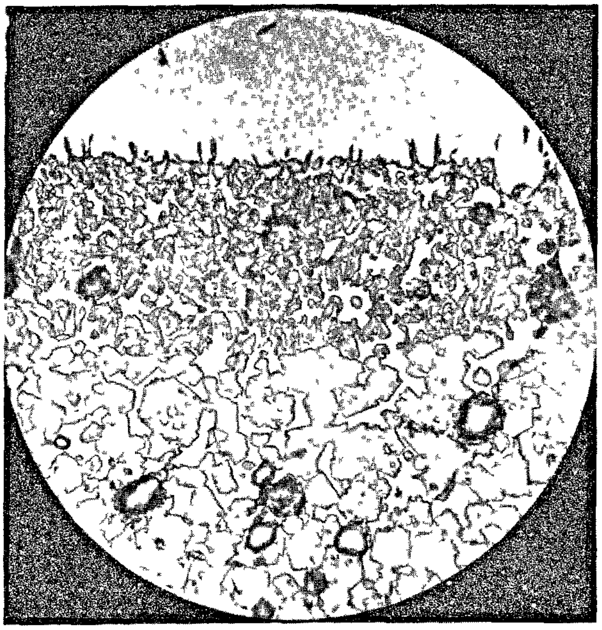

FIGURE 4. × *500. Test series B2. Clinker C1.*
Ash A1.—1,500 °C—10 sec.

chosen reaction times. The reaction temperatures chosen were 1,300, 1,400, and 1,500 °C, and the time of reaction was varied from 10 sec to 60 min.

After burning, the test specimens were cut, polished, and etched in the same way as the specimens of test series A, always insuring that the polished surface cut through the platinum wire.

For the tests, clinker of two compositions, one high in lime, C1, and one of low lime content, C2, were used. Two ashes were also used, one of normal composition, A1, and one with a special high content of CaO, A2. The compositions of the clinker and the ashes are given in table 3.

TABLE 3. *Compositions of clinker and ash used for test series A and B*

	Clinker		Ash	
	C1	C2	A1	A2
	%	%	%	%
SiO_2	19.7	24.8	48.8	39.1
Al_2O_3	5.5	3.6	27.2	20.0
Fe_2O_3	3.4	2.6	12.6	9.6
CaO	69.3	66.8	5.6	26.8
LSF	105	89	--------	--------
Free CaO	3.8	--------	--------	--------
C_3S	74.9	55.7	--------	--------
C_2S	0	29.2	--------	--------
C_3A	8.9	5.1	--------	--------
C_4AF	10.4	7.9	--------	--------
Ratio: CaO/SiO_2	--------	--------	0.12	0.69

General Description of the Reactions Between Ash and Clinker Substance

Figure 5, corresponding to a 1-hr reaction time at 1,500 °C between the clinker C1 and the ash A2, shows under small magnification (12 times) most of the briquet with the platinum wire in the middle of the depression. The uppermost layer is the original ash in which crystals of C_2S have already developed considerably, and below this is the reaction layer corresponding to the original clinker substance from which CaO has been removed.

There are indications that during the first part of the reaction time, presumably during the first few seconds, a thin layer of the clinker substance is dissolved directly into the molten ash. However, during further reactions between ash and clinker, certain characteristic zones of reactions are very quickly formed. These zones are clearly defined in relation to each other, and generally there are no signs of a continuous passing stage between one zone and the next.

Figure 6 shows the zones of reactions in greater enlargement. To the right of the picture the platinum wire can be seen, the top of which indicates the original border between ash and clinker substance. Similar zones are seen in figure 7. This photo is taken at some distance from the platinum wire so the wire itself does not appear in the photo.

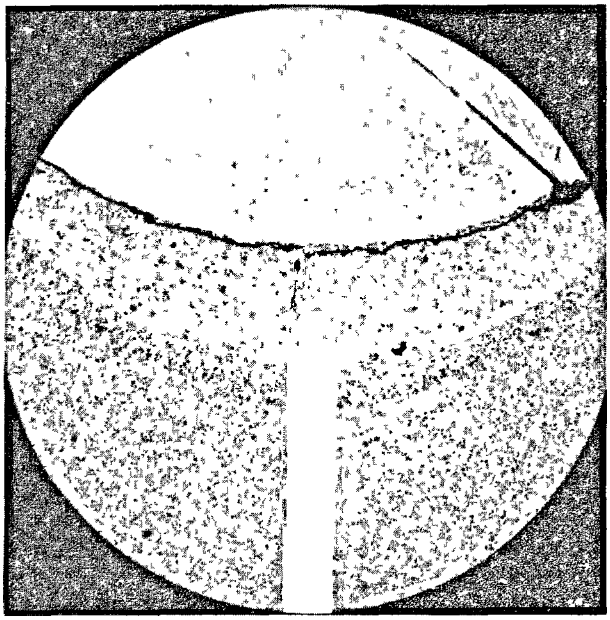

FIGURE 5. × *12. Test series B2. Clinker C1.*
Ash A2.—1,500 °C—1 hr—150 mg ash/cm².

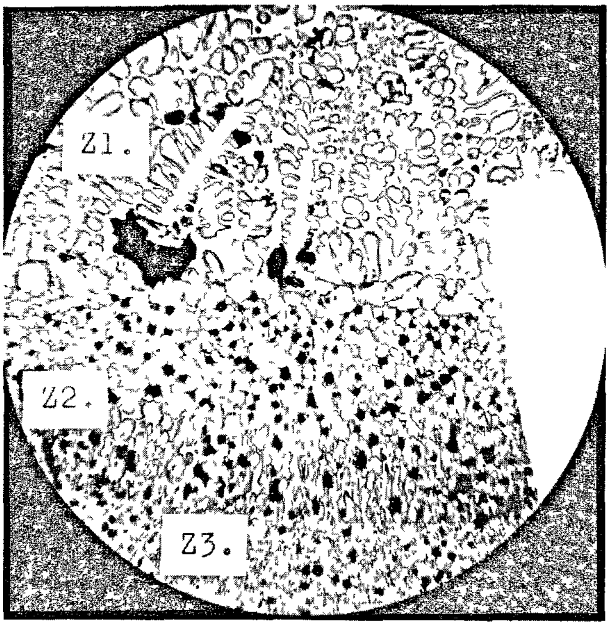

FIGURE 6. × *63. Test series B2. Clinker C1.*
Ash A2.—1,500 °C—1 hr—150 mg ash/cm².

Description of the Zones of Reactions

The uppermost zone, Z1, is the original layer of ash into which CaO has been absorbed with the formation of characteristic C_2S crystals. The next zone, Z2, comprises a layer of the original clinker substance from which crystals of free CaO and CaO from C_3S crystals have been extracted, with the transformation of this C_3S into C_2S crystals.

Farther down is found a zone, Z3, which is only characteristic for clinker of high lime saturation factor. This zone will contain the original clinker substance with its content of C_3S and, possibly, C_2S crystals. Only the crystals of free CaO have been removed. This zone is difficult to distinguish in a black and white photo but is clearly seen in a color photo.

Figures 8 and 9 show the border line between zones Z2 and Z3 in greater enlargement. Below the border line the great amount of well-developed C_3S crystals of the original clinker substance can be seen quite clearly, and above the border line, C_2S crystals formed by the extraction of CaO from the C_3S crystals.

Figures 10 and 11 show the border line between zones Z1 and Z2, also in greater enlargement. Above the border line can be seen the ash into which characteristic C_2S crystals have developed, and below the border line, the C_2S crystals remaining from the original C_3S crystals of the clinker.

Right on the border line there is a characteristic layer of coherent C_2S crystals of the same type which also develops on the outer border of a coarse grain of silica in an ordinary cement raw mix. In the great enlargement, figure 11, narrow channels are seen between these crystals, indicating the possibility of some transport of CaO by liquid diffusion. It must be assumed, however, that probably part of the transport of CaO through this layer takes place as diffusion through the solid C_2S phase.

It will further be noticed, from figure 9 and figure 7, that the C_2S crystals of zone Z2, positioned immediately above the border line between Z2 and Z3, have a typically elongated shape, showing that this shape is particularly characteristic of the initial reaction. Later these crystals are converted to the rounded shape generally seen in portland cement clinker. The elongated crystals, developed to a total length of 250µ or more, are seen only in the tests with the clinker C1 of high lime content. In the lower-lime clinker C2, with both C_2S and C_3S crystals, the elongated C_2S crystals do not develop to the same extent (see fig. 8).

During the reaction, CaO is given off from zone 2 to zone 1, thus the volume of zone 2 will decrease. It is assumed that this is one of the reasons why, as can be seen in figure 5, the border line between zones Z1 and Z2 is situated somewhat below the top of the platinum wire. Another reason is probably that by direct solution a thin layer of clinker has been dissolved by the ash during the very initial stages of the reactions.

A clinker such as C1, containing 3.8 percent of free CaO and 75 percent of C_3S, would by transformation of all C_3S crystals to C_2S and by giving off all the free CaO, shrink in volume by about 23 percent.

In figure 6 the thickness of zone Z2 has been measured and found to be about 510µ. Assuming a shrinkage of 23 percent the original thickness of that layer would have been 660µ. The distance from the border line Z2 and Z3 to the top of the platinum wire has also been measured and found to be about 700µ. Thus, it would seem that by direct solution a layer of clinker, corresponding to a thickness of 40µ, has been dissolved directly by the ash.

These figures correspond to a reaction temperature of 1,500° C. At 1,400° the dissolved layer is somewhat thinner. Furthermore, the dissolved layer is somewhat thicker in the case of ash A1, of low lime content, than in case of ash A2, but this is also to be expected.

In these calculations it has been assumed that the porosity of zone Z2 is the same as that of the original clinker. However, figure 5 indicates a somewhat greater porosity for zone Z2, which means that the dissolved layer would actually be slightly greater than found in the above mentioned calculations.

As the reactions proceed, the distinct border line between zones Z1 and Z2 is gradually obliterated, since the C_2S crystals in zone Z1 gradually assume the same rounded shape as in Z2. The disappearing of the border line Z1 and Z2 is generally found to take place earlier when smaller amounts of ash per unit area are used.

During the later reactions, when the ash layer has been saturated with CaO (with complete formation of C_2S) the transformation of C_3S into C_2S crystals in the clinker will stop, i.e., the border line Z2 and Z3 will not move further down into the clinker substance. However, in the case of the high-lime clinker C1, free lime from farther down in the clinker may be used for re-establishing crystals of C_3S in zone Z2 and in particular near the border line between zones Z2 and Z3. Such characteristic crystals of C_3S, which generally appear as particularly large-size crystals, can be seen in figures 12 and 13. In these figures, inclusions of the original C_2S substance may be seen in C_3S crystals of this type.

In the case of a long reaction time and a comparatively small amount of ash per unit area, this reaction may lead to a complete transformation of the C_2S in Z2 into C_3S. The transformation may even continue into zone Z1, the original ash layer, as seen in figure 14.

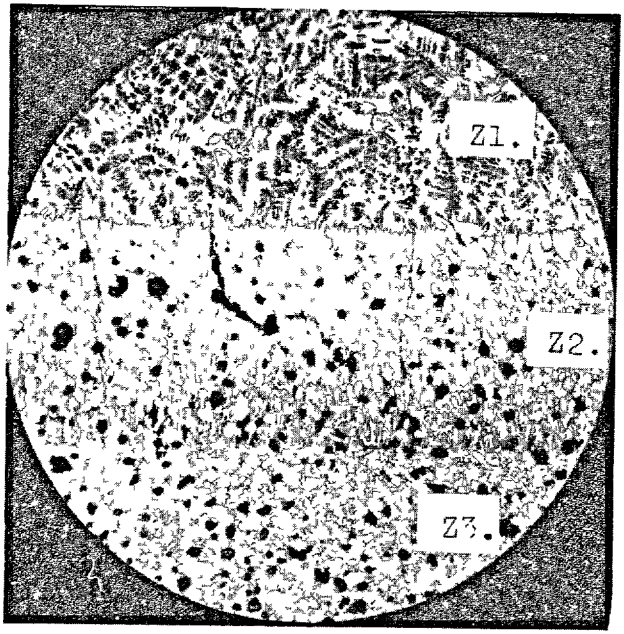

FIGURE 7. × *100. Test series B2. Clinker C1.*
Ash A2.—1,500 °C—6 min—150 mg ash/cm².

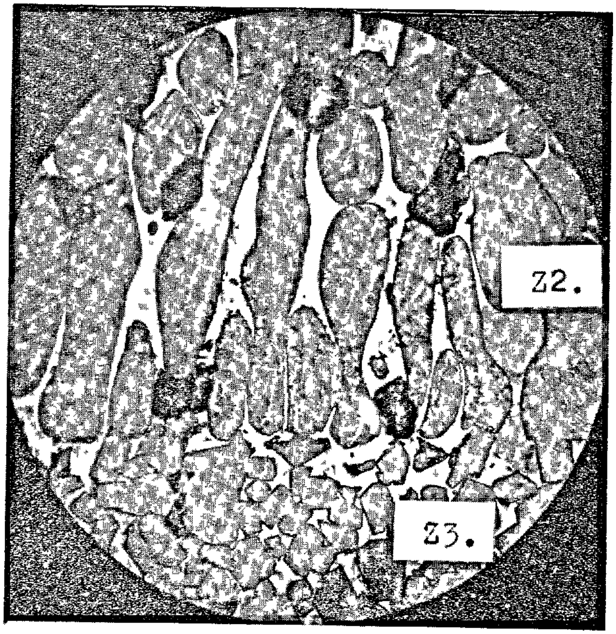

FIGURE 9. × *500. Test series B2. Clinker C1.*
Ash A2.—1,500 °C—1 hr—150 mg ash/cm².

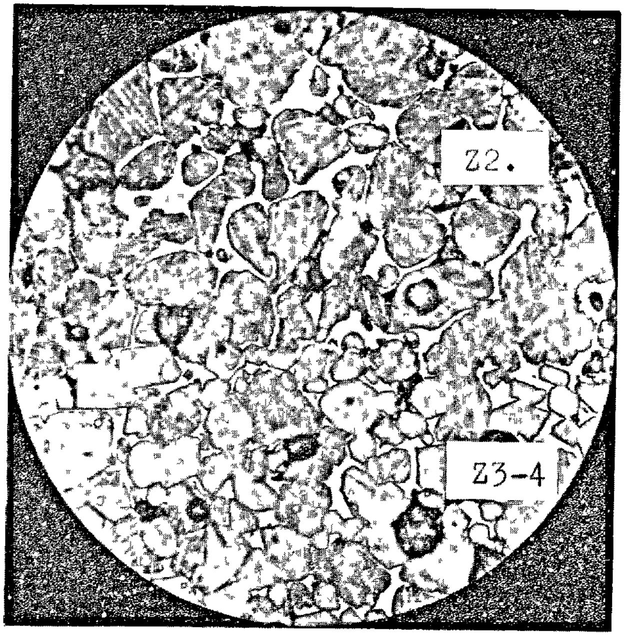

FIGURE 8. × *500. Test series B2. Clinker C2.*
Ash A1.—1,500 °C—6 min—150 mg ash/cm².

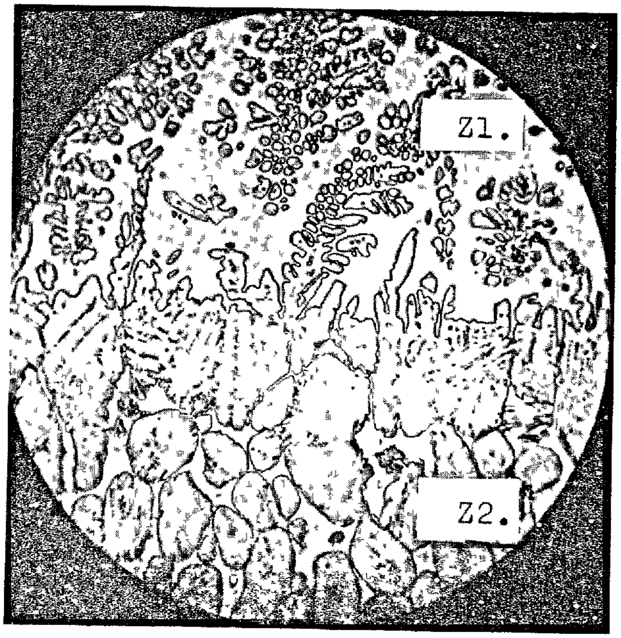

FIGURE 10. × *560. Test series B2. Clinker C1.*
Ash A2.—1,500 °C—6 min—150 mg ash/cm².

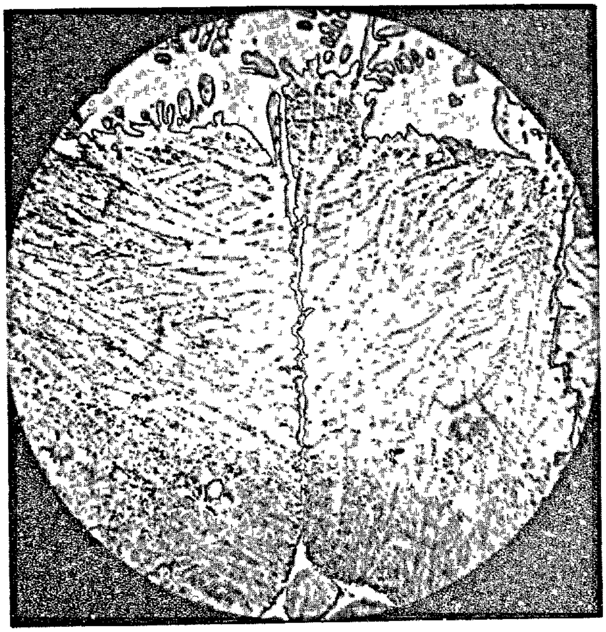

FIGURE 11. × *560. Test series B2. Clinker C1.*
Ash A2.—1,500 °C—1 hr—150 mg ash/cm².

FIGURE 13. × *500. Test series B1. Clinker C1.*
Ash A1.—1,400 °C—6 hr—50 mg ash/cm².

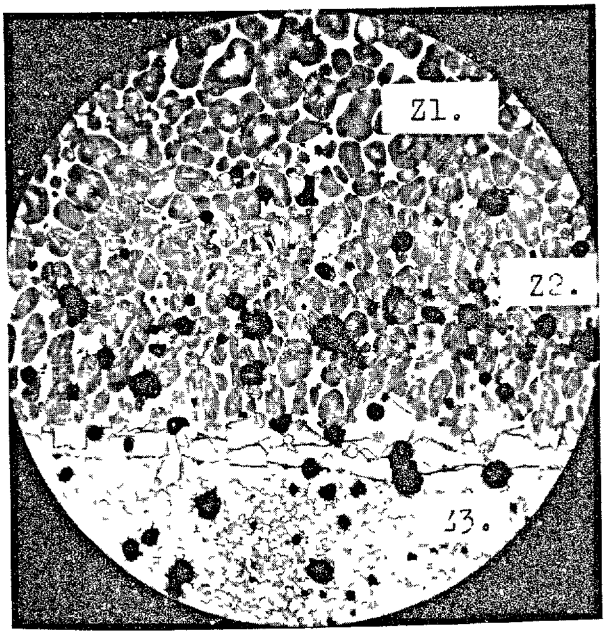

FIGURE 12. × *100. Test series B1. Clinker C1.*
Ash A1.—1,400 °C—6 hr—50 mg ash/cm².

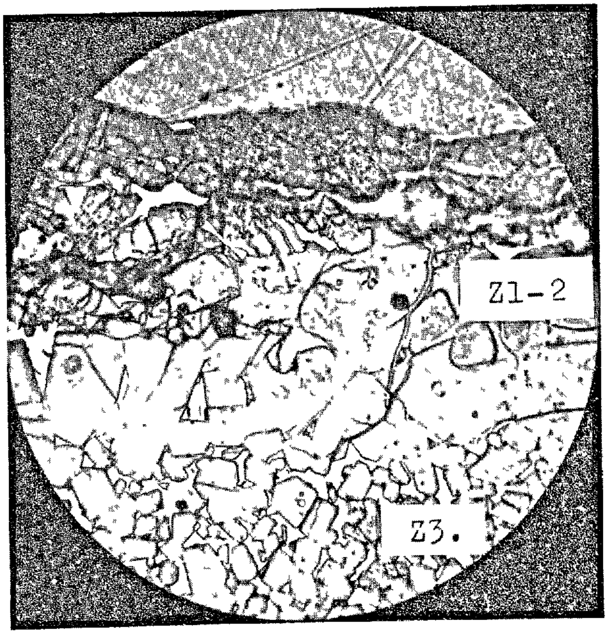

FIGURE 14. × *500. Test series B1. Clinker C1.*
Ash A1.—1,400 °C—1 hr—2.4 mg ash/cm².

Depth of the Zones Z2 and Z3

The graphs in figures 15, 16, and 17 show the depth of penetration of zones Z2 and Z3 as a function of the time of reaction, plotted on a double logarithmic scale. The depth of penetration of zone Z2 has been measured as the distance from the top of the platinum wire to the border line between Z2 and Z3, whereas for zone Z3 it has been measured as the distance from the border line Z2 to Z3 to the border line Z3 to clinker.

It will be seen that the depth of penetration "p" in relation to the time of reaction "t" is almost a straight line, indicating that the reaction takes place according to an equation of the following type:

$$p = Kt^k \qquad (3)$$

the constant "k" corresponding to the slope of the lines, and having values varying from 0.32 to 0.42.

The test series B1 (without the platinum wire), have shown that the zone Z3 may increase still further in thickness, and at 6 hr reaction time reach a value of up to 1,300 μ.

It must be assumed that the greater part of the transport of CaO, through the zone Z2, from the border line Z2 to Z3 to the border line Z1 to Z2, takes place as diffusion through the liquid between the C_2S crystals.

The diffusion may be estimated approximately in the following way:

An area, comprising one cm² of zones Z1, Z2, and Z3, is shown schematically in figure 18.

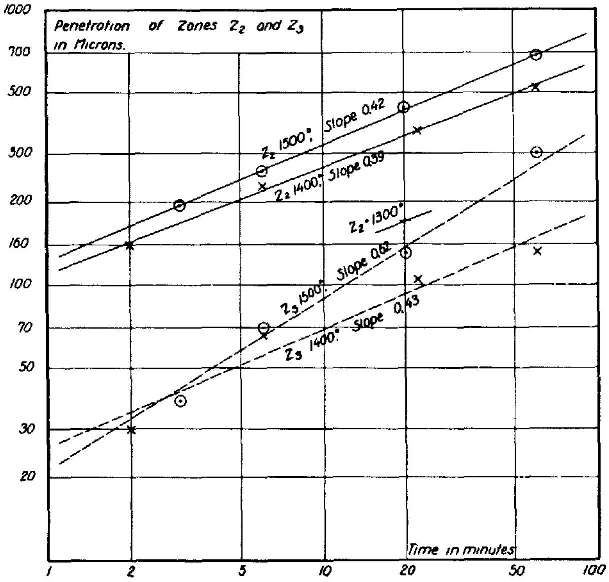

Figure 15. *Test series B2. Clinker C1—Ash A1.*

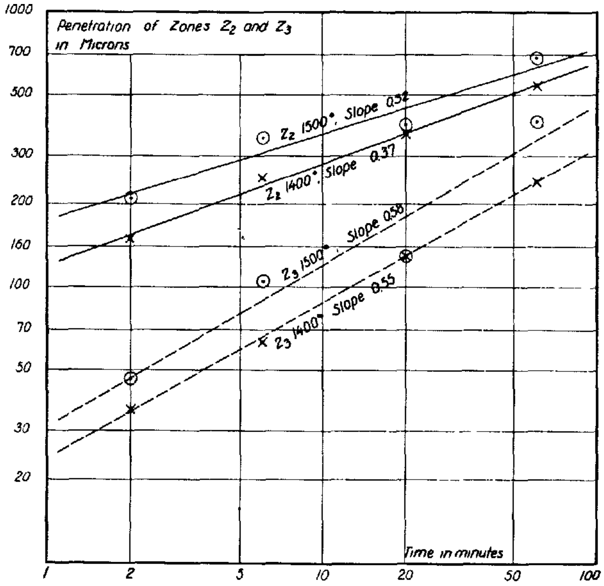

Figure 16. *Test series B2. Clinker C1—Ash A2.*

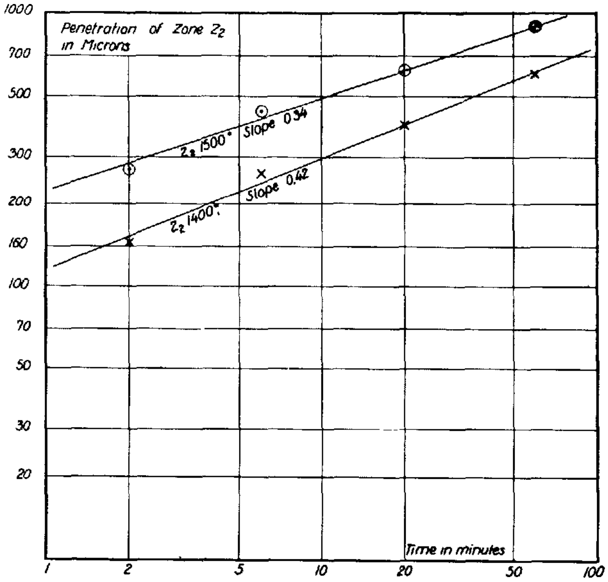

Figure 17. *Test series B2. Clinker C2—Ash A1.*

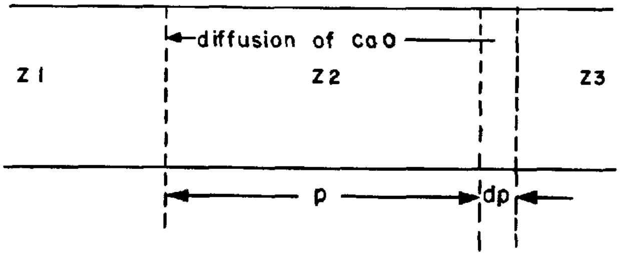

Figure 18. *Schematic representation of diffusion of* CaO.

At a certain time (t) the border line Z2 to Z3 is situated at a distance (p) from Z1 to Z2. In zone Z3, C_a g of CaO/cm^3 is assumed to be available for diffusion into zone Z1. Further, the concentration of CaO in the liquid phase at the border line Z1 to Z2 is taken as c_1 and at the border line Z2 to Z3 as c_0, assuming c_1 and c_0 to be constant.

During a time element (dt) the border line Z2 to Z3 moves a certain distance (dp), thus an amount of lime $C_a \times dp$ will move by diffusion into zone Z2.

The law of diffusion states that

$$C_a \frac{dp}{dt} = D \frac{c_0 - c_1}{p}, \qquad (4)$$

where D is the coefficient of diffusion. By integration, within the limits $t=0$, to $t=t$,

$$\frac{p^2}{2} = D \frac{c_0 - c_1}{C_a} t, \qquad (5)$$

or

$$p = k \frac{t^{\frac{1}{2}}}{C_a^{\frac{1}{2}}} \qquad (6)$$

are obtained, k being a constant.

The connection between p and t in general agrees with the results show in figures 15, 16, and 17. The reason why the lines shown on these figures have a slope which for the penetration of Z2 is somewhat below 0.5 may be that the figures for the penetration of Z2 should have been corrected for the thickness of the layer of clinker directly dissolved during the initial stages of the process. If a correction corresponding to about 50 μ is subtracted from all the figures, the slope of the lines will approach the value of 0.5.

The depth p, being a function of C_a, is in agreement with the fact that for the low lime clinker C2 a greater depth of penetration has been found than for the high lime clinker C1. The difference in penetration for the two types of clinker is, according to the graphs, somewhat smaller than the value calculated at 1,400°, and somewhat higher at 1,500 °C.

It would be natural to expect that as the lime content in the ash layer (zone Z1) increases, there would be a corresponding decrease in the rate of CaO absorption by the ash. However, this does not seem to be the case, at any rate not for the range of lime concentrations up to a ratio CaO/SiO$_2$ in the ash of about 1.5, as can be seen by comparing figures 4 and 5.

During one hour at 1,500 °C, the penetration of Z2 increases to a depth of about 700 μ in both cases, while the ratio CaO/SiO$_2$ in the ash layer increases from a value of 0.12 to about 0.7 in case of ash A1, whereas in case of ash A2 it increases from 0.7 to about 1.5.

Test Results in Relation to Industrial Experience

As a conclusion it would, of course, be of interest to judge how the various test results could assist in the general understanding of the various problems which are met in practice when burning portland cement clinker in a rotary kiln with coal of high ash content. The main problems arising from the use of such a coal would generally be (a) the tendency to ring formation in the kiln, thus disturbing its operation, and (b) the influence on the physical properties of the resulting cement, mainly through its strength and expansion properties.

The layer of ash precipitated onto the surface of nodules or clinker will for a certain time, as long as the lime content of the ash layer is low, have a melting point which is lower than that of the clinker. Therefore, in the burning zone there will be a tendency for this clinker covered with ash to stick together and to the surface of the lining; this behavior is well known. The tendency for the ash to cause these troubles will naturally be expected to be less the smaller the amount of ash per unit area of the clinker surface.

It has been seen that the molten ash has a pronounced tendency to penetrate into even the very small pores and cracks in the clinker. Thus as the porosity of the clinker increases, the area for reaction between ash and clinker also increases, thereby reducing the amount of ash per unit area of clinker. This means that the layer of ash would in a short time reach such a degree of lime saturation that the tendency for the clinker to stick either together or to the surface of the lining would be greatly reduced. It is also evident that the higher the temperature in the burning zone, the quicker the ash will react with the clinker.

Now it is a well-known fact that a high silica ratio as well as a high lime saturation will generally counteract the tendency to ring formation in cases where fuel of high ash content is used. Both these measures will. in fact, raise the burning temperature and, therefore, the speed of reaction between ash and clinker while furthermore, a high silica ratio will also increase the porosity of the clinker.

The porosity and the surface properties of the molten ash in relation to the clinker are, undoubtedly, very important factors in avoiding an excessive tendency to ring formation when using coal of high ash content in a rotary kiln.

As the tests show, the depth to which the ash is able to react with the clinker under the conditions prevailing in a kiln, is comparatively small, generally not more than about ½–1 mm. If it were not for the comparatively great porosity of the clinker and the tendency for the molten ash to penetrate into the pores, the ash would remain on the surface of the clinker and, undoubtedly, cause great inconvenience during the operation of the kiln.

Portland cement clinker burnt for instance to an average liter weight of 1,350 g (measured on a fraction from 5–10 mm in size) may have a total porosity of about 20 percent, of which open pores would amount to 16 percent. Thus there would be every chance for the ash to penetrate deeply and react with the clinker. However, the absorption of ash onto the nodules or the clinker and the resulting reactions will lead to certain inhomogeneities in the clinker, which will influence the physical properties of the cement made from the clinker in question.

The pores and the cracks in the surface of the clinker cannot be expected to be evenly distributed, and, therefore, in some places comparatively large amounts of ash will penetrate into the clinker, resulting in areas of C_2S crystals. Therefore, under equal conditions, the average lime saturation of the clinker cannot be kept as high, without the risk of getting clinker with a high content of free CaO, in the case of a fuel of high ash content, as it could have been with a fuel of lower ash content. Even with the same average lime saturation, however, the inhomogeneity of the clinker caused by the ash reactions may cause some reduction in the strength properties of the cement.

Concluding Remarks

Besides adding to the better understanding of the practical problems involved in the application of high-ash coal to the burning of portland cement clinker in a rotary kiln, the investigations have also contributed to the understanding of the mechanism of the reactions which take place during the formation of the clinker minerals during the burning process. In particular, the important part which the movement of CaO plays in the formation of the clinker minerals has been demonstrated.

Furthermore, it would perhaps be justified to point out once more the importance of the microscopical examination of portland cement clinker as a valuable instrument in the investigation of problems which it would be very difficult to solve solely by chemical analyses.

In the planning and execution of the tests which have been carried out in the laboratories of F. L. Smidth and Co. A/S., Copenhagen, very valuable assistance has been rendered by K. A. Simonsen, and further by A. F. Mansell, especially in compiling the test results.

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Paper II–S5. Solid Solution of Alumina and Magnesia in Tricalcium Silicate*

F. W. Locher

Synopsis

Mixtures of tricalcium silicate and tricalcium aluminate were burnt at 1,500 °C and quenched. The composition of the melt which is thus formed is indicated by the invariant point *D* at 1,470 °C of the ternary system $CaO–Al_2O_3–SiO_2$. As it is relatively poor in lime and, due to the rapid quenching, can not react with the solid phases C_3S and CaO, the mixture must contain a corresponding amount of free CaO, although practically no free CaO is present in the constituents C_3S and C_3A of the initial mixture. Consequently, the occurrence of free CaO indicates that the heated sample contained a liquid phase. As the liquid is formed principally from the aluminate that was not taken up into the C_3S, it can be determined with the help of the chemical-analytically determined content of free CaO what is the maximum amount of C_3A that can be taken up by the C_3S in solid solution. The investigations indicated a maximum of about 2 percent C_3A, equivalent to 0.7 to 0.8 percent Al_2O_3. The entering Al atoms occupy the positions of Si atoms. X-ray diffraction investigations revealed that the dimensions of the C_3S lattice were hardly changed, if at all, by the takeup of C_3A.

Magnesium ions can replace the calcium ions in the lattice of the tricalcium silicate, which are then present in the burnt mixtures as free CaO. With the help of the content of free CaO it was established that at 1,420 °C, C_3S can take up about 1.5 percent MgO, at 1,500 °C up to 2.5 percent MgO, and also if the mixture further contains 4 percent C_3A.

Résumé

Des mélanges de silicate tricalcique et d'aluminate tricalcique ont été soumis à une température de 1,500 °C, puis à un refroidissement trempé. La composition de la masse fondue ainsi formée est indiquée par le point invariant *D* (1,470 °C) du système ternaire $CaO–Al_2O_3–SiO_2$. Etant donné que le mélange est de teneur relativement faible en chaux et que, par suite du refroidissement rapide, il ne peut pas produire de réaction avec les phases solides C_3S et CaO, il doit contenir une quantité correspondante de CaO libre; bien qu'il n'y ait pratiquement pas de CaO libre dans les constituants C_3S et C_3A du mélange initial. Par conséquent la présence de CaO libre indique que l'échantillon soumis à la cuisson contenait une phase fondue. Puisque la masse fondue est principalement formée à partir de l'aluminate qui n'a pas été absorbé dans le C_3S, on peut déterminer (à l'aide de la teneur en CaO libre, laquelle est déterminée par méthode chimique analytique) la quantité maximum de C_3A qui peut être absorbée par le C_3S en solution solide. Les résultats des recherches indiquent un maximum d'environ 2 % C_3A, équivalent à 0.7–0.8 % Al_2O_3. Les atomes de Al qui sont entrés occupent la position des atomes de Si. Les études de la diffraction aux rayons X ont révélé que l'absorption de C_3A n'avait qu'à peine modifié les dimensions du réseau de C_3S, s'il y eusse aucune modification de ces dimensions.

Des ions de magnésium peuvent remplacer les ions de calcium dans le réseau de silicate tricalcique, ces derniers se trouvant alors sous forme de CaO libre dans les mélanges cuits. A l'aide de la teneur en CaO libre on a établi qu'à 1,420 °C,C_3S peut absorber environ 1.5% de MgO, à 1,500 °C il peut prendre jusqu'à 2.5% de MgO, également si le mélange contient de plus 4% de C_3A.

Zusammenfassung

Mischungen aus Tricalciumsilikat mit Tricalciumaluminat wurden bei 1,500 °C gebrannt und schnell gekühlt. Die Zusammensetzung der Schmelze, die sich dabei bildet, wird durch den Invarianzpunkt *D* (1,470 °C) des Dreistoffsystems $CaO–Al_2O_3–SiO_2$ angegeben. Da sie verhältnismäßig kalkarm ist und infolge der schnellen Kühlung nicht mit den festen Phasen C_3S und CaO reagieren kann, muß die Mischung eine entsprechende Menge freies CaO enthalten, obwohl in den Komponenten C_3S und C_3A der Ausgangsmischung praktisch kein freies CaO vorliegt. Das Auftreten von freiem CaO zeigt infolgedessen an, daß die erhitzte Probe eine Schmelzphase enthielt. Da sich die Schmelze im wesentlichen aus dem Aluminat bildet, das nicht in das C_3S eingebaut wurde, kann mit Hilfe des chemisch-analytisch bestimmten Gehalts an freiem CaO festgestellt werden, wieviel C_3A das C_3S höchstens in fester Lösung aufnehmen kann. Die Untersuchungen ergaben als Grenze etwa 2 % C_3A entsprechend 0,7–0,8 % Al_2O_3. Die eingebauten Al-Atome besetzen die Plätze von Si-Atomen. Röntgenographische Untersuchungen zeigten, daß die Abmessungen des C_3S-Gitters durch Aufnahme von C_3A nicht oder nur wenig geändert werden.

Magnesiumionen können im Gitter des Tricalciumsilikats die Calciumionen vertreten, die dann in den gebrannten Mischungen als freies CaO vorliegen. Mit Hilfe des Gehalts an freiem CaO wurde festgestellt, daß C_3S bei 1,420 °C bis zu etwa 1,5 %, bei 1,500 °C bis zu 2,5 % MgO aufnehmen kann, und zwar auch dann, wenn das C_3S außerdem 4 % C_3A enthält.

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Introduction

The formula

$$54CaO{\cdot}16SiO_2{\cdot}Al_2O_3{\cdot}MgO,$$

abbreviated to

$$C_{54}S_{16}AM$$

has been attributed by J. W. Jeffery [1] [1] to the alite of portland cement clinker. According to this formula, in 18 formula units of tricalcium silicate 2 Si atoms are to be replaced by 2 Al atoms and as charge compensation 1 Mg atom is to be placed in an intermediate lattice position. It was found, however, that it is not possible to produce a pure alite of this formula. Mixtures of this composition always contain after burning about 5 percent free CaO that does not decrease even after frequently repeated heating up to 1,500 °C.

This finding, which shows that the formula of J. W. Jeffery attributes too high a lime content to the alite, must be interpreted as follows: An Al atom entering into the alite in solid solution replaces a Si atom and can therefore bind 3CaO, that is to say, to one mole Al_2O_3 belong 6 moles CaO. In the lime-richest independent alumina compound, tricalcium aluminate, only 3 moles CaO are bound with 1 mole Al_2O_3. If the tricalcium silicate takes up less alumina in solid solution than is indicated in the aforementioned formula, tricalcium aluminate is formed, with a corresponding amount of free CaO.

Free CaO can also occur if the magnesium ions do not occupy intermediate lattice positions but replace the calcium ions in the lattice of the tricalcium silicate. However, this could only explain a free CaO content of about 1.4 percent. As about 5 percent of free CaO always occurred in burned mixtures with the composition $C_{54}S_{16}AM$, it was to be assumed that alite contains less alumina than is indicated in the formula. It was necessary, therefore, to investigate how much alumina tricalcium silicate can take up and whether an addition of MgO has an influence on the solubility of alumina in tricalcium silicate.

The point of departure for the determination of the maximum alumina content that can be taken up in tricalcium silicate was the following consideration. In mixtures of tricalcium silicate and tricalcium aluminate, heating to 1,470 °C yields a melt which contains all the tricalcium aluminate and only a small amount of tricalcium silicate. However, the alumina content of the tricalcium silicate will not participate in the formation of the melt. The composition of this melt at 1,470 °C is determined by the position of the invariant point *D* (1,470 °C) in the ternary system $CaO{-}Al_2O_3{-}SiO_2$ (fig. 1). According to the data given by G. A. Rankin and F. E. Wright [2] on the ternary system it contains

$$\begin{array}{r} 59.7\%\ CaO \\ 32.8\%\ Al_2O_3 \\ 7.5\%\ SiO_2. \end{array}$$

According to the investigations of E. Spohn [3] and H. Kühl [4], at sintering temperature the solid phases are in equilibrium with the melt. As the melt, however, is poorer in lime than the initial mixtures of tricalcium silicate and tricalcium aluminate, this condition being recognizable by the fact that point *D* lies on the low-lime side of the connecting line $C_3S{-}C_3A$, CaO must occur as a further solid phase. If the mixtures are cooled under equilibrium conditions, the CaO is re-absorbed by the melt, but with sufficiently rapid cooling it remains free. The occurrence of free CaO in the burnt and quickly cooled mixtures indicates, therefore, that a liquid phase was formed.

Accordingly, it should be possible to establish, with only the help of chemical determinations of the free CaO, how much tricalcium aluminate can be taken up into the lattice of the C_3S. The free CaO should also be able to furnish information as to whether the magnesium ions taken up by the C_3S occupy intermediate lattice positions, that is to say, enter additionally into the lattice, or whether they replace the calcium ions and displace an equivalent amount of CaO from the tricalcium silicate.

Method of Investigation

For the purpose of the investigations the compounds tricalcium silicate and tricalcium aluminate were prepared by the usual method and then mixed with each other in various proportions with or without an addition of MgO or CaO. All the mixtures were homogenized by repeated sieving and cautious grinding in a porcelain mortar, stirred with distilled water to a plastic paste, shaped into granules, burnt for one hour at 1,500 °C and then rapidly quenched in air. The burning temperature of 1,500 °C, which thus lay 30 °C above the temperature of the invariant point *D*, was chosen to ensure that all the tricalcium aluminate was melted. Consequently, although the composition of the melt also changed, the course of the boundary curve $C_3S{-}CaO$ (fig. 1) shows that principally only the C_3S content of the melt increased and that there was little change in the content of free CaO.

In the burnt mixtures the free CaO was determined by the method of B. Franke [5] in which process the CaO is dissolved in a mixture of acetoacetic ester and isobutyl alcohol and titrated with 0.1 N hydrochloric acid. In addition, a number of mixtures were investigated by X-ray diffraction with a Geiger-counter goniometer. The exact position of the lines was established with NaCl as standard substance.

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[1] Figures in brackets indicate the literature references at the end of this paper.

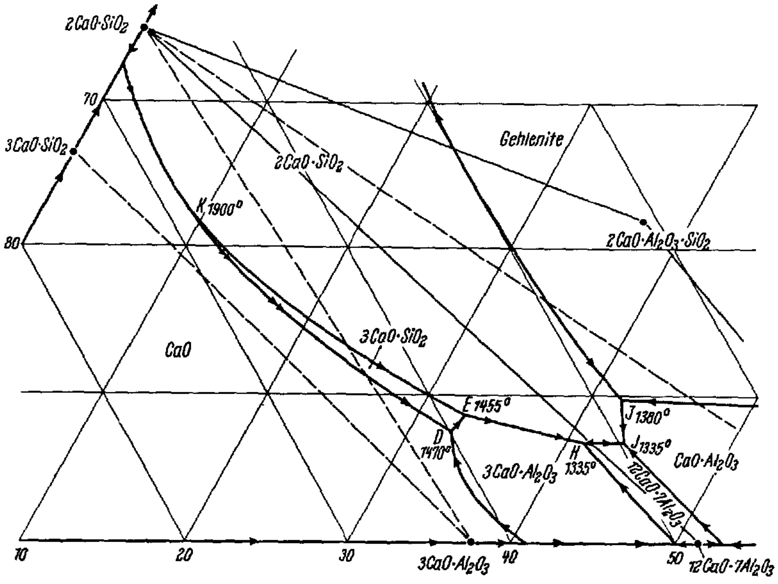

FIGURE 1. *Section of the ternary system CaO—Al_2O_3—SiO_2 with the invariant point D (1,470 °C), in which CaO, tricalcium silicate and tricalcium aluminate are stable beside each other.*

Results

The Amount of Tricalcium Aluminate Taken Up by Tricalcium Silicate

Figure 2 shows the results of tests with mixtures of tricalcium silicate without and with CaO or MgO and various amounts of tricalcium aluminate. It is seen that in mixtures of C_3S and MgO (C_3A content=0) the content of free CaO increases with the MgO content. This finding would appear to indicate that in the lattice of the pure tricalcium silicate the magnesium ions can replace the calcium ions. In mixtures of C_3S, C_3A, and MgO, the content of free CaO first decreases with increasing C_3A content, reaches a minimum value at about 2 percent C_3A, and then rises in a line with the C_3A content. This curve shows that C_3A contents of more than 2 percent already form a melt, that is to say, that the alite can contain approximately 2 percent C_3A at the most, i.e., 0.7 to 0.8 percent Al_2O_3.

The thin straight lines indicate the amounts of free CaO calculated on the assumption that the melt has the composition of the invariant point *D* in the ternary system CaO–Al_2O_3–SiO_2, that pure C_3S, C_3S with 2 percent or with 4 percent C_3A crystallizes in solid solution, and that in cooling, the melt no longer reacts with the solid phases C_3S and CaO. The chemically determined increase in the content of free CaO tallies very well with the calculated rise of the straight lines and thus shows that the occurrence of the free CaO in burnt mixtures of C_3S and C_3A can be explained by the formation of a melt poor in lime.

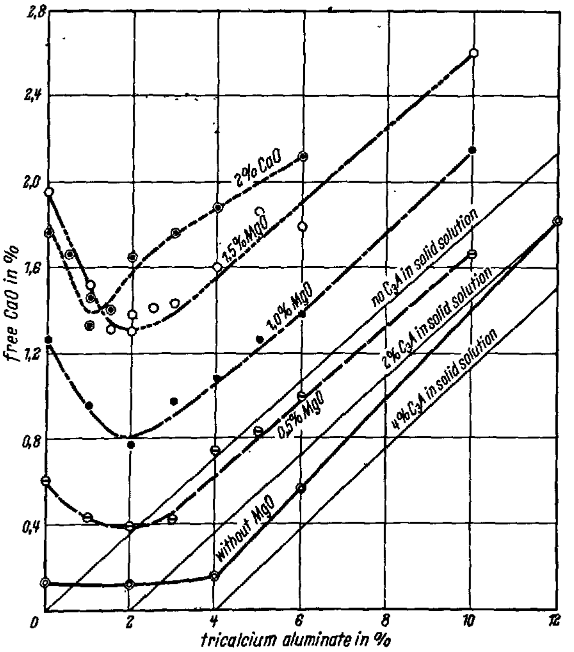

FIGURE 2. *Content of free CaO in mixtures of tricalcium silicate, tricalcium aluminate and MgO or CaO after burning at 1,500 °C and rapid quenching in air.*

Small MgO contents have only a slight influence on the position of the invariant point *D*. Investigations by H. F. McMurdie and H. Insley [6] showed that in the presence of 5 percent MgO the melt is still slightly poorer in lime at point *D*. The solid phases should, therefore, be richer in lime, i.e., in the formation of a melt more free CaO should occur in the system with MgO than in the MgO-free system.

In mixtures with less than 2 percent C_3A the free CaO decreases with an increasing C_3A content. This finding would appear to indicate that an MgO content stimulates the entry of alumina into the alite.

The Amount of MgO Taken Up by Tricalcium Silicate

It has already been pointed out in the foregoing section that free CaO is formed in mixtures of tricalcium silicate and MgO during heating. For the purpose of investigating the connection between the contents of MgO and of free CaO, the free CaO was determined in burnt mixtures of pure C_3S with various amounts of MgO. The results are presented in figure 3. It is perceived that the content of free CaO first rises steeply with an increasing MgO content, reaches a maximum value at a certain MgO content, then falls steeply, and, with still higher MgO content, continues to fall only slightly. This curve reveals that the magnesium ions are taken up into the C_3S lattice in place of the calcium ions, that is to say, they displace the calcium ions up to a maximum extent which depends on the temperature treatment. The higher the temperature the more MgO the C_3S lattice can take up.

In order to check whether the magnesium ions also displace the calcium ions if the lattice of the tricalcium silicate simultaneously contains alumina, three mixtures of 96 parts C_3S and 4 parts C_3A, to which had been added 1, 2, and 3 percent MgO, were burnt at 1,500 °C and after quenching as rapidly as possible in air, the content of free CaO was investigated. The results are shown by the thin curved line of triangles in figure 3. It is seen that with an addition of MgO the content of free CaO increases from 0.15 to 1.77 percent, showing that the magnesium ions also take the place of the calcium ions when there is a simultaneous takeup of Al_2O_3 and MgO.

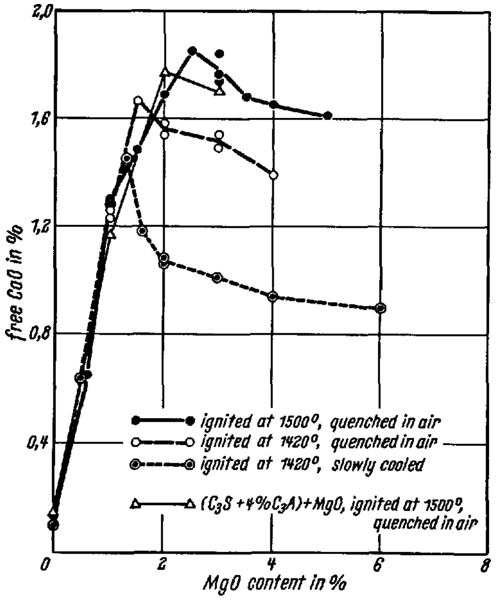

FIGURE 3. *Content of free CaO in burnt mixtures of tricalcium silicate with magnesium oxide.*

X-ray Diffraction Investigations

Figure 4 presents the Geiger-counter diagrams of a number of mixtures which were burnt at 1,500 °C. The two lower diagrams of pure tricalcium silicate and of an MgO-free mixture of C_3S and C_3A reveal, in agreement with the findings of W. Jander and J. Wuhrer [7], that the takeup of alumina in C_3S has no influence or only a very slight influence on the position of the lines, that is to say, on the dimensions of the crystal lattice. The two

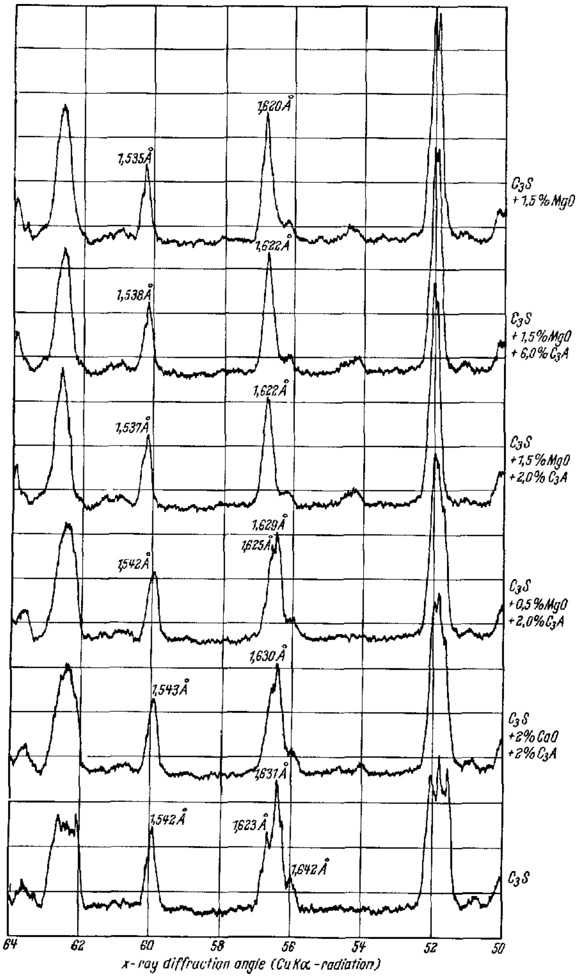

FIGURE 4. *X-ray diagrams of mixtures of tricalcium silicate, tricalcium aluminate and MgO or CaO after burning at 1,500 °C and rapid quenching in air.*

middle lines in the diagram of the C_3S–C_3A–CaO mixture at 1.630 A and 1.542 A ($(2\bar{2}13)$ and $(\bar{2}214)$, according to G. Yamaguchi and H. Miyabe [8]), in the diagram of the pure C_3S lie at 1.631 A and 1.542 A. The pattern of the lines changes, however, with glancing angles of reflection, 2θ, of about 51.5° ($d=1.76$ A) and 62.5° ($d=1.49$ A), which form multiplets in pure C_3S but occur in the mixtures as simple lines.

The top four X-ray diagrams of samples with MgO show, like the results of K. Koyanagi and T. Sudoh [9], that with a takeup of MgO the lattice of the tricalcium silicate contracts, this being recognizable by the fact that the two marked lines shift over to smaller d-values. The top three diagrams reveal that even alumina-free tricalcium silicate that contains 1.5 percent MgO already produces an X-ray diagram of an alite.

Discussion of Results

The tests led to the following results:

1. Tricalcium silicate cannot take up more than about 0.7 to 0.8 percent Al_2O_3, equivalent to 2 percent tricalcium aluminate, in its crystal lattice. The Al atoms here occupy the positions of the Si atoms. R. Naito, Y. Ono, and T. Iiyama [10] indicate approximately the same low values for the alumina content of the alite, i.e., 2.5 to 3.0 percent C_3A. These values were calculated on the basis of a diagram that was presented in a short review of the work of the Japanese scientists. A. Guttmann and F. Gille [11] found about 2.5 to 5.0 percent tricalcium aluminate in relatively pure alite samples which they produced from technical clinker by centrifuging with heavy solutions. H. E. Schwiete and W. Büssem [12] established on a selected part of a furnace coating with some 90 percent alite that about 4.5 percent tricalcium aluminate was contained in the alite in solid solution. Still higher values, namely 6 to 7 percent tricalcium aluminate, are indicated by W. Jander and J. Wuhrer [7]. This value tallies with the formula of J. W. Jeffery which attributes a 6.5 percent content of tricalcium aluminate to the alite.

2. Magnesium oxide can enter the lattice of the tricalcium silicate at 1,420 °C up to about 1.5 percent and at 1,500 °C up to 2.5 percent. As the content of free CaO increases hereby from about 0.1 percent in the pure C_3S to 1.5 to 2.0 percent it is assumed that the magnesium ions displace the calcium ions.

   According to K. Koyanagi and T. Sudoh [9] the tricalcium silicate can take up less MgO, namely, only 1.0 to 1.5 percent. They established this with the aid of X-ray diffraction investigations.

3. The investigations showed that MgO can enter into the tricalcium silicate independently of the Al_2O_3 and that it is not taken up additionally as charge compensation and placed on intermediate lattice positions, but that it replaces the calcium ions. The difference in charge between the quadrivalent silicon ion and the trivalent aluminium ion taken up in its place is therefore compensated in some other way. As the structure of the tricalcium silicate contains oxygens outside the tetrahedron it is probable that with the takeup of Al^{3+} an equivalent number of these oxygen positions will not be occupied.

The above work was published in somewhat more detail in Zement-Kalk-Gips, September, 1960, under the title "Die Einlagerung von Al_2O_3 und MgO in Tricalciumsilikat."

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Discussion

Guenter Ahlers

The purpose of this discussion is to report the results of some studies on the periclase content of portland cement. The difference between this and the total MgO content is an upper limit for the amount of MgO in the alite, since it is equal to the total combined MgO. It is felt that the fact that even this upper limit was found to be less than the amount indicated by Jeffery's formula is of some interest in relation to Dr. Locher's work on a simpler system.

The cement samples were analyzed for periclase by means of X-ray diffraction. The procedure was very similar to the one used by Copeland, et al. [1].[1] The samples were ground together with 10 percent silicon as internal standard in a vibratory ball mill. The material was vibrated into a sample holder, as described by Copeland and Bragg [2]. The ratio of the line areas of the (200) periclase line and the (311) silicon line was used for analysis. A calibration was obtained by adding three different known amounts of periclase to a cement sample, and obtaining the line intensity ratios to the standard line. The periclase used was obtained by heating C.P. basic magnesium carbonate at 950 °C. for several hours.

The chemical analysis[2] for MgO was done according to the usual ASTM procedure.

Eighteen cement samples from six different mills were analyzed. The results are shown in table 1. Each value is the average of three analyses. The uncertainties in the data are larger than the amount of combined MgO, and thus some of the differences are negative. The differences have an average of 0.05 percent MgO, and this is the best estimate of the average amount of combined MgO. Consideration of the scatter of the calibration data about a straight line and of the three analyses per sample leads to a probable error of ±0.17 percent for the average of the combined MgO. Allowing for some error in the chemical analyses, it then appears that on the average the amount of combined MgO does not exceed 0.3 percent, and probably is in the neighborhood of 0.1 percent.

TABLE 1. *Analyses of portland cement for periclase and total magnesium oxide*

Sample	Periclase X-ray	Total MgO chemical	Difference
	%	%	
I-1	1.24	1.21	−0.03
I-2	2.36	2.38	+.02
I-3	2.30	2.38	+.08
I-4	1.29	1.21	−.08
II-1	3.52	3.30	−.22
II-2	3.82	3.91	+.09
II-3	3.60	3.55	−.05
II-4	3.29	3.30	+.01
III-1	4.14	4.43	+.29
III-2	3.76	3.95	+.19
III-3	4.11	4.07	−.04
III-4	4.32	4.43	+.11
IV-1	2.94	3.02	+.08
IV-2	2.62	2.82	+.20
V-1	3.74	4.11	+.37
V-2	4.27	4.19	−.08
VI-1	4.09	4.13	+.04
VI-2	3.93	3.95	+.02

The samples all contained between 35 and 50 percent C_3S as calculated by the Bogue method, and on the average they contained 42.5 percent C_3S. Thus, if all the combined MgO combined with the C_3S, then the alite in the cements should on the average have contained 0.2 percent MgO, with a maximum possible content of 0.7 percent MgO. This is definitely less than Jeffery's value, and it is in good agreement with the amount of stabilizer used by Copeland, et al., [1]. Copeland's replacement of two SiO_4 groups in 54 such groups would result in about one third of one percent MgO.

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Discussion

E. Woermann

During our work on the effects of reduction on the equilibrium in portland cement clinker and especially on the alite phase [1] [1] it has been found that:

1. By action of reducing atmosphere in presence of iron-bearing compounds the free lime content of clinker—especially of clinker very rich in alite—is raised considerably.
2. Solid solution of Fe^{++} and Fe^{+++} in tricalcium silicate causes some changes in the lattice of the compound, resulting in a powder pattern resembling that of alite containing Mg^{++} and Al^{+++} in solid solution.
3. Solid solution of Fe^{++} in alite brings about an extremely high instability of this compound as compared with alite containing Mg^{++} in solid solution instead.

It seemed desirable to gain some further information on the influence of different ions on alite and its stability. Searching for some experimental method we tried to determine the influence of certain additions on the free lime content of our samples. Thus we made use of some methods very nearly resembling those of Locher.

Furthermore, as Mg^{++} and Al^{+++} are much easier to treat experimentally than Fe^{++} and

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[1] Figures in brackets indicate the literature references at the end of this paper.

[2] The author is indebted to the control laboratories of the Riverside Cement Company for these analyses.

[1] Figures in brackets indicate the literature references at the end of this paper.

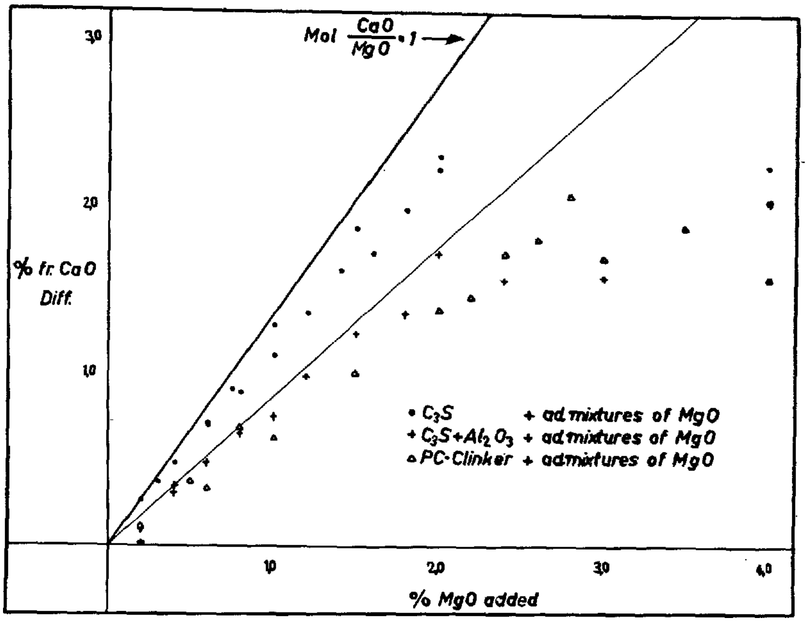

FIGURE 1. *Change in free lime content of* C_3S *and clinker resulting from addition of magnesia.*

Fe^{+++}, we started our experiments by testing the influence of magnesia and alumina on tricalcium silicate. Thus our results may directly be compared with those of Locher, and it seems that they compare very well (fig. 1).

In figure 1 the abscissa represents the amount of magnesia added to the charges, while the ordinate shows the change in content of free lime (=CaO difference) effected by this addition of magnesia as determined by analysis.

We find that after addition of magnesia to a sample of pure tricalcium silicate and burning until the value of free lime determined by analysis remains constant, this content of free lime is higher than in the original sample containing no magnesia. By plotting the results (fig. 1) we find that our points lie very close to a line which represents equivalence between the CaO of the ordinate and MgO of the abscissa. A slight deviation may partly be explained by experimental error, partly by lack of real equilibrium in the sample. Regarding the fact that nearly all of our points lie below the line, we may not exclude the possibility that there is a real deviation of our points from the line which, however, must be very small. We may conclude that up to a certain maximum limit of addition of MgO, Mg^{++} ions may replace Ca^{++} ions in tricalcium silicate. This is in perfect agreement with the results of Locher.

When MgO is added to a charge of C_3S containing alumina in solid solution we find, however, that after burning of the charge and determination of the free lime the points do not follow the line of equivalence of CaO and MgO any more, all of them lying distinctly lower, apparently following their own line of reference. This means that for any amount of magnesia added, *less* than the equivalent amount of lime is liberated. Thus, while still a greater part of the magnesium ions added is replacing calcium ions in the alite lattice, another fraction of the magnesium seems most probably to be included in the lattice of alite, other than by occupying Ca^{++} positions. Moreover there seems to exist a certain relationship regarding the amount of Mg^{++} substituting for Ca^{++} and of Mg^{++} included into the alite lattice.

Furthermore, figure 1 demonstrates that the limit of solubility of magnesium in alite is higher than in tricalcium silicate, while in both cases the maximum amount of lime that may be liberated by the magnesia is the same.

Considering the fact that alite is a major phase in portland cement clinker, we extended our studies to learn something about the influence of MgO on the phase composition of normal clinker. Plotting the points obtained from this experiment on the same graph (fig. 1) we find them closely following the alite line. Thus additions of magnesia in portland cement clinker may cause a rise of free lime content of about 2.0 to 2.5 percent. Considering this influence on the lime saturation of a clinker it seems to be important to include the value of MgO in any method for computation of cement composition.

The theory that a certain fraction of the Mg^{++} ions are included in the alite lattice other than by substituting for Ca^{++} may be supported by some observations on the decomposition of alite.

It seemed rather puzzling to find that a solid solution of ferrous iron in alite results in an extreme instability of this compound, so that it may hardly be possible to prevent the alite from being decomposed, while on the other hand alite containing magnesium in solid solution shows a comparatively weak tendency to decompose. Thus we tried to gain some more knowledge on the effect of admixtures of other divalent ions on alite.

Table 1 shows a list of divalent ions which have been tested for their influence on the stability of alite, arranged according to their ionic radii.

Table 1. *Influence of divalent ions on stability of alite*

Admixture	Ionic radius (after Ahrens 1952)	Disintegration of alite after cooling at 5 °C/min
Mg^{++}	0.66	−
Ni^{++}	.69	−
Co^{++}	.72	+
Fe^{++}	.74	+
Mn^{++}	.80	+

According to these results, Ni^{++} has much the same effect on alite as Mg^{++}, while Mn^{++} and Co^{++} resemble ferrous iron in exerting an accelerating influence on the decomposition of alite.

Thus, strikingly, all divalent ions with an ionic radius *greater* than about 0.7 A do exert this destructive influence on alite under given cooling conditions, some of them even to a still higher degree than Fe^{++}, which may lead to the conclusion that these ions were rather too *large* to be included into the lattice. By thermal expansion of the lattice during sintering temperature a certain amount of these ions may have been included in the lattice, but with subsequent cooling and contraction they induce a destruction of the lattice.

Since all of these ions are distinctly smaller than Ca^{++} (ionic radius=0.99 A) they cannot be too large as substituents for Ca^{++}. But assuming that these ions entered some of the holes in the lattice denoted by Jeffery [2] it may be imagined that really some ions may be too large for these holes. This observation thus confirms the theory that some of the Mg^{++} ions are included in the lattice of alite other than by substituting for Ca^{++}.

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Closure

F. W. Locher

It is to be expected that in the heating of mixtures of MgO and tricalcium silicate an equilibrium will occur between the MgO taken up in solid solution and the whole MgO present in the sample. The position of the equilibrium will depend on the following factors:

1. MgO concentration in the sample
2. Temperature treatment
3. Kind and amount of foreign ions present

It follows from this that the investigations hitherto carried out reveal only what MgO concentration in the sample is necessary to saturate the tricalcium silicate or the alite with MgO. They give no indication of the amount of MgO taken up in solid solution.

The investigations of G. Ahlers, for instance, show very clearly that the alite of the cement clinker takes up only very little MgO although relatively large amounts up to more than 4 percent were available to it. Taking into account that the aluminate ferrite phase also takes up MgO and, according to H. E. Schwiete and H. zur Strassen [1], thus give the cement its greenish color, and that, according to H. Müller-Hesse and H. E. Schwiete [2], the tricalcium aluminate can take up as much as 2.5 percent MgO it follows that the alite of the cement clinkers investigated by G. Ahlers can contain only an extremely small amount of MgO. The major part of the MgO was present as periclase. Nor is it to be expected, therefore, that in the mixtures used by E. Woermann, the MgO available was completely taken up by the tricalcium silicate or by the alite in solid solution. In this way it might also be explained why not all the MgO added to the mixture forms free CaO.

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Paper II–S6. Reaction Velocity in Portland Cement Clinker Formation [*]

Renichi Kondo

Synopsis

In the investigation of the burnability of portland cement, detailed studies on the reactions of clinker formation were performed, intending, first to clarify the differences in the reaction mechanism when selecting clays or granulated blast furnace slag as the sources of silica and alumina, and second to establish a method of measurement of reactivity. The results are as follows:

(1) The reaction between lime and clays containing quartz to form C_2S is noticeable above 1,100 °C. With reaction products burned in this temperature range, despite rapid cooling, slight expansion and dusting occur. The reactivity of highly siliceous clay is superior to that of low-silica clay combined with silica sand. Slag crystallizes out as melilite, and then absorbs lime to form C_2S. Considerable expansion occurs, but dusting can not be observed on cooling. The reactivity of the raw mixtures containing slag besides silica sand is excellent, especially in the stage of C_2S formation, up to 1,250 °C. The differences of reactivity due to the differing type of raw material diminished above about 1,250 °C to form C_3S.

(2) The rate of reaction in burning may be expressed by the formula, $(1-\sqrt[3]{1-x})^N=Kt$. At constant temperature, it seems that the contact-reaction and diffusion processes are predominant in the initial and successive stages respectively, because N is smaller and K is larger in the former than in the latter. N is found to have an abnormally high value of about 5, in contrast to the ordinary value of 2, K a minimum value at medium temperatures, and the activation energy a value as high as 200 kcal/mole. It may be speculated that these apparent abnormalities result from the too formal treatment disregarding two successive reactions leading to C_2S below and C_3S above about 1,250 °C.

(3) It is found that the amount of free lime remaining in the raw mixture sometimes passes through a minimum value during the burning at about 1,100 to 1,200 °C. This result is thought to be caused by the change of solubility of free lime in glycerin accompanying a change of state of the lime in burning at about 1,200 °C. The use of tribromophenol as a powerful solvent instead of glycerin resulted in the absence of a minimum.

Résumé

Après l'évaluation de 13 facteurs, au moyen d'expériences en ordre orthogonal combinées au hasard, des études détaillées concernant l'aptitude à la cuisson du ciment Portland ont été faites sur la réaction de la clinkérisation. Elles ont pour but d'abord de mettre en lumière la différence que produit dans le mécanisme de réaction le choix d'argiles ou le choix de laitiers de haut-fourneau granulés en tant que sources de silice et d'alumine, et ensuite d'établir une méthode de mesure de la réactivité. Les résultats sont les suivants:

(1) La réaction entre la chaux et les argiles contenant du quartz pour former C_2S est sensible au-dessus de 1,100 °C. Avec les produits de réaction à cet ordre de température, malgré le traitement de refroidissement rapide, on rencontre réduction en poussière et une expansion légères. La réactivité d'une argile à forte teneur en silice est supérieure à celle d'une argile à faible teneur en silice combinée à un sable siliceux. Le laitier se cristallise en melilite et absorbe ensuite la chaux pour former C_2S. A ce moment, une expansion considérable se produit mais on n'observe pas de réduction en poussière. La réactivité des mélanges bruts contenant du laitier, outre du sable siliceux, est excellente, spécialement au stade de la formation de C_2S, jusqu'à une température de 1,250 °C. La différence de réactivité due au type de matériaux bruts diminue au-dessus de 1,250 °C environ pour former C_3S.

(2) La vitesse de réaction dans la cuisson est exprimée par la formule, $(1-\sqrt[3]{1-x})^N=Kt$. A température constante, il semble que la réaction de contact et les procédés de diffusion sont prédominants respectivement aux stades initial et successif, parce que pour celui-là N est plus petit et K est plus grand que pour celui-ci. N montre une valeur anormalement élevée d'environ 5, contrastant avec sa valeur ordinaire de 2, K montre une valeur minimum à températures moyennes, et l'énergie d'activation montre une valeur aussi élevée que 200 kcal/mole. On peut se demander si ces anormalités ne proviennent pas du traitement trop conventionnel qui ne tient pas compte de deux réactions successives arrivant chacune à C_2S et C_3S, au-dessous et au-dessus de 1,250 °C environ.

(3) On observe que la quantité de chaux libre dans le mélange brut passe parfois par une valeur minimum durant la cuisson à environ 1,100–1,200 °C. On pense que ce résultat est causé par le changement de solubilité de la chaux libre dans la glycérine accompagnant le changement d'état de la chaux à la cuisson à environ 1,200 °C. Par conséquent on recommande comme dissolvant puissant le tribromophenol au lieu de la glycérine, ce qui évite la présence d'un minimum.

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[*] Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. *Contribution from the* Tokyo Institute of Technology, Japan.

Zusammenfassung

Das Brennen des Portlandzements hängt von 13 Faktoren, die durch Experimente mit Zufallskombinationen durch orthogonale Anordnung ausgewertet werden, ab. Untersuchungen über die Reaktion der Klinkerbildung wurden angestellt, die dem Zwecke dienten, die Unterschiede im Reaktionsmechanismus ausfindig zu machen, wenn Ton oder granulierte Hochofenschlacke das Rohmaterial für Kieselsäure oder Tonerde ist, und die auch dazu dienen sollten, eine Methode der Reaktionsgeschwindigkeitsmessung ausfindig zu machen. Die folgenden Ergebnisse werden erzielt:

(1) Die Reaktion zwischen Kalk und quarzhaltigen Tonen, die zur Bildung des C_2S führt, macht sich oberhalb 1,100 °C bemerkbar. Die Reaktionsprodukte, die bei einer solchen Temperatur erhalten werden, bringen eine leichte Ausdehnung und ein Zerrieseln hervor, die nicht durch ein schnelles Abkühlen überkommen werden können. Die Reaktionsfähigkeit eines Tones, der viel Kieselsäure enthält, ist größer als die eines Tones, der wenig Kieselsäure enthält, und den man mit Quarzsand gemischt hat. Die Schlacke kristallisiert zuerst als Melilit, und bindet dann Kalk unter C_2S–Bildung. Wenn sich das ereignet, nimmt eine beträchtliche Ausdehnung statt, aber ein Zerrieseln kann nicht beobachtet werden. Die Reaktionsfähigkeit der rohen Mischungen, die Schlacke mit Quarzsand zusammen enthalten, ist vorzüglich, besonders auf der Stufe der C_2S–Bildung, bis zu 1,250 °C. Die Differenzen, die man auf Grund der verschiedenen Rohstoffe beobachtet, verschwinden, wenn die Temperatur auf mehr als 1,250 °C erhöht wird, sodaß sich C_3S bilden kann.

(2) Die Reaktionsgeschwindigkeit beim Brennen wird durch die Formel $(1-\sqrt[3]{1-x})^N=Kt$ ausgedrückt. Bei konstanter Temperatur hat man den Eindruck, daß die Kontaktreaktion in der Anfangsstufe überwiegt, und daß die Diffusionsprozesse in den späteren Stufen die Oberhand gewinnen, weil nämlich N am Anfang klein ist, und weil K dann groß ist, in den späteren Stufen wächst N, während K kleiner wird. Bei nicht zu hohen Temperaturen wurde für N der ungewöhnlich hohe Wert 5 gefunden, der viel höher als der normale Wert 2 ist, während K durch ein Minimum geht, und die Aktivierungsenergie einen hohen Wert annimmt, bis zu 200 kcal/mole. Man kann annehmen, daß diese Ausnahmen in Wirklichkeit keine Ausnahmen sind, daß sie bemerkbar werden, weil man die Prozesse nur rein formell behandelt and zwei gekoppelte Reaktionen, die unterhalb und überhalb 1,250 °C stattfinden und in denen C_2S und C_3S entsteht, vernachlässigt hat.

(3) Es wurde gefunden, daß der Betrag des freien Kalks in der ungebrannten Mischung manchmal durch ein Minimum beim Brennen bei 1,110–1,200 °C geht. Es wird angenommen, daß dieser Effekt hervorgebracht wird durch eine Veränderung der Löslichkeit des freien Kalkes in Glyzerin, da er nämlich beim Brennen bei 1,200 °C seinen Zustand ändert. Es wird daher Tribromphenol als Lösungsmittel vorgeschlagen; es löst den Kalk genau so gut wie Glyzerin, und vielleicht sogar noch besser, und bringt dieses Minimum nicht hervor.

Introduction

In spite of abundant papers on the burning of portland cement clinker [1, 2],[1] there are rather few studies dealing mainly with the reaction velocity, a knowledge of which is believed to be most important for the improvement, and for the development of an entirely new design of the furnace. For instance, there is a future possibility of using the highly efficient suspension type or cyclone furnace heated with fuels or atomic energy.

The reaction velocity in the solid state has been investigated only for the simple systems [3], and similar studies have not yet been successfully applied to the formation of clinker.

Moreover, an abnormal fact has been reported [4] that the content of free lime takes a minimum value at a certain period during heating of the raw mixture at about 1,200 °C, but the causes could not be explained.

It has also been reported that a partial substitution of limestone and clay by blastfurnace slag can reduce the fuel consumption [5, 6], but the reaction process has not yet been demonstrated. This study was performed with the purpose of solving the problems mentioned above.

Burning of the Raw Mixtures

TABLE 1. *Chemical compositions and fineness of raw materials, percent*

	CaO	Al_2O_3	TiO_2	Al_2O_3 + Ti_2O_3	Fe_2O_3	Mn_2O_3	Fe_2O_3 + Mn_2O_3	SiO_2	MgO	S	Loss	Others	Fineness Blaine	Coarser than 88 μ
													cm^2/g	%
Limestone (L)	54.88	0.22	--------	0.22	0.64	--------	0.64	0.74	0.65	0.02	42.10	P_2O_5 0.07	3680	2.0
Siliceous clay (S)	3.35	13.86	--------	13.86	4.78	--------	4.78	65.96	1.74	.59	5.66		8190	0.1
High-aluminous clay (A)	tr.	29.50	--------	29.50	9.88	--------	9.88	48.20	0.62	tr.	12.36		20000	8.9
Granulated slag, coarse (C)	39.90	14.72	1.62	16.18	0.91	1.01	1.92	32.33	6.16	1.11	tr.		2950	tr.
Granulated slag, fine (F)	39.90	14.72	1.62	16.18	.91	1.01	1.92	32.33	6.16	1.11	tr.		4940	tr.
Silica sand (Q)	tr.	2.24	--------	2.24	.86	--------	0.86	94.88	0.40	tr.	0.65		5620	1.1
Blast-furnace dust (I)	1.40	3.57	--------	3.57	75.05	0.51	75.56	10.10	.82	0.21	2.83	C 4.18 ZnO 0.84 P_2O_5 0.10	4360	1.0

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[1] Figures in brackets indicate the literature references at the end of this paper.

Comparative burning studies were made using clays and granulated blastfurnace slag as raw materials for the sources of silica and alumina.

The chemical compositions and finenesses of the raw materials used in this experiment are shown in table 1.

The compositions of raw mixtures to be burned were H.M. 2.10, S.M. 2.42, and I.M. 1.90, i.e., C_3S 53–55, C_2S 23–24, C_3A 10–11, and C_4AF 9–10 percent, as illustrated in table 2.

The raw mixtures were pressed at 500 kg/cm^2 to form tablets with an area of 1 cm^2, height of 5.5 mm, and weight of 1 g. The burning conditions were in the range of 1,100 to 1,450 °C with 7 levels at 50 °C intervals, and in the range of 10 to 60 min. with 6 levels at 10 min. intervals. The burning was done in a carborundum electric furnace with an automatic temperature controller.

TABLE 2. *Combinations of raw materials*

Main raw material as the source of silica and alumina	Limestone	Siliceous clay	High-aluminous clay	Granulated slag, coarse	Granulated slag, fine	Silica sand	Blastfurnace dust
	L	S	A	C	F	Q	I
	%	%	%	%	%	%	%
Siliceous clay (S)	77.37	18.62	3.64	-------	-------	-------	0.37
High aluminous clay (A)	78.92	-------	12.12	-------	-------	8.56	.40
Granulated slag coarse (C)	66.95	-------	-------	23.74	-------	7.63	1.68
Granulated slag fine (F)	66.95	-------	-------	-------	23.74	7.63	1.68

(H.M. 2.10, S.M. 2.42, I.M. 1.90, C_3S 53–55, C_2S 23–24, C_3A 10–11, C_4AF 9–10)

Shrinkage During Burning

The shrinkage during burning is illustrated in figure 1. There is a tendency for the shrinkage to increase with rising temperature and with prolonged time, but expansion or dusting takes place also after burning at 1,100 to 1,350 °C. Dusting could not be found in the specimens containing slag. In connection with this fact, C_2S crystals formed from the quartz particles were generally large, while C_2S crystals from melilite as the devitrified product of slag were finely divided.

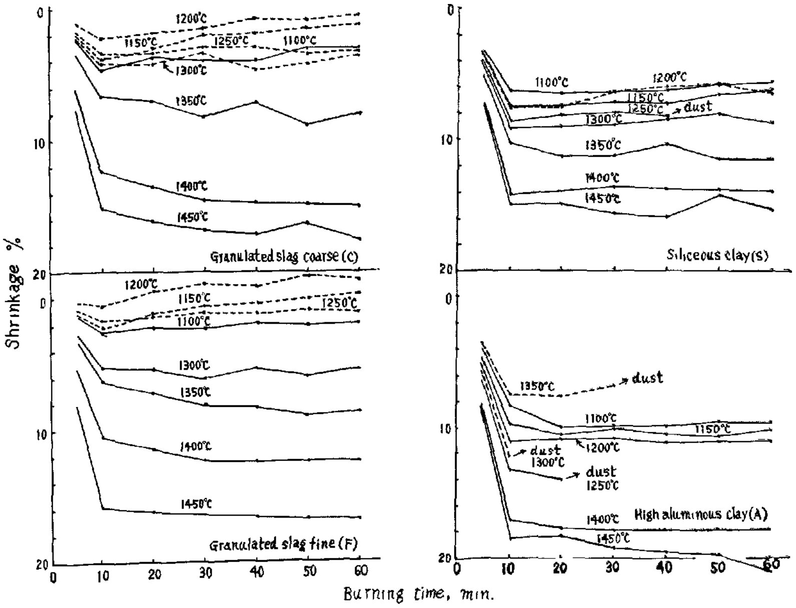

FIGURE 1. *Burning shrinkage.*

Changes of the Mineral Composition

The mineral composition of the raw materials and the changes of the mixtures in the burning process were determined by means of the reflecting and polarizing microscopes and also by the X-ray diffractometer. The principal results obtained were as follows:

Clay S contained quartz as a main constituent, together with feldspar, pyroxene, and a clayey mineral containing iron, and the maximum grain size before grinding was about 100μ. Clay A was composed chiefly of allophane containing iron, with a small amount of quartz, etc. Blastfurnace slag was almost entirely in the glassy state.

During the burning of the mixtures under about 1,000 °C, the component materials changed independently the reactions $CaCO_3 \rightarrow CaO$ and slag→ melilite taking place. In the mixtures containing clay S or clay A, the reaction $2CaO + \text{quartz} \rightarrow C_2S$ takes place at 1,100 to 1,200 °C, and then the reaction $CaO + C_2S \rightarrow C_3S$ above 1,300 °C. The resulting crystals were very fine at 1,350 °C but grew larger at 1,450 °C. In the mixtures containing Slag C or Slag F, the reaction $CaO + \text{melilite} \rightarrow C_2S$ occurred a little after the reaction $2CaO + \text{quartz} \rightarrow C_2S$ took place above about 1,100 °C, and all of the melilite disappeared with the reaction $CaO + C_2S \rightarrow C_3S$ at 1,300 °C.

Content of Uncombined Lime

The free lime content in samples was generally reduced with increased temperature and time of burning. An abnormal minimum value, however, sometimes appeared for samples burned at 1,100 to 1,200 °C. Figure 2 illustrates the results obtained.

The existence of a minimum value was reproducibly confirmed and this result was supposed to be based on experimental error in the determination of free lime. The degree of dispersion of lime tends to change in the range of 1,100 to 1,200 °C, consequently the solubility of lime in a solvent such as glycerin is expected to be different. By using tribromophenol as a somewhat more powerful solvent, it could be confirmed that this abnormal phenomenon is eliminated.

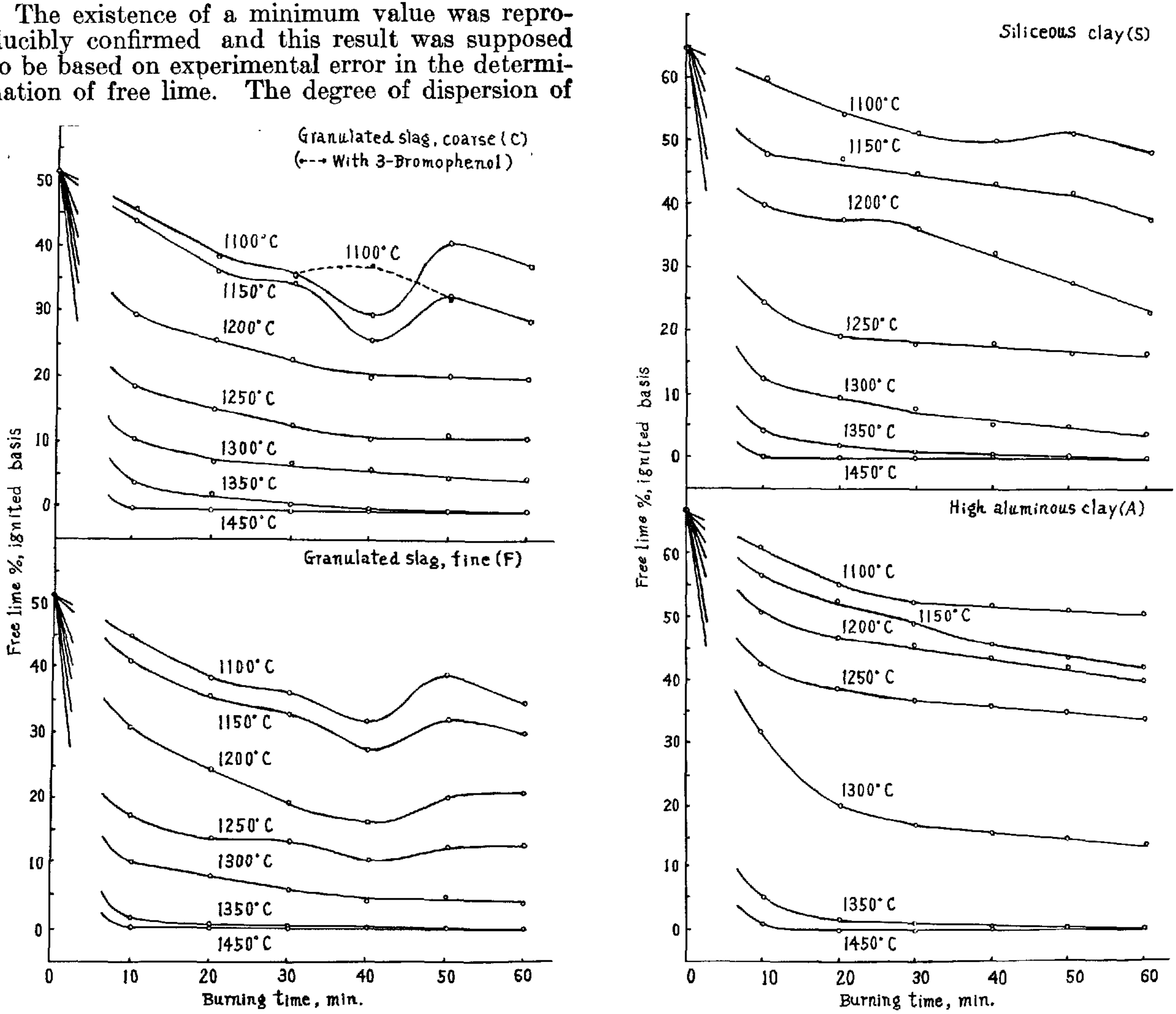

FIGURE 2. *Content of uncombined lime.*

The Reaction Velocity

The reaction ratios are shown in table 3, calculated from the results illustrated in figure 2.

Figure 3 shows the relationship between $1-\sqrt[3]{1-x}$ as the ratio of the depth of reaction to the mean radius of the particles, and t as the burning time, with temperature T as the parameter.

The equation $(1-\sqrt[3]{1-x})^2=Kt$ can be applied to the reaction velocity, if Jander's theory [3] holds. The lines are not parallel, however, and have a sharp bend, and the slope becomes gentle at high temperature where alite forms. It is therefore necessary to select the more general experimental formula $(1-\sqrt[3]{1-x})^N=Kt$. If the angle between the straight line and the ordinate is put as θ, then $N=\tan\theta$. The logarithm of the velocity constant K, i.e., log K, can be obtained by the length of the section between the original point 1,1 and the intersection of the abscissa with the straight line. The calculated values are shown in table 4.

The values of N and log K varied widely with the raw materials and the temperature and time

TABLE 3. *Reaction ratio x*

Temp	Time	Main raw material			
		S	A	C	F
°C	*min*				
1,100	10	0.05	0.08	0.10	0.10
	20	.16	.18	.27	.25
	30	.20	.22	.30	.29
	40	.21	.22	.32	.38
	50	.19	.23	.19	.25
	60	.25	.25	.26	.32
1,150	10	.26	.16	.14	.20
	20	.26	.20	.29	.30
	30	.31	.27	.32	.35
	40	.33	.34	.49	.47
	50	.34	.37	.36	.37
	60	.42	.37	.43	.43
1,200	10	.38	.25	.43	.40
	20	.43		.48	.50
	30	.44	.32	.55	.62
	40	.52	.36	.61	.69
	50	.57	.37	.50.	.61
	60	.65	.41	.57	.58
1,350	10	.62	.38	.64	.69
	20	.71	.42	.68	.73
	30	.71	.45	.74	.75
	40	.73	.47	.80	.80
	50	.75	.49	.75	.76
	60	.72	.50	.77	.73
1,300	10	.81	.53	.80	.80
	20	.85	.71	.86	.84
	30	.86	.75	.84	.88
	40	.93	.77	.88	.93
	50	.91	.79	.90	.88
	60	.93	.80	.90	.91
1,350	10	.92	.93	.93	.98
	20	.97	.97	.96	1.00
	30	.98	.98	.98	0.99
	40	1.00	1.00	.99	1.00
	50	1.00	1.00	1.00	1.00
	60	1.00	1.00	1.00	1.00
1,450	10	1.00	0.99	1.00	1.00
	20	1.00	1.00	1.00	1.00
	30	1.00	1.00	1.00	1.00
	40	1.00	1.00	1.00	1.00
	50	1.00	1.00	1.00	1.00
	60	1.00	1.00	1.00	1.00

of burning, especially at lower temperatures. At constant temperature, it seems that the contact reaction and the diffusion process are predominant in the initial and the successive stages, respectively, because N is smaller and K is larger in the former than in the latter.

The relation between the velocity constant and the temperature is shown in figure 4.

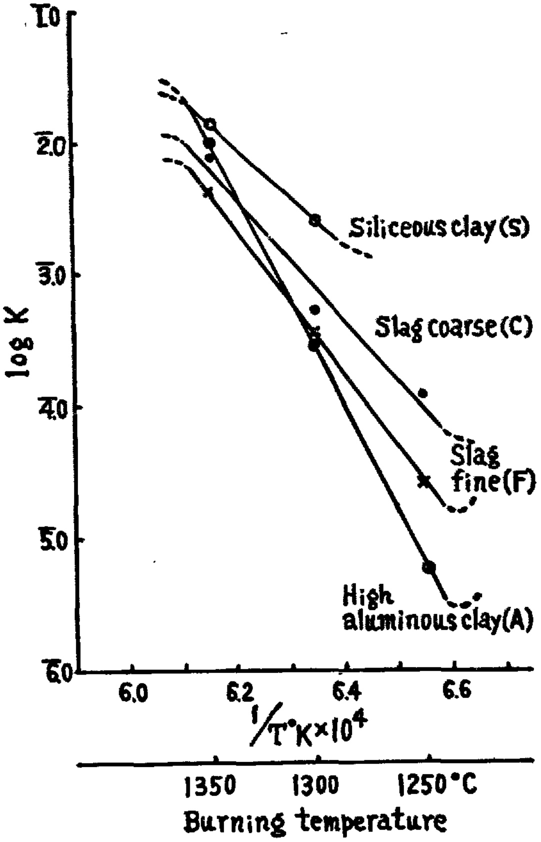

FIGURE 4. *Log K vs 1/t.*

It was found that the value of log K does not always increase with temperature, but passes through a minimum at about 1,100 to 1,250 °C.

The activation energy of the diffusion is calculated from the Arrhenius equation, log K=log A$-E/4.574$ T. If in this figure, the angle between the line and abscissa is put as θ, then tan $\theta=E/4.574$ T. The activation energy was cal-

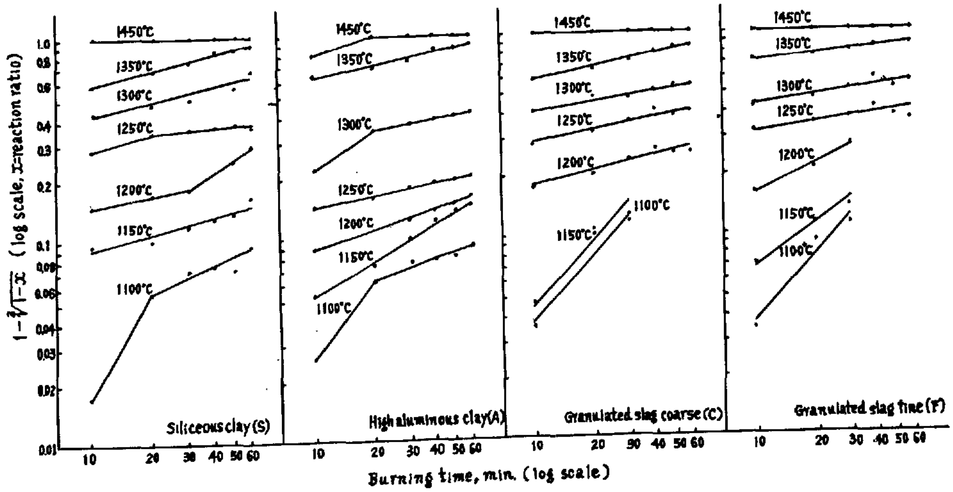

FIGURE 3. *Log* $(1-\sqrt[3]{1-x})$ *vs log t.*

Table 4. *Reaction order and velocity constant*

Temp	$\frac{1}{T^\circ K}\times 10^4$	Stage	Main raw material							
			S		A		C		F	
°*C*			*N*	log *K*	*N*	log *K*	*N*	log *K*	*N*	log *K*
1,100	7.29	Initial	0.6	$\bar{2}.00$	0.8	$\bar{3}.84$	0.9	$\bar{3}.80$	0.9	$\bar{3}.68$
		Later	2.2	$\bar{5}.89$	3.5	$\bar{5}.26$				
1,150	7.03		3.8	$\bar{5}.11$	1.6	$\bar{4}.87$	.09	$\bar{3}.87$	1.4	$\bar{3}.34$
1,200	6.80	Initial	4.9	$\bar{6}.80$	2.8	$\bar{5}.86$	4.2	$\bar{5}.70$	11.9	$\bar{3}.34$
		Later	1.5	$\bar{5}.50$						
1,250	6.56	Initial	3.0	$\bar{3}.08$	4.9	$\bar{6}.75$	5.5	$\bar{4}.15$	6.8	$\bar{5}.40$
		Later	11.7	$\bar{7}.40$						
1,300	6.35	Initial	4.4	$\bar{3}.42$	1.5	$\bar{2}.00$	5.7	$\bar{4}.69$	6.5	$\bar{4}.45$
		Later			5.3	$\bar{4}.46$				
1,350	6.16		3.7	$\bar{2}.11$	5.0	$\bar{2}.00$	4.8	$\bar{3}.90$	9.4	$\bar{3}.70$
1,450	5.80	Initial			2.7	$\bar{2}.80$				

($\log t = N(1-\sqrt[3]{1-x}) - \log K$)

Table 5. *Activation energy*

Raw material:	S	A	C	F
E……kcal/mole	180	380	210	240

culated in the range of alite formation at 1,250 to 1,350 °C, as shown in table 5.

The fact that the value of *N* was established at nearly 5, at higher temperature, apparently shows that the reaction mechanism is similar regardless of the difference of raw materials. The activation energy to form chiefly alite reaches 200 kcal/mole, which is considerably higher than the expected value. A much higher value was obtained with the composition A, which may be explained by the fact that the formation of C_2S is not sufficiently completed under 1,250 °C because of the inferior reactivity of the raw material.

Thus, the Jander formula cannot be applied to the burning of portland cement clinker, as *K* takes a minimum value at medium temperatures, and the values of *N* and activation energy reach very high values at higher temperatures. Such an abnormal result, however, is believed to be occasioned by the treatment, as there exists one sort of reaction, disregarding the reactions of the formation of C_2S and C_3S, taking place in 2 steps separately below and above about 1,250 °C. Reasonable results would be obtained, if we could distinguish the reactions $2CaO+SiO_2 \rightarrow C_2S$ and $CaO+C_2S \rightarrow C_3S$ and estimate the reaction ratios separately.

The author expresses his gratitude to President Toshiyoshi Yamauchi of Tokyo Institute of Technology for his invaluable advice and encouragement. He is also indebted to Mr. Toshio Tsuji for his assistance in carrying out the experiments.

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Paper II–S7. Solid Solutions of the Minerals of Portland Cement Clinkers*

N. A. Toropov

Synopsis

This account contains the results of experimental work by the author and his collaborators, establishing numerous cases of formation of solid solution between different constituents of portland cement clinker. The authors have established the dissolution of chromium in alite and belite, and of orthosilicates of barium and strontium and of calcium orthophosphate in belite, have determined the concentration limit of solutions of calcium aluminate in dicalcium ferrite, etc. These studies were accomplished with the aid of the polarizing microscope, X-rays, and thermal analysis.

Résumé

Cet exposé contient les résultats des travaux expérimentaux de l'auteur et de ses collaborateurs, établissant de nombreux cas de formation de solutions solides entre différents constituants du clinker de ciment portland. Les auteurs ont notamment constaté la dissolution d'oxydes de chrome dans l'alite et la bélite, d'orthosilicates de baryum, de strontium et d'orthophosphate de calcium dans la bélite, déterminé la concentration limite des solutions d'aluminate de calcium dans le ferrite bicalcique etc. Ces études ont été effectuées à l'aide du microscope polarisant des rayons X et de l'analyse thermique.

Zusammenfassung

In der Arbeit wird das Versuchsmaterial, das vom Verfasser und seinen Mitarbeitern zusammengetragen worden ist, beschrieben; sehr viele Beispiele von festen Lösungen der verschiedenen Portlandzementklinkerbestandteile in einander sind aufgefunden worden. Ganz besonders muß hervorgehoben werden, daß das Auflösen von Chromoxyden in Alit und Belit, und auch die Lösungsbildung des Bariumorthosilikats, des Strontiumorthosilikats und des Kalziumorthophosphats im Belit entdeckt worden sind; auch wurde die Maximumkonzentration des Kalziumaluminats im Dikalziumferrit bestimmt, und andere ähnliche Messungen wurden vorgenommen. Man hat in diesen Untersuchungen Röntgendiagramme und Thermoanalyse benutzt.

Results of some experimental work of the author and his collaborators are given in this report, from which it is seen that formation of solid solutions between different components of the portland cement clinker have been shown in numerous cases. In particular, the authors demonstrate the solution of chromic oxide in alite and belite, and of barium and strontium orthosilicates and calcium orthophosphate in belite; and the limited concentration of calcium aluminate solution in dicalcium ferrite was determined. These studies were made by the use of the polarizing microscope and by X-ray and thermal analyses. The varieties of cement clinker minerals obtained can be named: chromalite, chrombelite, barium belite, phosphate belite, and strontium belite. The results of these studies considerably reinforce the conception of minerals of portland cement clinker as solid solutions, not as definite compounds of simple chemical composition. The modern development of microscopical, X-ray, and thermal methods of examination of the polycomponent mineral systems, as well as of crystalline and amorphous phases formed in them, has made it possible to attain considerable progress in determining the mineralogical composition of portland cement clinker. The initial conceptions of this problem that have dominated for some decades (1915–1945), were principally based on the data obtained by the study of simple physicochemical systems formed by oxides of portland cement clinker. These conceptions favor the propagation of the theory that different clinker minerals are identified with simple silicates, aluminates, and calcium aluminoferrites formed in the respective physicochemical systems. In particular, this theory is assumed as a principle of the method for calculating the mineralogical composition of the clinker according to its gross chemical composition.

However, numerous experimental works in recent years show that this theory is only a first approximation to the solution of this problem. In reality, the chemical composition of the clinker minerals is more complicated. Mostly, they represent no simple chemical compounds but solid solutions formed between different compounds and oxides. As is known, the solution of aluminum oxide or calcium aluminates in alite and belite is a problem of great importance. Many investigators have dealt with this problem, including Jeffery [1] [1] who studied the crystalline structure of alite and tricalcium silicate. However, the close proximity of the optical properties of tricalcium silicate to those of tricalcium aluminate, as well as the absence of coloration, makes it diffi-

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Institute of Silicate Chemistry, U.S.S.R. Academy of Sciences, Leningrad, U.S.S.R.

[1] Figures in brackets indicate the literature references at the end of this paper.

cult to study their mutual solubility in solid solution. The thermal investigation of the phase diagram of the system $3CaO{\cdot}SiO_2$–$3CaO{\cdot}Al_2O_3$ is also difficult because of its pseudobinary character and the instability of these chemical compounds on heating to the melting point.

According to our opinion the possibility of partial dissolving of the aluminum oxide or a replacement of silicon atoms by aluminum atoms, with the supplementary introduction of magnesium atoms in the crystalline lattice of tricalcium silicate, finds its confirmation in the replacement of silicon by chromium in the structure of alite with the formation of chromalite, as we call it.

This replacement is a result of the interaction of the chromium oxide with basic silicates of calcium. Also, for example, during the study of samples of portland cement clinker with additions of chromite in small quantities (in the order of 3 to 5 percent of chromium oxide) obtained by S. S. Tcherepovski [2], we found already in 1933 that alite and belite crystals took on an intense bright-green emerald coloration. There was also observed a considerable augmentation of the index of refraction of the alite crystals from $n_m = 1.720 \pm 0.003$ to $n_m = 1.735 \pm 0.005$ and of belite from $n_m = 1.725$ to $n_m = 1.750 \pm 0.005$.

Later analogous observations were made by D. S. Belyankin and B. V. Ivanov [3] who had been studying structures of chromodolomitic refractories, produced by P. P. Budnikov. These refractories were obtained by firing of bricks prepared of mixtures of dolomite, chromite, and quartzite. In the chromalite crystals formed in this refractory, it was also possible to observe sometimes the formation of zonal structures with the internal substance consisting of discolored mineral of the belite type. The index of refraction of the chromalite varied within the limits $n_m = 1.745$ to $n_m = 1.760$–1.770. Chemical analyses of the refractory made by V. A. Moleva showed the presence of two chromium oxides: $Cr_2O_3 = 2.47$ percent and $CrO_3 = 5.79$ percent.

The formation of chromalite is of great interest in the study of the structure of chromite refractories, as well as for the knowledge of the service conditions of these refractories in furnaces for burning cement. According to Bunting [4] the ionic radii of trivalent aluminum (0.57A) and trivalent chromium (0.65A) are close together, and as a result there can be isomorphous, reciprocal, and complete miscibility of chromium oxide and aluminum oxide. This fact, according to our observations, appears to be an indirect indication of the possibility of solution of alumina (aluminum atoms) in the calcium silicates. It is also necessary to take into account the observations of V. V. Lapin [5], who showed the presence of feeble coloration of the alite crystals in clinkers; at the time of their burning there were introduced small additions of cobalt and nickel oxides. As is known, the solid solutions formed by dicalcium silicate have been the object of numerous and detailed observations. As a result, different authors obtained many varieties, α' and β, of the dicalcium silicate modifications, which represent themselves as various forms of the clinker mineral, belite.

In many works dedicated to the study of the solid solutions of dicalcium silicate, the solubility of the isolated oxides in the crystalline lattice of this compound has been investigated. However, the solubility of different oxides in a given case does not correspond at all with that of the orthosilicates of the same oxides in $2CaO{\cdot}SiO_2$. This is explained by the broad development of isomorphous interrelations between orthosilicates of the different elements, while the oxides of the same elements have a highly symmetrical structure. Therefore, in our work on solid solutions of dicalcium silicate, we considered it more expedient to study binary systems formed by this silicate with other orthosilicates rather than with different oxides. This procedure permitted us to establish the limited concentrations of solid solutions formed between orthosilicates under conditions of isomorphism. The study of solid solutions of dicalcium silicate with barium and strontium orthosilicates had been realized earlier in our laboratory. Toropov and Konovalov [6], with the help of a polarizing microscope, found evidence of the formation of a continuous series of solid solutions in the system dicalcium silicate–barium orthosilicate, and these authors also described the optical properties of these crystals (fig. 1). Later, we found similar crystals, which we named barium belites, in cements prepared with the addition of barium oxide.

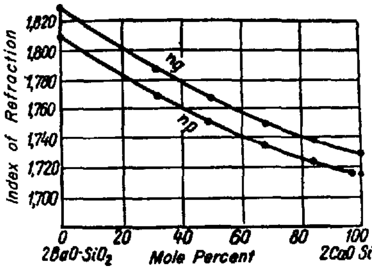

FIGURE 1. *Index of refraction as a function of composition in* $2CaO{\cdot}SiO_2$–$2BaO{\cdot}SiO_2$ *solid solutions.*

In 1953, Toropov and Borisenko [7] studied this series of solid solutions, called by us barium belites, in a more detailed way with the use of thermographic and X-ray analyses. Two series of samples were made for this purpose, namely: (a) by quenching from 1,450 °C, and (b) by annealing with slow cooling (1.5° per min, beginning from 1,450 °C) of the same samples in the platinum resistance furnace.

Data of thermographic investigations of the tempered samples are given in table 1.

Table 1. *Polymorphous transformations of dicalcium silicate, found by the method of thermal analysis*

No.	Composition		Temperatures of the polymorphous transformations	
	$2CaO \cdot SiO_2$	$2BaO \cdot SiO_2$	γ–α'	α'–α
1	2	3	4	5
	Mole %	*Mole %*	*°C*	*°C*
1	100	0	810	1,440
2	90	10	absent	1,340
3	80	20	absent	1,230
4	70	30	absent	1,130
5	60	40	absent	1,040
6	50	50	absent	950
7	40	60	absent	900
8	30	70	absent	Thermal effects not observed.
9	20	80	absent	
10	10	90	absent	
11	0	100	absent	

Transformations at 810 and 1,440 °C corresponding to the transformations $\gamma \rightarrow \alpha'$ and $\alpha' \rightarrow \alpha$-$2CaO \cdot SiO_2$ were found in the first sample. By addition of barium orthosilicate into the composition of the experimental solid solutions a stabilization down to low temperatures was observed on annealing the α' modification of $2CaO \cdot SiO_2$. The evidence of this stabilization is shown by: (1) The absence of disintegration of the sample on cooling, (2) the disappearance of the thermal effect corresponding to the transformation $\gamma \rightarrow \alpha'$-$2CaO \cdot SiO_2$, (3) the conservation (up to the concentration of 70 mole percent $2BaO \cdot SiO_2$) of the thermal effect corresponding to the transformation $\alpha' \rightarrow \alpha$-$2CaO \cdot SiO_2$. A lowering of the temperature of this effect, proportional to the increased addition of $2BaO \cdot SiO_2$, is characteristic of the formation of solid solutions.

The absence of the thermal effect for the samples containing more than 70 mole percent of $2BaO \cdot SiO_2$ shows that at this concentration the solid solutions of the type α'-$2CaO \cdot SiO_2$-$2BaO \cdot SiO_2$ become unstable even at high temperatures, but solid solutions of the type α-$2CaO \cdot SiO_2$-$2BaO \cdot SiO_2$ only are preserved at elevated temperatures.

Toropov and Konovalov [8] made an additional investigation of the system: dicalcium silicate–strontium orthosilicate where they also observed the formation of continuous solid solution. The same authors studied the optical properties of the crystals obtained (fig. 2). Later Toropov, Galakhov, and Bondar [9] studied the ternary system: calcium oxide–barium oxide–silica, in which they determined particularly the crystallization region of the barium belites, that is, the solid solutions of barium orthosilicate in dicalcium silicate. The development of production of portland cement containing barium and strontium oxides ("Edelzemente") permits the use of our physicochemical data for the determination of the mineralogical composition of the cements.

Solid solutions of calcium aluminoferrites are formed in the ternary system: calcium oxide–aluminum oxide–ferric oxide by the mutual dissolution of dicalcium ferrite, $2CaO \cdot Fe_2O_3$, and pentacalcium trialuminate in the solid phase, and probably of a small quantity of surplus calcium oxide in the crystal lattice of these solid solutions.

The first investigators of the system: calcium oxide–alumina-ferric oxide, Hansen, Brownmiller, and Bogue [10] found evidence of the formation of only a single ternary compound, tetracalcium aluminoferrite, $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, afterwards called brownmillerite. It forms a continuous series of solid solutions with dicalcium ferrite.

In subsequent studies, Lea and Parker [11] and Guttmann and Gille [12], investigating synthetic and clinker aluminoferrites, managed to obtain crystals with indices of refraction considerably lower than those of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. Therefore, in 1937 we undertook, together with Shishakov and Merkov [13], a special investigation of the pseudobinary system: brownmillerite-pentacalcium trialuminate, and ascertained a partial dissolution in brownmillerite of components with lower indices of refraction, namely, calcium aluminates.

A study of the system brownmillerite–pentacalcium trialuminate by microscope and X-ray methods permitted us to establish that the maximum quantity of pentacalcium trialuminate that can be dissolved in brownmillerite is 35 weight percent. The formula of the limited solid solution, consisting of 35 weight percent of C_5A_3 and 65 weight percent of C_4AF is $43CaO \cdot 16Al_2O_3 \cdot 7Fe_2O_3$. If the percentage of ferric oxide in brownmillerite is 32.8 weight percent, then the content of ferric oxide in this aluminoferrite is 21.7 percent. Aluminoferrite of this composition has the following indices of refraction: $n_g = 1.93$ and $n_p = 1.87$. The existence of these solid solutions was confirmed by the authors with the aid of X-ray analysis.

Almost simultaneously with our work, McMurdie [14] also demonstrated the existence of solid solutions between brownmillerite and pentacalcium trialuminate. But the limits of solubility found by him were considerably less. According to data of Yamauchi [15], who published his work at the same time, the existence of the solid solution of the composition $6.2CaO \cdot 2.2Al_2O_3 \cdot Fe_2O_3$ (21.8 weight percent of ferric oxide) would be possible.

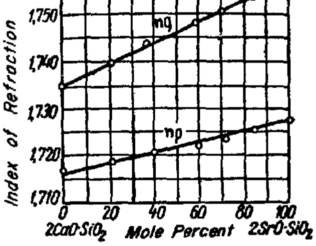

Figure 2. *Index of refraction as a function of composition in* $2CaO \cdot SiO_2$–$2SrO \cdot SiO_2$ *solid solutions.*

The results of the study completed by Toropov, Shishakov, and Merkov [13] had been repeatedly criticized until 1946, when Swayze [16] confirmed our results as well as those of Yamauchi. According to Swayze, a continuous series of solid solutions extends from $2CaO \cdot Fe_2O_3$ to the composition $6CaO \cdot 2Al_2O_3 \cdot Fe_2O_3$ (22.8 weight percent of ferric oxide) or $42CaO \cdot 14Al_2O_3 \cdot 7Fe_2O_3$. If this formula is compared with the formula $43CaO \cdot 16Al_2O_3 \cdot 7Fe_2O_3$ proposed by us in 1937, no great difference between them will be observed.

Furthermore, the last formula is considerably nearer to the aluminoferrite composition with maximum content of aluminate in solid solution (called limiting solid solution). Actually, according to Swayze the limiting solid solution should contain 22.8 weight percent of Fe_2O_3 but according to Toropov, Shishakov, and Merkov it contains 21.7 percent by weight. Thus, the composition proposed by Swayze as a final term of the series of solid solutions is only a first approximation to the limiting composition of the solid solutions. This fact becomes more evident if one examines the works of Italian investigators. Thus, Malquori [17], Cirilli and Burdese [18], studying by X-rays solid solutions of aluminoferrites, drew the conclusion that it is possible to obtain a homogeneous solid solution with a content of 20–21 percent of Fe_2O_3. Malquori [17a] proposed the following formula for aluminoferrite with the maximum content of aluminate: $6CaO \cdot 2.1Al_2O_3 \cdot 0.9Fe_2O_3$ (Fe_2O_3=20.7 percent).

The next work on this problem was done by Toropov and Boikova [19] in the Institute of Silicate Chemistry of the Academy of Sciences, USSR. The investigation of aluminoferrite solid solutions was performed mainly by the use of the polarizing microscope, this being the most precise method. The sensitivity of the roentgenographic method for the quantity determination of aluminates and aluminoferrites is not great and is limited to contents not lower than the following percentages in the mixture: C_4AF–15 percent, C_5A_3 and C_3A–6 percent [20]. Malquori, Cirilli, and Burdese disregarded the possibilities of the roentgenographic method for the quantity determination of aluminates and ferrites. It is also important to provide for sufficiently slow rate of cooling. The cooling velocity in our experiments was 1.5° per min.

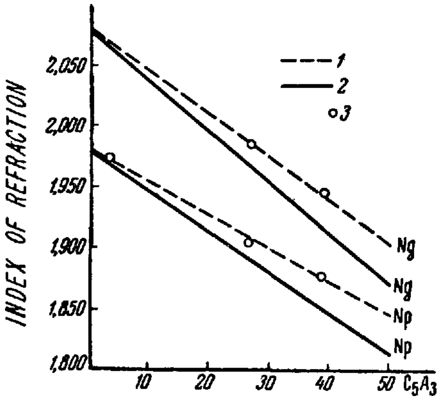

Figure 3. *Relation between indices of refraction of aluminoferrites and quantity of* C_5A_2 *incorporated in the solid solution containing* C_4AF.

-- A curve obtained on the supposition that the rhombic modification of C_5A_3 is incorporated into the solid solution.
— A curve obtained on the supposition that the cubic modification of C_5A_3 is incorporated into the solid solution.
° Experimental points.

At first we carried out experiments to establish which of the modifications α-C_5A_3 or α'-C_5A_3 was a part of the solid solution of aluminoferrites (together with an insignificant quantity of lime). It was natural to suppose that solid solutions of aluminoferrites are formed with the rhombic modification of pentacalcium trialuminate, which has a structure closer to that of $2CaO \cdot Fe_2O_3$.

To verify this hypothesis we have calculated a theoretical curve of index of refraction, drawing a chart of curves of variations of these indices as functions of the concentration of C_5A_3, for the α' form and for the α form (fig. 3).

This calculation is based on additivity, that is, on the existence of a linear relation between the composition of the solid solutions and their indices of refraction. As is known, such a relation is very clearly expressed for a whole series of systems with solid solutions. The experimental verification showed that it is necessary to consider α'-C_5A_3 as the aluminate component of the solid solution of aluminoferrites.

To answer a principal question, what is the maximum content of C_5A_3 in the solid solution, and also what are the limits of the reduction of the quantity of the ferric oxide in the limiting composition of the aluminoferrite, we have synthesized and studied samples containing 42, 32, 24, 20, 16, 14 and 12 weight percent of Fe_2O_3. In table 2 are given compositions of the mixtures.

Table 2

Sample No.	CaO	Al_2O_3	Fe_2O_3	$\frac{Al_2O_3}{Fe_2O_3}$
	Weight percent			
12	50.0	38.0	12.0	3.17
14	49.73	36.27	14.0	2.59
16	49.4	34.6	16.0	2.162
20	48.6	31.4	20.0	1.57
24	47.8	28.2	24.0	1.175
32	46.32	21.68	32.0	0.68
42	44.43	13.57	42.0	0.32

Each sample was subjected to four annealings with intermediate fine grinding. The samples were observed by the microscope in immersion and by reflected light, in polished sections. The study showed that the samples containing more than 20 percent of Fe_2O_3 consisted of homogeneous phases: solid solutions of the aluminoferrites.

Samples with 16, 14, and 12 weight percent of Fe_2O_3 contained, together with aluminoferrite, also the aluminates C_5A_3 and C_3A which were well identified in reflected light (when the section was etched with a solution of oxalic acid in alcohol). The indices of refraction of the aluminoferrites determined by immersion in liquids with a high index of refraction, continuously increased in the samples containing 14 and more percent of Fe_2O_3. Only samples with 14 and 12 percent of Fe_2O_3 attained a constant (minimum) value of indices of refraction. This permitted us to establish that the compositions of the aluminoferrites in these samples were the same. Therefore, we concluded we had attained the limiting composition of solid solution (with maximum content of aluminate). The maximum reduction of the indices of refraction of aluminoferrites is from $n_g=2.08$ and $n_p=1.98$ for $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ to $n_g=1.914$ and $n_p=1.854$ for the limiting solid solution.

The calculation based on the linear relation between the indices of refraction and the concentration of the solid solution gave a chemical composition of the limiting solution as follows: $7.8CaO{\cdot}3.24Al_2O_3{\cdot}Fe_2O_3$. Approximately, it can be represented by the following formula: $8CaO{\cdot}3Al_2O_3{\cdot}Fe_2O_3$ (ferric oxide, 17.5 weight percent).

A special roentgenographic study of this limiting concentration accomplished by Boĭkova and Poraĭ-Koshits [21] confirmed the results of the microscopical study. In figure 4 is shown the relative position of the characteristic peaks of the X-ray diagram obtained by the diffractometer. These curves are taken from samples of aluminoferrites with different contents of ferric oxide. (The number of the sample corresponds to percentage of ferric oxide.) As may be seen in figure 4, the position of the peak corresponding to pentacalcium trialuminate remains invariable. The position of the maximum for aluminoferrite is constant only in samples with a content of 12 and 14 percent of ferric oxide; if the content is more, then the peak is displaced, showing a change in concentration of the solid solution.

The choice of the formula, shown above, for the limiting solid solution is also confirmed by some crystallochemical considerations. Probably the relations of atoms in the elementary cell can be presented in the following way: $8CaO{\cdot}3Al_2O_3{\cdot}Fe_2O_3$ or $Ca_8Fe_2Al_6O_{20}$.

Büssem [22] thought that aluminum atoms in aluminoferrites are only in octahedral coordination. We consider that the point of view of Malquori and Cirilli corresponds better to reality. These authors think that aluminum atoms are to be found in aluminoferrites with coordination numbers four and six. In reality, this point of view is confirmed by the existence of the aluminoferrite solid solution of the type $Ca_8Al_6Fe_2O_{20}$. In this compound 4 aluminum atoms are in tetrahedral coordination and 2 in octahedral. The structural forms of the considered compounds can be represented as follows:

Chemical composition	Quantity of Fe_2O_3 in weight percent	Number of "molecules" in the elementary cell	Structural formulas
$2CaO{\cdot}Fe_2O_3$	58.8	4	$Ca_8Fe_4^{IV}Fe_4^{VI}O_{20}$
$4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$	32.8	2	$Ca_8Fe_4^{IV}Al_4^{VI}O_{20}$
$8CaO{\cdot}3Al_2O_3{\cdot}Fe_2O_3$	17.5	1	$Ca_8Fe_2^{IV}Al_2^{IV}Al_4^{VI}O_{20}$

For the composition $6CaO{\cdot}2Al_2O_3{\cdot}Fe_2O_3$ (ferric oxide 22.8 percent) or $6CaO{\cdot}2.1Al_2O_3{\cdot}0.9Fe_2O_3$ (ferric oxide 20.7 percent) it was impossible to establish a disposition of atoms in the elementary cell of the type $Ca_8Me_4^{IV}{\cdot}Me_4^{VI}{\cdot}O_{20}$.

It is necessary to consider that the formulas shown above express only a relation of oxides in aluminoferrites.

In 1958 Newkirk and Thwaite of the National Bureau of Standards, USA [23], published a new

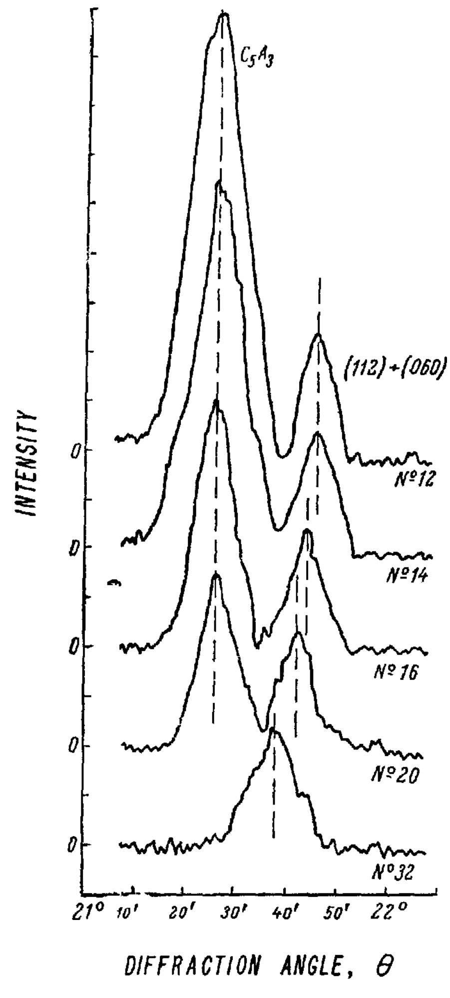

Figure 4. *Relative positions of calcium aluminate and calcium aluminoferrite lines.*

communication on solid solutions in aluminoferrites. According to the data of thermal and X-ray analyses the authors drew a conclusion that the limiting composition of the aluminoferrite solid solution corresponds to the formula $6.45CaO \cdot 2.31Al_2O_3 \cdot Fe_2O_3$. Thus, it corresponds to a composition occupying an intermediate position between the limiting compositions indicated by Malquori [17] and by us.

From our point of view, results of joint investigations by X-ray and microscope afford the greatest precision.

All examples, given above, show that the chemical nature of the different crystalline phases of portland cement clinker is very complex. Chemical phenomena in solid solutions are broadly developed, and there is a great possibility for variations of the structure and for chemical reactivity of the clinker minerals.

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Discussion

Myron A. Swayze

Dr. Toropov's approval of the petrographic microscope as the most precise instrument in checking homogeneity of the aluminoferrite solid solutions is heartily seconded by this writer, especially if powder mounts of these compositions are made in Hyrax resin. This material has a refractive index of 1.713, and thus allows observation of all the colorless clinker minerals with almost complete elimination of refraction shadows around these compounds. It has the further advantage of producing permanent mounts for everything except free CaO, which hydrates very slowly in contact with the solid resin.

High index resins for identification of particular compositions within the aluminoferrite solid solution series are not as reliable as X-ray analyses because of difficulty in standardizing these resins and the volatility of the lower index portion of these mixtures in preparing powder mounts. The X-ray patterns as shown in Toropov's figure 4 should furnish a much more exact indication of the A/F ratio of ferrite phases.

In this connection, it is regrettable that he fails to include compositions in table 2 between Fe_2O_3 contents of 20.0 and 24.0 percent, and that these compositions were not subjected to X-ray analysis. A study of this kind should automatically settle the present question of the minimum Fe_2O_3 content of the aluminoferrite series of solid solutions, by revealing C_5A_3 peaks when this minimum was passed.

Incidentally, the compositions shown in table 2 are not prepared from mixtures of C_5A_3 with C_2F or C_4AF at all, as might be concluded from the discussion, but are rather on or very close to a line of compositions running from C_2F to a hypothetical C_2A. Since this line of compositions is of such great interest, it is hoped that the author and his colleagues will fill in the information on compositions between 20 and 24 percent Fe_2O_3 and present these new data as a revision of the present paper.

Paper II–S8. Decomposition of Alite in Technical Portland Cement Clinker*

E. Woermann

Synopsis

The conditions occurring in technical clinker for the decomposition of alite to secondary belite and free lime have been traced. It is shown that alite tends to decompose only in such iron-bearing clinker samples as show typical indications of reducing heating conditions.

Laboratory experiments were conducted to confirm the hypothesis that the abnormal instability of alite is produced by ferrous iron ions entering the alite lattice.

Reducing conditions during the sintering process result in: dusting of clinker containing primary belite; a considerable increase in periclase; changing quantitative ratio of ferrite and aluminate; and a change of the properties of ferrite.

Under favourable conditions alite may decompose so rapidly that freezing of the high temperature equilibrium cannot be achieved simply by quenching in air.

The lower limit of stability of alite containing ferrous iron in solid solution is determined to be 1,183 °C (±5 °C). Alite containing ferric iron has been destroyed by annealing at a temperature of 1,180 °C.

Evidence has been offered that the Fe^{++} ions are for the greater part substituting for Ca^{++} ions in the alite lattice.

Résumé

Les conditions présidant à la décomposition de l'alite du clinker de l'usine en belite secondaire et en chaux libre sont connues. On montre que l'alite ne tend à se décomposer que dans les échantillons de clinker ferrifère qui donnent des indications typiques de chauffage réductif.

On a procédé à des expériences au laboratoire pour corroborer l'hypothèse que l'instabilité anormale de l'alite est produite par les ions de fer ferreux pénétrant le réseau d'alite.

Les conditions réductives au cours de l'agglomération par frittage donnent les résultats suivants: pulvérisations spontanée du clinker contenant du belite primaire; périclase extrêmement accrue; rapport quantitatif de ferrite et d'aluminate changeant; et un changement dans les propriétés du ferrite.

Sous des conditions favorables l'alite peut se décomposer si rapidement que le simple refroidissement à l'air est incapable de réaliser la fixation de l'équilibre à haute température.

La limite inférieure de stabilité de l'alite contenant du fer ferreux en solution solide est déterminée comme étant de 1,183 °C (±5 °C). L'alite contenant du fer ferrique est détruit par recuit à une température de 1,180 °C.

On présente de l'évidence que l'ion Fe^{++} remplace en partie le Ca^{++}, en entrant pourtant en partie les troux du réseau d'alite.

Zusammenfassung

Die Bedingungen, die in technischem Klinker zum Zerfall des Alit in sekundären Belit und freien Kalk führen, wurden untersucht. Es konnte dabei gezeigt werden, daß Alit vorwiegend in eisenführenden Klinkerproben, die typische Anzeichen reduzierender Brennbedingungen aufweisen, zum Zerfallen neigt.

Die Annahme, daß die abnormale Instabilität des Alit durch in das Gitter eintretendes, zweiwertiges Eisen verursacht wird, konnte durch Laboratoriumsversuche bestätigt werden.

Reduzierende Brennbedingungen rufen einige weitere, charakteristische Eigenschaften im Klinkerbild hervor: Klinker mit höheren Belitgehalten neigen zum Zerrieseln; die Periklasgehalte nehmen zu; das Mengenverhältnis Aluminat: Ferrit wird zugunsten des Aluminat verschoben; die optischen Eigenschaften des Ferrit sind verändert.

Unter günstigen Umständen kann Alit so schnell zerfallen, daß der Zustand bei Sintertemperatur auch durch Abschrecken an Luft nicht eingefroren werden kann.

Die Stabilitätsgrenze von Fe^{++} haltigem Alit liegt bei 1,183 °C (±5 °C). Alit mit Gehalten von dreiwertigem Eisen konnte durch Tempern bei 1180 °C zerstört werden.

Die Fe^{++} Ionen scheinen im wesentlichen Ca^{++} Ionen des Alitgitters zu vertreten.

Decomposition of Alite

During the last three decades much work has been devoted to the phenomenon of the decomposition of alite in portland cement clinker to secondary belite and free lime according to the simplified equation

$$3\ CaO{\cdot}SiO_2 \rightarrow 2\ CaO{\cdot}SiO_2 + CaO.$$

Except for the special case of admixture of CaF^2 to the clinker it has always proved necessary for the laboratory specimens to be tempered for a very long run—generally for several days—at temperatures between 1,300 and 1,000 °C before any decomposition of alite was detectable. Thus for these laboratory experiments time factors have been involved that are incomparable with any technical process.

Decomposition of alite in technical products, however, has been observed repeatedly during

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. *Contribution from the Hauptlaboratorium*, Portland-Zementwerke Heidelberg A. G., Germany.

FIGURE 1. *Idiomorphic crystal of alite (dark grey) partially disintegrated (diffused part).*

Shaft kiln clinker. Etched with dimethyl ammonium citrate. 1500 ×.

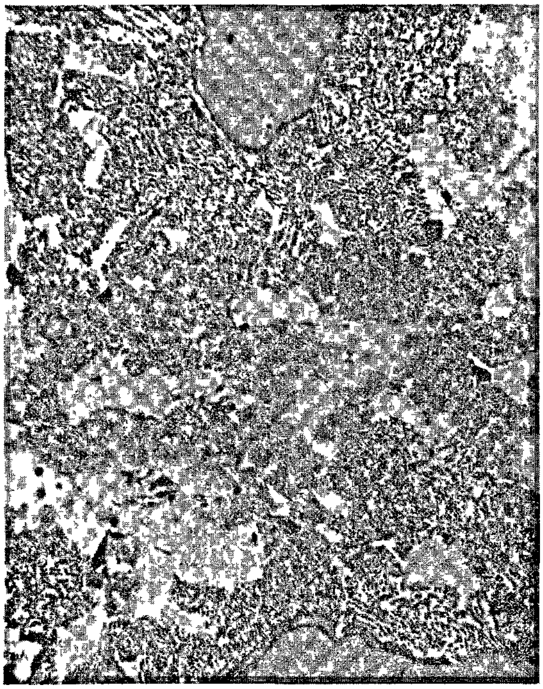

FIGURE 2. *Secondary free lime showing as fine black inclusions after exposure to moist air for 24 hr.*

Shaft kiln clinker. 200 ×.

FIGURE 3. *The same specimen as shown in figure 2.*

Intense decomposition of alite in a shaft kiln clinker. 50 ×.

microscopic control of shaft kiln and sinter grate clinker (figs. 1 to 4). Spohn [1],[1] Spohn and Woermann [2].

The products of this decomposition form intimate myrmekitic intergrowth structures, pseudomorphous after the primary alite, of very small, but even in single specimens widely varying dimensions. Typically the decomposition starts from certain centers that show relatively coarse intergrowth structures. From here it spreads like an infectious disease from one crystal to another, the intergrowth structures becoming ever finer with increasing distance from the centers until at last it is impossible to resolve them by optical methods. In this case the decomposition may still be detected in polished sections by the rough surface and the diffused reflection of the alite pseudomorphs and the quite different etching properties of the secondary products (fig. 5).

TABLE 1

Clinker	A	B	C	D
Alite	82.5	76.5	73.9	77.6
Decomposed alite	32.3	44.2	25.9	52.8
Secondary free lime	7.9	10.9	6.4	13.0
Primary free lime	5.0	3.3	2.4	1.1
Sum free lime (micr.)	12.9	14.2	8.8	14.1
Free lime (chem. anal.)	5.8	5.4	3.2	7.1

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[1] Figures in brackets indicate the literature references at the end of this paper.

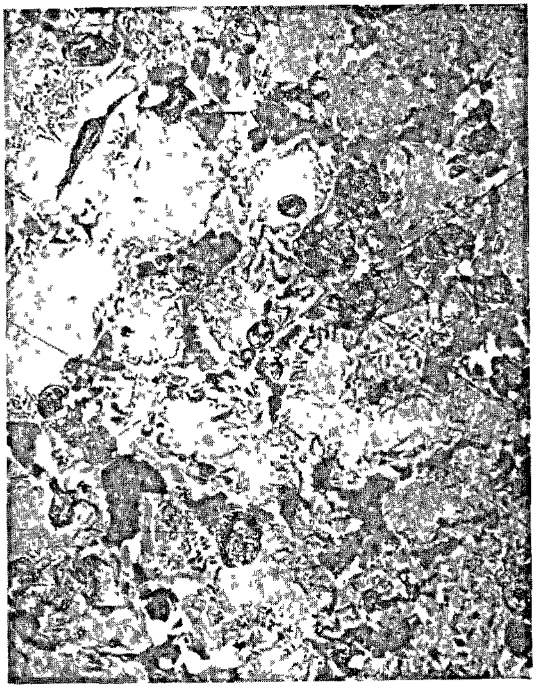

FIGURE 4. *Disintegration of alite starting from the crystal surfaces.*

Typical coating of the alite crystals by belite in spite of a high content of primary free lime. Sinter grate clinker. Etched with H_2O. 500 ×.

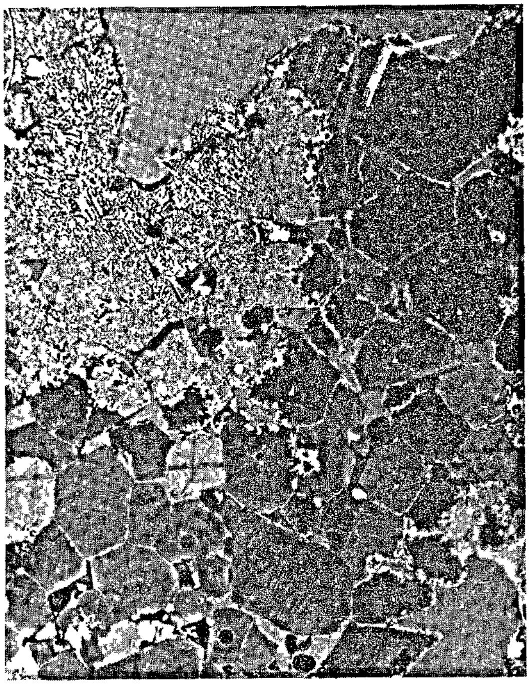

FIGURE 5. *Alite crystals (dark grey) being decomposed to belite (light grey) and free lime (black).*

The center from which the disintegration has started shows coarser structures. Shaft kiln clinker. Etched with H_2O 500 ×.

Methods of Investigation

The observation of these phenomena has only been possible by microscopic methods on suitably etched polished sections.

In thin sections, areas with decomposed alite were characterized by blurred dark spots. The decomposition products are in any case much finer than the thinnest practically attainable thin section (fig. 6).

The chemical determination of free lime must necessarily give values that are too low and will, in the case of the finest intergrowth-structures of the secondary products, fail altogether as a method for the detection of the decomposition of alite. Table 1 compares some values, obtained by analytical and microscopic methods, of free lime in clinker containing amounts of decomposed alite.

The phenomenon of the decomposition of alite in technical clinker has been described by several authors, e.g., Tröjer [3] and Alègre and Terrier [4]. In all cases slow cooling in the temperature interval below the stability limit of alite has been quoted as a determining factor. Tröjer observed decomposition of alite in clinker specimens containing relicts of coke or traces of a "sulfite" phase. From this he concluded that the burning of these inclusions in air would produce enough heat to prevent effective cooling of alite in the critical interval.

FIGURE 6. *In thin sections decomposition of alite may be recognized by dark blurred spots.*

Shaft kiln clinker. 200 ×.

The Causes of the Decomposition of Alite in Technical Portland Cement Clinker

Tracing the phenomena accompanying the decomposition of alite soon led to doubt that slow cooling alone is responsible for this effect in technically cooled clinker.

It was proved that alite may be destroyed even in cases of fast cooled clinker, as for example in sinter grate clinker, where the typical dendritic intergrowth of the matrix confirms the quenching from sintering temperature. The abnormal instability of alite seems to be sensibly dependent on other factors, e.g., the presence of foreign components that may enter the alite lattice. Some most typical characteristics may be observed in clinker showing structures of alite decomposition.

Generally the clinker is densely burnt, being of a light brown colour.

Under the microscope the ferritic phase shows a distinctly lower reflectivity than in normal clinker, a typical characteristic of reducing conditions during the sintering process.

At the same time some further compounds may be identified which can only be formed in reducing atmosphere, as for example calcium or iron sulfides (fig. 7).

Under conditions of extreme reduction, however, the ferritic phase disappears. All iron is transformed to the metallic state. The colour of the clinker is white. At the same time all structures of the decomposition of alite disappear.

Black, fully oxidized parts of the same sample, on the other hand, show a quite normal clinker with the usual combination of its components—a high reflectivity of the ferritic phase and eutectic intergrowth of ferrite and aluminate in the matrix—without any trace of decomposed alite. In some cases however fine lamellae are exposed in the alite crystals (fig. 8). They occur in three different—but apparently not equivalent—sets with strict crystallographic orientation with respect to the host. Coarser individual lamellae could be identified as belite.

Nearly all of the phenomena accompanying the decomposition of alite thus point to moderately reducing burning conditions, while on the other hand intense reduction, transforming iron to the metallic state, does not seem to exert an accelerating influence on the destruction of alite.

Furthermore the pseudomorphs after alite most frequently contain fine inclusions or margins of ferrite in addition to the belite and free lime to be expected here (figs. 9 and 10). Apparently iron is playing an active role in this reaction.

These observations lead to the conclusion that alite by action of moderate reduction and in the presence of iron—probably by introduction of ferrous iron into the alite lattice—is becoming highly unstable so that it will tend to decompose to belite, free lime and a ferritic phase, even under normal technical cooling conditions.

FIGURE 7. *Intense disintegration of alite in a specimen bearing calcium sulfide (white, round spots).*

Shaft kiln clinker. Etched with H_2O. 500 X.

FIGURE 8. *Fine lamellae of belite in three parallel sets in alite crystals.*

Shaft kiln clinker 500 X.

FIGURE 9. *Alite (medium grey relicts) being disintegrated to a myrmekitic intergrowth structure of belite (light grey), free lime (dark grey) and a ferritic phase (white).*

Shaft kiln clinker. Etched with H_2O. 500 X.

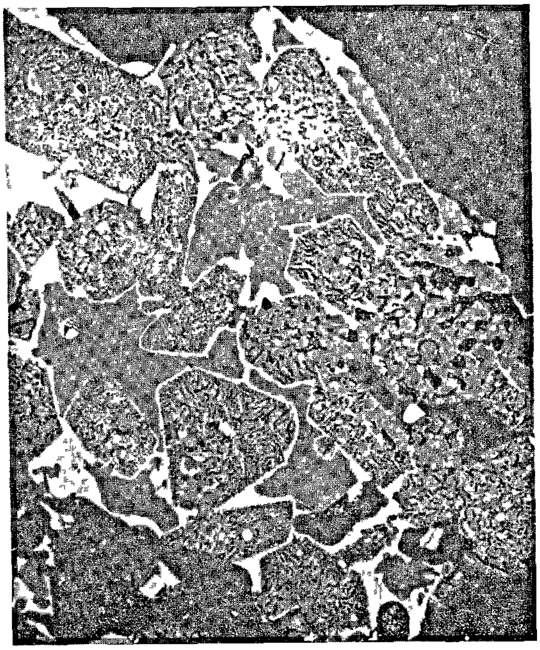

FIGURE 10. *Decomposed alite crystals with tiny inclusions and distinct margins of ferrite.*

Laboratory clinker. 500 X

Laboratory Experiments

It seemed desirable to prove the deduction, that the decomposition of alite under technical conditions is decidedly influenced by the action of Fe^{++}, by laboratory experiments.

Laboratory clinkers of very different compositions in the range of normal portland cement were prepared from pure chemical substances. Different fractions of each were subsequently treated according to the following scheme:

1. heated in air,	quenched
2. heated in air,	slowly cooled
3. heated in reducing atmosphere,	quenched
4. heated in reducing atmosphere,	slowly cooled

A uniform sintering temperature of 1,450 °C was chosen for all charges, which were kept at this point for 30 min, in some special cases even much longer. Quenching was achieved simply by droping the charge—about 7 g of clinker—from the maximum temperature to open air. Slowly cooled specimens were kept in the furnace, where the temperature dropped constantly at a rate of 5 °C/min until a temperature of 1,000 °C was attained.

Different methods were adopted to obtain moderate reduction in these charges. Either nitrogen containing small amounts of hydrogen was passed through the furnace tube or, with much better results, H_2O/H_2 or CO_2/CO mixtures were used. Excellent results were obtained by heating the charge in a closed iron crucible, but here it was most difficult to have control of the metallic iron of the crucible itself taking part in the reaction. Considerable difficulties have also been experienced with long run heatings in platinum crucibles and H_2O/H_2 gas, especially with high temperatures. The vapour pressure of FeO proved here to be high enough to cause considerable differences in composition of the charge before and after heating or in the composition of its outer shell and its centre. For these reasons the results of our experiments can have only a purely qualitative character. Never the less the deductions made from our experience with shaft kiln clinker were confirmed.

Clinker heated in air with subsequent quenching shows normal idiomorphic alite, round belite crystals and a most typical dendritic intergrowth of the matrix (fig. 11).

With heating in air and slow cooling a clinker is produced showing all well known characteristics: Alite is still fresh without any trace of decomposition. Aluminate and ferrite have crystallized separately. They show tiny exsolutions of belite (fig. 12).

The structure of clinker heated in reduced atmosphere and quenched (fig. 13) differs greatly from the above.

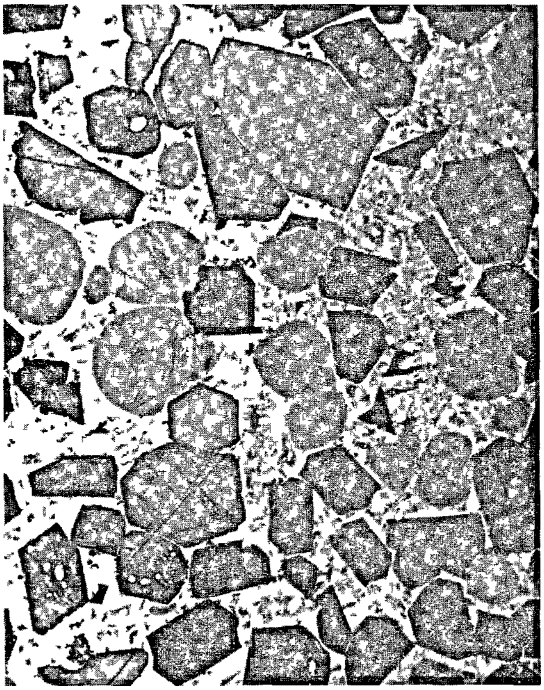

FIGURE 11 *Laboratory charge heated in air, quenched from sintering temperature*

Etched with H_2O 500 ×

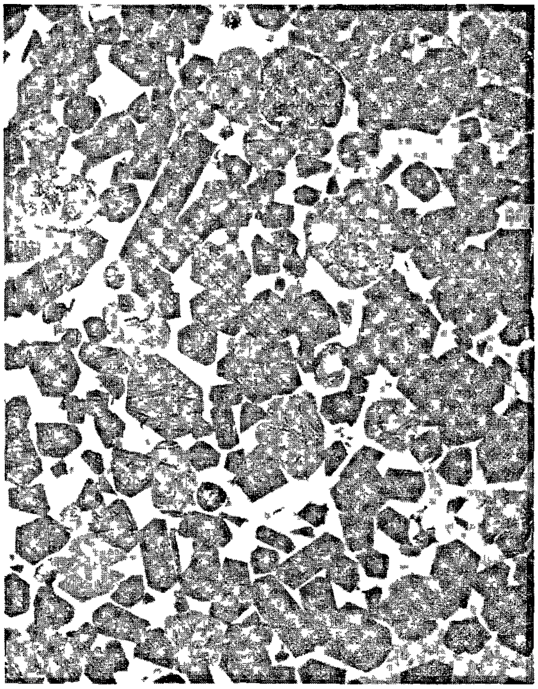

FIGURE 12 *Laboratory charge heated in air, cooled at a rate of 5°C/min*

Etched with H_2O 500 ×

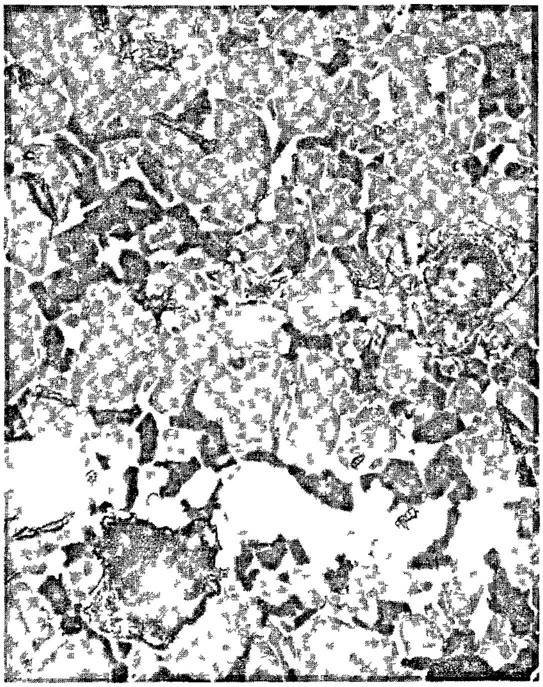

FIGURE 13. *Laboratory charge heated in reducing atmosphere, quenched from sintering temperature*

Etched with H_2O 500 ×

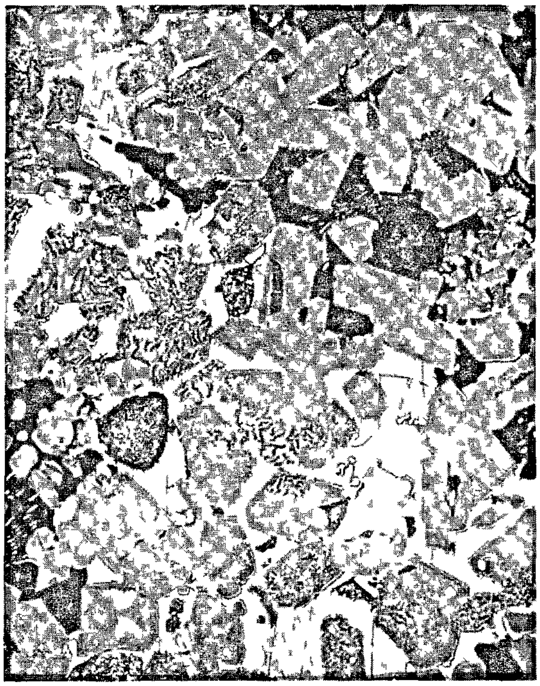

FIGURE 14 *Laboratory charge (initial composition analogous to that of figures 11–13) heated in reducing atmosphere, slowly cooled*

Inclusions of periclase (grey) and metallic iron (white) Etched with H_2O 500 ×

In spite of the fast cooling the phases of the matrix are distinctly separated from each other without showing the typical eutectic intergrowth structures. The etching properties are changed, the alite now being considerably less sensitive to the influence of water. No traces of decomposition are shown by the alite crystals in quenched charges. The content of free lime is always considerably higher than in oxidized charges of the parallel run. The alite crystals are coated—mostly after a thin ferrite seam—by a thick belite cover, a phenomenon that can be observed in some technical clinker as well. The melt must have been rich in silica and comparatively poor in lime. With quick cooling a resorption has been prevented.

Charges treated in a current of reducing gas during the heating and with subsequent slow cooling also produce highly characteristic structures (fig. 14). The most striking one is the decomposition of alite, which can be traced here in almost every charge: In 24 charges treated accordingly the degree of decomposition with respect to the original alite varied between 10 to 85 percent. Exceptions are noted only in clinker without iron or with very low iron content. Thus it is evident that here a combination of iron content, moderate reduction and slow cooling is a prerequisite for the decomposition of alite.

In some cases the structures of secondary belite and free lime are extremely coarse. Thus it may occasionally be difficult to detect their source (fig. 15).

Clinker containing MgO shows a distinctly lower rate of decomposition of alite, which could, however, never be prevented altogether. We may conclude that alite containing Mg^{++} cannot dissolve as much Fe^{++} as alite free of Mg^{++}.

Furthermore clinker containing Mg^{++} generally contains appreciable amounts of periclase, even if the parallel charge, run in oxidizing atmosphere, is altogether free of periclase. The periclase itself is characterized by high reflectivity and low polishing hardness. It thus obviously contains appreciable amounts of wüstite in solid solution.

The ferritic phase here possesses a considerably lower reflectivity than in analogous specimens heated in air. It is stable in the presence of metallic iron. The amount of aluminate increases on account of ferrite.

The massive belite seams around alite crystals shown by quenched specimens have disappeared completely. Obviously equilibrium conditions could be attained by resorption of belite by free lime.

Charges with a relatively low content of lime regularly tend to dust, even if samples of the same composition heated in oxidized atmosphere remain hard. This is in good agreement with the results of Suzukawa's [5] experiments, stating that the β–γ inversion of belite is sensibly promoted by small amounts of $2FeO{\cdot}SiO_2$ in solid solution with $2CaO{\cdot}SiO_2$. It has been established in technical clinker as well as in laboratory specimens that in general primary belite tends to dust much easier than belite derived from the decomposition of alite (fig. 16). Charges with high content of lime frequently remain hard, even if alite has been decomposed completely to secondary belite and free lime. It is obvious that dusting of a clinker specimen cannot be a direct measure for the degree of decomposition of alite.

FIGURE 15. *Coarse intergrowth structures in centers of decomposition.*

Inclusions of metallic iron. Laboratory charge. Etched with H_2O. 500 ×.

FIGURE 16. *Single grain from dusted clinker.*

The inversion to γ-C_2S has been limited to primary belite. Shaft kiln clinker. Etched with alcoholic HNO_3. 500 ×.

The Velocity of Decomposition of Alite

The rate of cooling of laboratory charges was chosen to be about 5 °C/min in order to pass the temperature interval between 1,450 to 1,000 °C in 90 min, corresponding to slow technical cooling conditions. Later some experiments were made in order to determine the tendency of alite to decompose even in shorter time intervals. Even after cooling at a rate of 10 °C/min a considerable amount of the alite is destroyed. The intensity of this decomposition is dependent on the composition of the specimen and on the heating temperature. Thus complete decomposition of alite could be observed in a sample prepared by heating a mixture of pure tricalcium silicate with 6 percent of ferrous oxide ($Fe_2O_3+Fe \rightarrow 3\ FeO$) in H_2/H_2O gas at 1,600 °C, although it was quenched subsequently in nitrogen (fig. 17). A charge of analogous composition was heated in air, where the first traces of decomposition could be observed only after annealing of the charge for 30 to 45 hr at 1,180 °C.

FIGURE 17. *Complete decomposition of a laboratory specimen after quenching from 1600 °C*

Etched with alcoholic HNO_3 1000 X

The Limit of Stability of Alite

A most favourable chance has been offered to determine the limit of stability of alite by a quick method by treating the alite with ferrous iron. Knowing, however, that the decomposition of alite containing Fe^{++} may occur very rapidly it seemed doubtful whether normal quenching would always succeed exactly in preserving the conditions of equilibrium of the temperature of annealing. Thus, after heating a charge at 1,500 °C, it was slowly cooled in reducing atmosphere until the temperature chosen for this run was attained. The furnace temperature having been kept at this point for 2 hr, the charge was oxidized and thus the phases stable at that temperature were preserved and the equilibrium safely frozen to room temperature.

The limit of stability of alite containing Fe^{++} has been determined by this method to be 1,183 °C (±5 °C). It seems, however, that this value is valid only for the special case of instabilization of alite by Fe^{++}. Attempts to decompose alite heated in air, by annealing, show that charges containing ferric iron are unstable at a temperature of 1,180 °C while those containing alumina and magnesia did not show any trace of decomposition after 120 hr annealing at this temperature. This is in good accordance with the observations of Welch and Gutt [6] who found that the limit of stability of alite may be shifted considerably by different admixtures.

The Fe^{++} Content of Alite

An attempt was made to determine the limit of solubility of Fe^{++} in alite. For this purpose pure tricalcium silicate containing admixtures of metallic iron and ferric oxide was heated to temperatures of 1500 °C and 1600 °C, respectively, while a water-vapor/hydrogen mixture of varying composition was passed over the charge. Succeeding inspections by analytical methods and by microscope always revealed that certain quantities of ferric iron or of ferric iron and metallic iron were present. It seems to be impossible to obtain a compound containing iron only in its bivalent state. Our analytical data, however, prove that at least 2.60 percent FeO together with 0.40 percent Fe_2O_3 may enter the tricalcium silicate as solid solution, thus producing the typical powder diagram of alite.

It has already been mentioned that considerable amounts of free lime are liberated by the reduction of iron-containing clinker. This phenomenon can be observed even much better in charges prepared from pure tricalcium silicate, containing no more than traces of free lime, and iron oxide only. After heating in reducing atmosphere, considerable

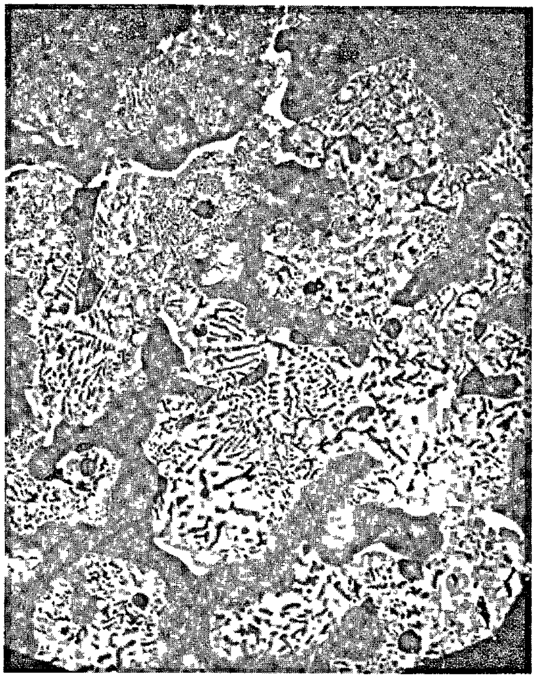

Figure 18. *Complete disintegration of iron-bearing alite in a laboratory charge resulting in a myrmekitic intergrowth of secondary free lime, belite, and ferrite.*

Primary and secondary free lime may easily be distinguished from one another. Etched with H_2O. 800 ×.

amounts of free lime are produced (fig. 18) while the phases of air-treated clinker in the parallel run consist of alite, belite, and ferrite. Thus it may be concluded that at least a considerable fraction of the Fe^{++} formed during this process replaces Ca^{++} of the tricalcium silicate.

The reoxidation at lower temperature of primarily reduced, iron-bearing alite produces characteristic structures which may help to arrive at an analogous deduction. Alite treated in this way shows three sets of fine, strictly parallel belite lamellae, strikingly similar to those described from technical clinker samples (fig. 19). This feature may be explained as follows:

Figure 19. *Three different sets of parallel belite lamellae follow the orientation of the alite crystal.*

Laboratory charge. Etched with H_2O. 1000 ×.

During the heating of the clinker under conditions of reduction, Fe^{++} ions have been replacing some of the Ca^{++} ions of the tricalcium silicate. Oxidation at lower temperatures transforms the divalent iron ions to trivalent ones which can no longer substitute for calcium. The ferric ion, on the contrary, changes its chemical nature from a cation to an anion, now detaching further amounts of divalent ions from the tricalcium silicate. As the formula of tricalcium silicate containing Fe^{++} as a substitute for Ca^{++} may be written $(Ca,Fe)_3SiO_5$ or $xCa_3SiO_5 \cdot yFe_3SiO_5$ the equation for this transformation will be

$$10\,Ca_3SiO_5 + 2\,Fe_3SiO_6 \xrightarrow[ox]{} 12\ Ca_2SiO_4 + 3\,Ca_2Fe_2O_5$$

or

$$10\ C_3S + 2\ f_3S \xrightarrow[ox]{} 12\ C_2S + 3\ C_2F,$$ (where $f=FeO$).

This clearly demonstrates the reaction forming belite lamellae in alite crystals at lower temperature, where the low mobility of the lattices prevents the complete separation of the resulting phases from one another as would have happened at higher tempertaures. Thus theoretically the oxidation of 1.0 percent Fe^{++} in alite will result in the transformation of tricalcium silicate to 6.17 percent dicalcium silicate. Again this reaction points to the substition of Ca^{++} by Fe^{++} in alite.

The Influence of Sulfides on the Stability of Alite

Sulfides are formed only under conditions of reduction, thus occasionally being encountered in samples showing disintegration of alite. Generally, however, they rather seem to repress this reaction.

Rather as a curiosity we want to present a photograph here (fig. 20), demonstrating the decomposition of alite in a clinker sample containing an unusually high amount of sulfides. Here belite, free lime, ferrite and an iron sulfide may be identified as disintegration products pseudomorphous after alite.

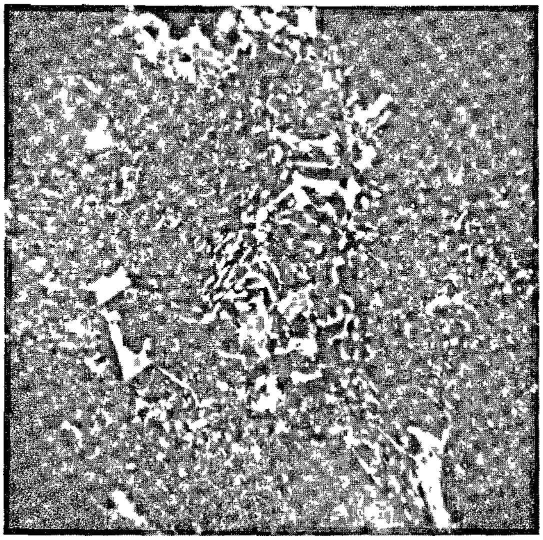

FIGURE 20. *Myrmekitic intergrowths of belite, free lime, ferrite, and iron sulfide pseudomorphous after alite.*
Oil, immersion, crossed nicols. 500 ×.

Decomposition of Alite in Clinker Containing Potassium

It is well known fact that the formation of alite is prevented when a certain limiting concentration of potassium in the clinker is passed. A belite phase and free lime are formed instead. (Zur Strassen [8])

This limit of concentration of potassium seems to be dependent on temperature in such a way that alite crystals may contain a higher amount of K^+ at higher temperatures without being destroyed. Thus there is a possibility that with lower temperature, in the equation alite$=$belite$+$ free lime the equilibrium may be shifted to the right. An alite crystal containing certain amounts of potassium will thus tend to decompose. Likewise a later addition of potassium to the clinker will result in a change of equilibrium.

The decomposition of alite by the influence of higher concentrations of potassium has been observed in laboratory clinker. The minimum amount of potassium resulting in this disintegration may even be attained by technical clinker. The author, however, has not yet found a sample in which the decomposition of the alite had to be ascribed without doubt to the fact that the limit of potassium content had been passed.

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Discussion

G. Ahlers

In this discussion it is desired to report on some other experiments on the decomposition of alite. It was felt that this decomposition, if it could be brought to completion, would be a way of obtaining a direct method of analysis for alite. Whereas it was found that normal clinkers did not decompose at an appreciable rate at any temperature, it was possible to decompose at least some cements quantitatively at 900 °C. The difference in the rate of decomposition between cement and clinker is due to the catalytic effect of $CaSO_4$ [1].[1] It was ascertained that the decomposition was complete by examining the cement after ignition by means of X-ray diffraction. After two hours at 900 °C, the alite lines were completely gone, there were strong CaO lines, and there were lines due to a substance which is believed to be some form of C_2S. The C_2S found was by no means the same material as that already present in the cement. Its pattern also did not agree too well with those reported for other forms of C_2S; however, this problem was not pursued any further.

The CaO formed during the decomposition was determined by the Bogue and Lerch modification of the Emley method [2]. The C_3S was calculated from this analysis by multiplying the free lime content by 4.072. This factor is based on the simplified reaction as written by Woermann; however, the error in the C_3S if one assumes Jeffery's formula to be correct would be only about 2 percent. Since this is an extreme assumption, it is felt that the factor for pure C_3S is a sufficiently good approximation.

It is, of course, conceivable that there are other minor reactions occurring under the suggested conditions in which CaO is involved. Notably there is a good possibility of a change in the composition of the ferrite phase. Indeed such a change was occasionally suggested by a change in the ferrite X-ray pattern. But nonetheless an estimate within several percent of the alite content could be obtained by this method. The results of 11 analyses are listed in table 1. They are compared with the results of Bogue calculations.

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[1] Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. *C_3S analyses by decomposition and by Bogue calculations*

This method	Bogue's method
47.8	45.5
53.7	49.5
19.0	21.0
50.1	48.1
56.2	54.8
55.8	53.1
48.0	55.8
55.7	57.3
50.1	48.2
60.7	61.1
56.2	51.2

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Closure

E. Woermann

According to the results of Ahlers' experiments it is possible to determine the amount of alite in a sample of portland cement by analyzing the free lime liberated by the decomposition of the alite during heat treatment in a laboratory furnace. For this purpose the amount of secondary free lime necessarily has to be determined most exactly and quantitatively.

At first glance this seems to be in contradiction to our statement, that it is impossible to trace the decomposition of alite in technical clinker by conventional analytical methods, because generally the intergrowth structures of secondary belite and free lime are much finer than the average grain size of cements.

It must be kept in mind, however, that the laboratory technique applied by Ahlers is totally different from any technical process.

(1) Ahlers points out the fact that normal clinker does not decompose at an appreciable rate at any temperature. In portland cement, however, alite may be quantitatively decomposed, owing to the catalytic action of the gypsum added.

(2) The samples of portland cement selected by Ahlers at one time have been cooled from sintering temperature in technical cooling aggregates—in most cases even at a relatively rapid rate. Only later they have been reheated to 900 °C in order to bring about the disintegration of the alite contained in these samples. Considering the influence of fast cooling on the properties of portland cement clinker, it does not seem improbable that rapid cooling may even affect the properties of alite itself. Thus alite seems to react more sensitively to this heat treatment than to the slow cooling from sintering temperature to about 900 °C that might occur in a technical process.

(3) From experiments of S. L. Meyers [1] and E. T. Carlson [2] we know that the age of the portland cement sample affects the tendency of the alite to dissociate, which is much less in the case of fresh material.

(4) Furthermore it should be borne in mind that the disintegration of alite in technical clinker is due to solution of divalent iron in the alite, which sensibly influences the velocity of the decomposition of the latter and thus at the same time, most probably, the coarseness of the intergrowth structures of the secondary products.

(5) During our own experiments it has repeatedly been observed that, while the disintegration products of alite in technical clinker form very fine intergrowth structures pseudomorphous after alite, these structures are very coarse in samples subjected to prolonged heat treatment according to the proposals of Ahlers. It is evident that in this case the amount of secondary free lime can be determined by conventional analytical methods. Thus our experiments are in good agreement with the results of Ahlers and of Meyers [1].

At this point it seems interesting to review the literature regarding the decomposition of alite and of tricalcium silicate. We find that nearly all research work devoted to this feature is done by reheating charges of the material in question, with or without further additions, at different temperatures. The recorded increase in the analyzed amount of free lime is accepted as a direct measure for the degree of disintegration of alite or of tricalcium silicate. (e.g., S. L. Meyers [1], E. T. Carlson [2], D. Steiner and B. Bartos [3], N. Yannaquis [4], F. W. Locher [5], J. H. Welch and W. Gutt [6], and others.) On the other side F. Tröjer [7], investigating the decomposition of alite in technical clinker, finds that in his samples the secondary free lime cannot be determined by conventional analytical methods because the structures of the secondary products are much too fine. Thus the belite to a considerable extent protects the free lime from being dissolved by the reagents.

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Paper II–S9. Note on the Behavior of Tetracalcium Aluminoferrite in an Atmosphere of Hydrogen*

P. Longuet

Synopsis

The weight losses attending the reduction of iron oxide compounds in a hydrogen atmosphere were recorded by thermogravimetric means. The strength of bond between Fe and O was thus revealed, with C_4AF apparently the most stable combination of those investigated. The iron formed by the reduction is quantitatively oxidized to Fe_2O_3 in an atmosphere of CO_2.

Résumé

Les variations de poids provenant de la réduction des composés oxydés du fer en atmosphère d'hydrogène sont enregistrées par thermogravimétrie. L'intensité de la liaison entre Fe et O est ainsi mise en évidence—AFC_4 apparaît comme le terme le plus stable. Le fer formé lors de la réduction est quantitativement oxydé en Fe_2O_3 en atmosphère de CO_2.

Zusammenfassung

Die Gewichtsverluste, die während der Reduktion von Eisenoxydverbindungen in einer Wasserstoffatmosphäre auftreten, wurden vermittelst thermo-gewichtsanalytischen Methoden registriert. Man konnte in dieser Weise die Bindungsfestigkeit zwischen Fe und O feststellen, und es ist auf diese Weise herausgefunden worden, daß augenscheinlich C_4AF die stabilste Verbindung ist. Alles Eisen, welches durch die Reduktion gebildet worden ist, wird in einer CO_2 Atmosphäre quantitativ zu Fe_2O_3 oxydiert.

Experimental Procedure

The use of thermogravimetric analysis as a method of phase analysis has led us to study the action of hydrogen on the reducible components in cement chemistry (alkali and alkaline earth sulfates, iron compounds, etc.). The present note deals with tetracalcium aluminoferrite and certain supplementary tests.

We used the Chevenard thermobalance which we have described elsewhere. We will simply say that the apparatus used permits continuous measurement of weight variation in a specimen subjected to a uniform temperature rise (300 °C per hr) in a definite gaseous atmosphere (air, H_2, CO_2, N_2, A . . . at atmospheric pressure).

The compounds subjected to tests were prepared by coprecipitation. A standard solution of nitrates with desired cations is precipitated *simultaneously* by ammonium carbonate. The precipitate obtained is dried, calcined at about 600 °C to constant weight, finely ground, and kept in an electric furnace for 20 to 30 hr at a temperature somewhat lower than the probable point of fusion. The composition is checked by chemical analysis, and, eventually, the phases present are identified by X-ray diffraction. A summary of our observations follows.

The Compound $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$

Figure 1a shows the curve for reduction of this compound in hydrogen. The trend is regular, without level stretches, as in the case of the reduction of a definite compound. The temperature at the start of the reaction is around 860 °C. This value is the highest encountered in the study of the ferric compounds. Figure 2 shows the behavior of Fe_2O_3 under the same conditions.

The compound obtained after reduction (cooling in an atmosphere of hydrogen) presents an X-ray diffraction pattern whose continuous back-

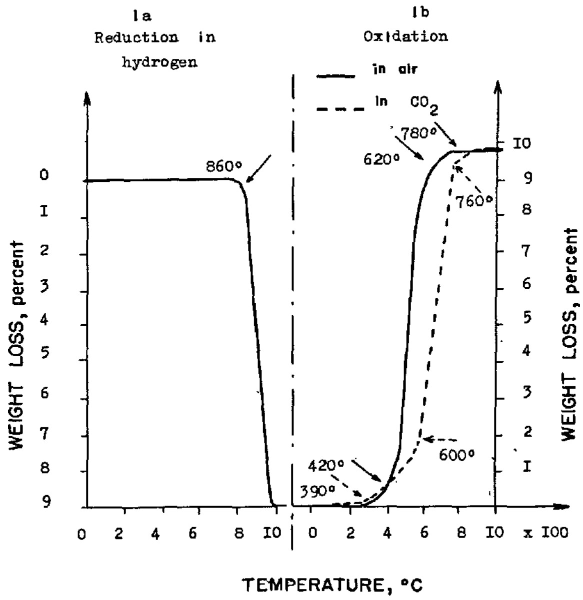

FIGURE 1. *Thermogravimetric analysis of* C_4AF.

Reduction in hydrogen, and oxidation in oxygen and carbon dioxide. Heating rate 300 °C per hr.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from Centre d'Études et de Recherches de L'Industrie des Liants Hydrauliques, Paris, France.

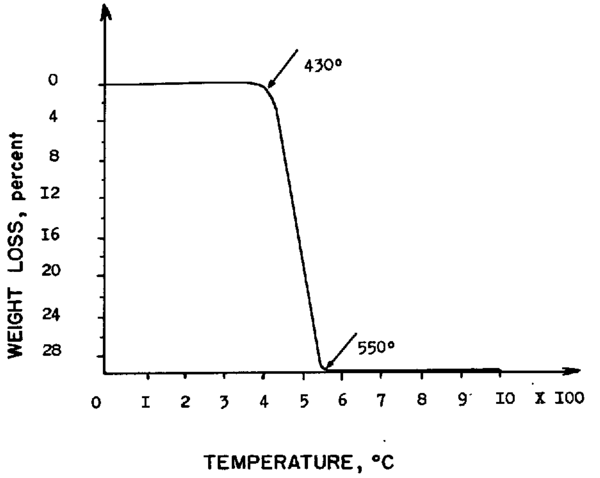

Figure 2. *Thermogravimetric analysis of* Fe_2O_3.
Reduction in hydrogen. Heating rate 300 °C per hr.

ground is rather pronounced, yet permits detection of the principal lines of metallic iron (Fe), tricalcium aluminate (C_3A), and calcium oxide (CaO). A quantitative determination of the lime thus liberated by fixation of water vapor at 200 °C at atmospheric pressure yields a value of the order of one mole CaO per mole of reduced C_4AF.

When heated in air the reduced compound oxidizes, following a regular curve (fig. 1b, solid line). Upon complete oxidation the compound presents an X-ray diffraction pattern analogous to the initial C_4AF product, although with a somewhat more pronounced continuous background. No free CaO is observed.

When heated in an atmosphere of CO_2 (we intended at the start to investigate the behavior of free CaO), the very finely divided iron of the reduced compound quickly takes part in oxidation-reduction reactions, finally becoming completely oxidized—the same final state as in air—without revealing any evidence of even partial carbonation of free lime (dashed curve, fig. 1b).

Supplementary Tests

No systematic study of the systems $CaO\text{-}Fe_2O_3$ and $CaO\text{-}Fe_2O_3\text{-}Al_2O_3$ was undertaken. Yet we must mention the behavior of certain compositions which we had occasion to examine.

A first binary composition comprising 80.9 percent Fe_2O_3 and 19.1 percent CaO (fig. 3).

Reduction begins at a lower temperature than that of the oxide. The trend of the curve reveals a succession of equilibria during the course of the reaction. The system is complex.

A second binary composition (64.1 percent Fe_2O_3 and 35.9 percent CaO) (fig. 4). The temperature increases at the start of the reduction. The trend is simpler and of a general type related to a sequence of two simple reactions.

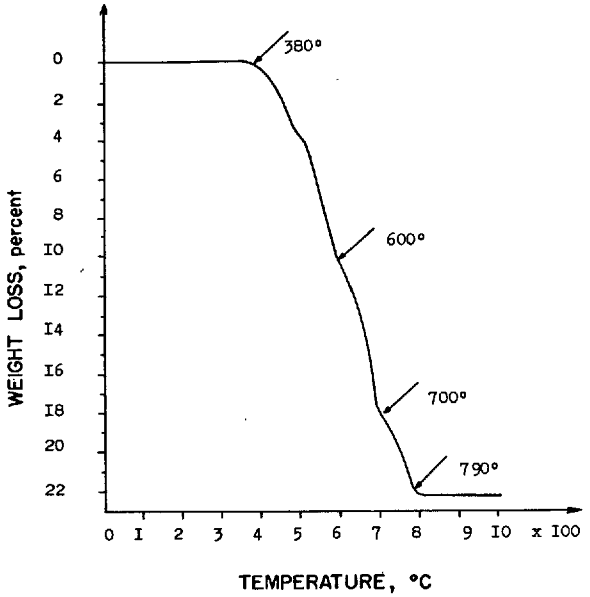

Figure 3. *Thermogravimetric analysis of* $CF_{1.49}$.
Reduction in hydrogen. Heating rate 300 °C per hr.

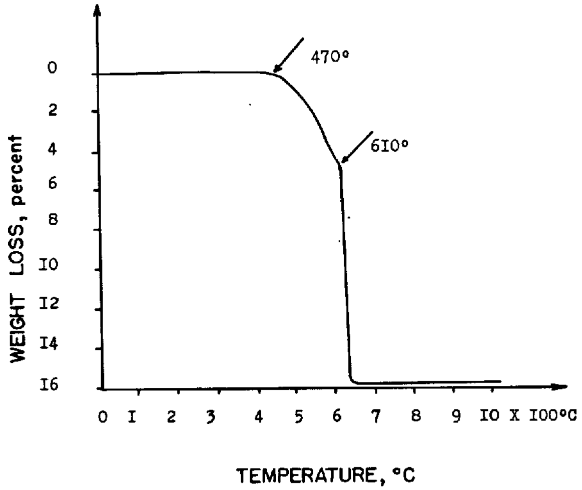

Figure 4. *Thermogravimetric analysis of* $C_3F_{1.88}$.
Reduction in hydrogen. Heating rate 300 °C per hr.

A ternary composition (Al_2O_3, 26 percent; Fe_2O_3, 31 percent; CaO, 43 percent or, expressed in millimoles per 100 g, Al_2O_3 257; Fe_2O_3 193; CaO 770). The composition presents the following ratios: $C/F=4$ and $A/F>1$. It corresponds to an addition of 64 mM of Al_2O_3 to 193 mM of C_4AF, with a ratio of excess A to C_4AF that amounts to 1/3.

The thermogram obtained in a hydrogen atmosphere (fig. 5) reveals two successive reactions which are clearly defined. One can see that the ratio of successive losses, 2.75/5.55, has essentially the same value as the ratio 64/(193–64). It seems as if the Al_2O_3 added to C_4AF forms an equivalent quantity of a ferric compound that

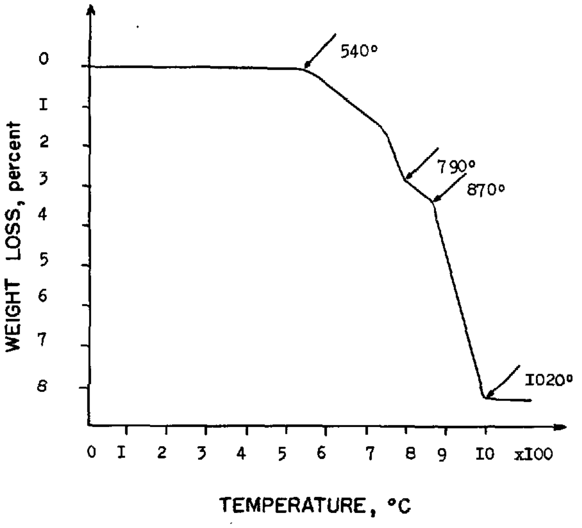

FIGURE 5. *Thermogravimetric analysis of* $C_4A_{1.33}F$.

Reduction in hydrogen. Heating rate 300 °C per hr.

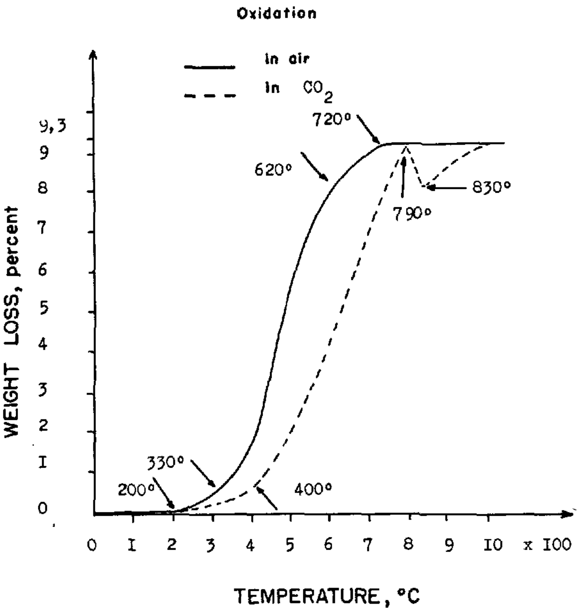

FIGURE 6. *Thermogravimetric analysis of reduced* $C_4A_{1.33}F$.

Oxidation in oxygen and in carbon dioxide. Heating rate 300 °C per hr.

is more easily reducible. The completely reduced composition yields an X-ray diffraction pattern with a very intense continuous background with only the principal lines of metallic iron visible. We could not detect free lime (the ratio excess $A/C_4AF=1/3$ permits acceptance of the hypothesis of formation of C_3A and Fe as end products of reduction).

Oxidation of the reduced composition in air yielded a regular curve (fig. 6, solid line). In a CO_2 atmosphere the curve presents a hook indicating a loss at the same temperature as at the end of the first reducing reaction (dashed curve, fig. 6). Whatever the cause of this hook (action of iron oxide on $CaCO_3$ formed during the reaction, disturbance of oxidation-reduction equilibria between the different iron oxides formed), it reveals the complexity of the system which does not smoothly attain its equilibrium as in the case of C_4AF.

Let us also mention that a comparison of the numerical values of the reduction and oxidation of the same reduced composition with the theoretical value derived from chemical analysis permits us to determine the losses of oxygen undergone by the composition during treatment at high temperature or, conversely, the formation of higher oxides during oxidation.

In summary, the action of hydrogen on some compositions in the two systems Fe_2O_3-CaO and Al_2O_3-Fe_2O_3-CaO suggests a classification of these compounds according to ease of reduction. This reactivity gives an indication—which could be a function of possible disturbances of equilibrium due to reduction—of the strength of the bonds between Fe and O in the composition under study. In the case of a pronounced difference the thermogram permits us to evaluate the relative amounts of the different forms present. We have thus revealed the stability of a compound corresponding to the formula C_4AF and the effect of an addition of Al_2O_3 to this compound. The oxidation curves in air or, even better, in CO_2 may permit us to state precisely the nature of the system under study. An examination of the products of the reduction yields interesting indications of the structure of the compound under study.

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SESSION III. CHEMISTRY OF HYDRATION OF CEMENT COMPOUNDS

Paper III-1. The Hydration of Tricalcium Silicate and β-Dicalcium Silicate at Room Temperature*

Stephen Brunauer and S. A. Greenberg

Synopsis

In the room temperature hydration of C_3S and β-C_2S, the hydration products are a calcium silicate hydrate and calcium hydroxide. Some of the properties of C_3S, C_2S, $Ca(OH)_2$ and the aqueous phase are presented, and the chemical and physical properties of the calcium silicate hydrate are discussed in considerable detail. This hydrate is a member of a series of hydrates, called tobermorites. The properties of other tobermorites are discussed in relation to those of the tobermorites produced in the hydration of C_3S and β-C_2S.

Data are given on the heats of hydration of C_3S and C_2S, and estimates are made of the entropies and free energies of hydration. Finally, the rates and mechanisms of hydration are discussed.

Résumé

Dans l'hydratation de C_3S et β-C_2S à la température du laboratoire, on obtient comme produits d'hydratation un hydrate de silicate de calcium et l'hydroxyde de calcium. L'exposé présente certaines propriétés de C_3S, C_2S, $Ca(OH)_2$, et la phase aqueuse, et discute de façon bien détaillée les propriétés chimiques et physiques de l'hydrate du silicate de calcium. Cet hydrate est membre d'une série d'hydrates, appelés tobermorites. Les propriétés d'autres tobermorites sont discutées par rapport à celles des tobermorites produits dans l'hydratation de C_3S et β-C_2S.

Des résultats sont donnés quant aux chaleurs d'hydratation de C_3S et de C_2S, et l'évaluation des entropies et des énergies libres d'hydration est faite. Enfin, les taux et mécanismes d'hydratation sont discutés.

Zusammenfassung

Bei der Hydratation des C_3S und des β-C_2S bei Zimmertemperatur sind die Hydratationsprodukte Kalziumsilikathydrat und Kalziumhydroxyd. Einige Eigenschaften des C_3S, des C_2S, des $Ca(OH)_2$ und der wäßrigen Phase werden besprochen, und die chemischen und physikalischen Eigenschaften des Kalziumsilikathydrates werden ganz ausführlich dargelegt. Dieses Hydrat ist nur eines einer Hydratreihe, die alle mit dem Namen Tobermorit bezeichnet werden. Die Eigenschaften der anderen Tobermorite werden in ihrer Beziehung zu den Tobermoriten, die bei der Hydratation des C_3S und des β-C_2S entstehen, diskutiert.

Die Werte der Hydratationswärmen des C_3S und des C_2S werden angegeben, und die Entropien und die freien Hydratationsenergien werden abgeschätzt. Schliesslich werden die Hydratationsgeschwindigkeiten und -mechanismen besprochen.

Introduction

In a discussion of the hydration of calcium silicates, it is customary to start by pointing out that tricalcium silicate and β-dicalcium silicate together constitute about 75 percent of a portland cement. To be sure, the reaction is vitally important, because the most important constituent of hydrated portland cement is a calcium silicate hydrate, and the most important constituent of concrete and mortar is hydrated portland cement. The present authors would like to point out that the hydration of calcium silicates is not only an important reaction but a fascinating one, as well. It is not a simple reaction, as will be seen, nor is it hopelessly complicated—but it is complicated enough to be interesting and challenging.

In every chemical reaction, the investigator is interested in three things: changes in matter, changes in energy, and the rate of change. In the present paper, the authors will attempt to report the status of the knowledge of these three aspects of the chemical reactions under consideration, as they see it. Before doing so, however, it seems appropriate to describe some of the pertinent properties of β-C_2S and C_3S.

Some Properties of the Two Calcium Silicates

1. The preparation of tricalcium silicate and β-dicalcium silicate was described by a number of early investigators; among them are Lerch and Bogue [1].[1] Most of the other investigators used slight modifications of this method. The modifications used in this laboratory are described in the literature, ref. [2, 3].

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Research and Development Laboratories of the Portland Cement Association, Skokie, Illinois.

[1] Figures in brackets indicate the literature references at the end of this paper.

2. The crystal structure of β-C_2S, together with the structures of the three other modifications of C_2S, was described by Nurse [4]. The structure of β-C_2S was determined by Mrs. Midgley [5]. The unit cell is monoclinic, with $a=5.48$, $b=6.76$, $c=9.28$, and the angle is 94°33′. Mrs. Midgley states that very slight modifications to the β structure produce an orthorhombic cell, and somewhat larger distortions and rearrangements produce a trigonal cell.

The unit cell contains four molecules. There are four SiO_4 tetrahedra in the cell, not linked with each other; in other words, β-Ca_2SiO_4 is an orthosilicate. Four of the eight Ca^{++} ions in the cell are alternately above and below the SiO_4 tetrahedra (Ca I), and the other four are in holes between the tetrahedra (Ca II). Nurse states, "Formally the co-ordination number of Ca I is six and of Ca II is eight, but the existence of holes fronting on the Ca ions means that the co-ordination is irregular and that O ions at distances greater than normal Ca-O bond lengths must also be considered as contributing to the co-ordination."

The specific gravity of β-C_2S is 3.28. β-C_2S occurs in nature as the mineral larnite.

The C_3S found in portland cement contains small amounts of Al_2O_3 and MgO as necessary constituents of its structure. This phase is called alite, and its crystal structure has been worked out by Jeffery [6]. The unit cell of alite is monoclinic, with $a=33.08$, $b=7.07$, $c=18.56$, and the angle is 94°20′. The cell contains 36 molecules of C_3S, in which four Si^{4+} ions are replaced by four Al^{3+} ions, and two Mg^{++} ions are located in holes to balance the charges. Thus, the chemical formula is $C_{54}S_{16}AM$.

The unit cell of C_3S itself is triclinic, and the crystal structure has not been worked out fully. The pseudostructure has the formula $Ca_3O(SiO_4)$. Bernal, Jeffery, and Taylor [7] state, "Each calcium ion is surrounded by six oxygens, arranged in such a way that the centres of five of them are in one hemisphere, with only one atom closing the gap on the other side. Large holes, equal in size and number to those occupied by the calcium ions, occur adjacent to the loosely coordinated sides of the calcium ions. The oxygen ions attached to silicon are each 3-coordinated on the other side by calcium ions, and those not attached to silicon are octahedrally coordinated by calcium."

The specific gravity of C_3S is 3.15. C_3S does not occur in nature.

3. The fact that β-C_2S occurs in nature, whereas C_3S does not, indicates greater stability of the former. This is borne out also by thermodynamic considerations.

Johannson and Thorvaldson [8] determined the heat of formation of C_3S from β-C_2S and CaO, and they found that the reaction was endothermic to the extent of 470 cal/mole at 20 °C. King [9] redetermined the same quantity and found a value of 3200 cal/mole at 25 °C. Brunauer, Kantro, and Weise [3] used a theoretically more correct calorimetric procedure and they corrected for impurities. Their value was 2100 cal/mole at 23 °C.

Todd [10] determined the low temperature heat capacities and the entropies at 25 °C for C_3S and β-C_2S. He obtained ΔS values of 1.5 and 1.8 e.u. for the formations from the oxides of C_2S and C_3S, respectively. These figures, combined with the ΔH value of Brunauer, Kantro, and Weise, lead to a ΔF of $+2000$ cal/mole for the conversion of β-C_2S and CaO to C_3S. Thus, C_3S is thermodynamically unstable with respect to β-C_2S and CaO.

Actually, C_3S is far more reactive than β-C_2S. Bernal, Jeffery, and Taylor [7] point out that, "The alkaline character of C_3S, together with the high lattice energy associated with a distorted Ca coordination, and possibly also the presence of "holes" in the structure, give the compound a high solubility and reactivity towards water." The authors mean "high energy lattice" instead of "high lattice energy". The term "lattice energy" is usually defined as the energy released when gaseous ions react to form a lattice; consequently, high lattice energy implies great stability.

The lattice energies of C_3S and β-C_2S were calculated in this laboratory. The reactions are

$$3Ca^{++}(g)+SiO_4^{4-}(g)+O^{--}(g)=Ca_3SiO_5(c) \quad (1)$$

$$2Ca^{++}(g)+SiO_4^{4-}(g)=Ca_2SiO_4(c) \quad (2)$$

and the lattice energies are $U_{C_3S}=-2570$ kcal and $U_{C_2S}=-1728$ kcal. The lattice energy of CaO, U_{CaO}, is reported to be -842 kcal [11]. The difference $U_{C_3S}-U_{C_2S}-U_{CaO}=-2570+1728+842=0$. Actually, this should be equal to the heat of formation of C_3S from C_2S and CaO, which is 2 kcal. The error in U_{C_3S} and U_{C_2S} may be 20 or even 200 kcal, but most of the error cancels on subtraction. Even so, the agreement is surprisingly close.

Stoichiometry of the Hydration of C_3S

A mixture of portland cement, C_3S, or C_2S with a limited amount of water is called a "paste". If the initially plastic paste is allowed to stand, in a few hours it "sets", then continues to harden for months, or possibly even for years. This type of hydration is called paste hydration. It attempts to simulate the hydration of portland cement, C_3S, and C_2S in concrete and mortar.

Brunauer, Copeland, and Bragg hydrated C_3S in two ways: in paste form, using a water/C_3S weight ratio of 0.7 [12], and in a small steel ball mill, using a water/C_3S weight ratio of 9.0 [13]. Brunauer, Kantro, and Copeland [14] further investigated the paste hydration of C_3S, and they also studied a third method of hydration. In this, a water/C_3S weight ratio of 9.0 was used, and the reaction was carried out in a polyethylene bottle rotated on a wheel at 30 rpm. Kantro, Brunauer, and Weise [15] reported further work on the ball-mill hydration of C_2S. All these reactions took place in a controlled temperature room, at 24±1 °C.

At complete hydration of C_3S, the stoichiometry of each of the three hydration reactions was represented by the equation:

$$2Ca_3SiO_5+6H_2O=Ca_3Si_2O_7{\cdot}3H_2O+3Ca(OH)_2. \quad (3)$$

Nevertheless, the three reactions were not identical. The ball-mill hydration produced a calcium silicate hydrate that was identical in crystal structure with the natural mineral afwillite. The paste hydration, as well as the hydration in the rotating bottle, gave a calcium silicate hydrate related to the natural mineral tobermorite.

The paste and the bottle hydration, which gave similar hydration products, will be discussed first, the ball-mill hydration later.

Calcium Hydroxide and the Molar CaO/SiO_2 Ratio in the Hydrate

1. The amount of calcium hydroxide was determined by X-ray quantitative analysis, using the method of Copeland and Bragg [16]. In almost every instance, the amount determined was smaller than that indicated by eq (3). It would have been a simple matter to assign the missing lime to the calcium silicate hydrate. In that case the molar CaO/SiO_2 ratio in the tobermorite-like hydrate would not be 1.5, as shown in the equation, but a variable amount, ranging from 1.52 to 1.75. However, certain lime extraction experiments indicated that this was not the correct explanation.

Franke [17] proposed a method for the determination of uncombined CaO and $Ca(OH)_2$ in hydrated and unhydrated calcium silicates and portland cements. A solvent mixture, consisting of acetoacetic ester and isobutyl alcohol, was refluxed with the sample, and, according to Franke, a single extraction removed all the free lime. The experience of Pressler, Brunauer, and Kantro [18] was that a single extraction did not come even close to removing all of the free $Ca(OH)_2$ from hydrated calcium silicates and portland cements. Variation of the ratio of acetoacetic ester to isobutyl alcohol or the time of refluxing did not solve the problem. However, by repeated Franke extractions on the same sample, the free $Ca(OH)_2$ could be determined with good accuracy. In these extractions a small part of the lime was removed from the calcium silicate hydrate, but the rate of removal of this lime was only about one-fiftieth of the rate of removal of calcium hydroxide. On this basis, a correction could be made for the lime removed from the calcium silicate hydrate. The multiple extraction method (M.E.M.) led to a CaO/SiO_2 ratio of 1.51 in the hydrate, which is the same as that shown in eq (3), within experimental error.

Later, Pressler, Brunauer, Kantro, and Weise [19] developed another modification of the Franke method for the determination of free $Ca(OH)_2$. In this, aliquot samples of the same material were treated with varying amounts of Franke solvent. In the solvent variation method (S.V.M.), again some lime was removed from the hydrate, but again a correction could be made for this. The two different methods led to the same results. The theoretical bases of the methods and the corrections are discussed in the papers [18, 19].

2. Brunauer, Kantro, and Copeland [14] found that the "missing lime", i.e., the difference between the stoichiometric quantity of $Ca(OH)_2$ indicated by eq (3) and the $Ca(OH)_2$ determined by X-ray quantitative analysis, was more easily extractable than the rest of the $Ca(OH)_2$. By the time half of the $Ca(OH)_2$ was extracted, all the missing lime was removed from the system, and X-ray analysis for $Ca(OH)_2$, combined with chemical analysis, indicated a molar CaO/SiO_2 ratio of 1.5 in the calcium silicate hydrate.

In spite of the easy extractability of missing lime, it may be argued that the tobermorite-like calcium silicate hydrate does contain this lime in a very loosely bound form. Several investigators, among them Kalousek and Prebus [20], reported the loosely bound lime as a part of the tobermorite-like structure. However, there are two types of experiments which point very strongly in the other direction.

It was stated earlier that the stoichiometry of the ball-mill hydration of C_3S was also represented by eq (3), but the calcium silicate hydrate was afwillite. In this case, X-ray quantitative analysis again gave $Ca(OH)_2$ values lower than that required by the equation. The missing lime was variable in amount, just as in paste and in bottle hydration, and the range of variation was also the same. There is no possibility here to ascribe the missing lime to the calcium silicate hydrate. Afwillite has a definite composition of $Ca_3Si_2O_7{\cdot}3H_2O$. The conclusion here is inevitable that the missing lime is $Ca(OH)_2$ in a noncrystalline form [15].

The second line of evidence is more direct. In the paste hydration of β-C_2S, as well as in the paste hydration of portland cements high in C_2S, at room temperature, tobermorite-like hydrates were obtained with molar CaO/SiO_2 ratios ranging up to 1.75. In the paste hydration of C_3S, at 50° and 80 °C, the molar CaO/SiO_2 ratios in the hydrate were 1.57 and 1.61, respectively. These results, as well as others, are shown in table 1. Henceforth, in this paper the tobermorite-like hydrates with CaO/SiO_2 ratios greater than 1.5 will be called high-lime tobermorites. In these high-lime tobermorites, the CaO in excess of the ratio 1.5 was just as firmly bound as the CaO below the ratio 1.5. It appears, therefore, that the missing lime is not a loosely bound part of a high-lime tobermorite, but $Ca(OH)_2$. Because it is not detected by X-rays, it must be noncrystalline.

3. Initially, it was thought that the missing lime was adsorbed on the surface of the calcium silicate hydrate [12]. This tobermorite-like hydrate has a very large specific surface area, able

to accommodate the missing lime. Nevertheless, later work [14] indicated that the adsorption of lime on the hydrate surface was small, probably because in the competition between $Ca(OH)_2$ and water for the surface, the latter is adsorbed preferentially. Kalousek and Prebus [20], in more quantitative experiments, also found that the adsorption of $Ca(OH)_2$ on tobermorite-like hydrates was small. Indirect evidence for the small adsorption of $Ca(OH)_2$ can be found in earlier work. Bessey [21], Taylor [22], and Greenberg [23] found that the CaO/SiO_2 ratio in tobermorite-like hydrates, prepared by the reaction of $Ca(OH)_2$ and silica, at or near lime saturation, was 1.5, within their experimental error. Although Greenberg alone measured surface areas, unquestionably, all three investigators obtained hydrates with large specific surface areas and, in all probability, the surface areas were different. Had the adsorption of $Ca(OH)_2$ been significant, the apparent CaO/SiO_2 ratios would have been variable and probably all greater than 1.5.

The only alternative that remained was to assume that the missing lime was amorphous calcium hydroxide [14]. The idea was not new. Heller and Taylor [24] found evidence of amorphous or poorly crystallized $Ca(OH)_2$ in the products of the reaction between $Ca(OH)_2$ and silica gel at 110 °C and higher. Grudemo suggested that a little dissolved silica may have entered the lattice of some of the $Ca(OH)_2$, disturbing or destroying the lattice.

Takashima [25] published a paper recently on amorphous calcium hydroxide. He prepared $Ca(OH)_2$ by the reaction of water with CaO; then he determined the total $Ca(OH)_2$ by one of the standard extraction methods and the crystalline $Ca(OH)_2$ by X-ray analysis. He found considerable differences between the two, depending on the kind of CaO used and on the temperature of slaking. The amount of crystalline $Ca(OH)_2$ ranged from 31 to 100 percent of the total. He attributed the difference to amorphous $Ca(OH)_2$. He also found that amorphous $Ca(OH)_2$ reacted with methanol, whereas crystalline $Ca(OH)_2$ did not. It is interesting to note the similarity of approach and results between Takashima's experiments and those performed in this laboratory. Neither side knew about the experiments of the other.

4. The conclusion from the above considerations is that eq (3) represents the stoichiometry of the hydration of C_3S at room temperature correctly, at least as far as the calcium hydroxide content and the molar CaO/SiO_2 ratio in the tobermorite-like hydrate are concerned. The same conclusion was reached by Graham, Spinks, and Thorvaldson [26] by a very different approach. They used C_3S labelled with radioactive Ca^{45}, and made it react with unlabelled saturated $Ca(OH)_2$ solutions. The rate of liberation of lime due to hydration and the rate of appearance of Ca^{45} in the solution indicated that the CaO/SiO_2 ratio in the calcium silicate hydrate was 1.5. A similar result was obtained when inactive C_3S was hydrated with active $Ca(OH)_2$ solutions.

A different conclusion was reached by van Bemst [27, 28], who reported that the calcium silicate hydrate produced in the hydration of C_3S had a variable CaO/SiO_2 ratio, ranging up to 2.0. He determined the $Ca(OH)_2$ released in the hydration by thermogravimetric analysis, but there is evidence that such a determination fails to account for the amorphous $Ca(OH)_2$. It was stated earlier that in the ball-mill hydration of C_3S the calcium silicate hydrate produced was afwillite, and the presence of noncrystalline $Ca(OH)_2$ was unquestionable. Greenberg analyzed the hydration products thermogravimetrically for $Ca(OH)_2$ and the analysis checked the X-ray analysis with remarkable accuracy. Thus, crystalline and amorphous $Ca(OH)_2$ appear to decompose in different temperature ranges.

Van Bemst [28] extracted the $Ca(OH)_2$ from a sample of C_3S hydrated at 60 °C. The maximum CaO/SiO_2 ratio that he reported for the extracted sample was 1.72. It was stated earlier that hydration of C_3S at higher temperatures leads to higher-lime tobermorites. In one preparation, a CaO/SiO_2 ratio of 1.63 was obtained at 80 °C in this laboratory (table 1). The error in this value and in van Bemst's value make the results not necessarily inconsistent.

5. In table 1, C–17 and C–18 represent a C_3S paste, 17-months old, dried under two different conditions. The paste contained no unhydrated C_3S. The molar CaO/SiO_2 ratio was determined for each, and the values 1.54 and 1.50 show the size of the maximum error in these determinations. In a similar manner, C–52 and C–53 represent another paste, 5-yr old, dried under the two different conditions. The ratios were 1.51 and 1.51. The average of the first two is 1.52, the average of the last two is 1.51. The excess over 1.50 may be experimental error, it may be a little adsorbed $Ca(OH)_2$, or it may be that the stoichiometry is not rigidly correct. Since one deals here with colloidal systems, as will be discussed later, such lack of accurate stoichiometry would not be surprising.

The four other C_3S pastes in table 1 indicate that the CaO/SiO_2 ratio increases slightly with increasing temperature of hydration.

Water of Hydration in the Hydrate

The water content of the calcium silicate hydrate depends on the drying conditions employed. Different investigators used different drying methods and reported different water contents.

The tobermorite-like hydrate has a very large specific surface area, of the order of 300 m^2/g. The surface is hydrophilic; the ions in the surface adsorb water readily. The water contents reported by most investigators consisted both of adsorbed water and of water of hydration, i.e., water which is part of the calcium silicate hydrate structure.

A complete physical separation of the two types of water is impossible. The hydrate is a colloid and, like other colloidal hydrates, it loses water from its structure continuously when equilibrated at lower and lower vapor pressures of water. The free energy of binding of the adsorbed water to the surface is variable, as in most adsorbent-adsorbate systems. Although the average free energy of binding of the combined water in the structure is greater than the average free energy of binding of the adsorbed water to the surface, the most firmly bound adsorbed water is held more strongly than the most loosely bound combined water. As a result, at lower vapor pressures some of the combined water is removed, while some of the adsorbed water is held by the hydrate.

When the products of the room temperature hydration of C_3S were dried at a water vapor pressure of 5×10^{-4} mm of mercury, which is the vapor pressure of ice at −78 °C, the molar H_2O/SiO_2 ratio in the tobermorite-like hydrate was always slightly greater than 1.0, averaging about 1.06 [14]. It is probable that part of the water in excess of 1.0 was adsorbed water. This method of drying will be referred to as (*D*)-drying, or dry-ice drying.

When the hydration products were dried at a water vapor pressure of 8×10^{-3} mm, which is the equilibrium pressure of $Mg(ClO_4)_2{\cdot}2H_2O$ and $Mg(ClO_4)_2{\cdot}4H_2O$, the H_2O/SiO_2 ratio in the hydrate was 1.40 [14]. This would correspond to a tobermorite of formula $Ca_3Si_2O_7{\cdot}2.80H_2O$. However, adsorption experiments showed that about 0.30 mole of water was adsorbed on the surface; thus, the corrected formula was $Ca_3Si_2O_7{\cdot}2.5H_2O$. This method of drying will be referred to as (*P*)-drying, or perchlorate drying.

It is obvious that at higher vapor pressures the tobermorite would contain more combined water and more adsorbed water. Such experiments were not performed to date, so the number of molecules of combined water in the hydrate at saturation pressure, or in liquid water, is somewhat conjectural. Bernal [29] proposed the structural formula $Ca_2[SiO_2(OH)_2]_2[Ca(OH)_2]$, indicating three molecules of water in a molecule of tobermorite, and experiments performed in this laboratory are consistent with his view.

Stoichiometry of the Hydration of β-C_2S

1. When β-C_2S was hydrated at room temperature in a small steel ball-mill, with a water/C_2S weight ratio of 9.0, at complete hydration the stoichiometry was represented by the equation

$$2Ca_2SiO_4+4H_2O=Ca_3Si_2O_7{\cdot}3H_2O+Ca(OH)_2. \quad (4)$$

The calcium silicate hydrate was identical with the tobermorite obtained in the paste hydration or bottle hydration of C_3S [14], discussed earlier.

When C_2S was hydrated at room temperature in a rotating polyethylene bottle, with a water/C_2S weight ratio of 9.0, in 162 days the products still contained 27.5 percent unhydrated C_2S, as determined by X-ray analysis (D–40 in table 1). The tobermorite had a molar CaO/SiO_2 ratio of 1.54, which is, within the experimental error, the same as that shown in eq (4). However, longer hydration at room temperature resulted in tobermorites of higher CaO/SiO_2 ratios (D–55, 56 and 69

TABLE 1. *Compositions of hydrated* C_3S *and* C_2S *preparations*

1	2	3	4	5	6	7	8	9	10	11	12
Preparation	Type of hydration	Material	Age	Temp.	Type of drying	$Ca(OH)_2$	$CaCO_3$	Minor constituents	Unhydrated material	CSH	Composition of CSH
				°C		%	%	%	%	%	
D–40	Bottle	C_2S	162 d	25	D	11.2	0.8	1.6	27.5	58.9	$C_{1.54}SH_{1.07}$
D–55	Bottle	C_2S	265 d	25	D	7.6	1.4	1.5	7.1	82.4	$C_{1.73}SH_{1.39}$
D–56	Bottle	C_2S	265 d	25	P	7.8	0.9	1.5	6.9	83 0	$C_{1.73}SH_{1.71}$
D–69	Bottle	C_2S	778 d	25	D	8.9	1.3	1.5	0.0	88.3	$C_{1.73}SH_{1\ 37}$
C–23	Paste	C_2S	17 m	25	D	9.1	0.5	1.6	27.5	61.3	$C_{1.65}SH_{1.15}$
C–24	Paste	C_2S	17 m	25	P	9.0	.6	1.6	27.0	61.8	$C_{1.65}SH_{1.43}$
C–51	Paste	C_2S	4¼ y	25	D	11.1	.9	1.6	12.9	73.4	$C_{1.63}SH_{1.09}$
C–29	Paste	C_2S	2 m 19 m	50 25	D	5.3	2.0	1.6	32.0	59.2	$C_{1.73}SH_{1.19}$
C–30	Paste	C_2S	2 m 19 m	50 25	P	6.2	1.6	1.6	31.5	59.1	$C_{1.70}SH_{1.44}$
C–57	Paste	C_2S	2 m 5 y	80 25	D	5.3	0.9	1.6	27.8	64.4	$C_{1.75}SH_{1.29}$
C–58	Paste	C_2S	2 m 5 y	80 25	P	5.8	.7	1.6	27.2	64.8	$C_{1.74}SH_{1.59}$
C–17	Paste	C_3S	17 m	25	D	38.5	.7	0.7	0.0	60.2	$C_{1.54}SH_{1.10}$
C–18	Paste	C_3S	17 m	25	P	38.6	.9	.6	.0	59.8	$C_{1.50}SH_{1.39}$
C–52	Paste	C_3S	5 y	25	D	38.8	1.2	.7	.0	59.3	$C_{1.51}SH_{1\ 09}$
C–53	Paste	C_3S	5 y	25	P	38.3	.8	.6	.0	60.3	$C_{1.51}SH_{1.46}$
C–27	Paste	C_3S	2 m 19 m	50 25	D	36.8	.8	.7	.0	61.8	$C_{1.58}SH_{1.13}$
C–28	Paste	C_3S	2 m 19 m	50 25	P	36.0	.9	.6	.0	62.5	$C_{1.57}SH_{1.46}$
C–55	Paste	C_3S	2 m 5 y	80 25	D	30.5	.5	.7	13.5	54.8	$C_{1.63}SH_{1.29}$
C–56	Paste	C_3S	2 m 5 y	80 25	P	31.1	.4	.7	13.2	54.6	$C_{1.59}SH_{1.81}$

in table 1). The ratio was 1.73 after 265 days, and it was the same after 778 days. These ratios are based on determination of $Ca(OH)_2$ by the two modifications of the Franke method, S.V.M. and M.E.M., discussed earlier. X-ray analysis always gave lower results for $Ca(OH)_2$ than Franke extractions, which indicates the presence of amorphous lime.

When C_2S was hydrated at room temperature in the paste form, with a water/C_2S weight ratio of 0.7, complete hydration was not obtained even in 4½ years. The CaO/SiO_2 ratio was 1.65 after 17 months (C–23 and 24), when the paste contained 27.5 percent unhydrated C_2S, and it was 1.63 after 4½ years (C–51), when the paste contained 12.9 percent unhydrated C_2S. These ratios are the same within experimental error. At higher temperatures, higher ratios were obtained, 1.72 at 50 °C (C–29 and 30) and 1.75 at 80 °C (C–57 and 58).

Funk [30], in the paste hydration of C_2S, with a water/C_2S ratio of 0.5, reported molar CaO/SiO_2 ratios averaging 1.77 at 50 °C, 1.88 at 100 °C, and 1.84 at 120 °C. He used a modification of the Franke method for the determination of $Ca(OH)_2$, which involved only a single extraction. The present authors wonder whether the $Ca(OH)_2$ was completely removed. Funk stated that the extraction results agreed with X-ray results. If there was amorphous $Ca(OH)_2$ in the hydration products, which seems likely, the X-ray results were also too low. It would be of interest to determine the $Ca(OH)_2$ in Funk's preparations by S.V.M. or M.E.M.

The reason for questioning Funk's ratios is found in a hypothesis of Taylor and Howison [31], which puts the upper limit of the ratios at 1.75. This hypothesis will be discussed in detail later. For all that, Funk's results may be entirely correct, and the reason for the small differences between his results and those obtained in this laboratory may possibly be found in the different water/C_2S ratios used.

2. The H_2O/SiO_2 ratio of the tobermorite of CaO/SiO_2 ratio 1.5, when subjected to (*D*)-drying, is close to 1.0, though usually somewhat higher. This is true whether the tobermorite comes from hydrated C_3S or C_2S.

For high-lime tobermorites, obtained in paste hydration and subjected to (*D*)-drying, the increase in CaO/SiO_2 ratio results in a corresponding increase in H_2O/SiO_2 ratio, i.e., adding a molecule of lime appears to be accompanied by the addition of a molecule of water. This is seen in table 1, column 12. For the eight (*D*)-dried pastes, four C_3S and four C_2S, the average excess of CaO over 1.5 was 0.13, and the average excess of water over 1.0 was 0.17. Funk [30] obtained similar results. He dried his hydrated C_2S preparations over P_2O_5 at 20 °C to constant weight. For 13 pastes, prepared at 50, 100, and 120 °C, the average of the excess for CaO was 0.33, and for H_2O, 0.36.

Tobermorite-Like Hydrates

When calcium hydroxide reacts with silica in water at room temperature, a calcium silicate hydrate of variable CaO/SiO_2 ratio is formed. The ratio, which depends on the concentration of lime in the solution, ranges from about 0.8 to 1.5. The same hydrates may be formed by other reactions, such as the reaction of calcium nitrate and sodium silicate, the hydration of C_3S or C_2S in large excess of water [22], and the reaction of ethyl orthosilicate with calcium hydroxide [32].

The hydrate system was studied by many investigators. Steinour [33], in an excellent review paper, reported the results of sixteen investigations. Although there is a vague general agreement between most of these results, they differ considerably in detail. The differences were probably caused, at least in part, by lack of adequate experimental techniques and lack of complete equilibration. However, probably there was a more subtle reason also, which will be discussed later.

The authors of this paper do not intend to present a full-scale discussion of the tobermorite-like hydrates. Nevertheless, a discussion of certain aspects of the system seems desirable in order to show how the tobermorites obtained in the hydration of C_3S and C_2S fit into the family of tobermorites.

Since the appearance of the above paper of Steinour, other investigations were published, by Taylor [22], by Kalousek [34] and by Grudemo [32]. The results of the first two are reproduced in figure 1. Again, there is a broad general agreement, but a disagreement in detail [35].

Taylor called the hydrate, ranging in CaO/SiO_2 ratio up to 1.5, calcium silicate hydrate (I) or CSH(I). It will be noted in figure 1 that the CaO/SiO_2 ratio in the hydrate rises sharply at lime saturation. Taylor called this high-lime hydrate calcium silicate hydrate (II) or C_2SH(II).

Claringbull and Hey [36] pointed out the similarity between Taylor's CSH(I) and the natural mineral tobermorite. There is no general agreement on nomenclature of calcium silicate hydrates as yet; some call the synthetic hydrates CSH(I) or hydrate I, others call them tobermorite minerals, tobermorite-like hydrates or simply tobermorites. The hydrates with CaO/SiO_2 ratios greater than 1.5 are called C_2SH(II), hydrate II, or high-lime tobermorites.

The most important difference between the curves of Taylor and Kalousek, from the point of view of the present discussion, is the difference in the vicinity of lime saturation. From a calcium ion concentration of about 11 millimoles per liter to lime saturation, Kalousek drew a flat curve, as shown in figure 1, corresponding to a CaO/SiO_2 ratio 1.33. Between a concentration of 15 millimoles per liter and lime saturation, Kalousek had three points on this curve and six points above

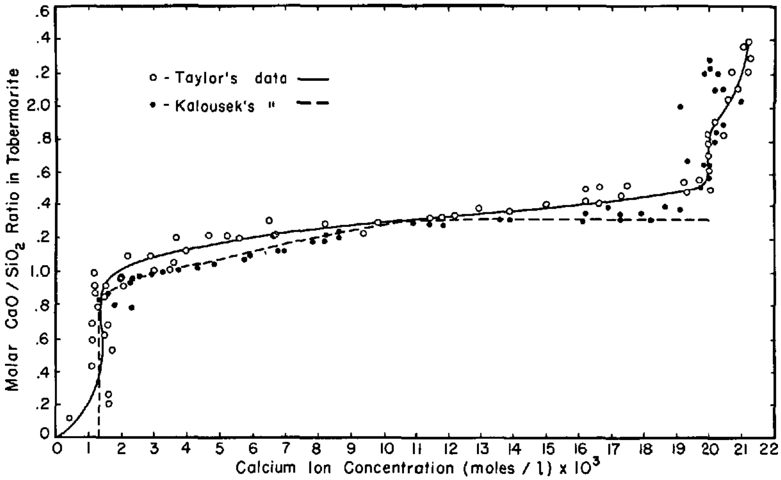

FIGURE 1. *Variation of the molar CaO/SiO_2 ratio in tobermorite with the calcium ion concentration in the solution.*

it. Taylor, on the other hand, obtained a continuous rise in CaO/SiO_2 ratio, reaching 1.5 at lime saturation. Grudemo [32], in one series of experiments, reached a maximum CaO/SiO_2 ratio of 1.45, in another, 1.56. Earlier work of Bessey [21] is in agreement with Taylor's curve, as well as later work of Greenberg [23], and as yet unpublished work performed in this laboratory.

Investigators for a long time debated the question whether the lime in excess of a CaO/SiO_2 ratio of 0.8 should be regarded as adsorbed or whether it is in solid solution. More recently, Brunauer, Copeland, and Bragg [12] pointed out that the extra lime cannot be regarded as physically adsorbed, and Taylor and Howison [31] advanced arguments for the extra lime being part of the crystal structure. Thus, the extra lime appears to be in solid solution—though it is a special type of solid solution, as will be seen later.

The high-lime end member of the tobermorite solid solution series, at lime saturation, has a CaO/SiO_2 ratio of 1.5, as Taylor's curve shows in figure 1. Beyond this point, one obtains the high-lime tobermorites, ranging in ratio up to 1.75, possibly higher. Kalousek and Prebus [20] contend that the tobermorite of ratio 1.5 should be regarded as the low-lime end member of the high-lime tobermorite series. There is considerable justification for this. The tobermorite obtained in the hydration of C_3S or C_2S, having a CaO/SiO_2 ratio of 1.5, resembles a high-lime tobermorite far more than the low-lime tobermorites. There seems to be a drastic change in morphology, in degree of crystallinity, as well as in other properties of the hydrate in the vicinity of lime saturation. This will be discussed later.

Crystal Structures and Densities of Tobermorites

1. The tobermorites are layer crystals. Their similarity to the clay minerals was pointed out by Taylor [22], to vermiculite by McConnell [37], and to montmorillonite by Grudemo [38].

The formula of the natural mineral tobermorite, found in Northern Ireland, is probably $Ca_4(Si_6O_{18}H_2)\cdot Ca\cdot 4H_2O$. Its crystal structure was determined by Megaw and Kelsey [39], who found that the layers were actually triple sheets, with some similarities to vermiculite. Taylor and Howison [31] describe the structure as follows.

"The central part of each layer, equivalent to the octahedral layer in a clay mineral, could be described as a distorted calcium hydroxide sheet divested of all its hydrogen atoms. This sheet is flanked on both sides by parallel rows of wollastonite-type chains, which are kinked in a plane perpendicular to that of the sheets. Only two-thirds of the tetrahedra in each chain are linked directly to the central CaO_2 sheet by sharing of oxygen atoms. The other third, which are held away from the CaO_2 sheet, will be called "bridging" tetrahedra. The composite 2:1 sheets so far described have the composition $Ca_4Si_6O_{18}$. Between them are the remaining or interlayer calcium atoms, and water molecules. The distribution of the hydrogen is uncertain. There may be more SiOH than is implied by the formula $Ca_4(Si_6O_{18}H_2)\cdot Ca\cdot 4H_2O$, with corresponding replacement of interlayer water by hydroxyl.

"To a good approximation, tobermorite from the above localities is orthorhombic with a—11.23, b—7.37, c—22.6 A, Z=4. The crystals are laths with length b (parallel to the chains) and cleavage (001) (the plane of the layers); a and b are both strongly pseudo-halved, and for many purposes a pseudo-cell with Z=1 may be used. This pseudocell is body centered. The longest observed basal spacing is therefore 002 (d=11.3 A), and corresponds to the thickness of a single 2:1 layer."

The CaO/SiO_2 ratio in the natural mineral is 0.83. In artificially prepared tobermorites, the ratio ranges up to 1.75, possibly higher. Throughout this wide variation in composition, such properties as density, index of refraction and X-ray diffraction pattern remain remarkably constant.

2. Taylor and Howison [31] measured the densities of tobermorites ranging in CaO/SiO_2 ratio from 0.81 to 1.50, and found no systematic trend to increase with the ratio. All of their density values were too low, as they themselves realized. They attributed the low densities to lack of complete penetration of the pore system by the liquid used for the measurements. This is doubtless correct, but there was another reason, too. Since their specimens were dried at a water vapor pressure of 6 mm, all of them contained adsorbed water. For example, the samples dried at 108 °C and 6 mm pressure probably had about half of their surface covered with adsorbed water. This is a considerable amount of water, because the specific surface of tobermorite is very large.

Taylor and Howison, nevertheless, believed that their conclusions as to the approximate constancy of the density was correct, and work in this laboratory confirms their conclusion [14]. The average density of five tobermorite preparations, having CaO/SiO_2 ratios of 1.50 and H_2O/SiO_2 ratios of 1.00, was 2.85 ± 0.02 g/cc. These were hydrated C_3S and C_2S preparations, dried at a water vapor pressure of 5×10^{-4} mm (*D*-drying). A tobermorite in a paste hydrated C_2S preparation, similarly dried, had a CaO/SiO_2 ratio of 1.65 and an H_2O/SiO_2 ratio of 1.15; its density was 2.85 g/cc. It is obvious that if in a given sized pseudo-cell molecules having compositions of $3CaO{\cdot}2SiO_2{\cdot}2H_2O$ are replaced by an equal number of molecules of composition $3.30CaO{\cdot}2SiO_2{\cdot}2.30H_2O$, the density must go up markedly. As the example shows, such molecule for molecule substitution does not happen.

The *a* and *b* dimensions of the pseudo-cell show a very slight shrinkage with decreasing water content [22]; but the change is so slight that for most purposes these dimensions can be considered constant. The *c* dimension, i.e., the distance between layers, shows a considerable variation, which will be discussed later. However, this alone cannot account for the constant density.

3. An ingenious hypothesis for the explanation of the constancy of density was advanced by Taylor and Howison. They suggest that as the CaO/SiO_2 ratio increases, calcium replaces silicon in the lattice. The "bridging" SiO_4 tetrahedra, which are not attached to the central CaO_2 sheet, are gradually removed or, more correctly, only SiO_2 is removed because two of the oxygen ions in each of the tetrahedra are common to adjacent groups. The removal of SiO_2 breaks the metasilicate chain. A calcium ion then enters the lattice, but not directly into the place of SiO_2, i.e., not into the layer, but between layers. Because the calcium ion has two positive charges and SiO_2 is neutral, to preserve charge balance, two hydrogen ions must also be removed. The overall replacement is SiO_2H_2 by Ca. Such a replacement would have a relatively small effect on the pseudo-cell weight, as table 2 shows.

In addition, some other features of the system would also be explained.

TABLE 2. *Replacement of* SiO_2H_2 *by* Ca

Pseudo-cell contents	$CaO:SiO_2:H_2O$	Pseudo-cell weight
I. $Ca_4Si_6O_{18}{\cdot}CaO_4H_{10}$	0.83:1:0.83	730
II. $Ca_4Si_{4.5}O_{15}{\cdot}Ca_{2.5}O_4H_7$	1.44:1:0.78	697
III. $Ca_4Si_4O_{14}{\cdot}Ca_3O_4H_6$	1.75:1:0.75	687

(a) The upper limit of the CaO/SiO_2 ratio would be 1.75, corresponding to the removal of all bridging tetrahedra. This is in complete agreement with findings in this laboratory. The highest-lime tobermorite, obtained in the paste hydration of β-C_2S, had a ratio of 1.75, as shown in table 1. The higher ratios of Funk [30] and van Bemst [28] were discussed earlier.

(b) The rate of equilibration between tobermorites and calcium hydroxide solutions is very slow. If increasing the lime content would involve merely uptake of lime between the layers, one would not expect such slow equilibration. However, according to the hypothesis, increasing the lime content would involve removal of SiO_2 from the layers, which may well be very slow.

Taylor and Howison realized that their hypothesis was probably an over-simplification of a very complex problem. This is true, as will be seen shortly. Nevertheless, the present authors believe that basically, though not in detail, the hypothesis of Taylor and Howison is correct. It is hard to visualize any other explanation for the constancy of density.

In several aspects, the hypothesis is not borne out by certain experimental findings.

(a) Taylor and Howison point out that the above described replacement would lead to gradual decrease in the crystallinity of the tobermorites. No such decrease was found by Grudemo [32] for synthetic tobermorites of ratios 0.98 to 1.36, nor in this laboratory for tobermorites of ratios 0.97 to 1.44. At least, as far as the layer spacings (*h k 0*) are concerned, the number, location and sharpness of the lines remains practically unchanged. There appears to occur, however, a sharp decrease in degree of crystallinity of the (*h k 0*) spacings around the ratio 1.5, which is associated with a change in morphology. From a ratio of 1.5 to 1.75 the morphology and the degree of crystallinity remain again constant. This will be further discussed later.

(b) The water contents indicated in table 2 for formulas II and III are much too low. For example, if 80 percent of the bridging tetrahedra would be removed, the tobermorite would have the formula $Ca_3Si_2O_7{\cdot}1.55H_2O$, which agrees with the formula in eqs (3) and (4), except for water.

The situation would be improved, if SiO_2H_2 were replaced not by Ca alone, but by Ca plus a water molecule. In this case, the formula of the above tobermorite would be $Ca_3Si_2O_7{\cdot}3.15\ H_2O$—close to that indicated by eq (3). There would be two other advantages in this addition to the hypothesis.

(1) The pseudo-cell weight would remain more nearly constant. The tobermorite obtained by 80 percent removal of the bridging tetrahedra would have a pseudo-cell weight of 724, and that obtained by 100 percent removal (formula III in table 2) would have a weight of 722. Such a high degree of constancy of density is indicated by the results obtained in this laboratory and cited earlier.

(2) Grudemo [32] showed that gradual increase in the CaO/SiO_2 ratio from 0.98 to 1.56 resulted in a gradual decrease in the *c* spacing from about 13.7 to about 10.4 A. Apparently, the calcium ions pull the layers closer to each other. Taylor [22], as well as many others, showed that increasing the water content resulted in an increase in the *c* spacing, ranging from 9.3 to more than 14 A. Brunauer, Kantro and, Copeland [14] pointed out that the decrease in *c* spacing caused by addition of a molecule of CaO is approximately equal to the increase in *c* spacing caused by the addition of a molecule of H_2O. It follows, therefore, that to keep the volume of the pseudo-cell constant, the addition of a calcium ion should be balanced by the addition of a water molecule.

Further evidence along these lines will be presented later.

(c) The removal of bridging tetrahedra would lead to a breaking up of the long metasilicate chains. This may be regarded as a partial depolymerization. When all bridging tetrahedra are removed, at $CaO/SiO_2=1.75$, all remaining silicon tetrahedra would be in the form of "dimers"; i.e., two tetrahedra joined at one corner (sharing one oxygen ion).

As a matter of fact, Greenberg and Pressler [40] found evidence of increasing depolymerization with increasing CaO/SiO_2 ratio. However, the depolymerization was far greater than that indicated by the Taylor-Howison hypothesis.

Various investigators [41] showed that most ortho and pyrosilicates readily dissolve in dilute HCl, whereas most chain, layer and three-dimensional structures of connected SiO_4 tetrahedra do not. Alexander [42] showed that one can distinguish between monomers, dimers and higher polymers in the solution by means of the rate of reaction of these species with molybdic acid. Using these techniques, Greenberg and Pressler obtained the results shown in table 3. In their experiments, 0.5 g. samples were dissolved in 200 ml. of 0.5 N hydrochloric acid at 0 °C. The percentage dissolved in 2 minutes is shown in column 2. The filtered solution was brought in contact with the molybdic acid reagent, and the extent of reaction in 2, 10, and 60 minutes is shown in columns 3, 4 and 5.

TABLE 3. *Solution properties of hydrated silicates*

1	2	3	4	5
Preparation	Percentage dissolved	Molybdic acid reaction		
		2 Min.	10 Min.	60 Min.
$Na_2H_2SiO_4 \cdot 8H_2O$	100	69.2	79.2	100
Hydrated C_3S	100	57.9	82.3	97.3
Tobermorite, 1.5	85.5	42.2	64.1	83.6
Tobermorite, 1.0	72.0	15.0	27.9	55.0
Tobermorite, 0.8	37.8	9.6	18.9	33.6
β-wollastonite	12.4	4.3	6.6	10.9

First of all, it is clear that hydrated C_3S behaves very much like $Na_2H_2SiO_4 \cdot 8H_2O$. Thilo [43] showed that the latter is an orthosilicate. At the other end, it is also clear that β-wollastonite behaves very differently, as one would expect for a metasilicate chain. The three tobermorites of table 3 were prepared by the reaction of calcium hydroxide and silica gel at 85 °C for 3 hr, with initial CaO/SiO_2 ratios of 1.5, 1.0, and 0.8. The solution behavior of these three tobermorites is intermediate between the two extremes.

It appears, therefore, that increasing depolymerization occurs with increasing CaO/SiO_2 ratio. The tobermorite of CaO/SiO_2 ratio 1.5, obtained in the hydration of C_3S, contains largely or wholly monomers, i.e., independent SiO_4 tetrahedra.

4. Whatever the genealogy of tobermorites may be, the tobermorite obtained in the room temperature hydration of C_3S or C_2S appears to contain no chains of SiO_3 but chains of SiO_4, very much like that postulated by Bernal [29]. The tetrahedra, very probably, are joined by hydrogen bonds. The hydrate itself is an orthosilicate, just as C_3S and C_2S are orthosilicates.

This particular tobermorite was called in all publications from this laboratory simply "tobermorite". Henceforth, to distinguish it from all other tobermorites, it will be called tobermorite (*G*). The name tobermorite gel was suggested by Taylor in private communication.

Tobermorite (*G*) is a very poorly crystallized hydration product. The natural mineral exhibits dozens of X-ray diffraction lines, as do the synthetic tobermorites prepared hydrothermally [24, 44]. Tobermorites, synthesized in suspensions at room temperature, show about a dozen diffraction lines. However, the tobermorites obtained in the room temperature hydration of C_3S and C_2S in this laboratory show only three diffraction lines. There is a very strong and very broad line with a maximum at 3.05 A, and two much weaker broad lines at 2.79 and 1.82 A. These spacings were obtained on samples dried at a vapor pressure of 5×10^{-4} mm. Heller and Taylor [44] found that these spacings have indices of (110), (200), and (020), respectively, and they reported the same spacings at 3.07, 2.81, and 1.83 A, on less strongly dried samples.

All three lines are (*h k 0*) spacings, i.e., spacings within the layer. Taylor [22] pointed out that drying results in a slight shrinkage of these spacings. The (020) spacing represents half the distance between Si atoms in the chain. Twice this distance, 3.64 A, is the *b* length of the orthorhombic pseudo-cell. Twice the (200) spacing, 5.59 A, is the *a* length of the pseudo-cell. The three lines in tobermorite (*G*) correspond to three of the strongest lines of all tobermorites.

Tobermorite (*G*) exhibits no basal spacing. In the first experiments performed in this laboratory, a paste-hydrated C_3S tobermorite sample, dried at 5×10^{-4} mm pressure, gave a *c* spacing of about 11 A and a density of 2.44 g/cc [12]. Never again was such a sample obtained. In dozens of preparations, obtained by hydration of C_3S and C_2S and dried at the same vapor pressure, the *c* spacing (002) was absent, and the average density was 2.86 g/cc [14].

Tobermorite (*G*), dried at 5×10^{-4} mm pressure, has the formula $Ca_3Si_2O_7{\cdot}2H_2O$. From the *a* and *b* lengths of the pseudo-cell and from the density, the *c* length can be obtained, and it is 9.3 A. Numerous investigators found this value for the *c* spacing of very strongly dried tobermorites; it appears to be the distance of closest approach of two layers.

Tobermorite (*G*), dried at 8×10^{-3} mm pressure, has the formula $Ca_3Si_2O_7{\cdot}2.8H_2O$. Calculation, using the density of 2.73 g/cc, leads to a layer-to-layer distance of 10.3 A. The extrapolated density of $Ca_3Si_2O_7{\cdot}3H_2O$ is 2.71 g/cc [15].

Even the three broad diffraction lines of tobermorite (*G*) do not represent the lowest limit of the degree of crystallinity of tobermorites. A tobermorite exhibiting a single broad diffraction band will be discussed in connection with the ball-mill hydration of C_3S.

5. It is seen in figure 1 that Taylor and Kalousek obtained tobermorites of different CaO/SiO_2 ratios at the same lime concentration in the solution. In earlier investigations, even greater variations were obtained [33]. To be sure, equilibrium is very slowly established for reasons discussed before. However, some investigators did approach equilibrium from both the high- and the low-lime directions, and still obtained somewhat different curves.

There are two factors that may cause such variations. One of these is difference in the structure and the degree of crystallinity of the tobermorite obtained in the reaction. For a given CaO/SiO_2 ratio, every recent investigator reports a somewhat different X-ray diffraction pattern; and even the same investigator reports somewhat different patterns for different methods of preparation. The formula SiO_2 does not define a chemical compound; quartz, crystobalite, and amorphous silicas have different free-energy contents and solubilities. Just so, the variations in the crystal structure of a tobermorite of a given CaO/SiO_2 ratio may cause variations in the free energy content and in solubility. Thus, it may happen, as figure 1 shows, that Taylor's tobermorite, with a ratio of 1.1, is in equilibrium with a calcium ion concentration of about 3 millimoles per liter, whereas Kalousek's is in equilibrium with a concentration of about 6 millimoles per liter.

A second factor is variation in the specific surface area of tobermorite. Very few investigators have measured surface areas; nevertheless, it is clear that considerable variations may be obtained. Two tobermorites, having the same CaO/SiO_2 ratio and the same crystal structure, would have different free energy contents and solubilities if they have different specific surface areas.

Water of Hydration in Tobermorites

1. When tobermorite (*G*), obtained in the hydration of C_3S or C_2S is (*D*)-dried, the CaO/SiO_2 ratio is 1.5 and the H_2O/SiO_2 ratio is slightly greater than 1.0. Part of the excess, as was stated before, is probably adsorbed water, held firmly on the most active part of the surface.

In agreement with Bernal's views [29], tobermorite (*G*) is an orthosilicate, with two hydrogens on two of the oxygen ions in the SiO_4 tetrahedra. According to his structural formula, $Ca_2[SiO_2(OH)_2]_2[Ca(OH)_2]$, two of the water molecules, in hydroxylic forms, are in the tobermorite layers—or in the $H_2SiO_4^{=}$ chains, constituting parts of the layers. The third water molecule, likewise in hydroxylic form, is between the layers.

On the basis of experiments performed in this laboratory, it appears more likely that the interlayer water is molecular; so Bernal's formula would be modified to $Ca_2[SiO_2(OH)_2]_2{\cdot}CaO{\cdot}H_2O$. With drying of increasing severity, the interlayer water is lost continuously. At (*P*)-drying, the formula is approximately $Ca_2[SiO_2(OH)_2]_2{\cdot}CaO{\cdot}\frac{1}{2}H_2O$, at (*D*)-drying, $Ca_2[SiO_2(OH)_2]_2CaO$. The density indicates that at (*P*)-drying the *c* spacing (interlayer distance) is 10.3 A, at (*D*)-drying 9.3 A. At (*D*)-drying all the interlayer water is removed, and the minimum distance between the layers is attained.

It was found in this laboratory [14] that tobermorite dried to this stage, even after soaking in water for a day, did not swell. Megaw and Kelsey [39] proposed that when a tobermorite having a *c* spacing of 11.3 A was dehydrated to a stage with a *c* spacing of 9.6 A, the metasilicate chains in one layer fitted into the grooves between those in the next adjacent layer. This would explain the strong attraction between adjacent layers, leading to the exclusion of water. Taylor and Howison [31] suggested that the packing would be similar in hydrates having *c* spacings of 10.3 A. Tobermorite (*G*), subjected to (*P*)-drying, gives a calculated *c*-spacing of 10.3 A. Upon soaking in water, it shows some swelling, but the swelling is very slow and very slight.

After (*D*)-drying, a tobermorite (*G*) molecule contains only the hydroxylic water attached to the SiO_4 tetrahedra in the layers, with the slight excess mentioned before. The water in the layers is far more firmly held than that between the layers. A tobermorite (*G*) preparation, dried over P_2O_5 for four weeks to constant weight, still had an H_2O/SiO_2 ratio of 0.95. Thus, at a vapor pressure of the order of 1/1000 of that used in (*D*)-drying, very little of the layer water was lost. The difference between 0.95 and 1.00 is only slightly greater than the experimental error.

It will be shown that tobermorite (*G*) is very finely divided in the *c* direction. This dimension of the crystallites—if one can call such poorly crystallized particles crystallites—is colloidal; it even verges on the molecular. On the other hand, the dimension of the particles in the *b* direction, i.e., along the silicate chains, is quite large, of the order of a micron or several microns. Thus, speaking with some license, tobermorite (*G*) is a colloid in the *c* direction but not a colloid in the *b* direction. It is interesting to note that interlayer water is lost continuously, as water is usually lost by colloids, but the water content of the orthosilicate chains remains almost constant over a wide range of vapor pressures.

2. It was shown earlier that in high-lime tobermorites the addition of lime to the structure always resulted in addition of water to the structure, in the approximate molar proportion of 1:1. If the modification of the Taylor-Howison hypothesis proposed in this paper is correct, the same should be valid for low-lime tobermorites as well. Experiments performed in this laboratory indicate that this is what happens. The results are shown in table 4.

TABLE 4. CaO/SiO_2 *and* H_2O/SiO_2 *molar ratios of low-lime tobermorites*

1	2	3	4	5	6	7	8
Preparation	Starting CaO/SiO_2	Reaction time (days)	Temp.	CaO/SiO_2	H_2O/SiO_2	ΔCaO	ΔH_2O
			°*C*				
F-29X	1.0	88	50	0.98	0.65	--------	--------
F-18X	1.0	165	23	.99	.67	0.01	0.02
F-20X	1.5	254	23	1.25	.90	.27	.25
F-27X	1.5	91	50	1.28	.93	.30	.28
F-23X	2.0	292	23	1.38	1.00	.40	.35
F-22X	2.0	75	50	1.44	1.07	.46	.42

Very pure lime and silica were used, in ratios 1.0, 1.5, and 2.0, and the reactions were carried out at 23 and 50 °C, for various lengths of time. One-half of the preparations were (*D*)-dried, the other (*P*)-dried. The results are given only for the (*D*)-dried samples; essentially the same results were obtained for the others. Ignition loss, CO_2, free SiO_2, and free CaO were determined for each preparation; thus, the ratios in columns 5 and 6 are quite accurate. The Δ values in the last two columns were obtained by comparison with F–29X which had the lowest CaO/SiO_2 and H_2O/SiO_2 ratios.

In contrast with these results, Taylor and Howison [31], confirming earlier work of Taylor [45], came to the conclusion that low-lime tobermorites, dried around 100 °C, have H_2O/SiO_2 ratios substantially independent of the CaO/SiO_2 ratios. Drying around 100 °C is not too different from (*D*)-drying. The present authors have no explanation for the very different results beyond what they stated earlier. The tobermorite system is a complicated one, to say the least. Differences in starting materials and experimental procedures lead to wide differences in the properties of the products. Much further work will be needed before this system will be, not fully, but adequately understood.

Morphology of Tobermorites

1. The first extensive electron optical studies of tobermorites prepared at room temperatures have been published by Grudemo [32]. The low-lime tobermorites consist predominantly of very thin crinkled foils; some of which are so thin that Grudemo estimated them to be of unit cell thickness. Some of these foils or sheets appear to roll, partially or completely, into tubes or fibers. Kalousek and Prebus [20] obtained similar electron micrographs, and came to similar conclusions. Gaze and Robertson [46] obtained tobermorite foils from hydrated portland cement, and they estimated that these foils were of the order of two molecules in thickness.

At lime saturation, the micrographs show predominantly tubes or fibers. Grudemo states, "In saturated and supersaturated lime solutions, a fibrous or needle-like growth of the crystals seems to be promoted, probably caused by a degeneration of the sheets into lath-like structures and by twisting and rolling of the crystal sheets."

Figure 2 shows electron micrographs of hydrated C_3S and C_2S preparations, obtained by Copeland and Schulz in this laboratory. Figures 2a to 2c show tobermorite (*G*), as well as occasional $Ca(OH)_2$ crystals, obtained in the paste-hydration of C_3S, and figures 2d to 2f, those obtained in the paste-hydration of β-C_2S. The pastes were dispersed by an ultrasonic generator, using 1,1,1 trichloro-ethane as the liquid. Almost complete dispersion was always obtained, and tobermorite (*G*) always appeared as fibers. The undispersed part was less than 10 percent, and it is probable that most of this also consists of fibers.

The micrographs give clear indications that the fibers are rolled-up sheets. Although in the photographs much of the distinctness of the original micrographs is lost, still enough is seen to show the correctness of this conclusion. Many dozens of micrographs show the rolling of the sheets, in different stages. The fibers are long and straight, most of them longer than 1μ. The magnifications are shown in the figure; the length of the line is 1μ.

It was stated earlier that the X-ray diffraction pattern of tobermorite (*G*) consists of only three broad (*h k 0*) lines and no (*0 0 l*) line. It seems reasonable to assume that the rolling of the sheets into fibers causes the great change in the degree of crystallinity of the substance. At any rate, the drastic change in morphology and in degree of crystallinity appear to be simultaneous.

2. Figures 2g and 2h show electron micrographs of C_2S hydrated in a polyethylene bottle rotated on a wheel for more than two years (*D*–69 of table 1). It will be noted that the particles look quite different from those obtained in the paste-hydration of C_3S and C_2S; instead of straight fibers, they are cigar-shaped. Again, almost all of the tobermorite was dispersed by ultrasonic treatment, and all dispersed material consisted of such cigar-shaped particles. The morphology of

Figure 2a. *Electron micrograph of hydration products of paste-hydrated* C_3S.

The length of the line in figures 2a to 2h is 1 micron.

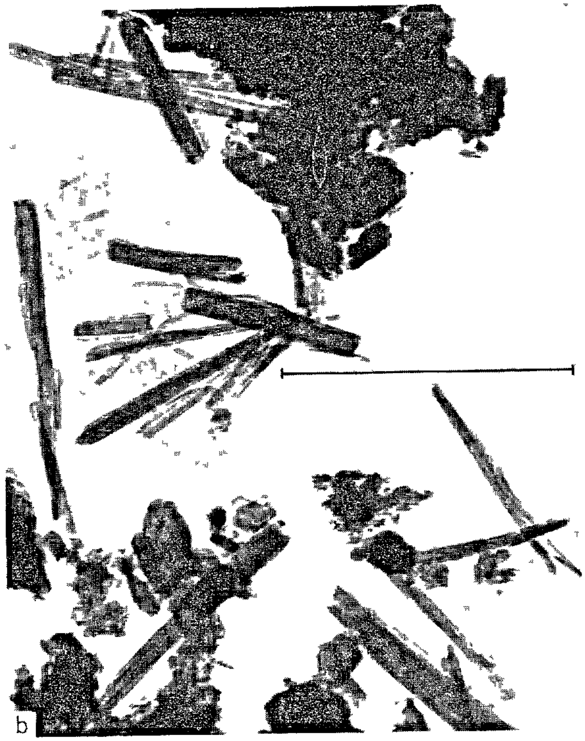

Figure 2b. *Electron micrograph of hydration products of paste-hydrated* C_3S.

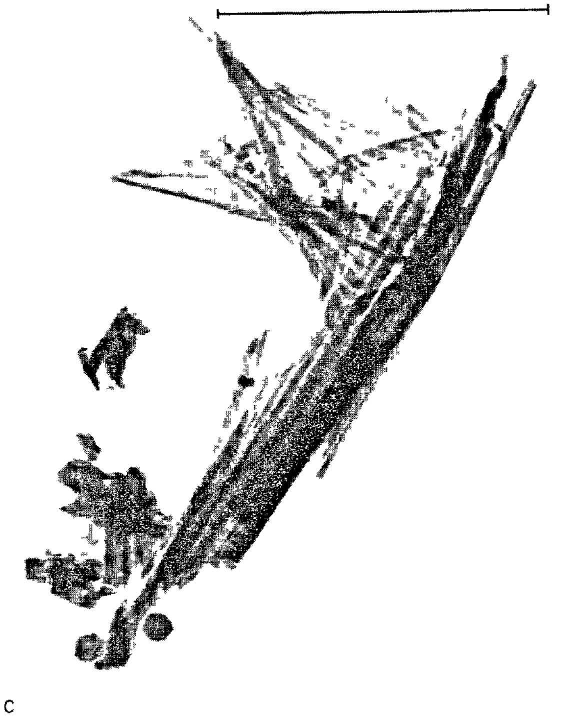

Figure 2c. *Electron micrograph of hydration products of paste-hydrated* C_3S.

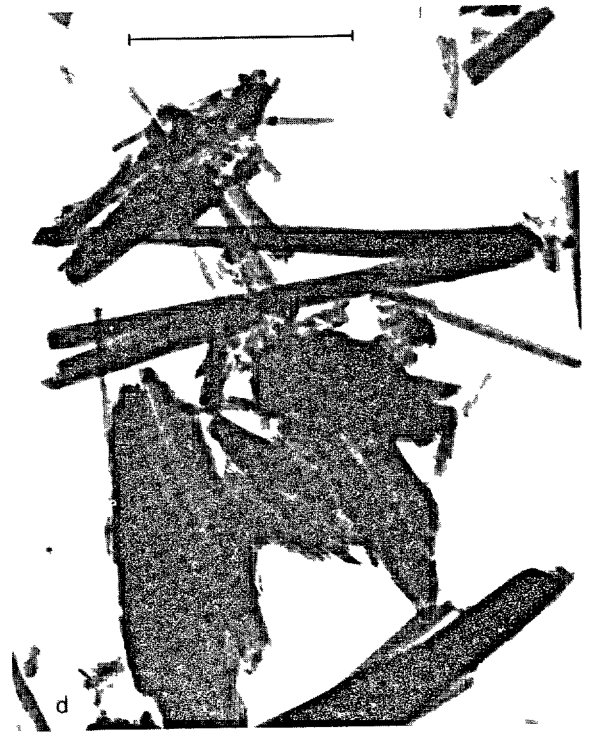

Figure 2d. *Electron micrograph of hydration products of paste-hydrated* C_2S.

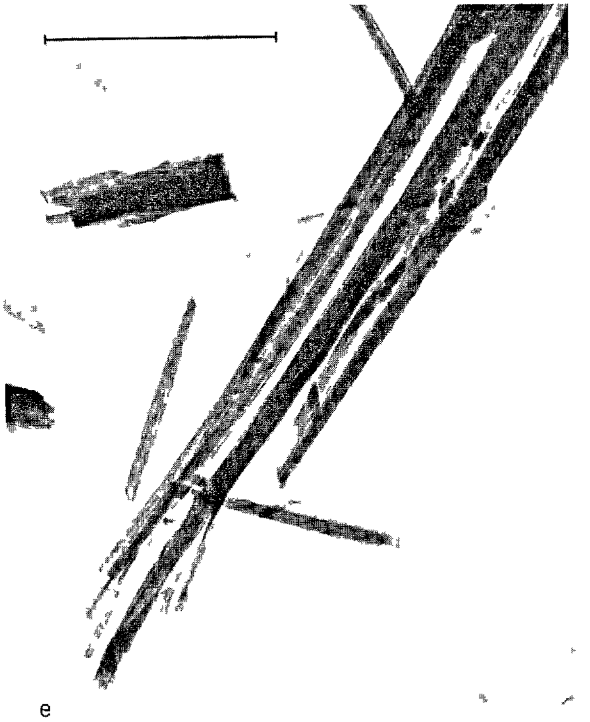

FIGURE 2e. *Electron micrograph of hydration products of paste-hydrated* C_2S.

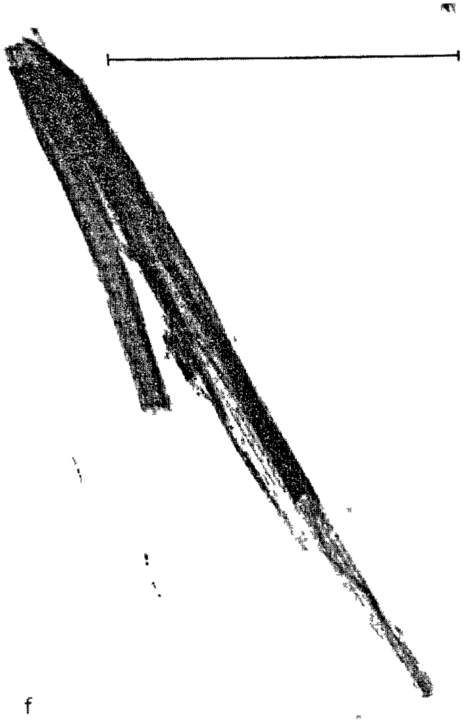

FIGURE 2f. *Electron micrograph of hydration products of paste-hydrated* C_2S.

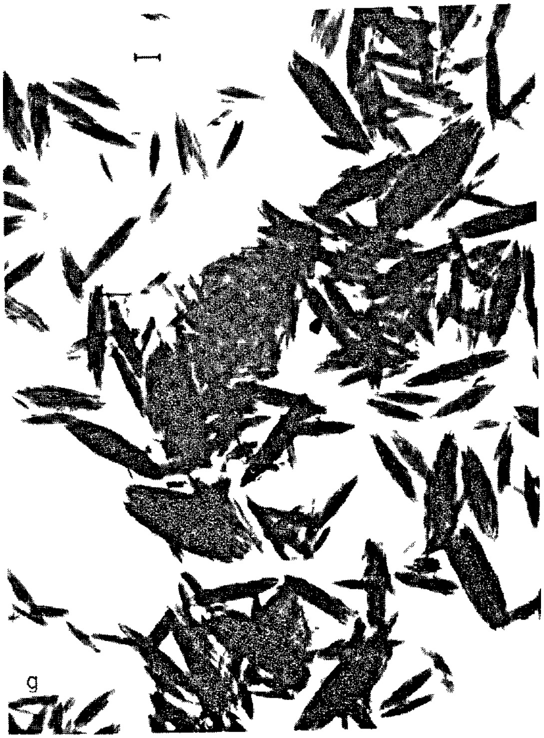

FIGURE 2g. *Electron micrograph of hydration products of bottle-hydrated* C_2S.

FIGURE 2h. *Electron micrograph of hydration products of bottle-hydrated* C_2S.

this preparation is identical with that of Taylor's C_2SH(II), published by Grudemo [32].

As a matter of fact, the material is identical with Taylor's C_2SH(II) in, probably, all respects. It is far better crystallized than the tobermorites obtained in the paste hydration of C_3S and C_2S; and, in fact, its X-ray pattern is the same as that of Taylor's C_2SH(II) [22]. Although initially Taylor believed that the CaO/SiO_2 ratio in this hydrate was close to 2, later he estimated it to be 1.75; and, as table 1 shows, the hydrate in *D*–69 has a ratio of 1.73. The water content of the hydrate in *D*–69 is higher than that of similarly dried high-lime tobermorites.

Preparation *D*–40, in table 1, presents an interesting transition between tobermorite (*G*) and C_2SH(II). The morphology of the hydrate in *D*–40 is the same as in *D*–69; nothing but cigar-shaped particles is in evidence. The composition, however, is the same as that of tobermorite (*G*), both with respect to CaO/SiO_2 ratio and H_2O/SiO_2 ratio. The X-ray diffraction pattern cannot be easily determined because of the 27.5 percent unhydrated C_2S in *D*–40; however, to the extent that it can be deciphered, it seems to be intermediate between that of tobermorite (*G*) and C_2SH(II). The *c*-spacing of the hydrate in *D*–69 exhibits a strong reflection at 9.9 A, in agreement with Taylor's value of 10.0 A (22) for C_2SH(II). Tobermorite (*G*) shows no *c*-spacing. The hydrate in *D*–40 gives such a weak line for the *c*-spacing that it is not quite certain that the line is there.

3. Hydrated C_3S and C_2S set and harden very much like hydrated portland cements; and, doubtless, the formation of tobermorite (*G*) is predominantly responsible for the setting and hardening of portland cements. Bernal [29] pointed out that the fibrous character of tobermorite presents a way for the reconciliation of the old Le Chatelier-Michaelis controversy on the nature of the setting of cement.

Le Chatelier emphasized the fibrous nature of the hydration products; Michaelis emphasized the gel-like characteristics. Bernal states, "We have long known from electron microscope results and the polymer systems that most of the things called gels were, in fact, very fine fibrous crystals; the characteristic gel of collagen (gelatin jelly) is simply a network of fine fibers holding water in between them . . . . One of the most important things to establish was that calcium silicate hydrate did form such a network . . .".

Bernal, Jeffery, and Taylor [7] state, "The rapid growth of long fibers might well lead to the production of interlocking crystals, similar in principle to those formed in gypsum plasters, but on a very much smaller scale."

The interlocking of tobermorite fibers may well explain the adhesion of the fibers to each other, but the adhesion of these fibers to the large $Ca(OH)_2$ crystals in C_3S, C_2S, and portland cement pastes, and to the much larger aggregate pieces in concrete probably requires a more detailed and more basic explanation. Nevertheless, the present authors do not doubt that Bernal's ideas constitute a good beginning toward the understanding of the strength of hardened paste and concrete.

4. Strength and dimensional stability are the two most important engineering properties of concrete, and both of these properties are probably strongly dependent on the properties of tobermorite.

Hardened portland cement paste swells when it imbibes water and shrinks when water leaves. Taylor and Bessey [47] showed that low-lime tobermorites can be hydrated and dehydrated reversibly up to about 100 °C, with a change in the interlayer spacing. Such reversible change in the interlayer spacing may occur in tobermorite (*G*) as well, though it cannot be demonstrated by X-rays since the *c*-spacing is absent.

The fibers of tobermorite are apparently rolled-up foils or sheets, and the sheet has a thickness of two or three layers, as will be shown later. Water can enter between these layers, with the result of swelling the fiber. Such a mechanism of swelling has been suggested by Bernal [29].

There are two other ways in which tobermorite may swell upon entry of water. Water may not only enter between the layers constituting a sheet, but it may also be adsorbed on the external surfaces of the sheet itself. Because the sheet is rolled up into a fiber, adsorption would also lead to swelling of the fiber. The third mechanism is entry of water into the spaces where fibers make contacts with each other, with the result of pushing the fibers away from each other. This mechanism would not involve swelling of the fibers.

It is quite likely that all three mechanisms contribute to the swelling of tobermorite, but much painstaking work must be performed before the relative importance of these mechanisms can be assessed.

Specific Surface Area and Particle Dimensions

1. It was stated earlier in this paper that tobermorites produced at room temperature were colloidal substances, with large specific surface areas. This large specific surface is one of the most important properties of tobermorite.

Powers and Brownyard [48] were the first who measured the specific surface areas and porosities of hardened portland cement pastes, and they were able to deduce highly significant correlations between these basic physical properties and such vitally important engineering properties as compressive strength, dimensional changes caused by changes in water content, permeability to water, and freezing and thawing of water in the pores. This work, as well as subsequent work performed in this laboratory along similar lines, is discussed by Powers in his review paper contributed to this symposium.

It was found in this laboratory that about 80 percent of the specific surface area of hardened portland cement paste is contributed by tobermorite. Although the other hydration products contribute the other 20 percent of the surface, it is clear that the surface dependent properties of hardened portland cement pastes are determined predominantly by the tobermorite surface.

Bogue and Lerch [49] showed that the compressive strengths of hardened C_3S and C_2S pastes increased progressively with increasing extent of hydration, as will be discussed later. The strength of hardened portland cement paste is about the same as that of hardened C_3S and C_2S pastes, and the strength of all three is essentially the strength of tobermorite.

Unquestionably, the other hydration products of portland cement make important contributions to the physical, chemical, and engineering properties of hardened portland cement paste. The present authors believe that it is also unquestionable that the contributions of none of the other hydration products, nor of all of them put together, equal in importance the contributions of tobermorite.

2. All investigators who published specific surface area values for tobermorites used the BET method [50]. Greenberg [23] used nitrogen adsorption, but nitrogen surface values for tobermorites are unreliable; in the great majority of instances they are too low. The incorrectness of the nitrogen surfaces was demonstrated by Brunauer, Kantro, and Weise [51], who showed that the nitrogen values frequently indicated negative surface energies, which is absurd. Apparently, the aggregation of the tobermorite sheets, or their rolling into fibers, or the aggregation of the fibers, or all these factors together create spaces inaccessible to nitrogen molecules, though accessible to water molecules.

Kalousek [52] used both nitrogen and water vapor for surface area determination, but he believed that nitrogen measured the external surfaces correctly. He attributed the difference between the two to the ability of water and the inability of nitrogen to penetrate between the layers of tobermorites. Originally, this opinion was shared by investigators in this laboratory [12], but later work necessitated the abandoning of this view [14]. As was stated earlier, strongly dried tobermorite (*G*) does not admit water between its layers even when soaked in water. In the adsorption experiments, the maximum relative humidity used was 33 percent.

The nitrogen surface values obtained in this laboratory ranged from 21 percent to 100 percent of the water surface values. The important fact is that the upper limit of the nitrogen surface values enables one to calculate the area occupied by an adsorbed water molecule on the surface of tobermorite.

The BET method gives a value for V_m, the weight of nitrogen or water that covers the surface with a complete adsorbed monolayer. In order to calculate the specific surface, one must know the area covered by a single adsorbed molecule. One can calculate the molecular area of nitrogen from the density of the liquid at -195.8 °C, the temperature at which the adsorption measurements are usually carried out. That the value thus obtained, 16.2 A^2, is really the correct area of an adsorbed nitrogen molecule has been confirmed by a great variety of experiments, among which the earliest, and still most impressive, is that of Harkins and Jura [53].

The molecular area of 16.2 A^2 for nitrogen has been adopted the world over, and because of the inert nature of nitrogen, the area applies to all adsorbents. The situation is not so simple, however, for water. The area calculated from the liquid density is 10.6 A^2, but this value cannot be applied to all adsorbents. Because of their strong dipole moments, the water molecules are oriented on ionic surfaces, with the result that the nature and the configuration of the ions of the surface influence the packing of the adsorbed molecules.

Naturally, it is easy to calibrate the water against nitrogen, when the nitrogen surface gives a correct area. Although this is the case for the great majority of adsorbent-adsorbate systems, it is not the case for tobermorites, as was shown above. Nevertheless, the upper limit of the nitrogen surface values can be used for such purpose. Using the largest nitrogen V_m value obtained for any tobermorite preparation, one calculates a molecular area of 11.4 A^2 for water adsorbed on the tobermorite surface.

There are three other comparisons that confirm this value.

(a) The molecular area of water adsorbed on a $Ca(OH)_2$ surface is 10.3 A^2 [54]; that adsorbed on a hydrous amorphous silica (silanol) surface is 12.5 A^2 [55]. The average of the two is 11.4 A^2. The surface of tobermorite is a sort of "chemical mixture" of the surfaces of the two others.

(b) The ball-mill hydration of C_3S produces the calcium silicate hydrate afwillite [13], as was stated before. Afwillite is a well crystallized product, with a specific surface area of about 16 m^2/g. Nitrogen and water give the same surface values for all afwillite preparations, if the molecular area of water is taken to be 11.4 A^2.

(c) Copeland determined the specific surface area of tobermorite by means of low angle X-ray scattering—entirely independently of adsorption. The water adsorption surface agrees with the value of Copeland, if the molecular area of water is taken to be 11.1 A^2. An uncertainty of 3 percent may arise in either set of experiments.

In the following discussion, all specific surface area values are based on water vapor adsorption, and the molecular area of water is taken to be 11.4 A^2.

3. Tobermorite (*G*), obtained in the hydration of C_3S and C_2S, consists of fibers, which are very probably rolled-up sheets. If the rolling of the sheets does not create spaces to which water cannot penetrate, the area measured by water adsorption for the fibers should be the same as that of the sheets prior to rolling. This area could be calculated from crystal structure data, if the thickness of the sheets were known.

Electron micrographs indicate that the sheets are very thin—of the order of a few layers, at most. Because the thickness is very small compared to the two other dimensions of the sheet, practically all of the surface area resides in the two sides of the sheet. The *a* and *b* dimensions of the orthorhombic pseudo-cell of tobermorite (*G*) are 5.59 and 3.64 A, respectively, when the composition is $Ca_3Si_2O_7 \cdot 2H_2O$ (in the (*D*)-dried state). If one places one molecule into the pseudo-cell and assumes that the sheet is one layer thick, the specific surface area is 755 m^2/g.

If the sheet is two layers thick, the specific surface area is 377 m^2/g. The largest specific surface area measured for any tobermorite (*G*) preparation made in this laboratory was 376 m^2/g [14]. Naturally, the almost exact agreement is somewhat fortuitous. Neglecting the edge areas makes the calculated specific surface a few percent less than the true surface. On the other hand, aggregation of the fibers, with possible bonding at the contact areas, may reduce the surface accessible to water molecules by a few percent. A third, and also small, factor will be considered shortly.

If the thickness of the sheet is three layers, the calculated specific surface, again neglecting edge areas, is 252 m^2/g. The smallest surface measured for any tobermorite (*G*) in this laboratory was 244 m^2/g [51]. Dozens of tobermorite (*G*) preparations gave specific surface area values between 244 and 376 m^2/g. Thus, the tobermorite (*G*) sheets always, or nearly always, consist of two or three layers. It was found in this laboratory that this conclusion is valid also for the tobermorite (*G*) in hydrated portland cements.

It is interesting to compare these results with those obtained for the low-lime tobermorites shown in table 4. Preparations F–29X, F–18X, F–27X, and F–22X had specific surface areas of 378, 249, 241, and 241 m^2/g, respectively. Apparently, the tobermorite sheets of the first one consisted of two layers, those of the last three, of three layers. However, the specific surface areas of F–20X and F–23X were 135 and 135 m^2/g, respectively, indicating sheets that are about 6 layers thick.

In contrast with tobermorite (*G*), each of the six preparations shows a *c*-spacing in the X-ray patterns. The lines are very broad for the first four preparations, but quite sharp for the last two. Apparently, 6 layers are sufficient to give a sharp diffraction line.

4. The above surface areas were measured on (*D*)-dried preparations. The surface areas obtained for (*P*)-dried preparations were always lower. The reason for this is that (*P*)-drying leaves a considerable amount of adsorbed water on the surface. If it is assumed that (*D*)-drying removes all adsorbed water, the amount of adsorbed water in (*P*)-dried samples can be calculated. Such a calculation leads to the result, reported earlier, that in $Ca_3Si_2O_7 \cdot 2.8H_2O$ about 2.5 H_2O is water of hydration and 0.3 H_2O is adsorbed water.

It was shown earlier that the H_2O/SiO_2 ratio in (*D*)-dried preparations is always greater than 1.0. The excess may be in part interlayer water not completely removed, and in part adsorbed water. It is quite likely that there is some adsorbed water in tobermorite (*G*) after (*D*)-drying, but judging from the amount adsorbed at (*P*)-drying, it must be small. Probably not more than 2 or 3 percent of the surface area is covered with water after (*D*)-drying.

This adsorbed water would make the specific surface areas determined by water vapor adsorption too small by a percent or two. It is clear that all three factors neglected in the basic calculations, preadsorption of water, adsorption on edge areas, and lack of adsorption on contact areas, are small, and they partly compensate for each other.

5. From the data given so far, certain conclusions can be drawn for the average dimensions of the tobermorite (*G*) sheets. If one calls the length of the average sized sheet in the direction of the silicate chains *B*, the length perpendicular to this *A*, and the thickness of the sheet *t*, the surface area per unit volume is given by

$$S=\frac{2(AB+At+Bt)}{ABt}. \tag{5}$$

S is the product of the specific surface area and the density, and *t* is about 20 A for the two-layer sheets and 30 A for the three layer sheets.

Solving for *B*, one obtains

$$B=\frac{At}{(S/2)At-(A+t)}. \tag{6}$$

It follows from eq (6) that

$$(S/2)At>A+t \tag{7}$$

and the lowest limit of *A* is given by

$$(S/2)At=A+t. \tag{8}$$

Because the fibers are rolled-up sheets, the average length of the fibers seen in electron micrographs gives the *B* dimension of the sheet. However, nothing can be said about the *A* dimension of the sheet on the basis of electron micrographs. Calculations based on eq (8) show that the *A* dimension of the average sheet cannot be less than 360 A for the two-layer tobermorite (*G*) and 515 A for the three-layer tobermorite (*G*).

If the average length of the fibers is 1 μ, the *A* dimension is 390 A for the two-layer sheet and 560 A for the three-layer sheet. If it is greater than 1 μ, as the electron micrographs seem to indicate, the *A* dimension is between 360 and 390 A for the two-layer sheets, and between 515 and 560 A for the three-layer sheets.

It can be seen from the above considerations that specific surface area, combined with other information, leads to reasonably good estimates of all three dimensions of the average tobermorite (*G*) particle.

Other Properties of Tobermorites

1. A most useful collection of X-ray powder data, as well as of a number of other properties of tobermorites, has been published by Heller and Taylor [56].

Extensive data on index of refraction are found in the papers of Taylor and Howison [31, 57]. The average index of refraction of tobermorite (*G*), obtained in the paste hydration of C_3S and C_2S, was 1.56 for each. Dr. L. S. Brown of this laboratory made the measurements.

2. Kalousek and Roy [58] and Kalousek and Prebus [20] reported infrared absorption data for tobermorites. Hydrothermally prepared and well-crystallized tobermorite absorbs infrared radiation at 2.9 and 6.2 μ; low-lime tobermorites of CaO/SiO_2 ratios 0.8 to 1.33 absorb at 2.9, 6.2, and 6.8 μ; and poorly crystallized high-lime tobermorites, with ratios 1.5 and higher, absorb at 2.9 and 6.8 to 7.0 μ. In addition, a broad band between 9 and 11 μ was present in all preparations. The 2.9 μ band was attributed to hydroxylic water, and the 6.2 μ band to molecular interlayer water.

In hydrated C_3S, van Bemst [28] found only a very broad infrared absorption band between 8.2 and 11.2 μ. A dissertation by Hunt [59], which includes infrared investigations of the hydration products of C_3S and C_2S, was not available to the present authors at the time of writing this paper.

3. Kalousek [34] applied differential thermal analysis in the study of the system lime-silica-water. Somewhat later, van Bemst published DTA curves for the hydration products of C_3S [28]. The method of hydration he used was very similar to that called "bottle" hydration in this paper. He obtained two endothermic peaks for the calcium silicate hydrate, a larger one at 150° and a smaller one at 335 °C. S. Gordon determined a DTA curve for preparation D–69 of table 1, and the curve was quite similar to that of van Bemst, with the large peak near 200° and the smaller one at 330 °C. It was shown earlier in this paper that the hydrate is probably identical with Taylor's $C_2SH(II)$. In contrast with this, Gordon's curves for paste-hydrated C_2S and C_3S (C–51 and C–52 of table 1) do not show the peak at 335 °C.

McConnell [37] obtained two distinct endothermic peaks for a natural mineral tobermorite at 128° and 249 °C. He attributed these peaks to "unbound" or interlayer water and "bound" water. The two peaks seem to fuse into a broad hump at or near 200 °C for D–69, C–51, and C–52.

The DTA curve of McConnell showed an exothermic peak at 851 °C, corresponding to the conversion of tobermorite to wollastonite. Van Bemst found that this peak shifted gradually from 840° to 920 °C, as the CaO/SiO_2 ratio in the tobermorite increased. He reported that lower-lime tobermorites converted into wollastonite, but high-lime tobermorites converted into β-C_2S.

4. A thermobalance was used by Greenberg [23], van Bemst [28], Nicol [60], and others for quantitative determination of the hydration products of C_3S and C_2S.

The differential thermobalance developed by DeKeyser [61] was employed by van Bemst [28] for the study of hydrated C_3S. He obtained endothermic peaks for the tobermorite at 70°, 250°, 310°, and 390 °C. He stated, "Differential thermogravimetric analysis indicates much better than thermal analysis the less important phenomena of thermolysis."

The present authors believe that infrared absorption, differential thermal analysis, thermogravimetry, and differential thermogravimetry may prove to be very valuable tools for the investigation of the properties of this complex system. However, much work will have to be done before all the infrared bands, and all the DTA peaks and differential thermobalance peaks will be definitely interpreted.

Aqueous Phase

1. The aqueous phase in contact with tobermorites of varying molar CaO/SiO_2 ratios has been studied by many investigators [33]. One of the often quoted investigations is that of Flint and Wells [62], who made silica sols react with $Ca(OH)_2$ at 30 °C. They plotted the amount of dissolved silicic acid as a function of the calcium ion concentration in the solution, and obtained a curve with an ascending branch at low calcium ion concentrations, followed by a sharp descent within a narrow calcium concentration range, and ending with a slowly descending, almost linear, curve at higher calcium concentrations. They found that the solid species in contact with the solution along the first branch was hydrated silica with some sorbed $Ca(OH)_2$; along the rest of the curve it was a calcium silicate hydrate with increasing molar CaO/SiO_2 ratios.

The first branch of the curve can be explained as increasing solubility of silica with increasing *p*H. Alexander, Heston, and Iler [63] found that the solubility of silica gel in NaOH solutions increased with increasing *p*H. They attributed the effect to the formation of $H_3SiO_4^-$ ions above *p*H 7. The equilibria can be expressed by the equations

$$SiO_2(s)+nH_2O(l)=H_4SiO_4aq. \tag{9}$$

$$H_4SiO_4aq.+nH_2O(l)=H^+aq.+H_3SiO_4^-aq. \tag{10}$$

The equilibrium constants are

$$K_1=a_{H_4SiO_4} \tag{11}$$

$$K_2=\frac{a_{H^+}a_{H_3SiO_4^-}}{a_{H_4SiO_4}} \tag{12}$$

where *a* refers to the activity of each species. The product of eqs (11) and (12) is

$$K_1K_2=K_3=a_{H^+}a_{H_3SiO_4^-}. \quad (13)$$

As the *p*H increases, a_{H^+} decreases, and $a_{H_3SiO_4^-}$ must increase. Thus the solubility of silica increases by the formation of $H_3SiO_4^-$ ions. Greenberg and Price [64] obtained similar results when $Ca(OH)_2$ was used instead of NaOH.

2. Along most of the descending branch of the Flint and Wells curve, the solution is in equilibrium with tobermorites of increasing CaO/SiO_2 ratios. Greenberg, Chang, and Anderson [65] investigated the solubilities of tobermorites of CaO/SiO_2 ratios 0.8, 1.0, 1.2, and 1.5, prepared at 85 °C by the reaction of $Ca(OH)_2$ and silica gel. The *p*H, the calcium ion, and the silicic acid concentration were determined for the solutions in contact with the tobermorites. Using the known dissociation constants of silicic acid and the Debye-Hückel limiting law, the activities of the calcium and $H_3SiO_4^-$ ions were calculated. For the tobermorite of ratio 0.8, the product

$$K_{sp_1}=a_{Ca^{++}}a^2_{H_3SiO_4^-} \quad (14)$$

was found constant and equal to $10^{-8.5}$ at 25 °C. For the tobermorites of higher ratios the product was not constant.

3. The relative amounts of H_4SiO_4, $H_3SiO_4^-$ and $H_2SiO_4^=$ species vary with *p*H in sodium and calcium silicate solutions. As the *p*H increases, H_4SiO_4 diminishes and $H_3SiO_4^-$ increases. At still higher *p*H values, $H_2SiO_4^=$ ions begin to appear in the solution, and their concentration increases with increasing *p*H. At a *p*H of 10.8 the $H_3SiO_4^-$ ion concentration is at its maximum, the H_4SiO_4 concentration is already small, and the $H_2SiO_4^=$ concentration is yet small. Beyond this *p*H, the $H_3SiO_4^-$ concentration diminishes and the $H_2SiO_4^=$ concentration increases, until eventually the latter ion takes over almost completely.

Greenberg, Chang, and Anderson [65] found that for their tobermorites of ratios 1.0, 1.2 and 1.5 the product

$$K_{sp_2}=a_{Ca^{++}}a_{H_2SiO_4^=} \quad (15)$$

was constant. Their values for pK_{sp_2} (the negative of the logarithm of K_{sp_2}) at 25 °C for two preparations with ratio 1.0 were 6.9 and 7.0, and for the preparations with ratios 1.2 and 1.5 were 6.9 and 7.0, respectively. The uncertainty in their pK_{sp_2} values was 0.1, so the solubilities of tobermorites with ratios ranging from 1.0 to 1.5 are the same within experimental error.

Greenberg, Chang, and Anderson obtained a pK_{sp_2} value of 7.0 for a tobermorite of ratio 1.0 at 40 °C. Thus, the solubility is approximately the same in the temperature range 25 to 40 °C.

4. Greenberg and his coworkers added 1.25- and 5.0-g samples of C_3S to 1,000 ml of water at 30 °C, and the mixtures were stirred. The K_{sp_2} values were determined as a function of reaction time. Initially, both samples indicated supersaturation with respect to tobermorite, but the supersaturation kept on decreasing. The 1.25-g sample gave a K_{sp_2} value of 10^{-7} after 20 hr. The 5-g sample reached a K_{sp_2} value of $10^{-6.9}$ after 200 minutes, and remained constant thereafter for the duration of the experiment (20 hr).

These experiments indicate that tobermorite (*G*) obtained in the hydration of C_3S, has the same solubility product, within the experimental error, as the synthetic low-lime tobermorites, with CaO/SiO_2 ratios 1.0 to 1.5.

It was noted that the solution in contact with the 5-g sample became supersaturated with respect to $Ca(OH)_2$ after 80 minutes of reaction time, and remained so for the duration of the experiment.

Energetics of the Hydration Process

Heats of Hydration of C_3S and β-C_2S

1. It is interesting that the first values for the heats of hydration of C_3S and β-C_2S were obtained by an indirect method. Woods, Steinour, and Starke [66] determined the heat evolved in the hydration of portland cements of different chemical compositions, and calculated by least squares analysis the heats assignable to the individual components. The values obtained were 136 cal/g for C_3S and 62 cal/g for C_2S. The cements were hydrated for one year.

Direct determinations were made by Lerch and Bogue [67]. They hydrated the compounds and obtained the values 120 and 62 cal/g for C_3S and C_2S, respectively. More recently, Verbeck and Foster [68], using the method of Woods, Steinour and Starke, obtained 117 and 53 cal/g for the heats of hydration of C_3S and C_2S, respectively. Their portland cements were hydrated for 6½ yr. The three sets of results are in reasonably good agreement, indicating that the heats of hydration of the two silicates in portland cements are approximately the same as the heats of hydration of the pure compounds.

Powers and Brownyard [48] pointed out that the calorimetrically determined heat of hydration of portland cement is a composite quantity. In the hydration process, a finely divided substance forms, called the "cement gel", and this gel adsorbs large amounts of water. The overall heat of hydration is the sum of the chemical heat of hydration and the heat of adsorption of water on the hydration products. Powers and Brownyard found that the heat of adsorption of water on two hydrated portland cements was about one-fourth of the overall heat of hydration.

All of the above heat determinations, as well as all others that will be reported in this paper, were made by a method proposed by Woods and Steinour [69]. Heats of solution of the unhydrated and the hydrated materials were measured in a calorimeter, and the heat of hydration was obtained as the difference.

All three sets of values given above for C_3S and C_2S are overall heats of hydration. Brunauer, Hayes, and Hass [2] determined the chemical heats of hydration by removing the adsorbed water from the hydration products prior to measuring their heats of solution. They did this by (*D*)-drying the preparations. The values obtained were 96.5 cal/g for the hydration of C_3S and 24.5 cal/g for C_2S. Lack of adequate knowledge of the system hampered these early determinations of the chemical heats of hydration. More accurate values are given in the present paper.

2. As a matter of fact, the overall heat of hydration of C_3S or C_2S is the sum of four terms, rather than two terms. For tobermorites of appreciable surface, the relation is

$$H_o = H_c - S + H_{\mathrm{H_2O}} + H_{\mathrm{Ca(OH)_2}} \qquad (16)$$

where H_0 is the overall heat of hydration, H_c is the chemical heat of hydration when a tobermorite of negligible surface is produced in the reaction, S is the surface energy of tobermorite, $H_{\mathrm{H_2O}}$ is the heat of adsorption of water, and $H_{\mathrm{Ca(OH)_2}}$ is the heat of adsorption of $Ca(OH)_2$. Because the adsorption of $Ca(OH)_2$ on tobermorite surfaces is small, the last term can be neglected. If the specific surface of a tobermorite is small, the last three terms on the right hand side can be neglected. If the specific surface of tobermorite is not small, the chemical heat of hydration is $H_c - S$.

The term S in eq (16) requires some elaboration. An atom, ion, or molecule in the surface layer of a substance has always greater energy than in the body of that substance. This excess energy is called surface energy. All solids and liquids have a part of their energies residing in their bodies, and a part residing in their surfaces. Ordinarily, substances have relatively small specific surface areas; consequently, the surface energy can be neglected. Only for colloids does surface energy constitute an appreciable fraction of the total energy.

The surface energy is usually expressed as ergs per cm^2 surface. The order of magnitude of the surface energy of a number of crystalline substances is 1,000 $ergs/cm^2$. If the specific surface area of a substance of this sort is 4 m^2/g, its surface energy is 1 cal/g. In most calorimetric work, the experimental error is far greater than 1 cal/g.

As was shown before, tobermorites prepared at room temperatures have large specific surfaces; so S can not be neglected. Furthermore, the specific surface areas are variable. The consequence of this is that the term "heat of hydration of C_3S" is indefinite, unless one specifies the surface area of the tobermorite (*G*) produced in the hydration.

The C_3S and C_2S used in this laboratory were very finely ground, with an average particle size of the order 10μ. Even so, the surfaces of C_3S and C_2S can be neglected without introducing an appreciable error. The specific surface area of tobermorite (*G*) is about 1,000 times greater than that of C_3S or C_2S. The surface area of the $Ca(OH)_2$ produced in the reaction can also be neglected. In the paste and the bottle hydration of C_3S and C_2S, $Ca(OH)_2$ separates out as large particles, some of which are even visible to the naked eye. Only in the ball-mill hydration of C_2S does $Ca(OH)_2$ acquire a sizable specific surface, but even there it contributes only about 2 percent of the surface of the hydration products [51].

Thus, in the hydration of the two calcium silicates, specification of the surface area of tobermorite is sufficient to define the energetics of the reaction. The specific surface area of tobermorite defines S and $H_{\mathrm{H_2O}}$ in eq (16).

In a reaction like that of silica gel with $Ca(OH)_2$, the situation is more complicated. Silica gels usually have even larger specific surface areas than tobermorites; so the specific surface area of the silica gel must also be specified.

3. The surface energy of tobermorite (*G*), with composition $Ca_3Si_2O_7 \cdot 2H_2O$, was determined by Brunauer, Kantro, and Weise [51], and it was found to be 386 ± 20 $ergs/cm^2$ at 23.5 °C. For a tobermorite of specific surface area of 300 m^2/g, the surface energy amounts to 27.7 cal/g. If one compares this with the heats of hydration of C_3S and C_2S given earlier, one realizes the magnitude of the surface energy contribution.

In earlier work in this laboratory, the surface energies of $Ca(OH)_2$ [54] and of hydrous amorphous silica [55] were found to be 1,180 and 129 $ergs/cm^2$, respectively. The surface energy of tobermorite (*G*) is very close to the geometric mean of these values. This was expected for two reasons: tobermorite (*G*) is chemically intermediate between $Ca(OH)_2$ and hydrous silica, and it is also intermediate structurally. The $Ca(OH)_2$ used in the experiments consisted of nearly perfect crystals, the hydrous silica was completely amorphous, and tobermorite (*G*) was very poorly crystallized.

In figure 3, the heat of solution of $Ca_3Si_2O_7 \cdot 2H_2O$ is plotted against the specific surface area of the tobermorite. The 14 points represent 14 preparations, 7 obtained from the hydration of C_3S and 7 from the hydration of C_2S. (The method of preparation is shown in table 5.) The slope of the straight line in figure 3 is the surface energy expressed in cal/m^2.

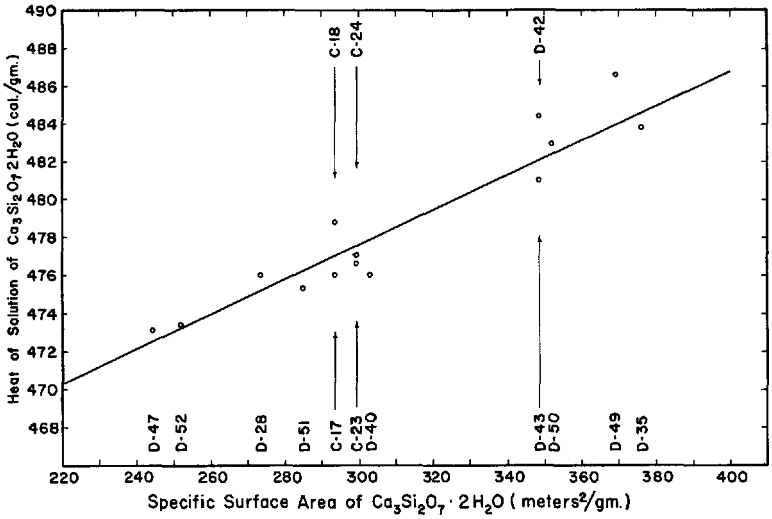

FIGURE 3. *Variation of the heat of solution of* $Ca_3Si_2O_7 \cdot 2H_2O$ *with specific surface area for 1.0-g samples.*

In the same investigations, the heat of the reaction

$$Ca_3Si_2O_7 \cdot 2H_2O(s) + H_2O(l) = Ca_3Si_2O_7 \cdot 3H_2O(s) \quad (17)$$

was also determined. It was found to be −7,600 cal at 23.5 °C. The surface energy of $Ca_3Si_2O_7 \cdot 3H_2O$ was not determined, because of experimental difficulties, but it was estimated to be close to that of $Ca_3Si_2O_7 \cdot 2H_2O$.

4. Using the heats of solution obtained for the above 14 preparations, the heats of hydration of C_3S and C_2S were calculated.

The tobermorites in 12 of the 14 preparations had CaO/SiO_2 ratios of 1.5, within the experimental error. The two exceptions were the two C_2S pastes, C–23 and C–24, in table 5, which had CaO/SiO_2 ratios of 1.65.

For the 7 C_3S preparations the heats of hydration were first calculated on the basis of the equation

$$2Ca_3SiO_5 + 5H_2O = Ca_3Si_2O_7 \cdot 2H_2O + 3Ca(OH)_2 \quad (18)$$

and for the 5 C_2S preparations, with tobermorites of CaO/SiO_2 ratio 1.5, on the basis of the equation

$$2Ca_2SiO_4 + 3H_2O = Ca_3Si_2O_7 \cdot 2H_2O + Ca(OH)_2. \quad (19)$$

All of the tobermorites contained more than two molecules of water per molecule; consequently, corrections were made by using the enthalpy change in eq (17), 420 cal/g of water. The tobermorites also had different specific surface areas but, using the surface energy given before, they were all corrected to a specific surface area of 300 m²/g. The heats of hydrations thus obtained are shown in table 5.

TABLE 5. *Heats of hydration of* C_3S *and* C_2S

For reactions shown in equations 18, 19, and 20.

C_3S designation	Method of hydration	Heat of hydration, cal/g C_3S	C_2S designation	Method of hydration	Heat of hydration, cal/g C_2S
C–17	Paste	77.5	C–23	Paste	7.7
C–18	Paste	76.0	C–24	Paste	7.5
D–35	Bottle	78.7	D–40	Bottle	8.8
D–42	Bottle	76.4	D–28	Ball mill	7.8
D–43	Bottle	78.5	D–47	Ball mill	6.9
D–49	Bottle	76.0	D–51	Ball mill	8.3
D–50	Bottle	77.5	D–52	Ball mill	8.4

For the two C_2S pastes the equation was

$$2Ca_2SiO_4 + 3H_2O = Ca_{3.30}Si_2O_{7.30} \cdot 2.30H_2O + 0.7Ca(OH)_2 \quad (20)$$

Corrections were made for specific surface area and for excess water in C–24, and the results are also shown in table 5.

It will be noted that the heat contents of the hydration products of C_3S are about the same, regardless of the method of preparation. The same is true for C_2S. More accurate determinations in the future may reveal differences, but for the time being the results may be averaged. The average heat of hydration for the C_3S preparations in table 5 is 77.2 cal/g C_3S, and for the C_2S preparations, 7.9 cal/g C_2S.

To obtain the heat of hydration for the reaction represented by eq (3), the enthalpy changes in the reactions shown in eqs (17) and (18) must be combined. The result is −42,850 cal at 23.5 °C, or 93.8 cal/g C_3S. A similar calculation for the heat of hydration of the reaction shown in eq (4) leads to a value of −10,320 cal at 23.5 °C, or 30.0 cal/g C_2S. These are the chemical heats of hydration of C_3S and C_2S, H_c-S in eq (16), when the tobermorite produced in the hydration has a specific surface area of 300 m^2/g. For a tobermorite with a different specific surface, correction can be made by using the surface energy of 386 $ergs/cm^2$.

5. No investigations were made to determine the heat of adsorption of water on the tobermorite surface, H_{H_2O}. A rough estimate can be made by comparing the H_c-S values with the H_0 values of Lerch and Bogue [67], given earlier. Their H_0 value for C_2S was 62 cal/g; subtracting 30.0 cal/g gives 32 cal/g C_2S for H_{H_2O}. A similar calculation for C_3S gives 26.2 cal/g C_3S for H_{H_2O}.

Comparison of eqs (3) and (4) shows that 1 g of C_2S gives 32.5 percent more tobermorite (G) than 1 g of C_3S. Thus, using 32 cal/g C_2S for H_{H_2O}, calculation would give 24.2 cal/g C_3S. The 2.0 cal/g C_3S difference between this and the value calculated above is well within the errors of the two sets of experiments.

The specific surface areas of the hydration products of C_3S and C_2S were not measured in the experiments of Lerch and Bogue. It is unlikely that the specific surface areas of their tobermorites were equal. If the tobermorite (G) in their hydrated C_3S had about 20 m^2/g greater specific surface than that in their hydrated C_2S, the 2-cal difference would be accounted for. It was shown before that the range of variation in the specific surface area of tobermorite (G) is about 6 times greater than this difference. Figure 3 indicates that the specific surface areas obtained in the hydration of C_2S tend to be smaller than those obtained in the hydration of C_3S.

Free Energies and Entropies of Hydration

1. No experimental determinations of the specific heats of tobermorite (G) have been made to date; consequently, the entropy change and the free energy change in the reactions represented by eqs (3) and (4) can not be accurately calculated. The best one can do at present is to make an educated guess at these quantities.

The difference between the free energies of hydration of C_3S and C_2S can be fairly accurately calculated.

It follows from eqs (3) and (4) that

$$2\Delta F_{C_3S}=F_T+3F_{Ca(OH)_2}-2F_{C_3S}-6F_{H_2O} \qquad (21)$$

and

$$2\Delta F_{C_2S}=F_T+F_{Ca(OH)_2}-2F_{C_2S}-4F_{H_2O} \qquad (22)$$

where ΔF_{C_3S} and ΔF_{C_2S} are the free energies of hydration of C_3S and C_2S per mole of C_3S and C_2S, respectively; and F_T, $F_{Ca(OH)_2}$, F_{C_3S}, F_{C_2S}, and F_{H_2O} are the free energies of formation of tobermorite (G), $Ca(OH)_2$, C_3S, C_2S, and H_2O, respectively. The difference is given by

$$\Delta F_{C_3S}-\Delta F_{C_2S}=F_{Ca(OH)_2}+F_{C_2S}-F_{C_3S}-F_{H_2O}. \qquad (23)$$

The values of $F_{Ca(OH)_2}$ and F_{H_2O} are -214.33 and -56.69 kcal, respectively [70], and those of F_{C_2S} and F_{C_3S} are -516.6 and -657.8 kcal, respectively. The last two values were calculated by using the heats of formation of C_2S and C_3S given by Barany, King, and Todd [71] and the entropy values of Todd [10]. The difference $\Delta F_{C_3S}-\Delta F_{C_2S}$ is -16.4 kcal. If one uses the value obtained by Brunauer, Kantro, and Weise [3] for the heat of decomposition of C_3S into C_2S and CaO, instead of King's value [9], $\Delta F_{C_3S}-\Delta F_{C_2S}$ becomes -15.3 kcal.

2. The entropies of $Ca(OH)_2$ and H_2O at 25 °C are 18.2 and 16.72 e.u., respectively [70], and the entropies of C_3S and C_2S are 40.3 and 30.5 e.u., respectively [10]. The entropy change in the hydration of C_3S and C_2S could be calculated, if the entropy of $Ca_3Si_2O_7 \cdot 3H_2O$ were known.

The entropy of tobermorite (G) can be estimated in the manner Latimer [72] estimates entropies. The entropies of CaO, SiO_2, hydroxylic water, and interlayer water in the tobermorite are estimated to be 9.8, 13.8, 8.7, and 10.4 e.u. per mole, respectively. These values lead to an estimate of 84.8 e.u. for $Ca_3Si_2O_7 \cdot 3H_2O$. To this, one may add 3.3 e.u. to account for the surface entropy of a tobermorite with a specific surface area of 300 m^2/g, and the figure may be rounded out to 90 e.u., to account for the low order of crystallinity of tobermorite (G). The estimate is probably good within ±5 e.u.

The entropy change in the reaction represented by eq (3), calculated from the above data, is -36.3 e.u., and that in the reaction represented by eq (4) is -19.7 e.u. It will be recalled that the equations refer to the hydration of two moles of C_3S and C_2S.

3. Using the ΔH values reported earlier, $-42{,}850$ cal for $2C_3S$ and $-10{,}320$ cal for $2C_2S$, the free-energy change in the hydration of $2C_3S$ at 23.5 °C is $-32{,}000$ cal, and in the hydration of $2C_2S$, $-4{,}400$ cal. The difference between ΔF_{C_3S} and ΔF_{C_2S} per mole is -13.8 kcal. This is to be compared with the more accurate value of -15.3 kcal, reported before. The agreement is not spectacular, but it is the best that the present authors can do with available data.

Rates and Mechanisms of Hydration

Rates of Hydration of C_3S and β-C_2S in Paste Form

1. Although there are sizable gaps in our understanding of the changes in matter and energy that occur in the hydration of C_3S and β-C_2S, there has been a steady and significant progress since 1952, the year of the Third International Symposium on the Chemistry of Cement. The situation is far less satisfactory in our understanding of the rates

and mechanisms of the hydration of C_3S and C_2S. Not enough work has been done, the results of different investigators do not agree, and few have attempted to interpret even their own results. A systematic and thoroughgoing investigation has been started in this laboratory, but the results will be available only in the future.

To be sure, the problem is not simple. The question immediately arises, how to measure the rate? The one direct method is to measure the amount of unhydrated C_3S or C_2S remaining in the system after various times by means of X-ray quantitative analysis, but only van Bemst [27, 28] and Kantro, Brunauer, and Weise [15] have used this method so far. The latter investigators used it in their study of the ball-mill hydration of C_3S. Van Bemst used the method extensively in studying what is called the "bottle" hydration of C_3S and C_2S in this paper, in which he employed a very large excess of water. By far the most important method of hydration is paste hydration, and the rates of hydration of C_3S and C_2S in the ball mill or in a bottle supply no information about the rates of paste hydration. Van Bemst published a few data on the paste hydration of C_3S [27]; these are the only rate data in the literature of paste hydration obtained by the direct method.

Other investigators have used indirect methods, such as the determination of the water of hydration, of the $Ca(OH)_2$ produced in the reaction, or of the heat evolved in the reaction. These methods would supply reliable information about the rate of disappearance of C_3S or C_2S only if the hydration products were the same throughout the entire reaction. It is easy to see, however, that the products in the early stages of the reaction may be different from those in the later stages. Reaction probably occurs both by direct contact of the surfaces of the anhydrous grains with water and by precipitation out of solution. The products of these reactions may be different, as van Bemst believes they are [28]. In different stages of the reaction, the relative amounts of the products forming by the two mechanisms may be different.

In the early stages, intermediate products may form on the surfaces of the grains, which differ in composition from the final products. Similarly, in the early stages, prior to the establishment of lime saturation in the solution, the tobermorite precipitating out of the solution may have a lower CaO/SiO_2 ratio than later. A C_2S paste, which hydrated for one day in this laboratory, had a CaO/SiO_2 ratio of 1.15 in the tobermorite. Lime saturation was established in much less than one day, but the tobermorite had not enough time to convert to the equilibrium product. The same C_2S hydrating for 17 months had a CaO/SiO_2 ratio of 1.65 in the tobermorite, as was shown earlier.

It is possible that changes in the hydration products may occur not merely for hours or days, but for months. Bogue and Lerch [49] found, for example, that microscopical examination of a C_3S paste hydrated for three months revealed complete absence of unhydrated C_3S grains, whereas the water of hydration indicated only about 80 percent hydration.

Practically all data in the literature on the rates of paste hydration of C_3S and C_2S were obtained by indirect methods. The foregoing considerations show that these data cannot be directly equated with the rate of hydration of C_3S or C_2S. When, at a certain age of paste, 30 percent of the ultimate amount of $Ca(OH)_2$ is liberated, it is possible that only 15 percent of the C_3S has reacted. On the other hand, it is also clear that a knowledge of the percentage hydration of C_3S by itself is not enough. Only if the unreacted C_3S, the water of hydration, the $Ca(OH)_2$, and the heat evolved at each stage of hydration are determined, can one acquire a real understanding of the process of hydration.

2. Ershov [73] summarized a part of the rate data in the literature by stating that C_3S hydrates to the extent of 15 to 20 percent in 1 day, 35 to 50 percent in 3 days, 45 to 70 percent in 7 days, 68 to 75 percent in 1 mo, and 85 to 94 percent in 6 mo; β-C_2S hydrates to the extent of 4 to 7 percent in 3 days, 8 to 10 percent in 7 days, 11 to 12 percent in 1 mo and up to 30 percent in 6 mo. Actually, the range of variation is far greater than these figures indicate. For example, the results of Bogue and Lerch [49] indicate 45 percent hydration of C_3S in 1 day, and the results of Knoblauch [74] indicate 86 percent hydration of C_2S in 4 mo.

Ershov did not attempt to analyze the causes of variation. Variations in the actual rates arise from different methods of preparation of the silicates, from differences in the fineness of grinding, differences in water/solid ratio employed and differences in the temperature of hydration. Variation in the results arise also from the different methods used for rate determination.

The effect of particle size on the rates of hydration was investigated by Anderegg and Hubbell [75]. For fractions with mean dimensions of 19, 22, and 25 μ for C_3S, and 18 and 22 μ for C_2S, the results indicated no difference in the rates of hydration, within their experimental error, from 3 hr to 28 days. Sloane, McCaughey, Foster, and Shreve [76] found no difference in the rates of hydration of three fractions of C_3S: 65 to 100 mesh, 100 to 200 mesh, and 200 to 300 mesh. In both sets of investigations, microscopical examination of the hydration products was used to determine the extent of hydration. In contrast with these results, Steinour [77] found a strong dependence of the rate of hydration of C_2S on particle size. A less than twofold increase in the specific surface led to a roughly twofold increase in the water of hydration at ages up to 42 days.

The most extensive work on the effect of water/solid ratio was done by Work and Lasseter [78]. Whereas most investigators used a single water/solid ratio, usually 0.50, or at best a narrow range, these investigators used a range from 0.06 to 1.00. They determined the rates by measuring the water of hydration and the $Ca(OH)_2$ evolved in the reaction. The rates of hydration of C_3S and C_2S increase markedly with water/solid ratio in the range of low water/solid ratios, but the increase is slight from 0.45 up. For 3-months-old C_3S pastes, they reported water of hydration values of 18.2, 19.0, and 20.4 percent for water/C_3S ratios of 0.45, 0.60, and 1.00, respectively. In this laboratory, for 72-days-old pastes, water of hydration values of 18.2, 19.0, and 19.3 percent were obtained for water/C_3S ratios of 0.45, 0.57, and 0.70, respectively.

The most extensive data on the effect of temperature were obtained by Schwiete and by Knoblauch [74, 79]. They found a slight increase in the rate of hydration of both C_3S and C_2S with increasing temperature from 20 to 65 °C. They calculated from their rate data energies of activation of 2.1 kcal for C_3S and 1.8 kcal for C_2S. Though these calculations are open to question, as will be seen later, there is no question about the positive temperature dependence of the rates of hydration. Schwiete and Knoblauch used a new method for the rate determinations, dynamic differential calorimetry.

Some data of van Bemst [27] indicate a slight negative temperature coefficient between 4 and 40 °C. For a C_3S paste, with water/solid ratio of 0.5, he obtained 52 and 65 percent hydration after 7 and 28 days at 4 °C, but only 40 and 47 percent hydration after the same periods at 40 °C. He measured the C_3S remaining by means of X-ray quantitative analysis.

From the foregoing, it seems probable that the large variations in the rates of hydration, pointed out earlier, are caused by differences in the methods of preparation of C_3S and C_2S. The nature of the raw materials used, the temperature of burning, the rate of cooling of the burn and, in the case of β-C_2S, the nature and the amount of stabilizer used, may have important effects on the rates of hydration. The effect of stabilizer was extensively investigated by Funk [30]. Steinour [77] investigated all of these effects for the rate of strength development of C_2S. He found that low temperature of burning and quick quenching were especially important in producing rapid strength development.

3. Among the data in the literature, probably those of Bogue and Lerch [49] and Work and Lasseter [78] illustrate the courses of the reactions best. They measured the rates by means of the water of hydration and the $Ca(OH)_2$ produced, but the results of Bogue and Lerch for $Ca(OH)_2$ are not reliable because they heated the hydration products to about 530 °C prior to the lime determination. It was found in this laboratory that such a heating resulted in a reaction between the lime and tobermorite (*G*). The fact that the free lime at complete hydration of C_3S indicated a CaO/SiO_2 ratio of 2.2 in the tobermorite of Bogue and Lerch is a clear evidence that free lime was removed from the products by heating prior to determination. Strangely enough, Work and Lasseter obtained the same values for free lime whether they heated the hydration products or not. This is another example that shows the complexity of the system. The free-lime values they obtained for C_3S after 6 mo of hydration indicated a tobermorite with CaO/SiO_2 ratio of 1.6, or somewhat less.

The "fixed water" of Bogue and Lerch for completely hydrated C_3S agrees well with the water of hydration obtained in this laboratory by (*D*)-drying. The 1-yr-old C_3S paste, with a water/C_3S ratio of 0.50, appears to be completely hydrated. If one uses the water of hydration as a measure of the percentage hydration, one obtains the values shown in table 6, row 1. In curve 1 of figure 4, the percentage hydration is plotted against the logarithm of time in days. The logarithmic scale is used just to be able to represent the data clearly from 1 day to 2 yr. The data of Bogue and Lerch indicate practically no hydration between 28 days

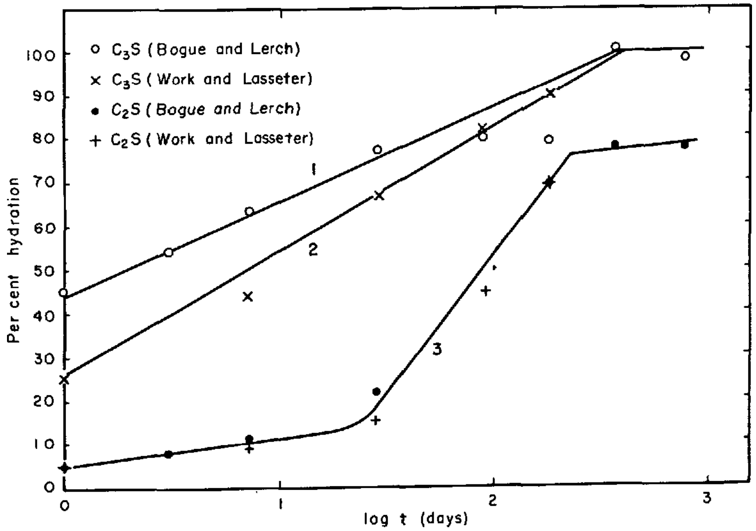

FIGURE 4. *Rates of hydration of* C_3S *and* C_2S.

TABLE 6. *Rates of hydration of* C_3S *and* β–C_2S

Water/solid ratio=0.50

	Substance	Investigators	Method of determination	Hydration, percent							
				1 day	3 days	7 days	28 days	3 mo.	6 mo.	1 yr	2 yr
1	C_3S	Bogue and Lerch	Water of hydration	45.3	54.2	63.2	76.8	80.0	78.9	100.0	97.9
2	C_3S	Bogue and Lerch	Strength	12.8	24.8	52.7	62.8	62.8	85.8	91.2	100.0
3	C_3S	Work and Lasseter	Water of hydration	24.2	----------	40.6	58.3	72.7	(90.0)	----------	----------
4	C_3S	Work and Lasseter	Calcium hydroxide	27.6	----------	47.8	75.8	90.0	(90.0)	----------	----------
5	β-C_2S	Bogue and Lerch	Water of hydration	5.0	7.7	10.8	21.6	56.6	68.8	(77.7)	77.0
6	β-C_2S	Bogue and Lerch	Strength	0.0	0.4	1.0	6.3	36.0	52.7	71.4	100.0
7	β-C_2S	Work and Lasseter	Water of hydration	5.3	----------	9.4	15.2	44.0	(68.8)	----------	----------

and 6 mo. Since no other data in the literature indicate such behavior, the curve was drawn by disregarding the 6-mo point. The 3-mo point is also somewhat too low.

Work and Lasseter obtained data only up to 6 mo. If it is assumed that their C_3S paste was 90 percent hydrated at that time, one obtains the percentage hydration values shown in table 6, rows 3 and 4. The first is based on water of hydration, the second on free $Ca(OH)_2$. It was shown above that the $Ca(OH)_2$ values of Work and Lasseter were fairly reliable. They did not use a water/C_3S ratio of 0.50, but interpolation between their ratios of 0.45 and 0.60 gave values for the ratio 0.50.

Plotting the average of the values shown in rows 3 and 4, table 6, gives curve 2 of figure 4. There are two notable differences between curves 1 and 2. The C_3S of Bogue and Lerch was 45 percent hydrated in 1 day; that of Work and Lasseter was only 26 percent hydrated. Both of these values are in agreement with values obtained by other investigators. A value of 41 percent hydration in 1 day was obtained by van Bemst [27] for one of his C_3S pastes, using X-ray analysis to determine the unhydrated C_3S. A value of 28 percent was obtained in this laboratory for a 1-day-old C_3S paste, using water of hydration and $Ca(OH)_2$ to measure the rate.

The second difference is that the C_3S of Work and Lasseter hydrates faster after 1 day than the C_3S of Bogue and Lerch. It is not certain that the former catches up with the latter in 1 yr—this is based on the somewhat uncertain assumption that the percentage hydration of the former was 90 percent in 6 mo. It is certain, however, that the slope of curve 2 is greater than that of curve 1.

4. The β–C_2S paste of Bogue and Lerch, likewise with water/solid ratio of 0.50, did not reach complete hydration in 2 yr. The extent of hydration after 1 yr was calculated on the basis of eq (19) of the present paper to be 77.7 percent, and the values in table 6, row 5, for other ages are based on this figure. It was assumed that the C_2S of Work and Lasseter, after 6 mo, was hydrated to the same extent as that of Bogue and Lerch, 68.8 percent, and the values in table 6, row 7, for other ages are based on this figure. As curve 3 of figure 4 shows, both sets of data can be represented by one curve.

It appears from the curves of figure 4 that the course of the hydration of C_2S is very different from that of C_3S. The initial hydration of C_2S is much slower; there is only 5 percent hydration in 1 day and 10 percent hydration in 7 days. The hydration appears to stop after about 1 yr, when about ¼ of the C_2S is still unhydrated. The most remarkable difference is in the time range from 3 days to 3 mo. In this period, the rate of hydration of C_3S diminishes strongly, whereas the rate of hydration of C_2S does not diminish at all.

In fact, both the data of Bogue and Lerch and those of Work and Lasseter indicate an increase in the rate of hydration of C_2S; the former a small increase, the latter a considerable increase. The average rates from the two sets of data are 0.40 percent C_2S per day from 7 to 28 days, and 0.51 percent C_2S per day from 28 days to 3 mo. Such an increase in rate is not unknown in reaction kinetics, and it is usually attributed to a catalytic effect of a hydration product.

The increase in rate appears to come about when 15 to 20 percent of the C_2S is hydrated. If a similar autocatalysis operates in the hydration of C_3S, it should occur in the course of the first day of hydration. Forbrich [80] actually found such an increase in rate for C_3S. Using a conduction calorimeter to measure the heat evolved, he obtained an initial heat evolution of about 1 cal/g C_3S per hour. The rate was still about the same after 4 hr, but then it began to climb, and it reached a maximum of about 3 cal/g C_3S per hour in 9 hr. The evolution of 1 cal/g C_3S corresponds to a hydration of about 0.8 percent.

As far as one can judge from the curves of Schwiete and Knoblauch [74, 79], their C_2S did not exhibit any autocatalysis.

5. Bogue and Lerch determined the compressive strengths of their hydrated C_3S and C_2S pastes. The strengths kept on increasing steadily from 1 day to 2 yr. Taking the compressive strength values at 2 yr as 100 percent, the percentages of the ultimate strength developed at different ages are shown in table 6, rows 2 and 6. The strength lags considerably behind the extent of hydration in the first 3 days for C_3S and in the first 3 mo for C_2S. Only when the hydration is about two-thirds complete, in 7 days for C_3S and in 6 mo for C_2S, does the percentage of the ultimate strength approach the percentage hydration. The

strength keeps on increasing after hydration stops; the increase between 1 and 2 yr is almost 10 percent for C_3S and about 40 percent for C_2S.

Steinour's results [77] for the early hydration and strength development of C_2S show that strength development lags behind extent of hydration up to 28 days, both for high and low surface C_2S.

Bernal, Jeffery, and Taylor [7] examined qualitatively, by means of X-rays, the hydration products of C_3S, and compared their results with the strength data of Bogue and Lerch. They came to the conclusion "that only a small amount of hydrate is needed in order to cement together the grains of the unchanged anhydrous compounds, and of the aggregate also, when this is present. Further reaction does not lead to any increase in strength and, indeed, could conceivably cause a decrease." The data of Bogue and Lerch, as well as those of Steinour, show that this conclusion is not correct.

The strength developed by a C_3S or C_2S paste at a given age shows as much variation from investigator to investigator as the extent of hydration, if not more. Ershov [73] finds, for example, that the ratio of the strength of C_3S to that of C_2S is "approximately 50 for specimens at the age of 3 days and about 5 for specimens aged 1 year." The results of Bogue and Lerch indicate that the ratio is about 50 at 3 days, but 1 rather than 5 at 1 yr. Ershov gives the ratios of the strengths at 28 days to those at 3 days the values 2 for C_3S and 6.7 for C_2S, whereas the values of Bogue and Lerch are 2.5 and 15, respectively.

Steinour's data [77] show especially well the magnitude of the effects of methods of preparation and fineness of grinding of C_2S on strength. Using a water/C_2S ratio of 0.40, he obtained compressive strengths ranging from 320 to 1,560 psi after 7 days, from 880 to 4,350 psi after 28 days, and from 2,270 to 11,250 psi after 6 mo.

Funk [30] hydrated C_2S with water vapor at 100 °C, and obtained a powder without any strength. He stated, "Electron micrographs show, in conformance with the loose structure of the preparations that water vapor action produces only loosely piled, acicular fibrous units. According to this, the high-lime tobermorite-like phase is not necessarily formed out of the solution phase. However, the aqueous solution phase must be present if hardening of the mass is to be produced."

Hydration in Excess Water

1. The most extensive data on the rates of hydration of C_3S with a large excess of water were obtained by van Bemst [28]. The ratio of water to silicate ranged from about 100 upward; in certain experiments saturated $Ca(OH)_2$ solution was used instead of water. The hydration was performed in polyethylene containers, constantly agitated in a thermostat. Temperatures of 25, 40, and 60 °C were employed. This method of hydration is similar to the "bottle" hydration used in this laboratory and described earlier in the present paper.

The course of the hydration of C_3S as observed by van Bemst may be summarized as follows. The silicate rapidly dissolves in water, and hydrate I, a low-lime tobermorite, is precipitated out of the solution. The CaO/SiO_2 ratio in the tobermorite is, presumably, the one that corresponds to the lime concentration in the solution according to figure 1 of the present paper; prior to lime saturation it is always less than 1.5. As the lime concentration in the solution increases, the solubility of C_3S diminishes, which results in a diminishing rate of hydration.

If at the time when saturation is reached the C_3S is less than half hydrated, the hydration virtually stops. There may be 30 or 40 percent unhydrated C_3S in the system, the solution may even be supersaturated with respect to $Ca(OH)_2$, and still there is no appreciable hydration between 28 and 56 days.

When the concentration exceeds 0.020 mole of CaO per liter, which corresponds to lime saturation at 25° and supersaturation at 40 °C, hydrate II appears as the hydration product of C_3S. At 60 °C this concentration was not reached in van Bemst's experiments, and only hydrate I was obtained. Van Bemst identified his hydrate II with Taylor's $C_2SH(II)$, and this is probably correct. It was shown earlier in this paper that the bottle hydration of C_2S in this laboratory resulted in a product that appeared to be identical with Taylor's $C_2SH(II)$.

When the hydration product is hydrate II, the rate is faster if less water is present. At a given temperature, the rate is fastest in a saturated lime solution. When water is used, lime saturation is reached faster if the amount of water is smaller; consequently, the rate is faster. Van Bemst concluded that the hydration was the fastest in the paste form, because of the very low water content.

Funk [30], investigating the hydration of C_2S at higher temperatures, also came to the conclusion that increasing the quantity of water diminished the rate. At 100 °C, with a water/C_2S ratio of 3, he obtained about 50 percent hydration in 10 days, and no appreciable further hydration took place in the next 20 to 30 days. On the other hand, with a water C_2S ratio of 0.5, complete hydration was obtained in 4 to 15 days.

In contrast with van Bemst and Funk, Brunauer, Kantro, and Copeland [14] found that bottle hydration, with a water/solid ratio of 9, was much faster than paste hydration, with a water/solid ratio of 0.7. Table 1 of the present paper shows that bottle-hydrated C_2S, D–40, reached the same extent of hydration in 162 days as paste-hydrated C_2S, C–23, did in 17 mo. Bottle-hydrated C_3S preparations reached 97 percent hydration in 48 days, whereas it takes more than 6 mo to reach that stage in the paste form.

Both van Bemst and Funk found that the rate of hydration increased with increasing temperature.

Van Bemst has advanced the hypothesis that hydrate I forms by precipitation out of solution, but hydrate II forms by reaction of the silicate surface with water. This may well be true, but further experiments are needed to test the hypothesis, as well as to explain the discrepancies in the experimental results discussed above.

2. The rate of hydration of C_3S in a small steel ball mill with a water/C_3S ratio of 9, was investigated by Kantro, Brunauer, and Weise [15]. Whereas the hydration of C_2S in the ball mill produces tobermorite (*G*) [14], the ultimate product of hydration of C_3S in the ball mill is afwillite [13].

The investigators used X-ray quantitative analysis to determine the amounts of C_3S and afwillite in the reacting system. In about 31 hr, the C_3S disappeared completely, but there was only about half as much afwillite produced as eq (3) of the present paper would indicate. The reason for this was that an intermediate compound formed first, which the investigators called hydrate III. It took about 25 days until the unstable hydrate III converted completely to afwillite.

The rate of disappearance of C_3S was found to be proportional to the surface area of the grains exposed to the steel balls. This indicated that hydrate III formed on the surfaces of the grains, and the rate determining step was the removal of the coating from the grains. The conversion of hydrate III to afwillite did not begin immediately upon the appearance of the former in the system. There was an induction period of about 6 hr which indicated an autocatalytic mechanism, i.e., a rate dependent on the concentrations of both afwillite and hydrate III.

The properties of hydrate III were found to be very similar to those of tobermorite (*G*) with respect to CaO/SiO_2 ratio, water content, heat of solution, heat of hydration, specific surface area, and surface energy. They differ only in two respects. Hydrate III shows only one very broad X-ray diffraction line, that corresponding to the strongest line of tobermorite (*G*), at about 3 A, whereas tobermorite (*G*) shows three diffraction lines. Hydrate III is unstable and converts to afwillite, whereas tobermorite (*G*) does not. A mixture of 50 percent C_2S and 50 percent C_3S by weight was completely hydrated in the ball mill. No X-ray quantitative analysis was performed on the hydration products, but inspection of the diffraction patterns indicated that tobermorite (*G*) and afwillite were present in the proportion corresponding to independent hydration of C_2S and C_3S.

Hydrate III appears to be a form of tobermorite with a structure so disordered that it exhibits only a single X-ray diffraction line. Just why it converts to afwillite rather than to a better crystallized tobermorite is not known at present.

Mechanisms of Hydration

1. When C_3S or C_2S is brought in contact with water, reaction may occur at the surfaces of the grains or in the solution phase. The surface of C_2S consists of Ca^{++} ions and SiO_4^{4-} groups, that of C_3S consists of these plus $O^{=}$ ions. These ions enter the solution as aqueous Ca^{++}, OH^- and hydrosilicate ions. When 0.25 g of C_3S was dissolved in 1 liter of water with vigorous stirring, in this laboratory, the electrical conductivity corresponded to the concentrations and mobilities of the Ca^{++}, OH^-, $H_3SiO_4^-$ and $H_2SiO_4^=$ ions for congruent solutions. Under other conditions, however, the different ions may dissolve at different rates.

In the solution mechanism, the hydrated ions form at the surface, diffuse away from the surface, react with each other to form tobermorite molecules, the molecules form nuclei, the nuclei grow, colloidal particles precipitate and flocculate. Practically nothing is known about the rates of these individual steps in the reaction.

Tobermorite may form directly on the surfaces of the silicate grains and may stay there. The hydrated grain surfaces may also serve as nuclei for the precipitation of tobermorite out of solution. In either case, a tobermorite gel coating would form on the surface, and the coating would grow in thickness with time. Whether further reaction proceeds on the surface or in solution, water and the ions must diffuse through this gel layer prior to reaction. Again, very little is known about the rates of the individual steps in this mechanism.

$Ca(OH)_2$ separates out of the solution as relatively large particles. These particles are overlaid by tobermorite gel and, not infrequently, they grow around and occlude tobermorite gel. When hydration is observed in a microscope, gel appears to form on the surfaces of the slide and the cover glass, at considerable distances from the grains. Such evidence shows clearly that a part of the tobermorite forms by precipitation from solution. On the other hand, hydration can also take place without the presence of liquid water. Funk [30] hydrated C_2S by water vapor at 100 °C and, in this laboratory, C_3S was hydrated by water vapor at room temperature. In these experiments, probably, the surface reaction mechanism is operative.

Not much is known about the relative importance of the two mechanisms in various stages of the reactions between the silicates and water. It is generally believed that, in the later stages of paste hydration, diffusion through the gel layer becomes the rate-controlling step, but it is not known when these stages are reached by C_3S and C_2S under different experimental conditions.

2. Le Chatelier [81] was the first to advance the solution and precipitation mechanism. Baikov [82] distinguished three steps in the hydration process. The first is the solution step, during which water becomes progressively saturated. The second is the "colloidization" step, during

which precipitation of colloidal particles takes place. This corresponds to the beginning of the setting process. The third is the "crystallization" step, during which the gels are transformed into crystalline aggregates. This is the period of hardening.

Though both Le Chatelier and Baikov advanced their hypotheses for the hydration of cements, subsequent investigators applied them to the hydration of calcium silicates as well. This is natural, since C_3S and portland cement are quite similar in their setting and hardening characteristics.

The Soviet investigators have adopted the Baikov hypothesis with various modifications and additions. A modern version of it is described by Rehbinder [83], who, on the basis of his own work and that of his coworkers, also distinguishes three stages in the hydration process. He states that "setting and hardening represent a complex of hydration processes developing in time, of a self-induced dispersion of cement particles (minerals of cement clinker), of a formation of coagulated thixotropic structures, and of the development on these as a base of a crystalline structure of new hydrated formations through crystallization out of a supersaturated water solution." These processes occur most rapidly in the hydration of C_3A, next comes C_4AF, then C_3S, and finally C_2S.

The first step in the hydration of C_3S or C_2S, accordingly, is the breaking up of the coarse grains into particles of colloidal dimensions. The grains have micro-cracks and other types of defects, and water and various ions, penetrating into the cracks and the weak spots of the lattice, produce dispersion. The surfaces of the dispersed colloidal particles are covered with hydration products. Rehbinder states, "The presence of a highly dispersed colloidal fraction appears, in this manner, as a necessary condition of the thixotropy of a coagulated structure." He identifies the setting process with the formation of a coagulating structure, which hardens reversibly, i.e., thixotropically.

The presence of the dispersed silicate particles and of the hydration products, which are very small, brings about a supersaturation of the solution. "A crystallization of new formations out of the supersaturated solution takes place as a result of the appearance and growth of surface nuclei of crystallization." Thus, on the coagulated structure as a base, at first a more or less open crystalline structure of the hydration products develops; however, as time passes, the crystalline structure becomes denser by the addition of further products of hydration. At this stage, the hydration progresses more slowly, because the unhydrated cores of the colloidal particles are covered by hydration products. This is the process of hardening which, in contrast with the setting process, develops an irreversible and much stronger crystalline structure.

The present authors are acquainted only with a small fraction of the literature on which the above conclusions of Rehbinder are based. Because of the shortness of time available for the writing of this paper and because the authors, unfortunately, do not read Russian, they have been handicapped in reporting the Soviet literature on the hydration of C_3S and C_2S. They hope that some of their Soviet colleagues will make up for this deficiency by attaching discussions or supplementary papers to the present paper. With respect to the above mechanism of hydration, they wish to make three comments, and they hope that Professor Rehbinder or one of his colleagues will clarify these points.

(a) In the paper cited [83], experiments are described showing that the surface of hydrating C_3A increases twenty-fold in the first 30–40 minutes. The present authors do not see that this reveals anything about the self-induced dispersion of C_3A particles; the growth of surface may be caused entirely by the larger specific surface of the hydration products. The specific surface area of tobermorite, for example, is about 1,000-fold greater than that of C_3S; 2 percent hydration, therefore, would cause a twenty-fold increase in the surface. This much hydration probably occurs in the first few minutes.

It is entirely reasonable to expect the kind of dispersion of grains described by Rehbinder, but it may be a relatively slow process. The autocatalytic processes in the hydration of C_3S and C_2S, described earlier, could be explained by such a splitting of the grains. Because the rate of hydration is proportional to the surface of the unreacted silicate in both the solution and surface reaction mechanisms, formation of new surfaces of the reactant would increase the rate. If grain splitting is the true explanation of autocatalysis, the rate of splitting becomes significant in hours for C_3S and in days for C_2S. This sort of splitting would have nothing to do with thixotropy, which is probably established in far shorter times.

(b) In general, the present authors do not see the connection between thixotropy and dispersion of the grains of the silicates. Thixotropy is caused by the appearance of tobermorite in the system. Lewis, Squires, and Broughton [84] point out that some clay suspensions in water, containing as little as 0.1 percent solids, exhibit thixotropy, and hydrating C_3S contains far more than this quantity of tobermorite immediately after mixing with water.

(c) Rehbinder seems to draw a clear-cut distinction between "coagulating structure" and "crystalline structure." As far as degree of crystallinity is concerned, tobermorite in the completely hydrated and hardened paste, i.e., in Rehbinder's "crystalline structure," is still very poorly crystallized; its X-ray diffraction pattern contains only three lines. The present authors wonder whether tobermorite in the early "coagulating structure" is any different in degree of crystallinity, or in any other respect, from the tobermorite obtained later.

3. Thixotropy, setting, and hardening are phenomena accompanying the formation of more and

more tobermorite in the hydrating system. According to current theory [85], thixotropic gels are made up of particles which are in contact at certain points only. The particles usually have the shapes of rods or plates; the rods probably form contacts at the ends, and the plates form contacts between oppositely charged edges and plane surfaces. The forces are van der Waals and electrostatic; they are sufficiently strong to hold the system together in a network structure at a low concentration of particles in the solution, but they are not so strong as to prevent breaking of the bonds between the particles by a small shearing stress. By changing the *p*H or the ionic strength of the solution in contact with the solid surfaces, Kruyt and his coworkers [86] were able to change the forces of attraction and repulsion between the particles in thixotropic gels.

Tobermorite consists of fibers or sheets; consequently, its morphology is suited for the formation of a thixotropic gel. Its surface is ionic, so both electrostatic and van der Waals forces are present. In some experiments performed in this laboratory, alite exhibited thixotropy by the time the first measurements could be made, which was 15 min after mixing with water. Tobermorite, obtained by the reaction of silica and $Ca(OH)_2$ in water at 85 °C, exhibited different degrees of thixotropy when the reaction was carried out with and without stirring. Also, when a thixotropic gel was obtained without stirring, shearing action transformed the gel into a sol, which on standing did not revert back completely to the original gel structure. This lack of complete reversibility in thixotropic properties may well be a characteristic of the tobermorite obtained in the paste hydration of C_3S as well.

One of the requirements for setting is that enough hydration products should form in the system, but this may not be the whole story. Bogue and Lerch [49] reported initial setting times of 3.7 and 4.7 hr for C_3S and C_2S, respectively, and final setting times of 6.0 and 24.0 hr, respectively. Although the extent of hydration was not determined by them for times less than 24 hr, it seems likely that more C_3S hydrated in 3.7 hr than C_2S in 4.7 hr. Another requirement for setting may or may not be the formation of chemical cross-links between tobermorite (G) fibers at the areas of contact. This may come about through calcium ions, or by hydrogen bonding, or by condensation of $Si(OH)_4$ groups, forming siloxane linkages. Even if such chemical linkages are present to a certain extent, the predominating forces must be electrostatic and van der Waals. That the binding between fibers is not very strong is indicated by the fact that Copeland was able to disperse completely hydrated and hardened C_3S and C_2S pastes by ultrasonic agitation.

A true understanding of the mechanisms of thixotropy, setting and hardening of C_3S and C_2S still lies in the future.

4. Hansen [87] has proposed that the hydration of the silicates occurs through diffusion of water into the solid and diffusion of lime out of it. The experiments of McConnell [88] and Nacken [89] appear to support this hypothesis. Jeffery [90] described McConnell's results as follows. "McConnell at Cambridge, in his investigations of Ballycraigy and Scawt-Hill minerals, has found bredigite (α-C_2S) and larnite (β-C_2S), hydrated to tobermorite (or plombierite, in his nomenclature). The hydrate occurs as pseudomorphs of the original C_2S crystals. In the case of larnite the characteristic delicate twinning is preserved in the hydrate, alternate lamellae extinguishing together under crossed nicols. . . . Much of the tobermorite occurs as a homogeneous flintlike sheath, up to five centimeters thick, round nodules of unaltered larnite. . . . McConnell concludes that detailed study of the gel so formed indicates that the process of hydration is a solid reaction which is effected by diffusion."

Nacken found similar evidence for the hydration of C_3S. He observed under the microscope that C_3S hydrated from the surface, then the reaction progressed inward. The product formed a pseudomorph of the original grain of C_3S.

A simple calculation shows that the tobermorite gel formed in the hydration of C_2S occupies considerably more space than C_2S itself. This is true, to a lesser extent, of C_3S also. This was pointed out by Powers [91]. It is clear, therefore, that the pseudomorphs observed by Nacken and McConnell could not contain all the tobermorite formed in the hydration of the particular C_3S and C_2S grains. It follows also that not only lime diffuses out of the solid, but silica as well.

5. Schwiete and Knoblauch [74, 79] found that the hydration of C_3S followed a reaction equation of the third order, and the order for C_2S was 1.5. They did not interpret the meanings of these orders. Plotting the logarithms of the rate constants against the reciprocals of the absolute temperatures, they obtained the energies of activation reported earlier in this paper. It is doubtful that the energies of activation thus obtained are energies of activation in the true sense of that term. The small positive temperature coefficients seem rather to indicate a diffusion controlled reaction mechanism.

Zur Strassen [92] interpreted the results of Schwiete and Knoblauch in terms of a diffusion mechanism. If the thickness of the gel layer is called y, one can make the simple assumption that

$$\frac{dy}{dt}=k \text{ and } y=kt. \tag{24}$$

This may happen when the reaction at the water-solid interface is slower than the diffusion of water through the gel layer. If water in the reaction zone is used up more rapidly than it is supplied by diffusion through the gel, one may assume that the rate is inversely proportional to the thickness of the gel layer,

$$\frac{dy}{dt}=\frac{1}{y}\,k \text{ and } y=k't^{\frac{1}{2}}. \tag{25}$$

Apart from an initial faster reaction in the first few days, the hydration of C_2S obeys equation 24 up to about 120 days. At that time about 80 percent of the C_2S is hydrated; after that time, the reaction slows down. On the other hand, the hydration of C_3S obeys equation 25, up to about 30 days. For C_3S also there is an initial higher rate and a final lower rate. The conclusion is that, throughout most of the hydration process, the reaction occurring at the interface is the rate controlling step in the hydration of C_2S, but diffusion through the tobermorite gel is the rate controlling step in the hydration of C_3S. The final slowing down in the hydration of C_2S is explained by the building up of the gel layer—when the layer becomes sufficiently thick, diffusion becomes the rate controlling step. However, the final slowing down in the hydration of C_3S is not explained.

Although zur Strassen's approach is undoubtedly an oversimplification of the problem, it constitutes a good beginning toward a quantitative treatment of the part of the hydration process which is diffusion controlled. However, much painstaking experimental and theoretical work must be performed before an adequate understanding of the mechanisms of the hydrations of C_3S and C_2S will be achieved.

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Paper III-2. Hydrothermal Reactions in the System $CaO-SiO_2-H_2O$ and the Steam Curing of Cement and Cement-Silica Products*

H. F. W. Taylor

Synopsis

The field is reviewed under the following headings: (I) Introduction and nomenclature; (II) Experimental methods; (III) Individual ternary phases; (IV) Some general considerations; (V) Hydration of C_3S, C_2S, and neat cement in pastes cured at elevated temperatures; (VI) Reactions occurring in lime-silica and cement-silica pastes cured at elevated temperatures. The aim of sections (I) to (IV) is to summarize existing knowledge and problems in the field of fundamental studies on the system $CaO-SiO_2-H_2O$ at or above 100 °C. These studies constitute the background for ones bearing more directly on technical practice which are reviewed in sections (V) and (VI). In section (V) the reactions in C_3S and β-C_2S pastes are chiefly considered; they serve as a model for the more complex ones occurring in neat cement pastes. In section (VI), reactions in lime-quartz pastes are similarly considered as a model for the case of cement-silica pastes.

The conditions under which poorly crystallized tobermorite minerals are formed hydrothermally are discussed, but not the constitution of these phases, as this is reviewed elsewhere in this symposium.

Résumé

La question est revue sous les titres suivants: (I) Introduction et nomenclature; (II) Méthodes expérimentales; (III) Phases ternaires individuelles; (IV) Considérations générales; (V) Hydratation de C_3S, de C_2S, et de ciment en pâte pure conservée à des températures élevées; (VI) Réactions qui se produisent dans les pâtes silice-chaux et silice-ciment conservées à des températures élevées. Les sections (I)-(IV) ont pour but de résumer les connaissances actuelles et les problèmes dans le domaine des études fondamentales sur le système $CaO-SiO_2-H_2O$ à 100 °C ou à une température plus élevée. Ces études constituent la base pour des études qui portent plus directement sur la pratique technique, et qui sont revues dans les sections (V) et (VI). Dans la section (V) ce sont surtout les réactions dans les pâtes de C_3S et de β-C_2S qui sont considérées; elles servent de modèle pour les réactions plus complexes qui se produisent dans les pâtes pures de ciment. Dans la section (VI) les réactions dans les pâtes quartz-chaux sont également examinées en tant qu'elles constituent un modèle pour l'étude des pâtes silice-ciment.

L'exposé examine les conditions sous lesquelles les minéraux tobermorites faiblement cristallisés sont formés hydrothermiquement, mais la constitution de ces phases n'est pas discutée puisqu'elle est revue dans une autre partie de ce symposium.

Zusammenfassung

Der Diskussionsgegenstand wird in den folgenden Kapiteln behandelt: (I) Einführung und Nomenklatur; (II) Experimentalmethoden; (III) Individuelle ternäre Phasen; (IV) Einige allgemeine Gesichtspunkte; (V) Hydratation des C_3S, des C_2S und der Purzementpasten, die bei höheren Temperaturen gelagert werden; (VI) Reaktionen, die sich in Kalk-Kieselerde und Zement-Kieselerde-Gemischen, die bei höheren Temperaturen gelagert werden, abspielen. Es ist der Zweck der Kapitel (I)-(IV), die vorhandenen Kenntnisse und die Probleme, die die Forschungen im System $CaO-SiO_2-H_2O$ bei und über 100 °C noch offengelassen haben, zusammenzufassen. Diese Forschungen haben große Bedeutung als das Grundwerk für andere, die den technischen Mann mehr interessieren, und die in Kapitel (V) und Kapitel (VI) besprochen werden. In Kapitel (V) werden überwiegend die Reaktionen in C_3S und in β-C_2S Pasten besprochen; sie sind Modelle für die komplizierteren Reaktionen, die in Purzementpasten auftreten. In Kapitel (VI) werden die Reaktionen in Kalk-Quarz-Gemischen in der gleichen Weise behandelt; sie dienen als das Modell für die Zement-Kieselerde-Gemische.

Die Bedingungen, unter welchen schlecht kristallisierende Tobermoritmineralien hydrothermisch gebildet werden, sind besprochen, aber auf den Phasenaufbau wird nicht näher eingegangen, weil dies in anderen Vorträgen dieses Symposiums behandelt wird.

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Introduction and Nomenclature

TABLE 1. *The hydrated calcium silicates (excluding the tobermorite group)* [a]

Name used in this review [b]	Probable or approximate composition			Principal other names in the literature [b]
	C	S	H	
Nekoite	3	6	7 or 8	
Okenite	1	2	2	
Z-phase [1,2]	1	2	2	CS_2H_2 [3].
Gyrolite	2	3	2	Centrallassite.
Reyerite	6	10	3	Truscottite.
Xonotlite	6	6	1	
Foshagite	4	3	1	
Afwillite	3	2	3	
Phase Z [4]	3	2	[d] 0	1.5 C/S gamma-type hydrate [5].
$C_6S_4H_3$ [c]	6	4	3	
Foshallassite [7] [c]	3	2	3	
Phase F [8] [c]	5	3	2	
$C_2S\alpha$-hydrate	2	1	1	$C_{10}S_5H_6$ [6], $C_2SH(A)$ [9], dicalcium silicate hydrate (I)[10].
Hillebrandite	2	1	1	$C_2SH(n=1.60)$ [6], $C_2SH(\beta)$ [9], C_2S β-hydrate [11], dicalcium silicate hydrate (II) [10].
Phase Y [4]	6	3	1	$C_6S_3H_2$ [6], $C_2SH(D)$ [9], $C_2SH_{0.5}$ [12,13].
Calcio - chondrodite [14].	5	2	1	Phase X [4].
Tricalcium silicate hydrate.	6	2	3	

[a] So-called "C_2S γ-hydrate" (synonyms: $C_2SH(C)$ [9], dicalcium silicate hydrate (III) [10], C_2S aq. [6], Phase X* [4], $C_2SH(CI)$, and $C_2SH(CII)$[13] is probably a mixture of calcio-chondrodite and Phase Z. So-called "CSH(A)" [9] is probably a quaternary phase containing CO_2, substantially identical with the mineral scawtite.

[b] References are given only where necessary to avoid confusion

[c] Phases described by only one investigator.

[d] *Phase probably varies in composition, perhaps over the range* C_3S_2—$C_6S_3H_2 \cdot$ aq.

TABLE 2. *The tobermorite group. Tentative system of classification and nomenclature*

C/S ratio	Degree of crystallinity		
	High	Low	Very low
	Complete X-ray powder pattern with *hkl* reflections.	Poor X-ray powder pattern with (mainly) basal and *hk* or *hkO* reflections.	Very poor X-ray powder pattern consisting of one or more *hk* lines or bands. No basal reflections.
Below 1.5 (near 0.83 when fully crystalline).	14-A tobermorite [a] 11.3-A tobermorite or tobermorite [b] 9.35-A tobermorite or riversideite	CSH(I) [d]	Plombierite.[e]
1.5 and over (probably 1.5–1.75 when fully crystalline).	"12.6-A tobermorite" [c] "10-A tobermorite" [c]	CSH(II) [f]	CSH gel.[g]

Notes and synonyms.

[a] Syn. plombierite [15].

[b] Syn. $C_4S_5H_5$ [6], well-crystallized calcium silicate hydrate (I) [16].

[c] The assumption that these species have $C/S > 1.5$ is purely tentative.

[d] Crumpled foils. CSH(I) is here short for "calcium silicate hydrate (I)" and does not imply CSH composition. Syn. CSH(B) [9], 0.8–1.33 C/S hydrate [17], etc.

[e] Gelatinous natural mineral of composition $C_{0.8}SH_2$ [18].

[f] Fibrous. CSH(II) is here short for "calcium silicate hydrate (II)" and does not imply CSH composition. Syn. $C_2SH(II)$ [19], C_2SH_2 [9], 1.5–2.0 C/S hydrate [17], etc.

[g] Short for "calcium silicate hydrate gel," the phase formed in C_3S pastes at room temperature; or any other similarly ill-crystallized material of similar composition. Syn. tobermorite (G) [20]. Hydrate (III) [21], etc.

An understanding of the chemistry of cement hydration at elevated temperatures rests first and foremost on a knowledge of the conditions of formation, crystal structures, and properties of the hydrated calcium silicates. The number of these phases is quite large, and it is not surprising that different investigators have evolved their own systems of nomenclature. Tables 1 and 2 show the names that will be used in this paper, together with the probable or approximate compositions of the phases, and the principal other names that have been used for them. The naming of the phases structurally related to tobermorite (table 2) is particularly difficult because some of them are badly crystallized and continuous variations in both composition and degree of crystallinity appear to exist. Any system of classification or nomenclature must therefore contain a large arbitrary element. That proposed in table 2 has been kept as simple as possible, and as knowledge increases further subdivisions will probably be needed. Thus there are indications of more than one variety of 11.3-A tobermorite, and the same is true of CSH(II) and perhaps of other cases. For certain purposes a more detailed terminology will thus eventually be needed. On the other hand, there is also an evident need for broader terms usable where it is impossible or undesirable to be more specific. Terms such as "tobermorite minerals," "tobermorite-like phases," and "tobermoritic material" have been used; some workers use the name "tobermorite" to include the entire group. In this paper the name "tobermorite" will (unless qualified) be restricted to the well crystallized phase with a basal spacing of about 11.3 A. The following broader terms will be used:

Tobermorite mineral: any phase or mixture of phases from the entire group.

CSH (short for "calcium silicate hydrate"): any phase or mixture of phases with a degree of crystallinity defined in table 2 as "low" or "very low." Assarsson [1, 2][1] used the term "phase B" in a roughly similar context; some workers refer to some or all such phases as "gels."

The name "crestmoreite" is used for the oriented intergrowths of tobermorite and apatite minerals which occur at Crestmore, Calif.

No attempt will be made in this review to discuss in detail all the earlier work on the CaO–SiO_2–H_2O system under hydrothermal conditions; for this purpose, earlier reviews [11,19,28] may be consulted.

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[1] *Figures in brackets indicate the literature references at the end of this paper.*

Experimental Methods

Hydrothermal synthesis and stabilities of phases. The early literature contains several reports of the hydrothermal synthesis of hydrated calcium silicates, but accurate identification of the products was impossible before the introduction of X-ray methods. Among the first significant studies were those of Thorvaldson and his co-workers [10, 22–24], Nagai [25–27], and Bessey [29]. Since then, many investigations have been reported. Flint, McMurdie, and Wells [6] made a notable advance in 1938 with the first systematic study covering a wide range of Ca:Si ratio. Starting materials that have been used include CSH made at or slightly above room temperature, anhydrous C_3S or C_2S, lime-silica mixtures, glasses, and other crystalline hydrated calcium silicates found as minerals or previously made hydrothermally. An important addition was made recently by Roy [30], who used CSH prepared below 100 °C and afterwards gently ignited. The crystallinity of CSH(I) and CSH(II) is reduced by heating at 400 to 600 °C, though it begins to increase again at 600 to 700 °C, when anhydrous crystalline phases begin to form [31]. Gels dried at 400 to 600 °C are probably particularly good starting materials for equilibrium studies because of their high reactivity and homogeneity and relative absence of pre-existing structure.

Most investigators until recently used closed bombs or autoclaves in which the pressure is generated internally. Stainless steel vessels have generally been used, though for the important temperature range below 200 °C sealed glass test tubes with silver inserts are equally satisfactory [39]. Where two fluid phases are present, the pressure is approximately defined by the saturated steam curve; where there is only one fluid phase it can be estimated from the degree of filling of the bomb [32].

Closed bomb techniques are simple, but have serious limitations. Except where saturated steam conditions exist, the pressure is often uncertain and sometimes uncontrollable. During a single run, the pressure and temperature cannot be varied independently. Combinations of high pressure and low temperature are not conveniently obtainable; below about 350 °C pressures higher than that of saturated steam cannot safely be obtained. These weaknesses have been largely overcome by the development of the Tuttle or cold-seal apparatus [33, 34], in which the pressure is externally applied, and can be controlled independently of the temperature. Pressures up to 70,000 psi and temperatures up to 900 °C are readily obtained.

Hydrothermal investigations can be divided broadly into equilibrium and nonequilibrium studies. The object of the first is to define the conditions of stability of the various phases. Two main types of equilibrium study have been made. Firstly, investigators using cold-seal apparatus have established stability relations between different solid phases in terms of P–T curves. Secondly, studies have been made of the compositions of solutions that exist in stable or metastable equilibrium with particular solid phases. Such studies are difficult because of the low solubilities involved, and have so far been made only at relatively low temperatures under saturated steam conditions [6, 35].

Nonequilibrium studies are particularly important in the range below 200 °C which is of direct technical importance. At these temperatures the approach towards equilibrium is slow, and often proceeds through formation of one or more intermediate phases [2, 36, 37]. The sequence of these phases is often markedly affected by small variations in experimental conditions; even minor variations such as the nature of the stabilizer in β-C_2S used as starting material can affect the phases produced under otherwise identical conditions [13, 38]. A given starting material may behave differently in pastes and in suspensions [39]. There are many other variable factors, some of which have been discussed by Kalousek [37].

Both equilibrium and nonequilibrium studies are important for understanding the processes of cement hydration. The equilibrium studies provide invaluable background material, but give little direct indication of the reactions likely to occur in pastes below 200 °C. These reactions show many complexities that could hardly be predicted by attempting to extrapolate P–T curves or other equilibrium data obtained at higher pressures and temperatures.

X-ray powder and optical studies. Since the last symposium, diffractometer methods have been widely introduced. They have clear advantages over film methods in speed and convenience, and, under favorable circumstances, in resolution and in precision of measurement of both spacings and intensities. It must, however, be stressed that they have disadvantages which should cause them to supplement and not supersede film methods. Diffractometer methods have so far proved less satisfactory for observing weak or diffuse reflections, especially at high angles. The surest method of indexing a powder pattern is direct comparison of powder and single crystal films made on the same camera. Occurrence of preferred orientation is more readily detected with suitable film methods. Lastly, where two or more phases occur and differ markedly in crystal size, assignment of lines to phases can often be based on the different textures of the lines when film is used, as the coarser particles give spottier lines. This ability is particularly valuable for studies of preparations made using quartz or β-C_2S, residual traces of which often give rough or spotty lines.

The specific gravity of an anhydrous or hydrated calcium silicate can usually be calculated to ±2 percent from the mean refractive index, using the

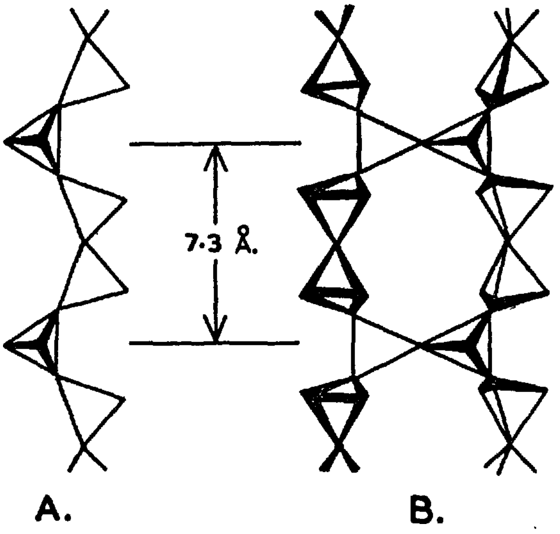

FIGURE 1. *Silicon-oxygen chains found in hydrated calcium silicates.*

A. Single Dreierkette. B. Double Dreierkette.

Lorentz-Lorenz equation [40]. This procedure has been used as an aid in determining composition [41], and to estimate the specific gravity where direct determination was impracticable [42].

Crystal-structure determinations. Major advances have been made since the London symposium in 1952. At that time, the only hydrated calcium silicates of which the structures were known were afwillite [43] and dicalcium silicate α-hydrate [44], both of which contain isolated $HSiO_4^{3-}$ groups. It was known that a group of hydrated calcium silicates had a repeat distance of about 7.3 A in one direction [19, 45], but the significance of this was not understood. Table 3 lists the compounds with this repeat distance. Anhydrous β-$CaSiO_3$ is included as it is the parent structure from which those of the hydrated compounds are derived. Its structure was established in 1954 by the work of Dornberger-Schiff, Liebau, and Thilo [46] on the isostructural compound $NaAsO_3$. Their results have since been confirmed by direct studies on β-$CaSiO_3$ [47–50]. These investigations disprove an earlier conclusion [51] that $Si_3O_9^{6-}$ rings were present.

TABLE 3. *Calcium silicates with a repeat distance of about 7.3 A*

Wollastonite	β-$CaSiO_3$
Parawollastonite	
Nekoite	$Ca_3Si_6O_{15} \cdot 7$ or 8 H_2O
Okenite	$Ca_3Si_6O_{15} \cdot 6H_2O$
Xonotlite	$Ca_6Si_6O_{17}(OH)_2$
Foshagite	$Ca_4Si_3O_9(OH)_2$
Hillebrandite	$Ca_2SiO_3(OH)_2$
Tricalcium silicate hydrate	$Ca_6Si_2O_7(OH)_6$
Tobermorite minerals:	
Tobermorite (11.3 A)	$5CaO \cdot 6SiO_2 \cdot 5H_2O$
14-A tobermorite	$5CaO \cdot 6SiO_2 \cdot 9H_2O$ (?)
9.35-A tobermorite (riversideite)	$5CaO \cdot 6SiO_2 \cdot 0$-$2H_2O$
CSH(I)	0.8–1.33[a]$CaO \cdot SiO_2 \cdot$aq.
Plombierite	$0.8CaO \cdot SiO_2 \cdot 2H_2O$
CSH(II)	1.5–2.0$CaO \cdot SiO_2 \cdot$aq.
CSH gel	

[a] Or 1.5 (?).

An essential feature of the structure of β-$CaSiO_3$ is the occurrence of metasilicate chains kinked so as to repeat at intervals of three tetrahedra (fig. 1a). This gives the characteristic 7.3 A repeat distance. Such chains have been called "Dreierketten" to distinguish them from metasilicate chains kinked in other ways, as for instance the "Zweierketten" of pyroxenes [52]. The German words are provisionally retained as they are not conveniently translatable. Kinking of silicon-oxygen chains in calcium silicates into Dreierketten, rather than into some other form, occurs because this gives a good fit with the dimensions of the CaO_6 polyhedron [52, 53].

Dreierketten have been proved to exist in tobermorite [54] and foshagite [55, 56], while xonotlite contains double Dreierketten (fig. 1b) analogous to the double Zweierketten of the amphiboles [57, 58]. It is reasonable to attribute the 7.3 A repeat distance in the other compounds of this group to the presence of Dreierketten or related structural groupings. Mamedov and Belov [59–63] have discussed theoretically the possible modes of condensation of Dreierketten with each other and with CaO_6 polyhedra, and on this basis have suggested structures for okenite, nekoite, tobermorite, foshagite, hillebrandite, and (in collaboration with Klebtsova) for tricalcium silicate hydrate. Although reasonable, these structures are not based on any direct experimental evidence from X-ray intensities; that proposed for foshagite does not satisfactorily explain the intensity data [56].

No further crystal-structure determinations of the hydrated calcium silicates have been made, but the structure of calcio-chondrodite [14] may be inferred by analogy with the known structure of chondrodite [64]. The latter mineral, which has the composition $(Mg,Fe)_5(SiO_4)_2(OH,F)_2$, is closely related structurally to olivine ($(Mg,Fe)_2SiO_4$), and a calcium analog of olivine exists in γ-C_2S [65]. Olivine and chondrodite are the only magnesium or iron silicates that are known to have exact calcium analogs. The reason for this is probably that they contain separate SiO_4^{4-} tetrahedra, which can be separated more widely to accommodate the larger calcium ion. The other typical magnesium or iron silicate structures, such as the pyroxenes, amphiboles, and micas, contain condensed anions of the Zweierkette or derived types. These cannot be expanded to accommodate calcium, which therefore plays only a limited role in these structures.

Electron microscopy and diffraction. Several early attempts were made to study hydrated C_3S or cement pastes by electron microscopy, but the results seem to have been vitiated by carbonation or other disturbing factors. Grudemo [66, 67] made the first systematic study of pure, hydrated calcium silicate phases using this method; subsequently several others have been made [17, 31, 38, 39, 41, 68–73, 76]. The method of selected-area electron diffraction has also been developed and applied to the study of hydrated calcium silicates

[31, 41, 70–74]. General surveys of this method have geen given [74–75]. More recent applications of electron microscopy and diffraction to the study of the hydrated calcium silicates are described by other contributors to this symposium.

Infrared absorption. Application of this method to studies on hydrated calcium silicates is recent, and the results appear promising. Data have been reported prior to this symposium for tobermorite and related phases [76–78], xonotlite [77, 79], calcio-chondrodite, Phase Y and Phase Z [4], afwillite [80], and $C_2S\alpha$-hydrate [76, 81]. It is too early to assess the significance of the results, or even to interpret them with certainty, but there seem to be distinct possibilities of using the method to determine the form in which constitutional water is present, and other structural features. Two promising extensions of the method are the study of single crystals using polarized beams (applied to afwillite [80]) and investigation of the effect of substituting deuterium for hydrogen (applied to $C_2S\alpha$-hydrate [81]).

Weight-loss curves and differential thermal analysis. Weight-loss curves of hydrated calcium silicates have been determined using dynamic or thermobalance methods [76, 78, 82, 83], and using quasi-static methods in which the temperature is maintained for lengthy periods at successively higher values. Buckle [84] has recently reviewed the theory and practice of the quasi-static method, and has compared its merits with those of the dynamic method. The latter is much faster and therefore alone suitable for most routine work, but the quasistatic method is probably better for most fundamental studies.

Mackenzie [85] has reviewed the technique of differential thermal analysis and its application to clay mineralogy. The method has been applied to the study of hydrated calcium silicates, especially by Kalousek and collaborators [5, 37, 86–91]. The value of both weight-loss and DTA studies is increased if they are supplemented by X-ray studies made either with high-temperature cameras, or on cooled material. It is important to control the atmosphere, and essential to exclude CO_2, in all of these studies.

Oriented transformations. This term will be used to describe reactions in which crystals of one substance are formed out of those of another in such a way that crystallographic orientation is substantially preserved. Heller [92] reported the first, exploratory studies in the CaO-SiO_2-H_2O system; the reactions she studied were mostly dehydrations effected by heating at ordinary pressures. Since then more such studies have been made [70–72, 93–97], and it has also been shown that some hydrothermal changes, such as that of tobermorite into xonotlite, occur or can occur in this way [98]. New experimental methods for the study of both thermal and hydrothermal transformations have been described [98–100]. Studies on oriented transformations provide a powerful means of linking crystal-structural information with chemical or phase-equilibrium data. From one such study it was concluded that the dehydration of a number of hydrated calcium silicates at about 700 °C involves rupture of Si-O rather than Ca-O bonds, with consequent migrations of silicon atoms or ions [94]. This conclusion enabled the prediction of the essential features of the crystal structure of foshagite, which were afterwards tested by classical X-ray methods [55, 56, 72].

Chemical extraction methods. There have been recent developments in methods for extracting uncombined $Ca(OH)_2$ [20, 101–103]. Some workers have also used methods for extracting uncombined silica, but the difficulties inherent in this procedure have been emphasized [104].

Individual Ternary Phases

Optical, X-ray powder, unit cell, specific-gravity, and other crystallographic data will not be listed as they were tabulated for most of the phases by Heller and Taylor [105] in 1956. Table 4 gives references to the principal additions or corrections to these data. Several new sets of powder data for other compounds have been published, but none differ significantly from the earlier data. The phases will be described roughly in order of increasing Ca:Si ratio, but this principle is sometimes departed from in order to group together related phases.

Okenite (CS_2H_2?) *and nekoite* ($C_3S_6H_{7\ \mathit{or}\ 8}$). These are the only two hydrated calcium silicates which are known to occur as well-defined natural minerals, but which have not yet been synthesized. Hydrothermal runs at low Ca:Si ratios little above 100 °C, which might be expected to yield them, appear to give instead compounds of the tobermorite or gyrolite groups together with hydrous silica. There has been one recent report of the

TABLE 4. *Crystallographic data for the hydrated calcium silicates. Principal additions or corrections to the compilation by Heller and Taylor [105]*

Phase	Nature of new data	References
Z-phase	X-ray powder data for new phase	[2,3]
	Sp. gr., refractive index	[3]
11.3-A tobermorite	Crystal structure	[54]
	Indexing of X-ray powder data	[71]
9.35-A tobermorite (riversideite).	Indexing of X-ray powder data, unit cell	[95]
Foshagite	Revised composition, unit cell, indexing of X-ray powder data	[72]
	Crystal structure	[55,56]
Phase F	X-ray powder data for new phase	[8]
Phase Z	X-ray powder data and optical properties of new phase	[4]
	Unit cell	See text.
Phase Y	X-ray powder data and optical properties of new phase	[4]
	Unit cell, specific gravity, indexing of X-ray powder data	[42]
C_2S γ-hydrate	Probably not a single phase	See text.
Calcio-chondrodite (Phase X).	X-ray powder data (indexed), unit cell, specific gravity, crystal structure (by analogy)	[14]
	Optical and X-ray powder data	[4]
Tricalcium silicate hydrate.	Indexing of X-ray powder data, unit cell, specific gravity	[41]

synthesis of nekoite [106], but it is based solely on optical evidence and cannot be considered established.

Okenite has been known as a mineral for over a century [70,107]. Nekoite is known only from one locality. It was originally described as okenite [108], but recent work has shown that it is a distinct species. It nevertheless resembles okenite in many ways and there is almost certainly a close structural relationship [70].

Published analyses indicate the formula CS_2H_2 for both minerals. A new analysis of nekoite suggests a higher water content, giving $C_3S_6H_7$ or $C_3S_6H_8$; the water is mostly lost by 200 °C, and there is infrared evidence to support the inference that it probably occurs in molecular form [109]. Synthesis is therefore most likely to be effected at low temperatures, possibly around 100 °C; prolonged reaction may be needed. This conclusion probably applies also to okenite.

Both okenite and nekoite form fibrous or markedly acicular crystals with one good cleavage in the prism zone and a 7.3 A repeat in the fiber direction [70]. On being heated at 800 °C, both minerals undergo oriented transformation giving β-$CaSiO_3$ [70,92]. Assuming the water to occur as molecules, the formulae of both minerals can be written $CaSi_2O_5 \cdot xH_2O$. These results strongly indicate the presence of Dreierketten condensed together to give infinite sheets of empirical composition $Si_2O_5^{2-}$. Mamedov and Belov [59] suggested a way of doing this which would explain the observed cell dimensions.

Gyrolite ($C_2S_3H_2$). *reyerite or truscottite* ($C_6S_{10}H_3$?) *and Z-phase* (CS_2H_2?). These three phases are structurally related; all form lamellar crystals with micaceous (0001) cleavage and are hexagonal or pseudohexagonal with *a* 9.73 A. They are most readily distinguished by their basal spacings, which are approximately 22.1 A for gyrolite [97,110], 18.7 A for reyerite [110,111], and 15.3 A for Z-phase [2]. Gyrolite and reyerite occur naturally [112–114]. Z-phase has not been found pure in nature, though some specimens of gyrolite probably contain minor amounts of it intergrown in parallel orientation [115]. The reported mineral centrallassite is identical with gyrolite, while truscottite is the same as reyerite [110]. The name reyerite has priority.

Doubts exist regarding the exact compositions of all three phases. Analyses of natural and synthetic gyrolites mostly agree reasonably well with the formula $C_2S_3H_2$ [112–115a], but Strunz and Micheelsen [110] have recently proposed the formula $C_3S_4H_3$. Analyses of natural reyerite or truscottite are hard to interpret because both of the known specimens are contaminated by other minerals which are difficult to separate. The formulae C_2S_4H and $2(CaO, MgO) \cdot 3SiO_2 \cdot 2H_2O$ have been suggested for truscottite (reyerite from Sumatra) while C_3S_4H has recently been proposed for reyerite from Greenland [110]. Harker [115a] recently found the composition of synthetic reyerite to be $C_6S_{10}H_3$. As will be seen later, reyerite is formed at relatively high temperatures, and the H_2O:Si ratio is therefore more likely to be 1:4 than 2:3. The Ca:Si ratio must be considered uncertain, though it appears definitely to be between 0.5 and 0.75. Harker's formula is perhaps the most probable.

Funk and Thilo [3] described a new phase in 1955, which they considered to have the formula CS_2H_2. Shortly afterwards, Assarsson [1,2] reported a new compound of uncertain but probably similar composition which he called Z-phase. Comparison of the X-ray powder patterns reported for these phases suggests that they are identical. Preliminary X-ray powder studies have been made in this laboratory of a specimen kindly provided by Funk. The powder data reported by Funk and Thilo were confirmed, but the patterns gave also a strong spacing of about 15 A, which was considered by Assarsson to be characteristic of Z-phase. The identity of the two preparations is thus confirmed. The similarity of the X-ray powder pattern to that of gyrolite suggests a structural resemblance, and the unit-cell or structural element is therefore probably hexagonal or pseudohexagonal with *a* 9.73, *c* 15.3 A, approx. The orthorhombic cell suggested by Funk and Thilo seems unlikely to be correct. It was based only on indexing of powder data.

Most of the data relating to the conditions of formation of these phases relate to saturated steam conditions, but Harker [115a] has briefly reported P-T curves defining the stabilities of gyrolite and reyerite, while Assarsson [116] made some runs in superheated steam. Gyrolite was first synthesized by Flint, McMurdie, and Wells [6] from gels and glasses with Ca:Si ratios in the range 0.5 and 0.66, at 150 to 400 °C. At 450 to 500 °C α-$CaSiO_3$ was obtained. They did not, however, distinguish gyrolite from reyerite; subsequent evidence suggests that the latter was probably formed at the higher temperatures. Subsequently, a number of workers have confirmed the formation of gyrolite, as distinct from reyerite or Z-phase, at temperatures mostly between 120 and 240 °C [1, 2, 8, 37, 79, 97, 104, 115a]. It appears to form very slowly at 120 °C, and more rapidly at 150 °C or above from gels or mixtures of lime with amorphous silica. The upper limit is at least 240 °C, though Harker's results show that gyrolite becomes unstable relative to reyerite and xonotlite above 220 °C; in the presence of excess silica, it becomes unstable relative to reyerite above 190 °C. Harker also found that formation of gyrolite was favored by the presence of up to 2 percent of alkali fluoride.

Buckner, Roy, and Roy [79] reported the formation of reyerite and gyrolite. together with other products, at 295 °C and 30,500 psi. This is the earliest report of the synthesis of reyerite. The inference that the phase is stable relative to gyrolite under these conditions was confirmed by Harker [115a], who showed that reyerite becomes unstable relative to xonotlite and silica above 355 °C at saturated steam pressure.

Jander and Franke [12] and Funk and Thilo [3] obtained products at 300 to 350 and 250 °C respectively, which could have been reyerite.

Peppler [35] determined the solubility relations at 180 °C for a preparation which he had identified as gyrolite; he found this compound to be metastable relative to xonotlite and hydrous silica at this temperature. This result seems to be incompatible with Harker's. Peppler had made his preparation by autoclaving an oxide mixture at 350° C, and it may therefore have consisted wholly or partly of reyerite.

Assarsson [1,2] obtained Z-phase by autoclaving mixtures of lime and amorphous silica at 140 to 240 °C. He could not prepare it at 120 °C, but his longest runs were only of 21 days' duration. He considered that it was an intermediate product in the sequence lime+silica gel→CSH(I)→Z-phase→gyrolite, and believed that it might have a stable field of existence at 130 to 150 °C. This is almost certainly too high, as gyrolite can be made at 120 °C. Funk and Thilo [3] obtained their product by autoclaving gels at 180 °C for 1 to 2 days; these conditions are comparable with those used by Assarsson.

These results indicate that Z-phase is the least, and reyerite the most, thermally stable of the three phases. The structural and compositional relations between the three compounds are not clear. The relationship does not appear to be simply one of varying numbers of water molecules between otherwise identical layers, since Z-phase has the shortest basal spacing but is formed at the lowest temperatures and is therefore presumably the most hydrous. Further studies on the compositions of all three phases are clearly needed.

Gyrolite loses three-quarters of its water below 450 °C; the structure undergoes relatively minor changes. The rest of the water is lost at 500 to 850 °C when oriented transformation occurs giving α-$CaSiO_3$ [97]. The principal water loss in reyerite probably also occurs around 800 °C [111]. A loss was also observed in a lower temperature range, but no change was detectable by X-rays, and this loss may have been caused by impurity. Z-phase loses one-half of its water by 100 °C, and the rest in two stages between 100 and 900 °C [3].

At present nothing is known about the crystal structures of these phases, but the oriented transformation of gyrolite to α-$CaSiO_3$ provides a possible clue, as the structure of the latter compound is known from work on the isostructural $SrGeO_3$ [117]. Another possible structural relation is with zeophyllite ($Ca_4Si_3O_{12}F_2H_6$) [96]. This mineral has also micaceous cleavage and is pseudohexagonal, with an *a*-axis not far from that of gyrolite.

Tobermorite ($C_5S_6H_5$). Crystalline tobermorite with a basal spacing of about 11.3 A occurs naturally in a pure form in Scotland [71,118] and N. Ireland [15], and in crestmoreite intergrowths at Crestmore, Calif. [108,119]. It is the essential constituent of most high-pressure steam-cured concrete and lime-silica products [37,120].

The first clearly described synthesis was made by Flint, McMurdie, and Wells [6]. They considered their product to be $C_4S_5H_5$ and remarked on its possible identity with the natural mineral. The next reported syntheses were by Heller and Taylor [16] and by Kalousek [37]. Heller and Taylor called their product "well crystallized CSH(I)." Taylor [119] showed that this preparation was essentially similar to the silicate constituent of crestmoreite, and Claringbull and Hey [118] showed that it was substantially identical with the pure, natural tobermorite from the type locality. These investigations established definitely the relationship between the natural and synthetic materials. Tobermorite has since been prepared by many other investigators [2, 68, 73, 76, 79, 82, 120, 121].

Among the more important of possible starting materials may be mentioned CSH(I), and mixtures of lime or cement with either quartz or amorphous silica. In the latter case, as is discussed later, reaction proceeds through intermediate formation of CSH(II) and CSH(I), or of phases similar to these. Formation of tobermorite under saturated steam conditions has been reported at temperatures varying between 110 [16] and 275 °C [6]. In the author's experience, it is most reproducibly formed by autoclaving a CSH(I) gel of appropriate Ca:Si ratio at 110 to 140 °C. Transformation to tobermorite at these temperatures is slow, periods of a month or longer usually being needed to complete the process, but a pure product can be obtained. It appears to persist indefinitely under these conditions, though whether it is truly stable is not known. It can be obtained more rapidly at higher temperatures, but is then definitely only an intermediate phase, and much care is needed to avoid partial or complete conversion into xonotlite or other phases. In pastes, it is reproducibly formed at 170 to 180 °C, though again only as an intermediate phase and probably rarely, if ever, free from other phases.

A broader view of the conditions of formation of tobermorite is obtained by considering the entire P–T field and not merely the curve defined by the pressure of saturated steam. Buckner, Roy, and Roy [79] showed that, at 12,000 to 25,000 psi, the equilibrium curve for the transformation of tobermorite to xonotlite, water, and possibly reyerite, lies at about 285 °C. This result points to the possibility of preparing pure samples of tobermorite both quickly and reproducibly by working at considerably higher pressures and temperatures than those commonly used hitherto. Under saturated-steam conditions, tobermorite begins to change to xonotlite at about 150 °C (75 psig). The same minimum temperature for the formation of xonotlite, to within ±10 °C., has been reported by several investigators. It is uncertain whether this temperature represents a point on the equilibrium P–T curve, or whether it is rate determined.

Electron micrographs of typical, synthetic preparations show well-defined flakes up to several microns across and possibly 200 A thick [17, 31, 68, 73]. The cleavage is (001) and there is in varying degrees a tendency to elongation parallel to *b*. Edges parallel in projection to (110) are often also developed. The selected-area electron-diffraction pattern is characteristic [31, 71, 73]. It shows the weak reflections indexable only in terms of the C-centered unit cell with *a* 11.3, *b* 7.3A approx, as well as the strong ones corresponding to the body centered pseudocell with halved *a* and *b*. The weak reflections are characteristic of tobermorite, but the strong ones are given by any sufficiently well-crystallized tobermorite mineral, including CSH(II), lying on (001) [31]. From selected-area electron-diffraction studies, Gard, Howison, and Taylor [31] found that tobermorite crystals sometimes lie superimposed one on the other in a relative orientation which suggested that their surfaces are derived from the Ca—O and not the Si—O part of the structure.

The main features of the crystal structure were established by Megaw and Kelsey [54], though some details are still uncertain. These investigators confirmed earlier suggestions of a layer structure in some respects analogous to that of vermiculite. They showed that each layer consists of a central Ca—O sheet covered on each side by rows of Dreierketten that form ribs. They likened the resulting complex layer to double-sided corrugated cardboard. Between these complex layers are more calcium atoms, and water molecules. The structure explains the observed morphology, and also the existence of higher and lower hydrates differing in *c*-spacing. Mamedov and Belov [60] suggested a modification of this structure involving the existence of Si—O—Si links between neighboring layers. It is not yet clear to what extent this modification is compatible with Megaw and Kelsey's experimental data. The question of the occurrence of such links is considered again later.

Infrared absorption data [76, 77] have been considered to support the view that both water molecules and bonded hydroxyl are present. Assuming Megaw and Kelsey's structure to be correct, the constitutional formula may be written as $Ca_4(Si_3O_9H)_2 \cdot Ca \cdot 4H_2O$. The hydroxyl is thus attached to silicon: the final $Ca \cdot 4H_2O$ denotes the interlayer material.

Most specimens of tobermorite change to 9.35-A tobermorite (riversideite) when heated to 300 °C at atmospheric humidity [15, 77, 95]. Taylor and co-workers [31, 71, 122], and Greenberg [82] obtained weight loss curves that were almost continuous, but McConnell [15] obtained a markedly stepped curve. More work is needed to decide the extent to which these differences can be explained by variation in experimental technique. On differential thermal analysis, Al-free tobermorite gives only a small exothermic peak or none at all at 800 to 850 °C [15, 68, 76, 91]. Al-substituted tobermorite, and also CSH(I), give a strong exothermic peak in this region [91].

Hydrothermal treatment of tobermorite with water causes oriented transformation to xonotlite without intermediate formation of riversideite [98].

Modified or anomalous forms of 11.3–A tobermorite. Kalousek [91] described the synthesis of tobermorite in the presence of reactive aluminous materials; he found that up to 4 or 5 percent of Al_2O_3 could enter the structure, the Al possibly substituting for Si. Al-bearing tobermorite differed from the pure compound in its thermal behavior, as mentioned above. At high Al-contents, there were also minor changes in the X-ray pattern, and the crystal size was reduced. Formation of tobermorite was accelerated, and conversion to xonotlite retarded by the presence of alumina.

Some other tobermorite specimens, both of synthetic and of natural origin, are anomalous in various ways. A natural specimen from Loch Eynort, Scotland, had a distinctly more fibrous form than is usual, with principal cleavage (100) [71]. The basal spacing of 11.3–A persisted right up to 800 °C, when β-$CaSiO_3$ was formed, even though all the water was lost below this temperature. The weaker electron-diffraction reflections, not indexable in terms of the pseudocell, differed from those of normal specimens. Some synthetic specimens free from alumina are also anomalous in that the 11.3–A spacing persists up to 800 °C [8]. In others, electron micrographs show, not the usual plates with conchoidal fracture, but plates that are composed of parallel laths imperfectly joined together [17,31]. These have been interpreted as CSH(II) fibres in course of forming into tobermorite [31] and, alternatively, as CSH(I) sheets showing incipient cleavage or breakdown [17]. There seems to be no evidence as to whether this morphology is correlated with persistence of the 11.3–A spacing except in the case of the Loch Eynort material.

Recent work shows that the Ca:Si ratio of tobermorite, as opposed to CSH(I), is not capable of wide variation, but it apparently can rise as high as 1.0 without any marked effect on the properties [17].

More work is needed before these anomalies can be explained. Clearly, however, the structure of tobermorite is capable of minor variations, which are difficult or impossible to detect by X-ray powder methods, but which markedly influence the morphology and behavior on dehydration. These variations can be caused by Al-substitution, but are not always due to this. It is tempting to speculate that they can be correlated with the formation of Si—O—Si links between the layers, possibly in the way suggested by Mamedov and Belov [60]. This correlation could account for the ability to undergo complete dehydration without shrinkage in *c*-spacing, and possibly also for the fibrous habit and the otherwise puzzling (100) cleavage of the Loch Eynort material.

9.35–A tobermorite (riversideite). $5CaO\cdot 6SiO_2\cdot 0\text{-}2H_2O$. This is formed when "normal" specimens of tobermorite are heated to 300 °C or above at ordinary humidity. The change in basal spacing is discontinuous [95]. The 9.35–A tobermorite also occurs naturally in some specimens of crestmoreite intergrowth; these were originally called riversideite [108], and this name has since been transferred to their hydrated calcium silicate constituent [15].

X-ray studies [95] confirm Megaw and Kelsey's suggestion [54] that the stacking of the layers differs from that in 11.3–A tobermorite; the ribs on the surface of one layer pack into the grooves on that of the next, whereas in 11.3–A tobermorite the layers pack rib against rib. They show also that formation of riversideite from tobermorite is accompanied by marked reduction in the degree of crystallinity.

When riversideite is formed at the minimum temperature of about 300 °C [95] the H_2O:Si ratio is about 0.3 according to McConnell's data [15] or below 0.2 according to data from this laboratory [31, 122]. All the water is expelled by 700 °C but the X-ray pattern shows little or no change between 300 and 700 °C. It has been concluded from this observation that interlayer Si—O—Si links are formed [95]. There is some evidence that part or all of the water is present as molecules [77, 95]. Riversideite has not been made hydrothermally. It should possibly be regarded as a metaphase, with no field of true stability.

14–A tobermorite. $C_5S_6H_9$ (?). This occurs in nature as the main constituent of many specimens of crestmoreite [119]. McConnell [15] suggested the name plombierite, but later [18] used this for a gelatinous phase of approximate composition $C_5S_6H_{12}$ which was of much lower crystallinity. Historical evidence favors its use for the gelatinous mineral, and it seems preferable not to use it also for the very different crystalline one.

The 14–A tobermorite has been synthesized from lime-silica slurries at 60 °C [77]. It probably consists of layers of tobermorite stacked rib against rib, as in the 11.3–A form, but separated by a further layer of water molecules. There cannot, therefore, be any interlayer Si—O—Si links. The H_2O:Si ratio of 1.5 suggested above is based not on experimental evidence, but on a plausible density of packing of the extra water molecules. Infrared absorption data have been reported [77]. Dehydration to the 11.3–A form occurs at 100 °C [122]; McConnell found the process to be reversible [15], but attempts by the author to rehydrate 11.3–A tobermorite have been unsuccessful.

10–A and 12.6–A tobermorites. Well-crystallized tobermorite minerals with these basal spacings occur in some specimens of crestmoreite [105]. The basal spacings suggest that the 10–A form may be a well-crystallized form of CSH(II) and that the 12.6–A form is a more highly hydrated form of this, but there is no proof.

Ill-crystallized tobermorite minerals. These phases, which are classified in table 2, are characteristically formed below 100 °C, and are therefore discussed elsewhere in this symposium. They have also been reviewed recently by the present author [123]. Some reference to them is nevertheless needed because they are also formed as intermediate products in hydrothermal processes. As such, they play an important part in the steam curing of cement.

CHS(I) is characterized by a low Ca:Si ratio, which can be anything from 0.8 to 1.33 or possibly 1.5, and by its morphology of thin, crumpled foils. It gives a strong differential-thermal-analysis peak at 800 to 850 °C. The basal spacing of material dried at 6 mm varies between about 10 and 14A, depending on Ca:Si and H_2O:Si ratios and on other factors not properly understood. The reasons for the variable composition are still uncertain; the material is in many ways a typical, semicrystalline basic salt and is possibly inherently inhomogenous.

CHS(I) is very easily formed and appears to persist indefinitely at room temperatures. Under hydrothermal conditions it seems to be a short-lived intermediate product, which recrystallizes rapidly to tobermorite or other phases. Thus, Kalousek and Prebus [17] showed electron micrographs of typical crinkly foils of CSH(I) made in 2 hr reaction of lime and diatomite at 175 °C; in contrast, Gard, Taylor, and Howison [31] obtained no evidence of CSH(I) in the products of 7 day reactions at 140 °C. They found only CSH(II) and tobermorite.

Plombierite is a natural mineral showing some resemblance to CSH(I), although there are distinct differences [18].

CSH(II) is characterized by a high Ca:Si ratio, which probably always lies within the range 1.5–1.75. The morphology is characteristically fibrous but varies with the mode of preparation; cigar-shaped bundles of fibres [20, 38, 66, 67], long, thin fibres [17, 31], and tubular forms [17] have all been observed. The basal spacing of material dried at 6 mm is about 10.5A. The degree of crystallinity, as evidenced by the X-ray pattern, tends to be lower than that of CSH(I), though the samples consisting of cigar-shaped bundles are better crystallized than the others. The crystal structure is unknown, but is clearly related to that of tobermorite. The possibility of a 1:1 layer structure, in contrast to the 2:1 layer structure of tobermorite, has recently been suggested [31]. If this structure is correct, CSH(II) stands in something like the same relation to the hydrated form of halloysite as does tobermorite to vermiculite.

CSH(II) is probably the initial product of reaction between lime and silica, under hydrothermal conditions as well as at room temperature. It seems to be more persistent than CSH(I), but is nevertheless only an intermediate phase, even at 100 °C. Various, more stable phases can crystallize directly or indirectly from it at 100 to 180 °C and the factors determining which of them will appear in any given case are not fully understood. Afwillite is probably the stable product below about 140 °C, and hillebrandite above this temperature, but neither forms readily and $C_2S\alpha$-hydrate is the most usual product over the whole temperature range. Other possible products include $C_6S_4H_3$ and "Phase F."

CSH gel is the product formed in β-C_2S or C_3S pastes cured at room temperatures. It is also formed as the first product in such pastes at higher temperatures, up to at least 180 °C [38,39]. It resembles CSH(II) closely in composition, and in some other respects, but differs so much in degree of crystallinity, and possibly also in morphology, that it seems wiser to distinguish between them. The phases crystallizing from CSH gel are similar to those formed from CSH(II). In neat cement or C_3S pastes, where a sufficient excess of $Ca(OH)_2$ is also present, tricalcium silicate hydrate is a further recrystallization product.

A natural mineral recently described by McConnell [124], and the sythentic "Hydrate III" described by Kantro, Brunauer, and Weise [21] each appear to be roughly similar in composition and crystallinity to CSH gel.

Xonotlite. (C_6S_6H). This phase occurs as a natural mineral in many localities. It is also one of the easiest of the hydrated calcium silicates to make in the laboratory. The first well established synthesis was by Nagai [27]; syntheses up to 1950 were reviewed by Taylor and Bessey [11]. Since then many more have been reported. Xonotlite is formed reproducibly from any sufficiently reactive starting materials of its own Ca:Si ratio at 150 to 400 °C under pressures of saturated steam. Its formation from lime and silica proceeds through intermediate formation of CSH(II), CSH(I), and tobermorite [2,16]. The equilibrium P–T relations between xonotlite and tobermorite have already been discussed. Figure 2 shows the P–T curve for the equilibrium between xonotlite and β-$CaSiO_3$ [79]. Peppler [35] studied solid-liquid equilibria for xonotlite at 180 °C under a pressure of saturated steam. He concluded that it was a stable ternary phase in the system under these conditions.

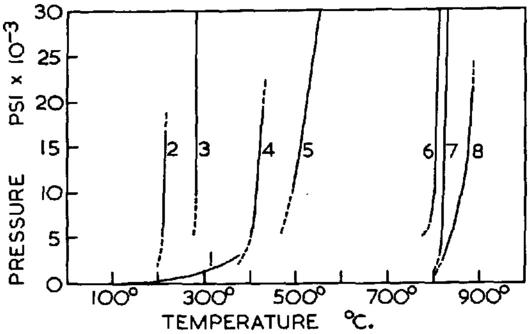

FIGURE 2. *P–T curves for some phase transformations in the* CaO-SiO_2-H_2O *system, obtained by Roy [4] and Buckner, Roy, and Roy [79].*

(1) H_2O liq.$\rightleftharpoons H_2O$ gas. (2) Afwillite$\rightleftharpoons$Phase Z$+H_2O$. (3) Tobermorite$\rightleftharpoons$xonotlite$+H_2O+$(?) reyerite. (4) Xonotlite$\rightleftharpoons\beta$-$CaSiO_3+H_2O$. (5) Tricalcium silicate hydrate$\rightleftharpoons$Ca-chondrodite$+Ca(OH)_2+H_2O$. (6) Phase Y$\rightleftharpoons\alpha'$-$C_2S+H_2O$. (7) Phase Z$\rightleftharpoons$Rankinite$+H_2O$. (8) Ca-chondrodite$\rightleftharpoons\alpha'$-$C_2S+CaO+H_2O$.

Xonotlite forms markedly fibrous or acicular crystals with a repeat distance of 7.3 A in the fiber direction. Synthetic crystals have a characteristically lath-like appearance in the optical or electron microscope [6,73]. These properties are satisfactorily explained in terms of the crystal structure, which was found by Mamedov and Belov [57,58] to contain double Dreierketten, of empirical formula $Si_6O_{17}^{10-}$ (fig. 1b) together with calcium and hydroxyl ions.

Published analyses of natural and synthetic xonotlites nearly all show higher water contents than that demanded by the formula $Ca_6Si_6O_{17}(OH)_2$ which is indicated by the X-ray structure determination; many indicate a composition of about C_5S_5H. Weight-loss curves [8,79] show approximately the theoretical loss of $1/6\ H_2O$:Si over the range 650 to 750 °C in which conversion to β-$CaSiO_3$ occurs, together with additional water that is lost gradually at lower temperatures. This circumstance suggests that the formula $Ca_6Si_6O_{17}(OH)_2$ is fundamentally correct, but that additional, more loosely bound water is usually or always present. The way in which this water is held is uncertain, although differential thermal analysis [79] and infrared absorption [77,79] constitute promising lines of approach. The question has also been discussed recently by Buckner, Roy, and Roy [79], and by Aitken and Taylor [8]. The dehydration reaction occurs by an oriented transformation, whether on heating at ordinary humidity [94] or under hydrothermal conditions [98].

Foshagite. (C_4S_3H). This phase was discovered as a natural mineral, and was originally believed to have the composition $C_5S_3H_3$ [125]. Its individuality as a species was at one time disputed, but was later established beyond doubt [6,72]. The original formula is, however, incorrect. Foshagite was first synthesized by Flint, McMurdie, and Wells [6] from glasses at 300 to 350 °C. under pressures of saturated steam. The synthesis has since been confirmed; Jander and Franke [12] made a product at 300 to 350 °C which was probably foshagite, while Gard and Taylor [72] prepared it at 500 °C and 6,000 psi, and Roy [4] at 450 °C and 15,000 to 30,000 psi. No P-T curves defining its stability range have been reported.

The crystals are markedly acicular, and the natural mineral forms long fibers [125]. There is a 7.3-A repeat distance along the fiber direction. The approximate crystal structure has been determined from X-ray fiber rotation photographs, and shows the presence of single Dreierketten together with calcium and hydroxyl ions [55, 56]. An alternative structure, involving double Dreierketten as in xonotlite [61], does not satisfactorily explain the X-ray intensities and other experimental data [56]. Foshagite is dehydrated at 650 to 750 °C, when it undergoes oriented transformation giving β-$CaSiO_3$ [92, 72]. There is also a tendency for β-Ca_2SiO_4 to crystallize, but the lime-rich product of this disproportionation is probably largely amorphous [56].

Afwillite. ($C_3S_2H_3$). This phase occurs as a natural mineral [126]. It forms short, prismatic crystals, and is remarkable among hydrated calcium silicates for its good crystallinity. Afwillite is a low-temperature product, which forms under pressures of saturated steam below about 160 °C. It was first synthesized by Bessey [11] at 98 °C. It has since been obtained by ball-milling of C_3S with water at room temperature [21, 127] and from lime-silica mixtures or β- or γ-C_2S at 110 to 160 °C [36, 128]. Its formation seems always to be slow. Heller and Taylor [36, 128] concluded from runs of 13 to 151 days' duration that afwillite was a stable phase at 110 to 160 °C, while Long and McConnell [124] obtained geological evidence that afwillite can exist in stable equilibrium with $Ca(OH)_2$ and solution at relatively low temperatures.

Although afwillite is probably a stable product, it is not readily prepared. Its formation from lime-silica mixtures, β-C_2S, or C_3S probably involves the intermediate formation of CSH(II) or similar material. As has already been noted, this compound changes more readily into other metastable but highly persistent phases, especially $C_2S\alpha$-hydrate. Under a pressure of saturated steam, afwillite probably becomes unstable relative to xonotlite and hillebrandite at about 140 °C. At higher pressures (fig. 2) it apparently remains stable until above 200 °C; the immediate decomposition products were unidentified, but at 300 °C and above Phase Z was obtained [4].

When afwillite is heated at atmospheric pressure, dehydration takes place at 275 to 285 °C [126, 129]. An oriented transformation occurs, giving γ-C_2S [92, 93, 129]. A preliminary discussion of the mechanism of this transformation has been given [93], but the question is complicated by the formation of one or more unstable, intermediate phases, a full explanation of which is not yet available [129]. On heating further to about 650 °C, a further oriented transformation occurs, giving an anhydrous, poorly crystalline form of Phase Z [4, 129]. This product was called "Phase Y" by Heller [92] (not the same as Roy's Phase Y!). At about 1,000 °C, rankinite is obtained [92]. The dehydration of afwillite has also been followed by differential thermal analysis [129].

Megaw [43] determined the crystal structure of afwillite; it is built from Ca^{2+} ions, H_2O molecules, and separate $HSiO_4^{3-}$ tetrahedra. Afwillite is structurally related to bultfonteinite ($Ca_4Si_2O_{10}H_6F_2$ [130]), but not closely to any other of the ternary phases. Infrared studies [80] support the results of the X-ray structure determination.

Phase Z. (C_3S_2—$C_6S_3H_2$ (?)). This phase was first described by Roy [4, 131], and must be distinguished from Z-phase (of Assarsson). It has not yet been reported as a natural mineral. Roy believed it to be C_9S_6H, but subsequent work suggests a variable composition, one end of the presumed solid-solution series being anhydrous. Roy made Phase Z from gels, and from afwillite, in runs of 1 to 14 days' duration (mostly 1 to 3 days) at about 300 to 830 °C and 2,000 to 20,000 psi. As already mentioned, an anhydrous variety of Phase Z is also produced when afwillite is heated in air at 650 °C. Work in this laboratory, on a specimen kindly provided by Roy, which had been made hydrothermally at 715 °C and 16,500 psi, showed that this specimen lost no weight in the range 100 to 1,400 °C. The material formed under such conditions is therefore anhydrous. In contrast, specimens made at lower temperatures and pressures appear to have higher Ca:Si ratios and to be hydrated. This result can possibly be attributed to hydrogarnet-type replacement of Si by 4H, which would give compositions trending towards $C_6S_3H_2$; further work is in progress to test this hypothesis. The so-called "C_2S γ-hydrate" or "$C_2SH(C)$" is probably a mixture containing the lime-rich, hydrated form of Phase Z as one constituent; this is discussed later.

The stability relations of Phase Z are not fully established. Roy obtained curves (fig. 2) for the upper stability limits of afwillite and of Phase Z, and it might be inferred that the latter was stable in the intervening field. However, longer runs appeared to give different products [132], and Phase Z may be unstable relative to Phase Y and other compounds, such as wollastonite or foshagite, over part or all of this range.

Roy [4] gave optical, X-ray powder, and infrared absorption data for Phase Z. The approximate unit-cell parameters have been determined in this laboratory from a combination of selected-area electron diffraction and X-ray work; the cell is orthorhombic or pseudoorthorhombic, body centered, with *a* 5.07, *b* 11.3, *c* 23A approx; the crystals are flaky with (001) cleavage. The unit-cell contents, for the anhydrous form of the phase, are 8 [C_3S_2]. The *a* and *b* dimensions are about the same as the corresponding ones for γ-C_2S and calciochondrodite, and Phase Z is evidently related structurally to these two compounds.

Incompletely characterized phases with Ca:Si near 1.5. Three apparently different phases of roughly similar compositions have each been reported only once. "$C_6S_4H_3$" was described by Flint, McMurdie, and Wells [6], who made it from glasses and from CSH(II) at 150 to 200 °C. They gave optical data, and the X-ray powder pattern was later reported [133]. "Phase F," of possible composition $C_5S_3H_2$, was reported by Aitken and Taylor [8] as a product formed in lime-quartz pastes cured at about 165 °C. Its formation was irreproducible, some specimens of lime giving it and others not. "Foshallassite," of approximate composition $C_3S_2H_3$, was reported as a natural mineral by Tschirwinsky [7]. The sum of the analysis was only 97.15 percent and the mineral was possibly zeophyllite.

Dicalcium silicate α-hydrate. (C_2SH). This phase is not known as a natural mineral; it was first isolated by Thorvaldson and Shelton [22] from steam-cured cement mortars. Early preparations are reviewed by Taylor and Bessey [11]. The compound has since been obtained by many investigators at temperatures usually between 100 and 200 °C under pressures of saturated steam [2, 5, 13, 36, 76]. The most usual starting materials have been lime-silica mixtures, gels, β- or γ-C_2S, or C_3S; in the last case, $Ca(OH)_2$ is also obtained. C_2S α-hydrate is readily formed from any of these starting materials; crystallization is further assisted by seeding [13]. Its formation is probably always preceded by that of CSH(II) or similar poorly crystallized material, and it is thus one of the several phases that can form from this below about 200 °C. Under most conditions it seems to be the most readily formed, and it is a common if not universal phase in steam-cured cement or lime-silica pastes of sufficiently high overall Ca:Si ratio. Its presence in steam-cured products is undesirable; this is considered later. Although C_2S α-hydrate crystallizes so readily, it does not seem ever to be produced as a stable phase. Below about 140 °C under saturated steam conditions, it is probably unstable relative to afwillite and $Ca(OH)_2$, while above 140 °C it is probably unstable relative to hillebrandite [2, 36]. Its transformation to these phases is slow.

The crystal structure has been determined [44] and indicates the constitution $Ca_2(HSiO_4)OH$. Infrared studies have been made of normal and deuterium substituted material [76,81]. Under favorable conditions, C_2S α-hydrate crystallizes well; Vigfusson, Bates, and Thorvaldson [23] made crystals up to 0.5 mm in size by treating quartz or silica glass plates with lime water in silver vessels at 170 °C. It forms orthorhombic tablets or plates of characteristic appearance. When formed in pastes, it is sometimes poorly crystallized. Buckle and Taylor [39] reported that its crystallization in autoclaved C_3S or β-C_2S pastes was gradual, cryptocrystalline material being initially formed. There is evidence of variable composition [2,5]. This seems unlikely to occur in fully crystalline material if Heller's structure is correct, but might occur in imperfectly crystalline material. Dehydration of C_2S α-hydrate occurs on heating in air of ordinary humidity at about 450 °C; weight-loss [76,84] and differential thermal analysis [5,76] studies have been made. The product is unoriented β-C_2S [92].

Hillebrandite. (C_2SH). This occurs as a natural mineral. The first established synthesis was by Nagai [27] in 1932. Hillebrandite has since been prepared by many investigators [2,5,6,11,23,35,73]. For a time there was doubt as to whether the natural and synthetic products were identical; but it was shown [11] that this was because the early powder data for the natural mineral were incorrect. Later work [36] revealed slight differences between the powder patterns of natural and synthetic materials. These have never been explained, but there can be no doubt that the two relate to essentially the same species.

Hillebrandite is one of the more troublesome of the hydrated calcium silicates to prepare. It has been obtained starting from lime-silica mixtures, gels, and β-C_2S, but there seems to be no record of its having been made from γ-C_2S or from C_3S. All of the preparations have been made at saturated steam pressures, usually in the range 150 to 250 °C. As has already been stated, the initial product of such reactions is probably CSH(II). Hillebrandite seems to crystallize from this not as an immediate product, but through intermediate formation of C_2S α-hydrate [2,5,36]. It forms slowly at 140 °C [36], and more rapidly at higher temperatures; but above about 160 °C "C_2S γ-hydrate" is often more readily formed. Kalousek, Logiudice, and Dodson [5], commenting on the difficulty of preparing hillebrandite reproducibly, believed that the physical state and reactivity of the silicic acid were important factors. One recent careful investigation [13] did not yield hillebrandite, even though its formation might have been expected under the conditions used. There is some evidence that hillebrandite is the stable phase in contact with water and saturated steam at about 140 to 180 °C. Heller and Taylor [36] obtained an apparently pure specimen by a 166-day treatment of β-C_2S at 140 °C. Peppler [35] determined its solubility relations at 180 °C, and from experiments of 6 months' duration concluded that it was a stable ternary phase at this temperature.

Hillebrandite forms fibrous crystals with a 7.3-A repeat distance, and almost certainly contains Dreierketten. The ionic formula is therefore possibly $Ca_2(SiO_3)(OH)_2$. Mamedov and Belov [62] suggested that double Dreierketten occur, giving $Ca_{12}(Si_6O_{17})(OH)_{14}$, or $C_{12}S_6H_7$. Further work is needed to test these two hypotheses. Dehydration occurs at 520 to 540 °C giving unoriented β-C_2S; Toropov, Nikogosyan, and Boikova [134] showed that there was an intermediate, amorphous stage, and believed that this supported Mamedov and Belov's suggested structure. Differential-thermal-analysis data have been obtained [5,134]. Kalousek, Logiudice, and Dodson [5] considered that variable Ca:Si ratio occurs, and further suggested the possibility of a solid-solution series embracing also foshagite and tricalcium silicate hydrate. Subsequent unit-cell determinations [41, 72, 135] show, however, that the three species are quite distinct. The possibility of limited variability of composition can nevertheless not be ruled out, at least for badly crystallized material.

Phase Y. (C_6S_3H). This phase is not known in nature. It was described by Roy [4, 131]; unit-cell and dehydration data were afterwards given [42]. It has since been shown [136] that several preparations of earlier workers were probably substantially identical with phase Y. These are $C_2SH_{0.5}$ of Jander and Franke [12], $C_6S_3H_2$ of Flint, McMurdie, and Wells [6] and van Valkenburg and Rynders [137], also called $C_2SH(D)$ [9], $C_2SH_{0.5}$ of Funk [13], and $C_2SH(D)$ of Buckle [84]. The evidence for this statement is based on: (1) optical data, which are substantially the same for all, apart from the preparation of Flint *et al*, which was a pseudomorph and might well be anomalous; (2) comparison of X-ray single crystal photographs for the actual preparations made by Roy, Funk, and Buckle; (3) comparisons of new X-ray powder photographs for these preparations, along with the published data of Jander and Franke and of Flint, McMurdie, and Wells. The X-ray powder data published previously for these preparations seem to have been inaccurate in varying degrees, and new data will be reported elsewhere. Other properties are well described by Roy [4] and Dent Glasser and Roy [42]. They obtained good evidence for the H_2O:Si ratio 1:3; other recent results are compatible with this ratio [13, 84].

Roy [4] obtained her preparation at high temperatures and pressures, typically at about 790 °C and 10,000 to 25,000 psi. The other workers used lower temperatures and pressures. Jander and Franke, Funk, and Buckle all worked at about 350 °C under pressures of saturated steam (2,450 psi) while Flint, McMurdie, and Wells worked at 450° C and 6,000 psi. Roy used as starting materials β- and γ-C_2S and gels; Jander and Franke used mixtures of lime and quartz; Buckle used β-C_2S; Flint, McMurdie, and Wells used C_2S α-hydrate; Funk found that his product was formed irreproducibly from α- or α'-C_2S, rarely from β-C_2S, and never from γ-C_2S. At high temperatures under hydrothermal conditions, Phase Y is decomposed giving α'-C_2S. Roy [4] obtained a P–T curve (fig. 2) for this transformation, which occurs at about 810 °C at 20,000 psi. Phase Y is also dehydrated giving β-C_2S when heated at about 700 °C under atmospheric humidity; weight-loss curves have been reported [42, 84].

Phase Y forms short, prismatic crystals, which often show simple twinning across a plane in the prism zone. The crystal structure is unknown. The repeat distance of 6.73 A in the prism direction suggests a resemblance to β-C_2S, but the transformation is unoriented [42]. The high dehydration temperature of 640 to 700 °C [42, 84] suggests that the hydroxyl is ionically bound, giving $Ca_6(SiO_4)(Si_2O_7)(OH)_2$. Roy [4] obtained infrared data, but these have not been interpreted in detail.

Calcio-chondrodite (*Phase X*). (C_5S_2H). This is not known as a natural mineral. It was first described by Roy [4, 131] and, somewhat later, by Buckle and Taylor [14]. Funk's "$C_2SH(CII)$" [13], discussed in the next section, also seems to have consisted largely of this phase. Roy called her product "Phase X," and considered it to be $C_8S_3H_3$; Buckle and Taylor called theirs calcio-chondrodite, with the formula C_5S_2H. They showed from a unit-cell determination that it was structurally analogous to the well established mineral, chondrodite ($(Mg,Fe)_5(SiO_4)_2(OH,F)_2$) and their formula was based on this analogy and supported also by other data. Comparison of the reported X-ray powder and optical data shows that the two preparations are substantially identical. There is, however, an error in the optical data given by Buckle and Taylor; the sign of elongation should be negative (as stated by Roy) and not positive.

Roy obtained calcio-chondrodite from various starting materials mainly at 400 to 800 C° and pressures above 5,000 psi. She obtained P-T curves (fig. 2) defining its stability relative to tricalcium silicate hydrate and to α'-C_2S. At lower pressures, it is formed at considerably lower temperatures; if, as seems likely, "C_2S γ-hydrate" is a mixture containing calcio-chondrodite, the latter can be obtained from β- or γ-C_2S at temperatures as low as 180 °C.

Calcio-chondrodite forms prismatic crystals which resemble those of olivine in appearance. They often show twinning across a plane in the prism zone. Roy [4] reported infrared data. Buckle and Taylor [14] reported a weight-loss curve and showed the dehydration products to be γ-C_2S and CaO. The formation of γ- and not β-C_2S, considered along with the structural similarity, suggests the probable occurrence of an oriented transformation, but this was not experimentally verified.

"C_2S γ-hydrate." ($C_2SH_{0.2-1}$). This name is used for the product most often obtained when β- or γ-C_2S or lime-silica mixtures with Ca:Si=2, are autoclaved at 200 to 300 °C under saturated steam pressures. It has been reported by many investigators [5, 6, 11, 24, 36, 76]. Recently, Roy [4] has described an essentially similar "Phase X*," and Funk [13] a "$C_2SH(CI)$" and "$C_2SH(CII)$." The material crystallizes badly, and the only recorded crystallographic data are a mean refractive index and an X-ray powder pattern. Both of these, and also the H_2O:Si ratio, vary slightly from one sample to another. Weight-loss [84] and differential-thermal-analysis [5, 76] data have been obtained, and also infrared data [76].

The X-ray pattern resembles that of calcio-chondrodite. Both Roy [4] and Buckle and Taylor [14] considered the possibility that the two substances were related. The general formula for the calcium chondrodite series is $2\frac{1}{n}CaO{\cdot}SiO_2{\cdot}\frac{1}{n}H_2O$ and the lower limit of Ca:Si ratio is thus provided by γ-C_2S. C_2S γ-hydrate cannot therefore be simply a member of this series. It is, however, so badly defined a substance that there is no convincing reason to believe that it is a single phase. The fact that its X-ray powder pattern is approximately reproducible proves nothing, because almost all the preparations have been made from starting materials of the same Ca:Si ratio. Indeed, when this ratio is lowered [5], there is an apparently gradual change to a pattern now identified as belonging to Phase Z.

It thus seems possible, as Roy [4] suggested, that C_2S γ-hydrate or "Phase X*" is a member of the calcium-chondrodite series mixed with a phase having Ca:Si$<$2. She suggested that hydrous silica might be present. It seems more probable to the author that these and similar products are mixtures of calcio-chondrodite and Phase Z. With increasing temperature of preparation, the Phase Z would become poorer in lime, and the proportion of calcio-chondrodite would therefore increase. In agreement with this hypothesis, Funk's C_2SH(CII), made at 250 to 350 °C, gave an X-ray pattern close to that of calcio-chondrodite, whereas his C_2SH(CI), made at 200 °C, gave a pattern resembling that of Phase Z.

C_2S γ-hydrate seems to form particularly readily from γ-C_2S. This is understandable if it is a mixture of two phases, both of which are structurally related to γ-C_2S, and which could thus be formed by oriented transformation. The difficulty of making hillebrandite from γ-C_2S can probably be explained by the fact that C_2S γ-hydrate forms more easily, and is not decomposed until temperatures well above those at which hillebrandite can be formed.

Tricalcium silicate hydrate. ($C_6S_2H_3$). This phase does not occur as a natural mineral but is reproducibly prepared by hydrothermal treatment at 200 to 450 °C of C_3S, or other starting materials of similar Ca:Si ratio [4,6,10,24,29,41]. Below 200 °C, C_2S α-hydrate and $Ca(OH)_2$ usually are formed, although tricalcium silicate hydrate has been made from C_3S in freshly mixed pastes as low as 75 °C [39]. Above about 450 °C, calcio-chondrodite is formed; Roy [4] determined a P-T curve defining the upper stability limit of tricalcium silicate hydrate (fig. 2). Under saturated-steam conditions, tricalcium silicate hydrate is not easily obtained free from C_2S α-hydrate or calcio-chondrodite. Curve 5 (fig. 2), on extrapolation downwards, may roughly coincide with the saturated-steam curve. If this is so, pure samples could better be obtained by working at pressures above this curve.

There has been considerable doubt about the H_2O:Si ratio of this compound, and the value 2 has often been assumed. Recent work [41] supports earlier indications that the true value is 1.5. Tricalcium silicate hydrate forms long, fibrous crystals [6,41]. The repeat distance of 7.48 A in the fiber direction [41] is similar to that of wollastonite and other calcium silicates containing Dreierketten. Buckle, Gard, and Taylor [41] suggested that the relatively high dehydration temperature of 420 to 550 °C indicates ionic binding of the hydroxyl, giving the constitutional formula $Ca_6(Si_2O_7)(OH)_6$. The $Si_2O_7^{6-}$ groups could be placed with their long axes parallel to the fiber direction, giving Dreierketten with one tetrahedron in three missing, as is known to occur in cuspidine [138] and tilleyite [139]. Mamedov, Klebtsova, and Belov [63] developed this hypothesis further and postulated a complete crystal structure, but this has not been experimentally tested.

The weight-loss curve [41] suggests that the water is lost in two stages; this has not been explained. The products of dehydration are γ–C_2S and CaO; the formation of γ–C_2S could be taken to indicate a structural relationship, as with calcio-chondrodite. Further study of the mechanism of this transformation is needed.

Some General Considerations

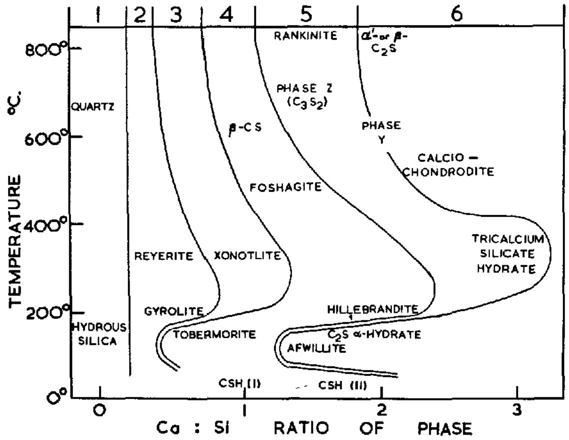

Figure 3. *Approximate temperatures of formation of the better established hydrated or anhydrous calcium silicates under hydrothermal conditions.*

Saturated steam conditions are assumed below 374 °C.; for other reaction conditions, see text. Curves group phases according to known or probable degree of condensation of anion. (1) Frameworks. (2) Sheets. (3) Double chains. (4) Single chains or rings. (5) Si_2O_7 groups. (6) Isolated tetrahedra.

The relationships between structure and the conditions of formation and of dehydration. Available knowledge of the CaO–SiO_2–H_2O system is quite inadequate to permit the drawing of anything approaching a true phase equilibrium diagram for the system as a whole. The results most important to cement chemistry can, however, be summarized by plotting the Ca:Si ratio of each phase against the temperature at which it is most readily formed (fig. 3). For this purpose it was assumed that: (1) below 374 °C the pressure is that of saturated steam, and above 374 °C it is about 5,000 psi, (2) reactive starting materials are used, such as CSH(I), β–C_2S, or C_3S, (3) reactions are carried out in aqueous suspension, and (4) sufficient time is allowed for the formation of *apparently* stable products (a few months below 150 °C, falling to a few days at 800 °C).

The curves in figure 3 group the phases according to the known or probable degree of condensation of the anion. They are necessarily somewhat speculative, mainly because many of the crystal structures are unknown. Certain trends nevertheless seem clear. Above about 200 °C, a low degree of condensation is favored by increase in Ca:Si ratio and increase in temperature. This trend is a consequence of the fact that, in these relatively high-temperature phases, water when present occurs as ionically bound hydroxyl, the proportion of which tends to decrease as the temperature is raised. The dislocation of the curves below 150 to 200 °C is explained by the fact that in low temperature products, water can also occur as Si–O–H or H_2O.

A relation between structure and temperature is also apparent in the conditions of dehydration at ordinary humidity under quasi-static conditions. Where the water occurs partly or wholly as H_2O or Si–O–H (tobermorite, nekoite, gyrolite, afwillite, C_2S α-hydrate), dehydration occurs below about 450 °C. In some cases, it begins below 100 °C. Where the water occurs entirely as ionic OH^-, dehydration occurs at higher temperatures. The dehydration temperature tends to increase as the water content decreases; in $Ca(OH)_2$, with the highest water content, it is about 400 °C [84], while in reyerite, xonotlite, foshagite, Phase Y, and calcio-chondrodite, which have low water contents, it is around 700 to 800 °C. Hillebrandite and tricalcium silicate hydrate are intermediate cases. A rough correlation between temperatures of hydrothermal formation and of dehydration at ordinary humidity is to be expected, as the dehydration of a hydrous phase under the two types of conditions is essentially the same process. In general, it occurs at considerably higher temperatures when atmospheric humidity is used; the dehydration of xonotlite to β-$CaSiO_3$, for instance, occurs at about 700 °C under these conditions but about 400 °C under hydrothermal conditions. This relationship is the opposite of what would be expected from extrapolation of P-T curves (fig. 2) to very low water-vapor pressures. It must be concluded that dehydration temperatures at ordinary humidity are usually determined by kinetic and not equilibrium considerations, and that the dehydration process is strongly catalyzed by water or steam under hydrothermal conditions.

The influence of CO_2 *contamination in hydrothermal studies on the* CaO-SiO_2-H_2O *system.* It is difficult entirely to avoid contamination of hydrated calcium silicate preparations by CO_2, and under technical conditions this is often virtually impossible. A knowledge of the influence of CO_2 on the system is therefore important. In principle, there appear to be three possible effects as regards the phases formed:

(1) *The* CO_2 *is present entirely as* $CaCO_3$.—Where more than a few percent of CO_2 is found by chemical analysis, the lines of calcite, or vaterite, or both can nearly always be found in the X-ray pattern. Crystallization in the form of vaterite seems to occur particularly readily in the presence of hydrated calcium silicates.

(2) *The* CO_2 *enters into the structure of a hydrated calcium silicate.*—This possibility is suggested by analogy with the hydrated calcium aluminates, some of which can accommodate CO_3^{2-} ions with relatively minor changes in structure, apparently through replacement of $2OH^-$ by CO_3^{2-} together with adjustment in the number of water molecules [140]. This replacement is thus most likely to occur in tobermorite minerals and other low-temperature phases. Gaze and Robertson [68] suggested that CO_3^{2-} could enter into the structure of tobermorite, but more recent evidence [141] indicates that all the CO_2 in tobermorite preparations can be attributed to calcite, aragonite, or vaterite.

(3) *New phases are formed, in which* CO_2 *is an essential constituent.*—There are three known phases of this type: spurrite, tilleyite, and scawtite.

Scawtite was originally found as a natural mineral and has been considered to have the formula $Ca_7(Si_6O_{18})CO_3 \cdot 2H_2O$. More recently, other specimens have been found with somewhat different compositions. McConnell and Murdoch [142], in a review of the subject, concluded that these variations in composition could best be explained by assuming replacement of tetrahedrally coordinated Si by C in triangular coordination; they proposed the general formula $Ca_{14}(OH)_4(Si_{16-x-y}C_{4x/3}H_{4y})O_{44}$. This cannot be right, as it implies that the carbon is trivalent; confusion has arisen between coordination number and oxidation state. The formula can also be criticized on the ground that it presupposes a structural relation to the amphiboles, which, as already seen, is unlikely for a calcium silicate. The unit cell [143, 144] suggests the presence of Dreierketten rather than Zweierketten. The correct formulation of scawtite thus awaits further work. The hypothesis of replacement of Si by C, in a broad sense, nevertheless appears highly probable, and the possibility thus exists of finding or preparing a scawtite low in CO_2.

Flint, McMurdie, and Wells [6] prepared a phase which they considered to be $CaO \cdot SiO_2 \cdot H_2O$ under saturated steam conditions at 150 °C. Other workers have since obtained the phase under comparable conditions [16, 76, 79]; it appears to form from tobermorite at or just below the transition temperature to xonotlite. Bogue [9] called it CSH(A). Its X-ray pattern is very like that of scawtite [143, 144]. Buckner, Roy, and Roy [79] suggested that it was in fact identical with scawtite. This identity appears probable in view of the results for the natural mineral described above. The nonreproducibility of formation of CSH(A) further accords with the hypothesis that its synthesis depends on CO_2 contamination.

Tilleyite ($Ca_5(Si_2O_7)(CO_3)_2$) and spurrite ($Ca_5(SiO_4)_2(CO_3)$) are anhydrous phases and form at higher temperatures. Both occur naturally and have also been synthesized. In a series of studies [145–146], Tuttle and Harker obtained P_{CO_2}-T curves for phase transformations in the anhydrous ternary system CaO-SiO_2-CO_2. They synthesized both spurrite and tilleyite at high temperatures and pressures of CO_2. McConnell [147] showed that they could also be made at somewhat lower temperatures in the absence of excess CO_2 but with water at high pressures also present.

All the studies discussed in the remaining sections of this review relate to saturated steam pressures.

The immediate products of hydration of C_3S *and* β-C_2S *in pastes.* When pastes of C_3S or β-C_2S are cured at 100 to 200 °C, the immediate products do not seem to differ greatly from those formed at ordinary temperatures. With most specimens of β-C_2S, and probably all specimens of C_3S, these products are CSH gel and $Ca(OH)_2$. The constitution and composition of the CSH gel is discussed elsewhere in this symposium [20], and will not be considered in detail here. Interpretations still differ, but it seems certain that Ca : Si is always between 1.5 and 2.0; there is evidence that it rises within this range as the curing temperature is increased [20, 38]. With this qualification, CSH gel formed at 100 to 200 °C seems to differ little from the corresponding product formed at room temperature.

Funk [38] has recently shown that the behavior of β-C_2S on hydration in pastes at 20 to 120 °C depends on the stabilizer present. With some stabilizers, including the commonly used 0.5 percent B_2O_3, CSH gel and $Ca(OH)_2$ were formed. Funk described β-C_2S made using these stabilizers as "completely stabilized." It seems probable that the β-C_2S in cement clinker is normally of this type. When certain other stabilizers were used, such as 0.2 percent Na_2O, the β-C_2S inverted on curing to give a modified form of γ-C_2S. These samples of β-C_2S were called "insufficiently stabilized." These effects were substantially independent of temperature within the range stated. Later work [13] showed the γ-C_2S to be anomalous in several respects. It had a composition, after drying over P_2O_5 at 20 °C, of 1.8 to $2.0\ CaO \cdot SiO_2 \cdot 0.5$–$1.0\ H_2O$, showed minor abnormalities in its X-ray pattern, and tended, more readily than did normal γ-C_2S, to change further giving CSH gel.

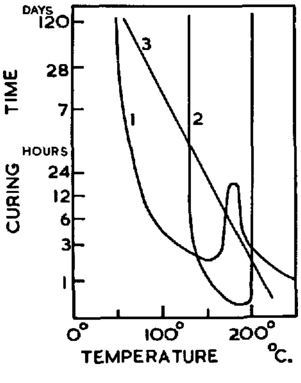

Figure 4. *Phases detected in* C_3S *pastes cured at 20 to 250 °C.*

(1) Lower limit of formation of tricalcium silicate hydrate. (2) Lower limit of formation of C_2S α-hydrate. (3) Upper limit of occurrence of unreacted C_3S. $Ca(OH)_2$ was nearly always found for temperatures below 200 °C. $Ca(OH)_2$ and CSH gel were the only hydrated phases detected below and to the left of curves 1 and 2.

Subsequent reactions in β-C_2S *pastes.* When "fully stabilized" β-C_2S is hydrated at ordinary temperatures in pastes to give CSH gel and $Ca(OH)_2$, no further reactions occur at any detectable rate. This is still true at 100 °C. Above about 120 °C, however, C_2S α-hydrate crystallizes from the gel. Buckle and Taylor [39] were able to detect this phase by X-ray methods after 5 days at 120 °C. It formed increasingly rapidly as the temperature was raised and was found after 12 hours at 180 °C. The β-C_2S used was rather coarsely ground, and C_2S α-hydrate might be expected to form more rapidly if the particle size was similar to that of the β-C_2S in cement. No other phases were detected in the products of runs at or below 180 °C, with curing times up to 28 days. Unchanged β-C_2S was found in all these products, and CSH gel and $Ca(OH)_2$ were also probably always present. These reactions show that hydration of β-C_2S in pastes at 100 to 180 °C proceeds in the way that might be expected from the fundamental studies discussed previously in this review. CSH gel and $Ca(OH)_2$ are the initial products. and above 120 °C C_2S α-hydrate crystallizes from them. Both processes occur more slowly than in suspensions, and the subsequent changes to give equilibrium products such as afwillite or hillebrandite do not occur in the times used in practice.

Subsequent reactions in C_3S *pastes.* Buckle and Taylor [39] studied the phases formed in C_3S pastes cured at 20 to 200 °C; they also made a few runs at higher temperatures. X-ray, optical, and weight-loss methods were used. They confirmed that CSH gel and $Ca(OH)_2$ were the immediate products, at least up to 200 °C. They were the only products for times up to 5 hr at 100 °C, or 30 min at 170 °C. With longer curing times, C_2S α-hydrate, or tricalcium silicate hydrate (TSH), or both were formed, as shown in figure 4. The exact positions of the curves in figure 4 apply only to the particular sample of C_3S used in the investigation. Other samples would possibly behave somewhat differently.

Figure 4 shows that C_2S α-hydrate is formed at 130 to 200 °C, and TSH in two ranges above and below 180 °C. These results do not differ appreciably from those found with suspensions except for the existence of the low-temperature range of formation of TSH at 50 to 170 °C. This range is not found with suspensions; Buckle and Taylor showed, in addition, that it did not occur with aged C_3S pastes that had already been cured for several years at room temperature. They concluded that TSH was formed at these temperatures as a non-equilibrium product. The only other investigators who have reported the formation of TSH below 180 to 200 °C appear to be Keevil and Thorvaldson [24], who were able to prepare it at temperatures as low as 110 °C by autoclaving initially dry C_3S powder in saturated steam. These conditions thus appear to resemble those existing in a paste.

Buckle and Taylor also made optical studies on C_3S pastes. In general, pastes cured below 200 °C consisted of a gelatinous or cryptocrystalline matrix in which were embedded crystals of unreacted C_3S and of hydrated phases. In pastes cured under sufficiently mild conditions of time and temperature, this matrix consisted of CSH gel together probably with cryptocrystalline $Ca(OH)_2$; under more severe conditions, it probably also contained cryptocrystalline C_2S α-hydrate or TSH, or both. These phases, and also $Ca(OH)_2$, segregated gradually from the matrix as curing proceeded. In pastes cured above 200 °C, the matrix had largely or completely disappeared and only crystalline phases were observed.

The reactions occurring in C_3S pastes can be summarized as follows. The initial products are CSH gel and $Ca(OH)_2$; at first they are so intimately mixed as to be barely distinct phases, but crystals of $Ca(OH)_2$ gradually separate. Two further processes can then occur under appropriate conditions. Firstly, at 130 to 200 °C, the CSH gel is transformed into C_2S α-hydrate. Crystallization of this phase is probably a gradual process. It is probably cryptocrystalline at first and, when in this state, can possibly have a nonstoichiometric composition, as was suggested by Kalousek, Logiudice, and Dodson [5]. The formation of C_2S α-hydrate probably occurs through an internal rearrangement within the CSH gel and does not depend much, if at all, on reaction with the $Ca(OH)_2$ crystals. It therefore occurs readily, even in aged pastes. Secondly, TSH can be formed. Because TSH has a high Ca:Si ratio, this process depends on reaction between the CSH gel and $Ca(OH)_2$. It therefore does not occur below 180 to 200 °C, except in fresh pastes where the $Ca(OH)_2$ crystals are still small, and which are thus still relatively homogeneous. Above 180 to 200 °C complete recrystallization of the material occurs within a few days. This results in the formation of TSH, or at higher temperatures, of calcio-chondrodite and $Ca(OH)_2$; these phases are probably then formed as equilibrium products.

The compressive strengths of autoclaved C_3S *and* β-C_2S *pastes.* Assuming typical curing times of 12 to 24 hr, the strengths of β-C_2S pastes increase continuously with curing temperature up to at least 200 °C; those of C_3S pastes, in contrast, decrease markedly when the curing temperature exceeds 180 to 200 °C. C_3S pastes cured below 180 to 200 °C are stronger than β-C_2S pastes, but for higher curing temperatures the reverse is true [39, 148]. This phenomenon is readily explained. Development of strength in C_3S or β-C_2S pastes without added silica seems to depend on the formation of an adequate proportion of the matrix. With either compound, the sequence of reactions is one in which the matrix is first formed and afterwards destroyed. β-C_2S reacts so slowly that the first process is still the dominant one, even after many hours' curing at 200 °C; strengths at this temperature are therefore greater for typical curing times of 12 to 24 hr than at lower temperatures. C_3S reacts more rapidly, so that the second process occurs extensively after a few hours at 180 to 200 °C. This causes the strengths of C_3S pastes cured for typical periods at 200 °C to be much lower than those of pastes cured for similar times at lower temperatures.

Hydrothermal curing of neat cement pastes. The first systematic study of the hydrated phases produced in neat cement pastes cured hydrothermally was made by Kalousek and co-workers [86–88]. They based their conclusions principally on the results of differential-thermal-analysis studies. With cements cured at 100 °C and above, any separate hydrated aluminate or sulfoaluminate phases that were initially formed were quickly decomposed. There was evidence that at 100 °C, ettringite persisted for up to 30 min; a $C_4AH_{13}-C_3A{\cdot}CaSO_4{\cdot}12H_2O$ solid solution was then formed, and was at a maximum in 2 hr, but this also had disappeared within 4 hr. The product of this reaction, which Kalousek called "Phase X," was a gel containing all the oxide components of the cement. At curing temperatures above 100 °C, no separate hydrated aluminate or ferrite phases at all were found. A particularly careful search was made for C_3AH_6 or hydrogarnet solid solutions, but these were not found, although a number of different cements were examined after differing curing times at temperatures between 120 and 175 °C. C_2S α-hydrate was, however, detected in cements cured at these temperatures.

Kalousek believed that Phase X formed at or above 100 °C differed from the corresponding phase formed at lower temperatures, though perhaps only in porosity. It seems to be essentially the same as CSH gel, modified by the incorporation of Al_2O_3 and the other minor components of the cement.

Kalousek [37] and Kalousek and Prebus [17] afterwards reported X-ray and electron microscope studies on neat cement pastes cured at 50 to 120 °C. With one cement, cured according to a plant cycle at 50 to 80 °C, they obtained evidence of the formation of CSH gel, fibrous CSH(II), $Ca(OH)_2$, hillebrandite, and, possibly, C_2S α-hydrate. An oil-well cement cured at 120 °C also appeared to yield hillebrandite. The reported formation of this phase can be compared with that of TSH from pure C_3S under similar conditions [39]. It is tempting to suppose that the phase formed in the cements may in reality have been TSH, as the X-ray patterns of TSH and hillebrandite are difficult to distinguish in a complex mixture. On the other hand, cements may very well differ from pure C_3S in their behavior. In either case, Kalousek's observation seems to provide further evidence that certain hydrated phases are sometimes formed in pastes at temperatures much lower than those at which they are formed in suspensions.

Sanders and Smothers [120] made X-ray studies on a neat cement paste cured for 24 hr at 182 °C.

They found CSH gel, $Ca(OH)_2$, C_2S α-hydrate, and unreacted C_3S and β-C_2S.

These results suggest that the behavior of neat cements in the autoclave is not too different from that of β-C_2S or C_3S; the successive formation of a modified form of CSH gel and of C_2S α-hydrate, together with $Ca(OH)_2$ in each case, seems established. More work is clearly needed to establish definitely whether, and if so in what form, the Al_2O_3 and other minor constituents are incorporated in the CSH gel. It would also be interesting to know whether separate aluminate phases, such as C_3AH_6, hydrogarnets, or $C_4A_3H_3$ can be detected if curing temperatures above 200 °C are used.

Hydrothermal Reactions in Lime-Silica and Cement-Silica Pastes

Introduction. The studies on neat cement, C_3S, and β-C_2S pastes described in the previous section are of direct technical interest only up to temperatures little above 100 °C. When higher curing temperatures are used, low strengths are obtained unless finely divided quartz or other reactive forms of silica are added to the cement. Small additions of silica cause a decrease in strength, but larger additions, of 40 to 70 percent on the weight of the cement, cause a marked increase [149]. These variations in strength can be compared with the overall Ca:Si ratio of the mix. For most neat cements, this ratio is around 3. Minimum strengths are obtained when it is around 2, and maximum strengths at 0.8–1.0. Comparable results for lime-quartz pastes have recently been obtained [150]. These results indicate that the bonding material in autoclaved products has a lower Ca:Si ratio than the CSH gel which serves this purpose in products cured at lower temperatures. As will be shown, it is also much more crystalline. This fact accounts for the lower drying shrinkages that are found with autoclaved products.

Autoclaved lime-silica pastes. These are of direct technical importance because they include sand-lime bricks, lightweight heat-insulating materials, and other commercial products. They are also of interest because they provide a means of studying the most important of the processes that occur in cement-silica pastes while avoiding the complications inherent in a multicomponent system.

Bessey [151] reported optical studies on sand-lime bricks, and also made estimates of the Ca:Si ratios of the bonding material based on soluble silica determinations. He found that the bonding material was sometimes gelatinous, sometimes crystalline, and that its Ca:Si ratio varied from 0.97–1.77. The gelatinous material was probably CSH gel, while the appearance of the crystalline one suggests that it may have consisted of xonotlite. Taylor [152] showed from X-ray and chemical studies that a tobermorite mineral was present in a commercial lightweight sand-lime block. The X-ray data can be reinterpreted in the light of present day knowledge as indicating the presence of crystalline 11.3-A tobermorite. The overall Ca:Si ratio of the bonding material was shown from soluble silica determinations to be 1.28. A poorly crystallized tobermorite mineral of higher Ca:Si ratio than tobermorite itself was therefore probably also present and undetected by the X-ray determination.

A more systematic investigation was made by Kalousek [90] who prepared blocks from lime and silica, and also from other starting materials; he examined the products mainly by X-rays, differential thermal analysis, and soluble-silica determinations. His X-ray results confirmed that crystalline tobermorite was a frequent constituent of autoclaved pastes in which the bonding material had a Ca:Si ratio below 1.3. His differential-thermal-analysis results showed that CSH(I) was also present, as there was a strong exothermic peak at 840 to 860 °C. Where the Ca:Si ratio of the bonding material exceeded 1.3, the differential-thermal-analysis results showed the presence of C_2S α-hydrate.

Kalousek [37] later showed that the reaction between lime and silica involved the intermediate formation of CSH(II) and CSH(I), or of phases similar in composition to these. The reactions of $Ca(OH)_2$ with quartz and with silicic acid were followed using X-rays, differential thermal analysis, soluble-silica determinations, specific-surface measurements and electron microscopy. The reactions were studied in slurries with a water-to-solids weight ratio of 3.5, but it seems probable that the results are in general applicable also to pastes. For mixes of Ca:Si mole ratio 0.8, using either quartz or silicic acid, the initial product had the approximate composition $C_{1.75}SH_n$. Kalousek considered that this was usually CSH(II), but that in some cases where quartz was used, a poorly crystallized form of C_2S α-hydrate was formed instead. In either case, this lime-rich phase then reacted with more silica, giving in succession compounds of the compositions $C_{1.25}SH_n$, CSH_n, and $C_{0.8}SH_n$, followed by tobermorite. The specific surface rose to a maximum with the formation of $C_{0.8}SH_n$, and afterwards fell sharply with the crystallization of tobermorite. At first, Kalousek considered that the compositions $C_{1.25}SH_n$, CSH_n, and $C_{0.8}SH_n$ corresponded to distinct compounds, but later [17] he regarded these as being all essentially the same phase, with a Ca:Si ratio variable between 0.8 and 1.33. This is the phase called CSH(I) in this review.

Kalousek found that the rates of these successive transformations depended on the exact nature of the starting material. In particular, the transformation of CSH(I) into tobermorite was more rapid with quartz than with silicic acid. He attributed this difference to the higher silica concentrations in solution likely to be obtained with silicic acid, which he believed would make the

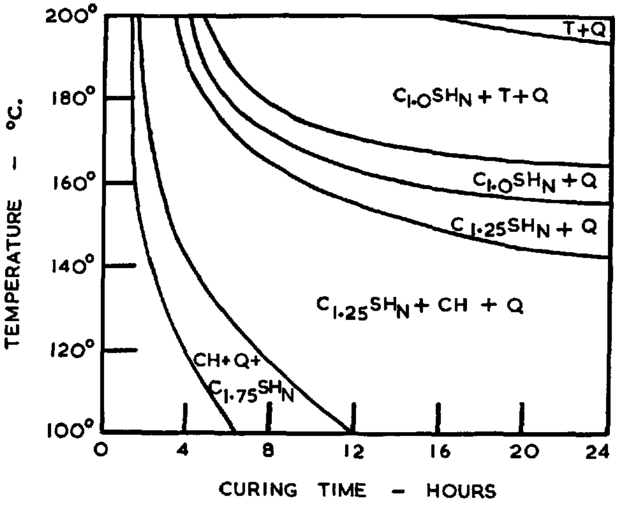

FIGURE 5. *Phases detected in lime-quartz pastes* (*Neese [121]*).

Ca:Si molar ratio 0.33, specific surface of quartz 4514 cm²/g. Q=quartz, T=tobermorite, CH=$Ca(OH)_2$.

CSH(I) more stable relative to tobermorite. He found also that the presence of reactive Al_2O_3 favored the formation of tobermorite.

In the main, these results have been amply confirmed by the work of later investigators. It may, however, be doubted whether C_2S α-hydrate is ever an initial product in the lime-silica reaction. Other workers have considered that the initial product is always a poorly crystallized tobermorite mineral, and that C_2S α-hydrate forms from this as a second-stage product [2, 8, 36]. As stated previously, Kalousek's results, though obtained on slurries, probably apply in other respects to pastes. Rates of reaction may be somewhat different, and the intermediate products may be less well crystallized in pastes. The high-lime tobermorite mineral, in particular, is probably CSH gel rather than CSH(II) when formed in pastes.

Neese and associates [106, 121] studied the phases produced in lime-quartz pastes, using chemical, X-ray, and optical methods, as well as differential thermal analysis, weight-loss curves, and dilatometry. They prepared pastes with molar Ca:Si ratios of about 0.33 and 0.66, as well as ones using cement, which are discussed later. Typical results are shown in figure 5. They confirm Kalousek's views on the intermediate formation of CSH(II) and CSH(I).

Aitken and Taylor [8] also studied the phases produced in lime-quartz pastes. They investigated a wider range of Ca:Si ratios than did Neese, and also extended the autoclaving periods to longer times, but did not attempt to distinguish between different, poorly crystallized tobermorite minerals, which were collectively called CSH. Other products obtained were tobermorite, xonotlite, gyrolite, C_2S α-hydrate, hillebrandite, and "Phase F." From the results of this study, together with those already described, the principal features of the lime-quartz reaction in pastes autoclaved under saturated steam pressures at 100 to 200 °C can be summarized as follows:

(1) The initial reaction gives CSH(II) or CSH gel, with a Ca:Si ratio of at least 1.5. In pastes of low overall Ca:Si ratio (e.g., 0.8–1.0), the lime therefore disappears before the quartz.

(2) At low overall Ca:Si ratios, the CSH(II) reacts with more silica to give CSH(I). When first formed, this probably has a Ca:Si ratio of 1.25. The value drops gradually to 0.8 as reaction proceeds.

(3) The CSH(I) recrystallizes to tobermorite. The rate of this process depends greatly on the temperature. At 175 °C tobermorite can be detected within 12 hr, but at 125 °C (the lowest temperature at which it has been found in a paste) several days' reaction is needed. This process occurs more quickly if reactive aluminous materials are present, but more slowly if silica gel is substituted for the quartz.

(4) If the temperature is high enough, the tobermorite is changed into xonotlite. This phase has been detected in pastes cured at 165 °C, but its formation under these conditions is slow. It is not formed to a detectable extent in less than 24 hr below 180 to 190 °C.

(5) At overall Ca:Si ratios below 0.83, unreacted quartz remains after all the CSH(II) and CSH(I) have been converted into tobermorite. Reaction of tobermorite or CSH(I) with residual quartz can occur, giving gyrolite. This reaction, however, is very slow, probably because it can only take place at the interface of the quartz and the tobermorite. Gyrolite can nevertheless sometimes be detected in pastes with Ca:Si$\leq$0.67 after one or more days' autoclaving at 165 to 200 °C. Its formation under these conditions is not very reproducible. Xonotlite is sometimes formed when gyrolite might be expected, presumably because the tobermorite alters to xonotlite more quickly than it can react with the quartz.

(6) If overall Ca:Si exceeds 1.2–1.3, there is not enough quartz to convert all the CSH(II) into CSH(I). A different set of reactions thus occurs, which begins with recrystallization of the CSH(II). The usual product of this recrystallization is C_2S α-hydrate which is formed slowly at 125 °C and more quickly at higher temperatures.

(7) "Phase F," of possible composition $C_5S_3H_2$, seems to be an alternative recrystallization product of CSH(II), but its formation is irreproducible; it was formed most often at around 165 °C [8].

(8) At sufficiently high temperatures, C_2S α-hydrate or phase F can alter to hillebrandite. This phase is formed to a detectable extent in pastes cured for 1 to 2 days at 165 to 200 °C.

Autoclaved cement-silica pastes. The pioneer work of Thorvaldson and Shelton [22] showed that C_2S α-hydrate can be formed in cement-silica pastes. Later work, however, has shown that formation of this phase is associated with low mechanical strength, and that satisfactory strengths are obtained when tobermorite is formed.

Kalousek and co-workers [17, 86, 88, 90] studied autoclaved cement-quartz pastes using differential thermal analysis, X-ray diffraction, and chemical methods. They showed that addition of small proportions of fine quartz to the cement, before autoclaving for 24 hr at 175 °C, increased the proportion of C_2S α-hydrate in the product and decreased that of $Ca(OH)_2$. With about 9 percent of quartz (on the weight of cement) the yield of C_2S α-hydrate was at a maximum, and formation of $Ca(OH)_2$ was eliminated. At this composition, the strength is at a minimum [149]; Kalousek concluded that low strength was correlated with formation of C_2S α-hydrate. When more quartz was added, formation of C_2S α-hydrate was reduced and ultimately eliminated, tobermorite being formed instead. Maximum formation of tobermorite occurred at about the compositions known to give the highest strength [149]. High strength was thus attributed to formation of tobermorite.

Sanders and Smothers [120] obtained closely similar results. They autoclaved cement-quartz pastes for 24 hr at 182 °C and made X-ray studies and strength tests on the products. The hydrated phases were detected, and in some cases estimated quantitatively, using a diffractometer. Ten-percent addition of quartz effected a maximum in the formation of C_2S α-hydrate and a minimum in strength; 35 percent addition of quartz effected a maximum in the formation of tobermorite and a maximum in strength. Less tobermorite was formed if curing was at 159 °C, and none at all if it was at 125 °C, or if silica gel was substituted for the quartz.

Neese, Spangenberg, and Weiskirchner [106] studied the phases produced in pastes cured at 151 to 197 °C, with quartz:cement weight ratios of 1.5 and 3.0. They reported the formation of CSH(I), tobermorite, and nekoite. The detection of nekoite was based only on optical evidence, and must be considered doubtful.

In none of the investigations described in this section were any hydrated aluminate or ferrite phases detected; in particular, C_3AH_6 and other hydrogarnets were not found. It therefore appears probable that, as with autoclaved neat cement pastes, the minor components of the cement are incorporated into hydrated silicate phases.

The results discussed in this section show that when cement-silica pastes are autoclaved at 150 to 200 °C, the cement behaves to a first approximation as a source of lime and silica. The phases produced are the ones that would be formed in lime-silica pastes with the same Ca:Si ratio. Typical neat-cement pastes have a Ca:Si ratio of about 3; addition of 9 to 10 percent of quartz, which gives a maximum yield of C_2S α-hydrate, lowers the overall ratio to about 2, while 40 to 70 percent additions, which give a maximum yield of tobermorite, lower it to 0.8–1.0. The mechanism of the process also is probably not very different from that occurring in lime-silica pastes. Differences between cement and lime can be expected to arise because of the different physical state of the reactants, and because of the presence of Al_2O_3 in the cement, but they do not seem to affect the essential features of the reaction.

The fact that high strength in autoclaved cement-silica products is associated with formation of tobermorite shows that crystalline as well as gelatinous phases can have good cementing properties, though the behavior of C_2S α-hydrate shows that this is not true of all crystalline phases. The reason for this behavior is still not understood.

Note on Further Investigations

The author much regrets that he became aware of a group of papers from the U.S.S.R. too late to discuss them in this review. They are, however, included in the list of references [153–166]. References 153 and 154 deal mainly with the lime-silica reaction, 155 to 160 with the hydrothermal curing of C_3S or β-C_2S pastes with or without added silica, and 161 to 166 with the hydrothermal curing of cement or cement-silica pastes.

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Discussion

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The discussion below concerns only the reactions with saturated steam in the temperature range 100 to 240 °C, planned by the present author and published 1956–60 [1].[1]

If compounds that are in real equilibrium with the surrounding phases were to be prepared, solutions of ions heated to the required temperature would have to be used; such experiments would be impossible to perform practically. The experiments must therefore be realized with other types of components, not forgetting the fact that the relevant conclusions may be drawn only if all premises are taken into consideration. When components are used in the solid state as colloids or as crystals instead of ions, we introduce some new reaction types that could, however, be clearly explained if a sufficiently good knowledge of possibilities for the formation of the phases is available, and if it is used correctly.

In most cases the solid phases, silica and calcium hydroxide, are mixed with water and afterwards autoclaved as slurries or pastes. It has been suggested that mixtures of amorphous silica of different origin give different results. In our laboratory we have investigated some silica samples, dried on the steam bath or heated in an air bath 300 to 400 °C. The same results have always been obtained, independent of the kind of silica; the only precaution we took was to grind and sieve the silica before mixing it with the calcium hydroxide or oxide. A slurry in which a certain part of the solids could precipitate was avoided. The autoclaves, in which the platinum crucibles were hung on a silver gallows, were equipped with manometers for pressure control and valves for evacuation. The heating-up period was always performed according to a program in which the reaction temperature was reached with the least delay. In this way the experiments could be reproduced without difficulty. When quartz or silicates were used, the surface area per gram of the mineral was always determined, and it was also necessary in this case to limit the added amount of water.

The reaction between lime and silica will begin when the silicate ions are dissolved from the small lumps of amorphous silica or from the crystals of the well-crystallized compounds (quartz, feldspar, mica). The ions are monomeric and have the configuration $[SiO_4]^{4-}$. The ions will immediately be saturated by Ca ions as far as the supply of these ions in the surroundings will allow. These reactions between silicate ions and Ca ions are the initial ones that always take place in every system containing CH–S–H. Up to the present, three compounds with varying lime content are known to occur as initial phases in the systems between 100 and 250 °C, having the initial configuration according to the schematic representation below and finally crystallizing as phases established by X-ray measurements.

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[1] Figures in brackets indicate the literature references at the end of this paper.

$\left[\mathrm{H_4}\right]^{4+}\cdot\left[\mathrm{SiO_4}\right]^{4-}$	$\left[\begin{matrix}\mathrm{H_3}\\ \frac{1}{2}\mathrm{Ca}\end{matrix}\right]^{4+}\cdot\left[\mathrm{SiO_4}\right]^{4-}$	$\left[\begin{matrix}\mathrm{H_2}\\ \mathrm{Ca}\end{matrix}\right]^{4+}\cdot\left[\mathrm{SiO_4}\right]^{4-}$	$\left[\mathrm{Ca_2}\right]^{4+}\cdot\left[\mathrm{SiO_4}\right]^{4-}$
tetrahydrogen orthosilicate	trihydrogen hemicalcium silicate	dihydrogen calcium silicate	dicalcium silicate
Crystallizing as Ca compounds	Z-phase $\mathrm{CaO{\cdot}SiO_2{\cdot}2}$ or $\mathrm{3H_2O}$	Tobermorite $\mathrm{CaO{\cdot}SiO_2{\cdot}H_2O}$	α-dicalcium silicate monohydrate $\mathrm{2CaO{\cdot}SiO_2{\cdot}H_2O}$

After this crystallization, other reactions set in giving products of other kinds characteristic for the system in question.

The System Lime–Amorphous Silica–Water

The Low-Temperature Phases (<150 °C)

The formation of the three compounds at the saturation of the silicate ion, the Z-phase, the tobermorite phase, and the α-dicalcium silicate monohydrate phase, depends on the supply of lime. In most cases some silica seems to remain uncombined. Only one of the three phases can be in equilibrium with silica, apart from the mixture corresponding to an invariant point (two silicates + silica). At present it seems to be impossible to establish the silicate in equilibrium with silica by running experiments over a long period; other methods must be used.

This system gives the best survey of the reactions, and observations in other systems have to be based on the results; the formation of the phases is illustrated in the scheme shown in figure 1.

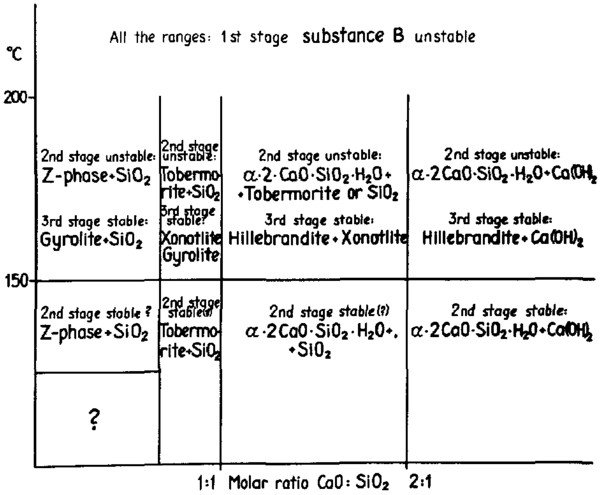

FIGURE 1. *Reactions in the system* $\mathrm{Ca(OH)_2}$*–amorphous silica.*

The High-Temperature Phases

Since the low-temperature phases always occur at higher temperature during a short period of time, they can be recovered as transition compounds. In these cases they reach the range of the high-temperature phases because of a rather slow rate of crystallization. The temperature of the transition phases is now considerably higher than their own real highest temperature of formation. The position of the substances in the thermochemical system of the compounds leads to a production of heat caused by the recrystallization. From the thermochemical point of view the compounds formed by these reactions must be stable phases. Figure 1 shows these high-temperature phases (gyrolite, xonotlite, and hillebrandite); the final high-temperature products will contain the phases in proportions that can be calculated from the compositions of the initial mixtures.

The System Lime–Quartz–Water

As mentioned above it is necessary to know the supply of lime per unit area of mineral surface, if the products formed are to be estimated. A survey of the reactions is presented in figure 2.

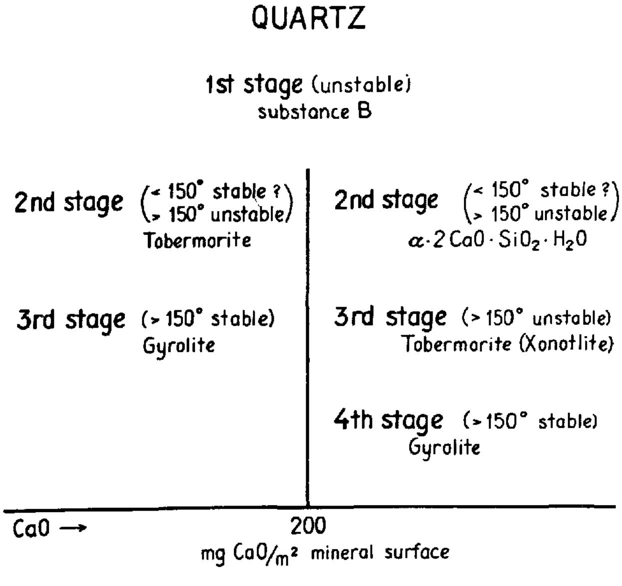

FIGURE 2. *Reactions in the system* $\mathrm{Ca(OH)_2}$*–quartz.*

The general course of the reactions noted in the system lime-amorphous silica-water can also be followed here. The compounds first formed depend to a high degree on the supply of lime; mixtures poor in lime yield the tobermorite phase as first compound; the mixtures rich in lime, on the other hand, the α-dicalcium silicate hydrate. The boundary between these two ranges corresponds approximately to about 200 mg CaO/m^2 mineral surface. The sequence of crystallization products is the same as in the system with amorphous silica; on the assumption that solid quartz remains during the autoclave treatment the principal reaction will lead to formation of the compound poorest in lime, the gyrolite phase, at 150 to 250 °C.

In some points the system with quartz differs from that with amorphous silica. In the quartz system the hemicalcium silicate, the Z-phase, has not been recovered. There are two possible explanations of this. The Z-phase may not be a stable phase, in which case it would not be formed. Secondly, in the system with amorphous silica the production of silicate ions is abundant, in the system with quartz or silicates the supply of ions is regulated by the rate of dissolution from the surface of the crystals. Probably this rate is not sufficiently high to yield a hemicalcium silicate. Thus, the initial reaction will be extremely dependent on the state of the lattice of the reacting surface. Investigations with varying reacting surface combined with the state of the lattice have not yet been performed; they should be very elucidating for the explanation of the system.

Among the products compounds appear that would not be expected in the correct formation of solids outlined above. Small amounts of xonotlite and hillebrandite occur, possibly also other compounds. In the heterogeneous system with quartz, pores and cavities will always occur, rendering available possibilities for special compounds not subjected to the diffusion of ions which is a condition for a homogeneous reaction product. The low rate of transformation also tends to preserve these compounds.

The System Lime–Silicate–Water

For the present, only the systems with feldspar and muscovite have been investigated systemtically. The systems of this kind require special considerations.

The attack of lime on the surface of the crystals depends even in this case on the supply of lime per unit area of the mineral surface. Mixtures poor in lime yield monocalcium silicate (the tobermorite phase), and those rich in lime the α-dicalcium silicate hydrate. The boundary between these ranges corresponds to about 100 mg CaO/m^2 for feldspar, and less than 25 mg CaO/m^2 for muscovite (fig. 3). Further treatment at temperatures 150 to 250 °C leads to the formation of gyrolite, in agreement with the sequence of crystallization found for the system with quartz.

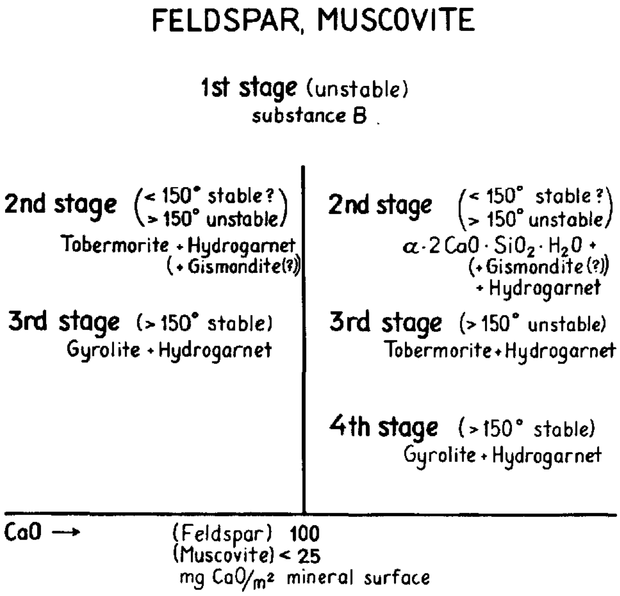

FIGURE 3. *Reactions in the systems* Ca(OH)$_2$–*feldspar and muscovite.*

The silicates contain other components than silica, in the above two cases alumina and alkalies. The alkalies do not influence the reactions to a noticeable degree. Alumina reacts with lime chiefly forming hydrogarnets. The hydrogarnets vary considerably in composition during the autoclave treatment. The compound first formed has the approximate composition $3CaO{\cdot}Al_2O_3{\cdot}1{\cdot}5SiO_2{\cdot}3H_2O$; later during the treatment the composition is changed to about $3CaO{\cdot}Al_2O_3{\cdot}0.5SiO_2{\cdot}5H_2O$. When the attack of lime on the mineral is vigorous (high temperature, easily attacked mineral lattice), the hydrogarnets are registered as bands in the X-ray photographs; with a slow attack the bands are divided into sets of distinct lines, showing a rhythmical crystallization of the compound.

At low temperature ($<$150 °C) a new compound appears, having a characteristic line at 10A, possibly indicating a zeolite (gismondite). This compound has not been shown in products autoclaved at higher temperatures. Some other unidentified lines occur also in the X-ray photographs. This part of the system is not investigated sufficiently, probably the occurrence of some other compounds can be established.

The Diffusion Layers

When the minerals react with calcium hydroxide, the crystal surface will immediately be covered with a cryptocrystalline layer, in the present paper designated substance B. It is identical with the substance formed when calcium hydroxide reacts with amorphous silica. The substance has been considered identical with the tobermorite phase, and its varying lime content is explained as an excess of lime adsorbed on tobermorite crystallites of low frequency with lattice units similarly oriented especially in the *c* direction. From the results of the investigations described above, however, the conclusion must be drawn that the substance B is a mixture of several substances. When lime reacts under hydrothermal conditions with silicates containing alumina or ferric oxide, these components will occur in the substances.

The thickness of the layers represents the formation rate of the solids, and the boundary concentration of lime will give a certain idea of the production of ions. The importance of the diffusion layers has been emphasized earlier in a paper concerning the system Ca almuinate–solution [2]. The same reaction types will always be found in every heterogeneous solid-liquid system, and without a detailed knowledge of the properties of the solids formed and the sequence of crystallization the character of the final reaction products cannot be shown. The reaction conditions at the crystal surface depend on the attacking agent, in this case the lime, and experiments in which the supply of lime per unit area of the crystal surface is unknown are of very little value for an understanding of the observations.

The reaction layers are of two types forming monocalcium or dicalcium silicates as first crystallizing product. The boundary concentration of lime is only approximate, but it gives a good conception of the resistance of the mineral lattice to the attacking agent and a possibility of calculating the amounts of the hydration products, at the point where the products change properties.

The three minerals investigated (quartz, feldspar, and mica) show varying resistance to the attack of lime, The most resistant mineral is quartz (200 mg CaO/m^2 mineral surface), then feldspar (100 mg CaO/m^2), and least the mica (<25 mg CaO/m^2). The thickness of the layers is listed in table 1. It is calculated on the assumption that the lime is equally distributed over the mineral surface, disregarding pores and cavities.

TABLE 1. *Thickness of the reaction layers at the boundary.* CaO *concentration at the boundary: with quartz, 200 mg* CaO/m^2; *with feldspar, 100 mg* CaO/m^2; *with mica, 25 mg* CaO/m^2

Character of the layer	Quartz	Feldspar	Muscovite
	mm	*mm*	*mm*
Monocalcium silicate (tobermorite)	2.1×10^{-4}	0.6×10^{-4}	0.2×10^{-4}
α-dicalcium silicate	1.2×10^{-4}	1.4×10^{-4}	0.2×10^{-4}
2:3 calcium silicate (gyrolite)	2.5×10^{-4}	----------	----------

The first layer formed is the tobermorite or α-dicalcium silicate hydrate afterwards transformed into the gyrolite compound. The aluminous silicates also yield hydrogarnets. The thickness of the layers at the concentration boundary has a magnitude of 0.1 – 2.5 × 10^{-4} mm.

The Z-Phase

The Z-phase, first prepared by the present author, is mentioned by Taylor as identical with the substance $CaH_4Si_2O_7$ prepared by Funk and Thilo [3]. The preparation method of these authors is irrelevant for the present system. The spacings given by Funk and Thilo are listed in table 2 together with new measurements of the Z-phase made by the present author. The spacings agree in some cases, in others not. The symmetry of the Z-phase is probably not orthorhombic, but monoclinic or triclinic. Considering the different methods of preparation it would be surprising if the two substances were identical.

TABLE 2. *X-roy data on hemicalcium silicate hydrates*

Z-phase (Assarsson) $CaO \cdot 2SiO_2 \cdot 2$ or $3H_2O$ (autocl. 140 °C, 24 hr)			$CaH_4Si_2O_7$ (Funk and Thilo) (autocl. 180 °C, 24 hr)		
I	*d*	*hkl*	*I*	*d*	*hkl*
s	15.1	100	w	8.32	001
m	8.35	001	www	5.02	200
m	5.070	300	m	4.18	002
w	4.390		ww	3.82	010
ww	4.165	002	ww	3.35	300
w	3.786	010?	s	3.03	210
w-m	3.357		ww	2.77	003
bd w	3.80–3.36		www	2.52	400
ww	3.142		www	2.26	013
m	3.033	500	www	2.08	004
bd w	3.14–3.03		ww	1.92	020
br w	2.778	003	www	1.87	403, 313
w	2.410	----------	s	1.82	502
w	1.911	020?			
s	1.817				
br w	1.336				
w	1.192				
			According to Funk and Thilo		
			orthorhombic		
$a=15.16$			$a=10.04$		
$b=3.79?$			$b=3.82$		
$c=8.330$			$c=8.32$		

The Tobermorite Phase

The tobermorite phase prepared by autoclaving mixtures of lime and amorphous silica has been considered to have the composition shown in some mineral species, corresponding to $C_5S_6H_5$. When mixtures of lime and amorphous silica, having the molar proportion $CaO:SiO_2=0.80:1$ and 0.85:1, are autoclaved at 180 to 200 °C, the tobermorite phase should be formed in an almost pure condition. The products, however, contain considerable amounts of the gyrolite compound. The synthetic tobermorite compound should therefore be a monocalcium silicate.

Some experiments performed in order to establish the formation of the tobermorite in the presence of alumina and kaolinite showed that the spacings of tobermorite do not change on addition of these compounds and that the formation of the tobermorite takes place in a normal manner and to the expected extent if the reaction surface area per grams of mineral is taken into consideration.

Other Compounds

The compounds mentioned in this paper are limited to three low-temperature phases (Z-phase, tobermorite, and α-dicalcium silicate hydrate) and three high-temperature phases (gyrolite, xonotlite, and hillebrandite). The high-temperature phases are the only ones occurring in equilibrium at about 150 to 250 °C. The equilibrium of the low-temperature phases is not yet established. Besides these compounds, however, some others occur that obviously belong to the system but have not yet been prepared synthetically. Their formation conditions must be extraordinary and outside common methods of preparation. They are okenite, nekoite, truscottite, foshagite, perhaps partly also afwillite and others. In the experiments on which the above results are based the lattice of the initial silicates does not contain lime. The compounds formed by autoclave treatment of mixtures with lime must therefore be independent of the configuration of the lattice of the silicate, and the calcium silicate hydrates are formed according to the normal conditions (figs 2 and 3). On the other hand, when the silicate lattice initially contains calcium ions, the positions of the ions are already occupied to some degree, a certain part of the formation energy is consumed and the conditions for the formation of hydrated products are limited. When the surplus of formation energy between the stable and unstable compounds in question is insignificant, the phases formed at the hydration behave as metastable compounds, and the real equilibrium is not reached. This relation is characteristic for the system; it seems to be the explanation of the somewhat contradictory results given in the literature. Ions extraneous to the pure systems can also cause results of this kind.

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[2] G. O. Assarsson, Proc. Symposium on the Chemistry of Cement, Stockholm, 1938, p. 452; Geological Survey of Sweden, Yearbook **27,** No. 379 (1933), ibid. Yearbook **30,** No. 399 (1936), Zement, **26,** 293 (1937), ibid. **29,** 1 (1940).

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Discussion

H. Grothe, G. Schimmel, and H. zur Strassen

The following discussion presents a report of some observations on tobermorite formed in sand-lime bricks. The electron-microscope investigations described [1] [1] are of interest for the hydrothermal reaction between quartz and lime [2].

Method of Investigation and Results

When sand-lime bricks were formed, polished quartz crystals were embedded in them. After the reaction the bricks were crushed and the crystals carefully taken out. Then a quickly hardening resin was poured on the crystal surface, which could be taken off from the quartz crystal after hardening. In this process the fine reaction layer of calcium silicate hydrate which had formed on the quartz surface adhered at least partially to the resin. To that side of the resin facing the quartz a carbon film was applied by sublimation in vacuum. When dissolving the resin the carbon film remained with the adhering crystals which could be put on a specimen screen of the electron microscope for investigation.

The photographs belonging to this investigation were made during a test series in which the reaction temperature was kept constant at 195 °C.

After a reaction lasting for 1 hr, diffraction diagrams showed some strong reflections of a tobermorite-like phase. After a reaction period of 3 hr fibrous crystals formed (fig. 1) from which single-crystal diffraction patterns could be obtained. The diffraction diagram shown in figure 2, which was obtained from 2 crystals slightly twisted against each other, shows—apart from the strong reflections (*h* and *k* even)—likewise weak ones (*h* and *k* odd) as they can be observed in a similar, but not identical way when tobermorite is produced hydrothermally [3]. The crystal rests on the (001) surface. The long axis of the lath-shaped crystal is the *b* axis corresponding to the tobermorite structure [4].

FIGURE 1. *Micrograph of the reaction product after 3 hr.* Magnification 10,000.

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[1] Figures in brackets indicate the literature references at the end of this paper.

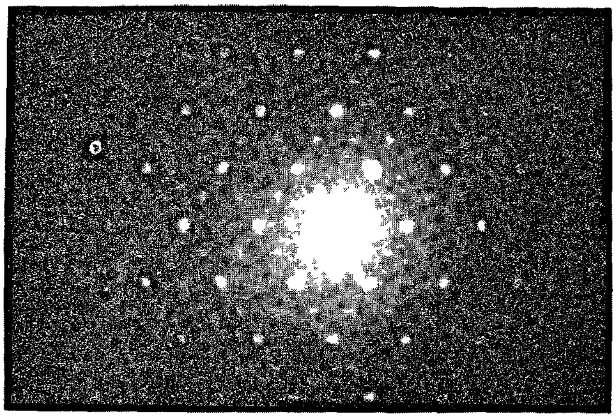

FIGURE 2. *Single-crystal diffraction pattern of the reaction product after 3 hr.*

Crystal lying on (001), *b*-axis vertical.

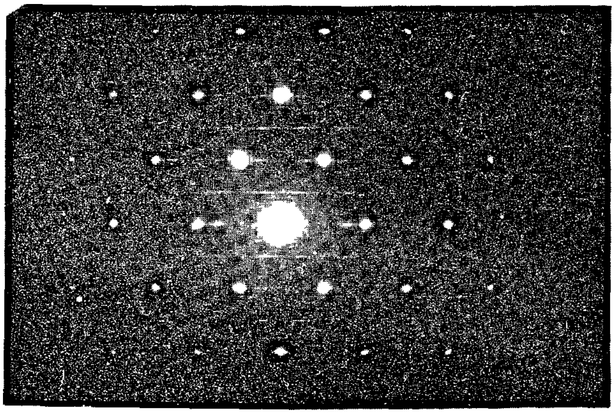

FIGURE 3. *Single-crystal diffraction pattern of the reaction product after 4 hr.*

Crystal lying on (001), *b*-axis vertical.

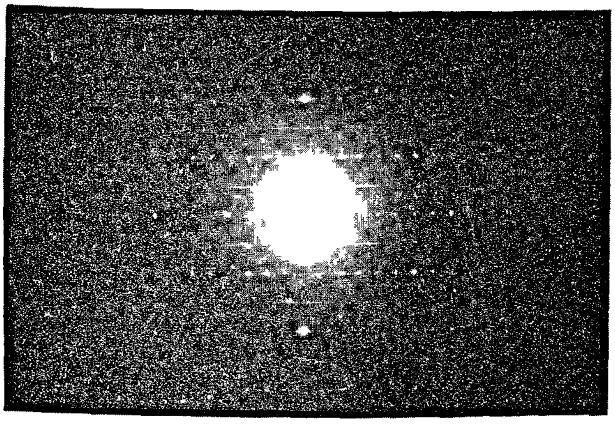

FIGURE 4. *Single-crystal diffraction pattern of the reaction product after 5 hr.*

Crystal lying on (100), *b*-axis vertical.

After 4 hr (fig. 3) a characteristic disorder phenomenon sets in, in the reaction product, which after 3 hr could be observed at best as traces. In the crystal which has the same orientation as in figure 2 the odd zones have become distorted to form continuous lines running parallel to the *a* axis; likewise the strong reflections of the even zones show elongations. The crystals show the same disorder arrangement after a reaction time of 5 hr. Figure 4 shows the diffraction pattern of a crystal lying on (100). Here the odd zones running parallel to the *c* axis consist of continuous lines.

Since the resolving power of the electron microscope reaches down to the order of the basal spacing, it was attempted to make a direct micrograph of the same crystal, the diffraction pattern of which is shown in figure 4, by the strongest magnification possible. In figure 5 is a closeup into the crystal running parallel to the *a* axis, and the alternating light and dark streaks show clearly the various horizontal layers. The periodicity of the basal spacing in the *c* direction obtained by direct observation is in good agreement with the 11.3 A measured by electron diffraction.

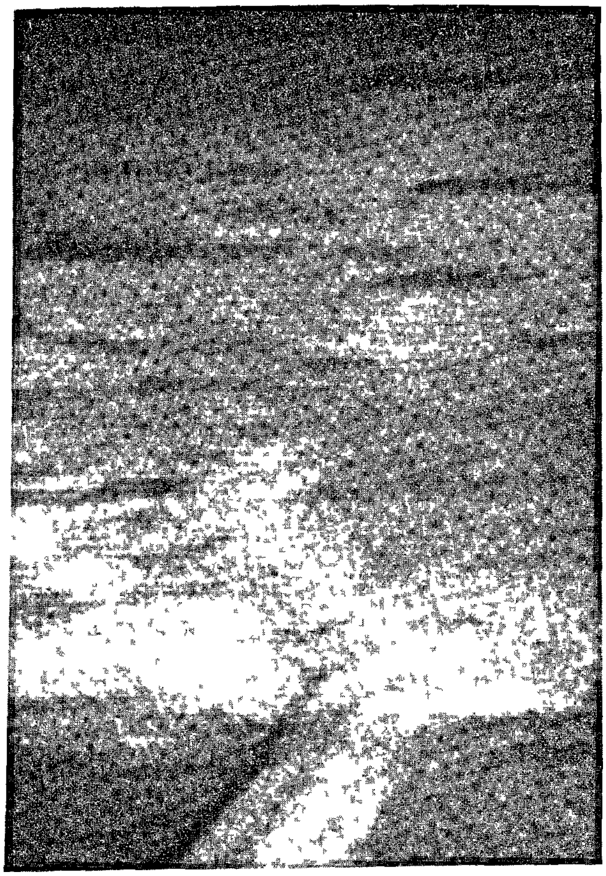

FIGURE 5. *Electron micrograph of the same crystal as shown in figure 4*

Crystal lying on (100), *b*-axis horizontal Magnification 880,000.

Discussion of Results

At first we considered the reaction product formed after 4 and 5 hr to be tobermorite of the "anomalous" Loch Eynort type [3], for two reasons: the single-crystal diffraction patterns show the disorder phenomena characteristic for this type, and almost all specimens have the same inalterable basal spacing of 11.3 A. In two cases only a shrinkage of the layer distance down to 9.5 A occurred, as is to be expected in case of a "normal" tobermorite due to dehydration under electron bombardment [3, 5].

Dr. Gard [6], however, drew our attention to the fact that the strong reflections of the diffraction diagram (fig. 4) do not follow the extinction rules of tobermorite, but those of foshagite. Dr. Gard assumed that the phase should be foshagite.

For other reasons even the formation of foshagite is not plausible: The layer distance of foshagite is not 11.3 A as observed here, but 14 A, and the area of foshagite ranges only beyond 300 °C [2, 7], whilst the tests described here had been running at 195 °C.

A new discussion with Dr. Taylor had the result that the reaction product after 3 hr should be normal tobermorite, which after a longer reaction period changed to a new phase unknown to date. This new phase should be closely related to tobermorite; probably the two phases differ only in the arrangement of the metasilicate chains.

The strength carrier in the sand-lime brick is the tobermorite. Changing to the new well-crystallized phase causes a decrease in the strength.

References

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Discussion

D. M. Roy and R. I. Harker

Introduction

In his review paper H. F. W. Taylor [1][1] has emphasized the importance of equilibrium studies at relatively high water-vapor pressures as background information for understanding cement hydration processes, and has described many of the results which have been completed since the last symposium.

It is now possible to present a tentative series of diagrams describing the phase assemblages which develop at successively higher temperatures for all lime:silica ratios in this system. The results of equilibrium studies at The Pennsylvania State University (chiefly on that part of the system with lime:silica molar ratios of 1.0 or more) and at the Johns-Manville Research Center (on compositions in which this ratio is less than 1.0) can be combined with each other and with data in the literature to provide an overall picture for the CaO-SiO_2-H_2O system. This can best be done by presenting a series of triangular diagrams which show the various assemblages as steps in a dehydration series in a manner analogous to that of Roy and Osborn [2] for the Al_2O_3-SiO_2-H_2O system and to that of Bowen and Tuttle [3] for the MgO-SiO_2-H_2O system. It would be imprudent to claim that all the assemblages shown represent the ultimate equilibria, especially at the lower temperatures. They do, however, represent stages which are well beyond what are obviously metastable equilibria and are of pratical significance. There is some evidence that by increasing the duration of runs, some of the earlier dehydration steps may be made to take place at slightly lower temperatures, but the order in which they take place is not changed substantially from that given below. Above 400 °C most of the reactions involving the more lime-rich phases can be made to proceed in either direction.

Many of the assemblages are not appreciably affected by moderate changes of pressure because the P–T curves for the dehydration reactions are more or less parallel to each other and, at the higher pressures, to the pressure axis on a P–T diagram. However, where there is evidence that the low-pressure (i.e., saturated steam) assemblages are different from the high-pressure assemblages at a given temperature, then the low-pressure compatibility triangles are marked in dotted lines. The effect of pressure on the assemblages involving a calcium hydroxide-rich liquid is not known but below 100 bars calcium hydroxide dissociates instead of melting (Wyllie and Tuttle [4]).

It must be emphasized that the triangular diagrams do not attempt to show every step in the dehydration series but only those for which there is experimental evidence. *Where evidence for the actual order of successive steps is lacking, they are all introduced in one combined step in the series.*

Up to the melting point of calcium hydroxide, we are concerned only with the stability of solid phases in equilibrium with extremely dilute fluids (liquids or vapors). The solubility of lime in the vapor phase at high temperatures is very low and, although the solubility of silica is probably higher, the diagrams would have to be greatly enlarged at the H_2O apex to show the true composition of the

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[1] Figures in brackets indicate the literature references at the end of this paper.

vapor. On the triangular diagrams, therefore, the solid phases all have lines running towards the H_2O apex (see Majumdar and R. Roy [5]), indicating that essentially pure H_2O is a coexisting phase.

Where there is some uncertainty in the interpretation of the experimental results or the natural rocks, dashed lines have been used. In those diagrams which show a calcium hydroxide-rich liquid, the dashed lines indicate the approximate phase boundaries as determined by preliminary experiments.

Dehydration Steps

Up to temperatures somewhat below 100 °C, CSH(I) and CSH(II) usually develop from reactive starting materials. Therefore, the first triangle shows CSH(I)–SiO_2 and CSH(II)–CH joins. These CSH phases are poorly crystallized and so far have defied precise definition in terms of structure and composition. Doubts may be cast on their true stability—hence, the dashed lines in triangle IA. More hydrated phases are, of course, known. These include okenite, nekoite, (Taylor [1]) and plombierite (as defined by McConnell [6]) found in natural rocks, and Funk and Thilo's [7] $CaH_4Si_2O_7$, probably Assarsson's [8] Z phase and CSH(II) with compositions extending towards C_2SH_4 approximately (Heller and Taylor [9]), produced in laboratories.

Triangle IB summarizes the assemblages, including natural minerals, which are probably closer to equilibrium at these very low temperatures than are the poorly-crystallized synthetic phases (see Long and McConnell [10]).

In a narrow temperature range, 100 to 160 °C approximately, CSH(I) gives way to better crystallized tobermorites ($C_4S_5H_4$ to $C_5S_5H_5$), gyrolite ($C_2S_3H_2$) develops from C/S molar ratios less than 0.8, and afwillite ($C_3S_2H_3$) and hillebrandite (C_2SH) can be synthesized. At saturated steam pressures in this range $C_3SH_{1.5}$ has also been synthesized, but it may not be stable until about 185 °C at higher pressures and, therefore, is shown in triangle II with the dotted tie lines. The formation of each phase involves an individual reaction, but lack of evidence prevents individual triangles from being drawn to represent each one. At the upper limit of this temperature range (160 °C), therefore, the assemblages in triangle II are indicated.

Between 160 and 200 °C in saturated steam (see dotted lines in triangle III), xonotlite + H_2O appears to become more stable than tobermorite (Nagai [11], Foret [12], Flint, McMurdie, and Wells [13], Heller and Taylor [14], Peppler [15]). Peppler's runs of several months' duration indicate that xonotlite and hillebrandite are stable rather than afwillite.

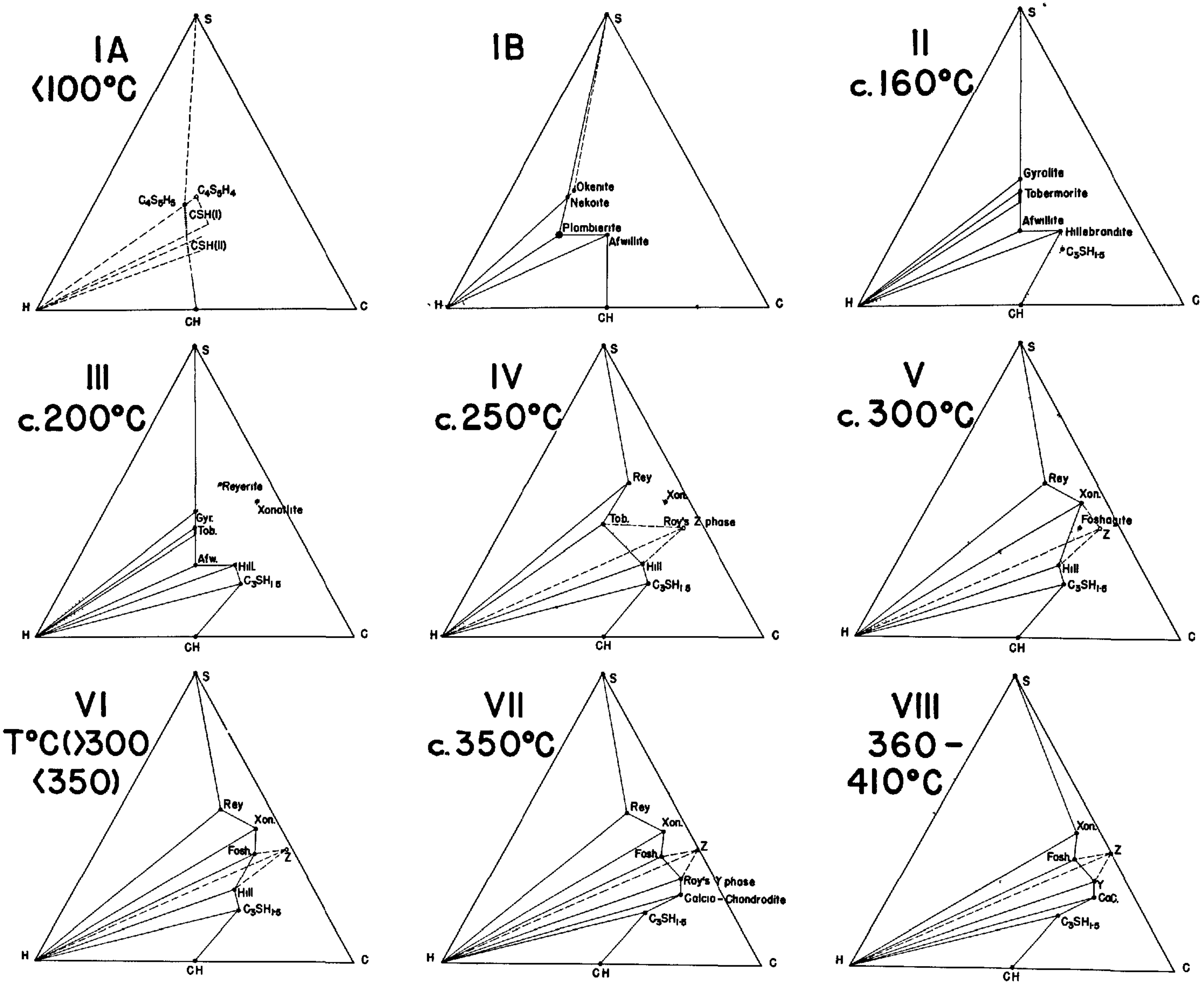
Also, in this range, gyrolite becomes unstable in the presence of excess silica, and, as a result, reyerite ($C_3S_5H_{1.5}$) tends to form (Harker [16]). With a mineralizer (2 percent of NaF) quite well-crystallized reyerite can be produced, but with no mineralizer long runs (one month) produce gyrolite-reyerite mixtures which are probably metastable and which from their nonintegral basal spacings appear to consist of randomly mixed layers on a very small scale (Brown and MacEwan [17]).

At elevated pressures (see continuous lines in triangle III), gyrolite+silica have persisted together to about 210 °C in runs of similar duration; therefore, the gyrolite-silica join remains at high pressures in triangle III. At high pressures, the stability of tobermorite is raised considerably (Buckner, Roy, and Roy, [18]) so that a gyrolite-xonotlite assemblage is stable at low pressures but not at high pressures.

Between 200 and 250 °C several reactions take place until finally at about 250 °C, the assemblages indicated in triangle IV are in equilibrium. The assemblage gyrolite+silica, already not stable at 200 °C at saturated steam pressures, now reacts to form reyerite+H_2O at high pressures (above 15,000 psi). Then gyrolite alone becomes unstable, breaking down to reyerite+xonotlite+H_2O around 220 °C at saturated steam pressures and to reyerite +scawtite (presumably reyerite+tobermorite if CO_2 could be kept out) a little above 230 °C at high pressures, 15,000–40,000 psi (Harker [16]). Afwillite breaks down to Roy's phase Z ($C_3S_2H_{0-0.33}$)+H_2O at about 220 °C above 5,000 psi (Roy [19]), but work at high temperatures and pressures of 30,000 psi or greater suggests that this phase Z may be metastable—hence, the dashed lines emanating from Z in triangle IV and subsequent triangles. The P–T curve for the breakdown of afwillite and that for the breakdown of gyrolite would be very close to each other on a P–T diagram and at present cannot be shown separately.

Triangle V represents conditions at about 300 °C. Above 290 °C high pressure fails to preserve the stability of tobermorite and tobermorite gives way to xonotlite (+reyerite) at all pressures at least up to 30,000 psi. Little work has been done on the lower limits of stability of foshagite (C_4S_3H)+H_2O, but that of Flint, McMurdie, and Wells [13] in saturated steam indicates that with rising temperature the formation of foshagite follows that of xonotlite, and that at low pressures it comes in definitely below 300 °C. If the P–T curve for its formation has a normal positive slope, as one might expect from a consideration of the volume relations, then it should form at lower pressures (dotted lines) before it would at higher pressures with rising temperature. High-pressure runs are needed to verify this conclusion.

Triangle VI represents the appearance of foshagite at high pressure at some temperature between 300 and 350 °C. One of the major equilibrium problems among well-crystallized phases in this system is that concerning the relative stabilities of foshagite and Roy's Z-phase. If Z is truly stable then its formation at temperatures lower than those covered by the hillebrandite-xonotlite and the hillebrandite-foshagite assemblages is difficult to explain.


IA
<100°C
S
$C_4S_5H_5$
$C_4S_5H_4$
CSH(I)
CSH(II)
H
CH
C
IB
S
Okenite
Nekoite
Plombierite
Afwillite
H
CH
C
II
c.160°C
S
Gyrolite
Tobermorite
Afwillite
Hillebrandite
$C_3SH_{1.5}$
H
CH
C
III
c.200°C
S
Reyerite
Xonotlite
Gyr.
Tob.
Afw.
Hill.
$C_3SH_{1.5}$
H
CH
C
IV
c.250°C
S
Rey
Xon.
Tob.
Roy's Z phase
Hill
$C_3SH_{1.5}$
H
CH
C
V
c.300°C
S
Rey
Xon.
Foshagite
Z
Hill
$C_3SH_{1.5}$
H
CH
C
VI
T°C(>300
<350)
S
Rey
Xon.
Fosh.
Z
Hill
$C_3SH_{1.5}$
H
CH
C
VII
c.350°C
S
Rey
Xon.
Fosh.
Z
Roy's Y phase
Calcio-Chondrodite
$C_3SH_{1.5}$
H
CH
C
VIII
360–
410°C
S
Xon.
Fosh.
Z
Y
CaC.
$C_3SH_{1.5}$
H
CH
C

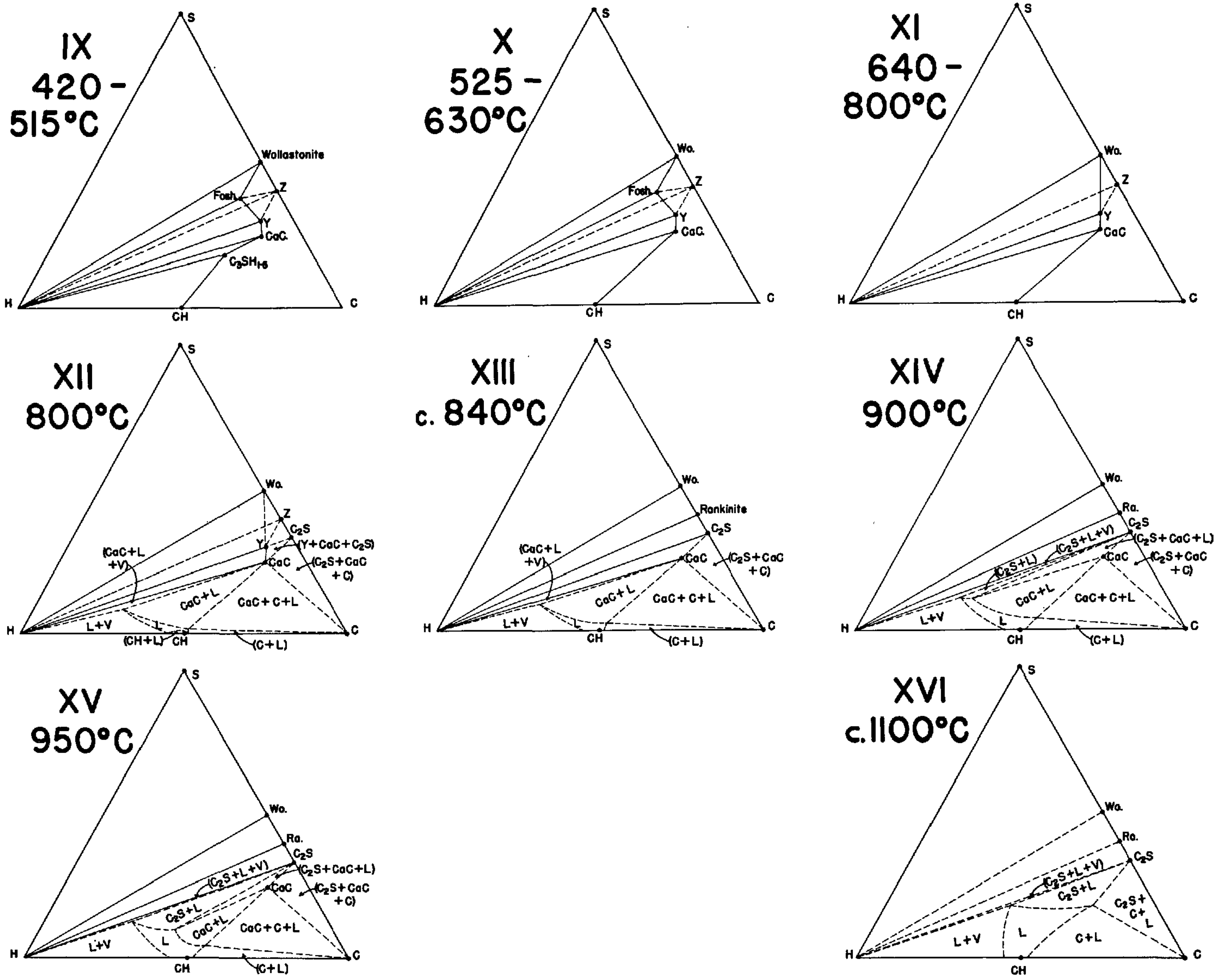


FIGURE 1. *The system* CaO-SiO_2-H_2O, *showing some of the compatibility triangles for the temperatures and temperature ranges indicated at saturated steam pressures (dotted lines) and at high pressures, about 15,000 psi (continuous lines).*

Triangle IB shows the most hydrated (lowest temperature) crystalline phases known. Dashed lines indicate some uncertainty in the equilibria as explained in the text. It has been impossible to show every step in the dehydration series and in several instances more than one reaction has taken place between two adjacent triangles. All phases are written in full the first time they appear and thereafter are abbreviated approximately. L—Liquid, V—Vapor (essentially H_2O), C—CaO, S—SiO_2, H—H_2O, and CaC stands for Calcio-Chondrodite or C_5S_2H.

The next step occurs when $C_3SH_{1.5}$ breaks down at 520 °C (at 15,000 psi), and the calcio-chondrodite-calcium hydroxide join is established, see Roy [19]. Triangle X represents the equilibrium assemblages between 525 and 630 °C.

At about 635 °C (and 15,000 psi) foshagite breaks down to wollastonite+Z+H_2O, but at higher pressures the product is Y+wollastonite+H_2O (Roy, unpublished data), suggesting metastability of the Z-H_2O join which is shown as a dashed line in triangle XI as in all others containing Z. The temperature is based on data obtained using three different starting materials: the natural mineral from Crestmore, synthetic foshagite having a 4:3 CaO:SiO_2 ratio, and a gel having the same ratio.

Reactions in the Presence of Liquid and Further Dehydration Steps

Curves for decomposition of the following phases at successively higher temperatures were given by Roy [19]: Y-phase$\rightleftharpoons\alpha'$-$C_2S+H_2O$; Z-phase$\rightleftharpoons$rankinite; and X-phase (calcio-chondrodite, C_5S_2H, or CaC)$\rightleftharpoons\alpha' C_2S+CaO+H_2O$, and these data form part of the bases of the next four triangles. However, after Wyllie and Tuttle [4] described the phenomenon of melting of $Ca(OH)_2$ under elevated H_2O pressures it became apparent that the field of $Ca(OH)_2$ liquid must enter the ternary system, at least above 815 °C (the eutectic for the system $Ca(OH)_2$-H_2O at 15,000 psi), and additional information was necessary to more completely describe the equilibria. Preliminary data have therefore been obtained by the authors to investigate the probable extent of the liquid field in the ternary system at 800, 900 and 950 °C and the equilibria among the crystalline phases at these temperatures at 15,000 psi.

The next four triangles represent an attempt to present the data in a reasonable manner, although the data are by no means complete, as indicated by the dashed lines. Triangle XII shows the proposed stability relations at 800 °C and 15,000 psi, where both Z-phase and Y-phase persist in the presence of H_2O vapor, and Y-phase+calcio-chondrodite (CaC)+H_2O are stable together. A small field of $Ca(OH)_2$+liquid exists, and the liquid field extends into the ternary system, but not as far as the CaC-H_2O join. A fairly large field where CaC is the primary phase in equilibrium with liquid is found at this temperature.

Roy's [19] Y-phase (C_6S_3H) comes in below 350 °C at the expense of hillebrandite. Unlike foshagite (which may occur in nature intimately intergrown with hillebrandite, e.g., see Taylor [20]), the Y-phase cannot occur in equilibrium with hillebrandite +H_2O except along a univariant P–T curve. Its formation therefore probably represents a more advanced stage in the dehydration series than the development of foshagite. Phase X of Roy [19] or calcio-chondrodite (C_5S_2H or "CaC") becomes stable in this temperature region and can be in equilibrium with Y or $C_3SH_{1.5}$ depending on the exact C/S ratio. Since it has never been positively identified as coexisting with hillebrandite and the individual steps involving the incoming of Y and of CaC have not yet been differentiated they are shown as coming in together in triangle VII.

At 335 °C reyerite breaks down to xonotlite+silica+H_2O (Harker [16]). As might be expected from a consideration of ΔV for the reaction, the P–T curve is nearly parallel to the pressure axis on a P–T diagram. Triangle VIII therefore represents the equilibrium assemblages after the breakdown of reyerite but before the breakdown of xonotlite.

It is convenient from now on to consider the various successive steps isobarically with rising temperature, as the saturated steam curve has no meaning above the critical point of water. The following triangles therefore apply at approximately 15,000 psi.

At 415 °C (and 15,000 psi) xonotlite decomposes to wollastonite+H_2O and dehydration in the silica-rich half of the system is complete. Triangle IX shows the equilibrium assemblages between 420 °C and 515 °C with foshagite now coexisting with wollastonite.

It is noteworthy that the occurrence of wollastonite with hillebrandite has been reported (at Velardena, Mexico, Wright [21]), whereas experimental work indicates that in the CaO-SiO_2-H_2O system wollastonite+hillebrandite+H_2O should not be in equilibrium, and no wollastonite-hillebrandite-H_2O compatibility triangle is seen in this series. The experimental and natural observations, however, may not really be in conflict for the following reasons: (1) It has been recently shown that natural hillebrandite and foshagite are frequently intergrown and difficult to identify separately, and that at least part of the Velardena "hillebrandite" is really foshagite (Heller and Taylor [9]). (2) At Velardena the wollastonite occurs in veins cutting the "hillebrandite" and thus may not be in equilibrium with the hydrated mineral.

Between the temperatures of triangle XII (800°) and XIII (840 °C) three changes take place in the following order: (1) At 815 °C Y-phase decomposes to $\alpha' C_2S+H_2O$ and $\alpha' C_2S$+CaC+Vapor are probably stable together for a narrow temperature interval. (2) At 820 °C Z-phase converts to rankinite. As discussed before, Z-phase may not be truly stable, in which case wollastonite+Y-phase could be stable together above the decomposition of foshagite as shown in triangle XI, and rankinite would form at 815 °C above the decomposition of Y-phase. (3) Finally, at 835 °C $Ca(OH)_2$ is entirely melted, and the equilibria at 840 °C are probably as shown in triangle XIII.

Triangle XIV shows the proposed equilibria at 900 °C, where C_2S exists as a primary phase in equilibrium with liquid, the field becoming larger with increasing temperature largely at the expense of the CaC+L field. At 950 °C the C_2S primary phase field is even larger (triangle XV) and the CaC+L field is smaller, suggesting that CaC melts incongruently. It should be reemphasized that the dashed lines in the past four triangles indicate that the relations described are of a highly tentative nature except for the high-silica portions.

The temperature of final melting of calciochondrodite has not been determined; however, it should be complete by 1,100 °C, and the final triangle XVI is a purely hypothetical representation of suggested equilibrium relations after the last hydrous phase is absent. In the event that CaC melts congruently, this diagram would be slightly modified with the liquid area more closely approaching C_2S.

The writers express their appreciation to Dr. O. F. Tuttle for his aid in determining the liquidus relations involving $Ca(OH)_2$, and to Dr. R. Roy for help with the manuscript. Part of the work was supported by the National Science Foundation Grant G–4648 at the The Pennsylvania State University. The authors are furthermore indebted to the staff of the Johns-Manville Research Center for their encouragement and assistance and especially to Messrs. J. P. Pellicane, Jr., and J. P. McGourty.

(Contribution No. 60–52, College of Mineral Industries, The Pennsylvania State University, University Park, Pennsylvania.)

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Discussion

G. C. A. Schuit and R. Wyatt

The essential point in the hydration of the calcium silicates seems to be the hydrolytic fission of the Ca—O—Si bond, hence

$$H_2O+\text{—}Ca\text{—}O\text{—}\overset{|}{\underset{|}{Si}}\text{—}\longrightarrow\text{—}Ca\text{—}OH+HO\text{—}\overset{|}{\underset{|}{Si}}\text{—} \tag{1}$$

or alternatively

$$H_2O+Ca^{2+}(SiO_4)^{4-}\longrightarrow Ca(OH)^{+}+(HOSiO_3)^{3-}. \tag{2}$$

If this would continue to the ultimate end we would obtain the formal reaction

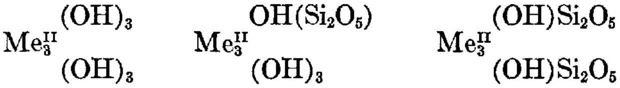
$$Ca_2(SiO_4)+4H_2O\longrightarrow 2Ca(OH)_2+Si(OH)_4$$

$$Si(OH)_4\longrightarrow SiO_2+2H_2O. \tag{3}$$

There is a great similarity in structure between the orthosilicates and hydroxides, thus suggesting that the two structures are largely or completely intermiscible. This is explicitly stated by Wells [1] for the Mg_2SiO_4-$Mg(OH)_2$ case where a continuous series of minerals $(Mg_2SiO_4)_m\cdot(Mg(OH)_2)_n$ (the chondrodite series) exists.

It may therefore be predicted that the hydration product is somewhere in between the orthosilicate and a mixture of SiO_2 and $Ca(OH)_2$.

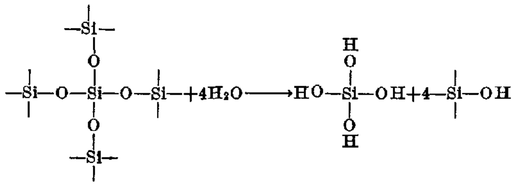
Starting from the other side, e.g., from a reaction of $Ca(OH)_2$, H_2O, and SiO_2 we obtain, as shown by Brunauer et al., a product that resembles tobermorite and that possesses a structure very similar to the layer structure of montmorillonite. This reminds us of some older work by Feitknecht and Berger [2] and Strese and Hofmann [3] for the Mg-compounds and by Van Eyk van Voorthuijsen and Franzen [4] for the Ni-compounds. The evidence shows that there can be formed *kaolinite-* (or antigorite-) type and *montmorillonite*-type compounds even at relatively low temperatures. The two types differ fundamentally in the fact that in the kaolinites we find the tetrahedral silica layer only on one side of the octahedral metal hydroxide layer while it is present on both sides in the montmorillonite-type clays



$$Me_3^{II}\begin{matrix}(OH)_3\\(OH)_3\end{matrix} \qquad Me_3^{II}\begin{matrix}OH(Si_2O_5)\\(OH)_3\end{matrix} \qquad Me_3^{II}\begin{matrix}(OH)Si_2O_5\\(OH)Si_2O_5\end{matrix}$$

hydroxide antigorite montmorillonite

One might visualize the formation of these layer structures as occurring in two steps



$$-\overset{|}{\underset{|}{Si}}-O-\overset{\overset{|}{-Si-}\\ |\\ O\\ |}{\underset{|\\ O\\ |\\ \underset{|}{-Si-}}{Si}}-O-\overset{|}{\underset{|}{Si}}-+4H_2O \longrightarrow HO-\overset{H\\ O\\ |}{\underset{|\\ O\\ H}{Si}}-OH+4-\overset{|}{\underset{|}{Si}}-OH$$

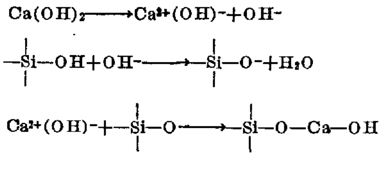
$$HO-Me-OH+Si(OH)_4 \longrightarrow HO-Me-O-Si(OH)_3+H_2O \qquad (4)$$

The structure thus formed is a precursor of the ideal hydrosilicates (kaolinite, montmorillonite). It can, under favorable circumstances be converted into them by the two-dimensional interpolymerization of $Si(OH)_3$ groups

$$-\overset{|}{\underset{|}{Si}}-OH+HO-\overset{|}{\underset{|}{Si}}- \longrightarrow -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-+H_2O \qquad (5)$$

Four remarks have to be added in this connection.

a. Reaction (4) is to be considered a formal representation; in reality it will be more plausible to state it as



$$Ca(OH)_2 \longrightarrow Ca^{2+}(OH)^-+OH^-$$

$$-\overset{|}{\underset{|}{Si}}-OH+OH^- \longrightarrow -\overset{|}{\underset{|}{Si}}-O^-+H_2O$$

$$Ca^{2+}(OH)^-+-\overset{|}{\underset{|}{Si}}-O \longrightarrow -\overset{|}{\underset{|}{Si}}-O-Ca-OH$$

b. Close packing of O^{2-} of OH^- puts a limit to the number of O^{2-} or OH^- ions in the tetrahedral Si-layers. Hence the stoichiometry relations will be premontmorillonite structure, $Me_3(O\overset{*}{H})_4(SiO^*(OH)_3)_2$; montmorillonite structure, $Me_3(O\overset{*}{H})_2(Si_2O_2^*O_3)_2$; in which the asterisk marks the O ions in the octahedral layer, the others being the oxygens at the outerside of the tetrahedral layer.

c. Reaction (4) will probably occur in a random manner, i.e., the $Si(OH)_3$ groups will occur on both sides of the octahedral layer deriving from the hydroxide layer, thus simulating a montmorillonite layer.

d. The protons of the "acid" OH groups connected to the Si will be changed by the Ca^{2+} ions because the protons react with the "basic" OH groups on the metal cation. The Ca^{2+} and H_2O then becomes located between the sandwich layers of the hydrosilicate structure as stated in various papers in this Symposium (Brunauer and Greenberg; Kurczyk and Schwiete). This should occur in such manner that the Ca^{2+} ion should remain in six-coordination with O^{2-}. In a faulty layer structure this would involve incorporation of H_2O, the water molecules fitting then in the vacancies of the outer O^{2-} and OH^- layers.

Our final conclusion is therefore that the hydration of β-Ca_2SiO_4 and the reaction of $Ca(OH)_2$ and silica gel would lead to the same products. These products possess a layer structure that is derived from $Ca(OH)_2$ and $Si(OH)_3$ groups or two-dimensional SiO layers (Si_2O_5) on both sides of the octahedral layer. The tetrahedral Si-O layers are random structures. If enough $Ca(OH)_2$ is present, parts of the structure will be pure $Ca(OH)_2$; on other parts we have SiO layers, isolated $Si(OH)_3$ groups, or structures in between. The outer OH groups, pertaining to the Si-layer, have partially replaced their protons with Ca^{2+} which involves an incorporation of H_2O in the structure.

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Closure

H. F. W. Taylor

I believe that Dr. Roy and Dr. Harker have made a valuable contribution in showing that much of our present knowledge of equilibria in the C–S–H system can be represented on compatibility triangles. There are no significant points of data or of interpretation in their contribution with which I disagree. The triangles at 800 °C. and above are especially valuable, as they summarize the first results of a new line of study, which is clearly going to provide a link between the existing studies on the hydrated and anhydrous systems.

Dr. Assarsson has put forward a most interesting view of the initial stages of the hydrothermal reactions between lime and siliceous materials. His suggestion that ions such as $H_3SiO_4^-$ and $H_2SiO_4^{2-}$ are initially formed, to relative extents that depend on the supply of calcium and silicate ions, appears reasonable enough; one might expect $H_3SiO_4^-$ ions to condense extensively giving the probably lamellar anions in Z-phase, $H_2SiO_4^{2-}$ somewhat less extensively to give the chains characteristic of the tobermorite group, and SiO_4^{4-} (or $HSiO_4^{3-}$?) not at all, to give C_2S α-hydrate. There is, however, a certain conflict of opinion, and perhaps also of evidence, as to what are the first detectable solid products. Most investigators have assigned this role to a poorly crystallized, lime-rich tobermorite mineral of the CSH(II) variety, which subsequently reacts with more silica if this is available. Dr. Assarsson's suggestion that this stage can be bypassed if enough silicate ions are available ought to stimulate much new research on a difficult experimental problem.

Some minor points of Dr. Assarsson's contribution demand comment. Gyrolite, xonotlite, and hillebrandite are not the only ternary phases stable in contact with saturated steam at 150 to 250 °C; reyerite and tricalcium silicate hydrate should be added. Contrary to his statement, afwillite, foshagite, and reyerite (or truscottite) have all been synthesized. Dr. Assarsson disagrees with my view that his "Z-phase" and the "$CaH_4Si_2O_7$" of Funk and Thilo are identical. Of course, one cannot be certain, but the X-ray data which he quotes impress me more as regards similarities than differences. This is the more true if one takes into account our observation that the specimen prepared by Funk and Thilo gives a spacing of about 15A, as well as those originally reported by them. Neither the unit-cell data given by Dr. Assarsson, nor those proposed by Funk and Thilo, can be considered significant, as in both cases they were derived merely by attempting to index the powder data. With such complicated and poorly crystallized structures, the chance of obtaining in this way a unit cell that is even simply related to the true one must be very small. Single-crystal data, or failing that, help from analogy with a substance of known unit cell, are essential. The similarities between the patterns for Z-phase and that of gyrolite are such as to suggest that the two compounds have closely related layer structures. If this is so, Z-phase is hexagonal or pseudohexagonal, with approximate parameters $a=9.73$, $c=15.1$A.

I think that I agree with some of the concepts expressed by Drs. Schuit and Wyatt. The tobermorite structure is indeed derived very broadly from that of $Ca(OH)_2$, the most important difference being the substitution of silicate ions for hydroxyl on both sides of the elementary layer. When a tobermorite mineral is precipitated from aqueous solution, there is presumably a competition between silicate and hydroxyl ions for places in the surfaces of these layers. Under not too basic conditions above 100 °C, the silicate ions eventually win (probably through a complicated mechanism involving several intermediate stages), and 11.3–A tobermorite is formed. Under more basic conditions, the competition is more nearly equal, and both hydroxyl and silicate ions may be expected to find places in the layer. When this happens under conditions favoring crystallization, as in suspensions treated hydrothermally, CSH(II) is formed; I believe this may have a relatively well-ordered, halloysite-like structure in which one side of the layer contains only silicate ions and the other hydroxyl. Under conditions not favoring crystallization, as in normally cured cement pastes, the product resembles CSH(II) in composition, but is considerably less ordered. It seems possible that, in this case, both silicate and hydroxyl ions are attached in a largely random manner to both sides of the layer. This would explain the observed very low degree of crystallinity.

The contribution of Drs. Grothe, Schimmel, and zur Strassen is of exceptional interest. It is becoming increasingly clear that there is more than one form of 11–A tobermorite, and that in some cases at least, these forms are difficult or impossible to distinguish by X-ray powder methods. Because of the differences in morphology, it is possible that they make very different contributions to the strength and other mechanical properties of autoclaved cement products. Further study of them is therefore of practical as well as theoretical importance.

My colleague, Dr. J. A. Gard, has pointed out that the lath-like tobermorite obtained by Drs. Grothe, Schimmel, and zur Strassen after 4 or 5 hours' autoclaving (their figs. 3, 4, and 5) is apparently not quite the same as the Loch Eynort mineral. In the latter, the (100) face of the reciprocal pseudocell (obtained by ignoring the streaky layer lines with k odd) is centered, whereas in the synthetic material (fig. 4) it is primitive. Assuming figures 3 and 4 relate to the same phase, the latter would appear to be a tobermorite in which the pseudocell is C-centered with $c=11.3$A, and not, as in the Loch Eynort and all other known 11.3–A tobermorites, body-centered with $c=22.6$A. Such a pseudocell would correspond to a different kind of packing between each 11.3–A layer and its neighbors, and there is no obvious structural reason to suppose that this is impossible. Since the pseudocell is different, this variety of 11.3–A tobermorite would probably be distinguishable by X-ray powder methods. Further study of this material would be of the greatest interest.

Hydration of Calcium Aluminates and Ferrites

F. E. Jones

Synopsis

Some of the literature of cement hydration bearing on the development of hydrated calcium aluminates and ferrites is reviewed, with some reference to the more complex sulfo- and chloroaluminates and ferrites which may be formed in the presence of calcium sulfate added as retarder, or calcium chloride added to hasten development of strength in a concrete.

Discussion is first based broadly, not on individual hydrated compounds, but on three basic crystal lattices which play a dominant role in cement hydration, and on various solid solutions based on these structures. The place of individual compounds or possible compounds in these structures is discussed in the light of available information, and conclusions are drawn as to compounds or solid solutions which can be formed.

Only the two ternary systems $CaO-Al_2O_3-H_2O$ and $CaO-Fe_2O_3-H_2O$ are discussed in detail. The more recent literature on the former system is considered fairly exhaustively, more particularly in the light of a recent study by Jones and Roberts. The latter system has received much less study and is experimentally much more difficult using normal "phase-rule" techniques, owing to the very slight solubility of the relevant iron compounds. Formation of hydrated ferrites by the action of solutions on anhydrous compounds "in situ" is much more important than in the corresponding $CaO-Al_2O_3-H_2O$ system. Recognition of this, and indirect approach based on analogy yields, however, a useful picture of the realities and possibilities of hydrated iron compound and solid solution formation in the cement-water system.

A simplified picture of hydrated calcium aluminates or ferrites and solid solutions, including reactions with sulfate or chloride, is presented. On present evidence, aluminates appear to be restricted within the range 22 to 100 °C to $C_4A \cdot 19H_2O$ and $C_2A \cdot 8H_2O$ both metastable, however, with respect to $C_3A \cdot 6H_2O$. Below 22 °C, $C_2A \cdot 8H_2O$ is replaced by $CA \cdot 10H_2O$. Above about 100 °C only stable $C_3A \cdot 6H_2O$ and possibly a high-temperature $C_2A \cdot 3H_2O$ hydrate is formed up to about 215 °C, and above 215 °C, $C_4A_3 \cdot 3H_2O$. Corresponding hydrated ferrites are limited to metastable $C_4F \cdot aq.$ and $C_3F \cdot 6H_2O$, the latter requiring some Si or Al or both in the structure to stabilize it. Solid solutions and compounds or solid solutions with sulfate or chloride are also discussed.

Résumé

L'exposé passe en revue une partie de la littérature de l'hydration du ciment en cequi concerne le développement de ferrites et d'aluminates de calcium hydratés. Référence est fait aux sulfo- et chloro-aluminates et ferrites plus complexes qui peuvent se former en présence de sulfate de calcium ajouté en qualité de retardateur, ou de chlorure de calcium ajouté pour hâter le développement de la résistance d'un béton.

La discussion est d'abord largement basée non pas sur les composés individuels hydratés, mais sur trois réseaux fondamentaux qui jouent un rôle prépondérant dans l'hydratation du ciment, et sur différentes solutions solides basées sur ces structures. La position des composés individuels ou des composés possibles dans ces structures est examinée à partir des informations disponibles, et des conclusions sont tirées quant aux composés ou aux solutions solides qui peuvent être formés.

On discute en détail seulement sur les deux systèmes ternaires $CaO-Al_2O_3-H_2O$ et $CaO-Fe_2O_3-H_2O$. La littérature la plus récente qui traite du premier de ces systèmes est étudiée à fond, tout particulièrement à l'aide d'une étude récente de Jones et Roberts. On a étudié tant moins le second système. A cause de la solubilité très faible des composés du fer pertinents, l'expérimentation de ce système-ci en utilisant les techniques normales du règle des phases se trouve beaucoup plus difficile. La formation de ferrites hydratés par l'action de solutions sur les composés anhydres "in situ" est beaucoup plus importante que dans le système correspondant $CaO-Al_2O_3-H_2O$. La reconnaissance de ce fait et une approche indirecte basée sur l'analogie présentent cependant un tableau utile des réalités et des possibilitiés de la formation de composés hydratés ferriques et d'une solution solide dans le système ciment-eau.

Un tableau simplifié des ferrites ou aluminates de calcium hydratés et des solutions solides est présenté, comprenant les réactions avec sulfate ou chlorure. D'après l'évidence actuelle, les aluminates, entre 22 et 100 °C, semblent limités à $C_4A \cdot 19H_2O$ et $C_2A \cdot 8H_2O$, tous deux métastables cependant quant à $C_4A \cdot 6H_2O$. Au-dessous de 22 °C, $C_2A \cdot 8H_2O$ est remplacé par $CA \cdot 10H_2O$. Audessus de 100 °C environ et jusqu'à une température d'environ 215 °C, seulement $C_3A \cdot 6H_2O$ stable (et peut-être un hydrate $C_2A \cdot 3H_2O$ de haute température) est formé, et au-dessus de 215 °C, $C_4A_3 \cdot 3H_2O$. Les ferrites hydratés correspondants sont limités au métastable $C_4F \cdot aq.$ et au $C_3F \cdot 6H_2O$. La stabilisation de la structure de ce dernier exige du Si ou de l'Al ou des deux. Les solutions solides et les composés ou les solutions solides avec sulfate ou chlorure sont également discutés.

Zusammenfassung

Ein Teil der Literatur der Zementhydratation, der sich mit der Entwicklung des hydratisierten Kalziumaluminates und -Ferrites befäßt, wird besprochen, und die mehr komplizierten Sulfo- und Chloroaluminate und Ferrite, welche in Gegenwart des Kalziumsulfates, wenn dieses als Verzögerer benutzt wird, gebildet werden, oder wenn diese Produkte entstehen, wenn Kalziumchlorid einem Zement beigemischt wird, um seine Festigkeit zu erhöhen, werden kurz erwähnt.

Die Diskussion ist auf einer breiten Grundlage gehalten, daher werden zuerst nicht einzelne hydratisierte Verbindungen, sondern die drei Grundkristallgitter besprochen, die die vorherrschende Rolle in der Zementhydratation spielen, und die verschiedenen festen Lösungen, die von diesen Strukturen zusammengesetzt werden, werden erörtert. Die Rolle der einzelnen Verbindungen oder der Verbindungen, die möglicherweise vorhanden sein könnten, wird unter Bezugnahme auf alle Kenntnisse, die man heutzutage davon hat, besprochen, und Schlüsse werden gezogen, welche Verbindungen oder feste Lösungen überhaupt geformt werden könnten.

Nur die beiden ternären Systeme $CaO-Al_2O_3-H_2O$ und $CaO-Fe_2O_3-H_2O$ werden ausführlicher besprochen. Die neuere Literatur, die sich mit dem ersten System befäßt, wird in allen Einzelheiten erörtert, und große Aufmerksamkeit wird den neuesten Untersuchungen von Jones und Roberts geschenkt. Dem anderen System ist in der Literatur weniger Beachtung geschenkt worden, die Experimente hier, wenn man normale Phasenregeltechniken benutzen will, sind viel schwieriger, weil die Eisenverbindungen, mit denen man arbeiten muß, nur wenig löslich sind. Die Bildung der hydratisierten Ferrite als Folge der Wirkung der Lösungen auf wasserfreie Verbindungen *in situ* ist hier von größerer Wichtigkeit als in dem entsprechenden $CaO-Al_2O_3-H_2O$ System. Wenn man sich dessen bewußt ist und die Fragen mit Analogie-schlüssen zu lösen versucht, kann man sich doch ein gutes Bild davon machen, was in Wirklichkeit vorgeht, und wenn es möglich ist, daß hydratisierte Eisenverbindungen und feste Lösungen in einem Zement-Wasser-System geformt werden.

Eine vereinfachte Idee betreffs hydratisiertem Kalziumaluminat oder -Ferrit und fester Lösungen, welche die Reaktionen mit Sulfate oder Chloride umfäßt, wird angegeben. Auf Grundlage der jüngsten Forschungen kann man sagen, daß nur zwei Aluminate zwischen 22 und 100 °C vorkommen können, nämlich $C_4A \cdot 19H_2O$ und $C_2A \cdot 8H_2O$, die jedoch beide nur metastabil sind und in $C_3A \cdot 6H_2O$ übergehen wollen. Unterhalb 22 °C wird $C_2A \cdot 8H_2O$ durch $CA \cdot 10H_2O$ ersetzt. Oberhalb ungefähr 100 °C ist nur $C_3A \cdot 6H_2O$ stabil, und es ist möglich, daß ein Hochtemperaturhydrat $C_2A \cdot 3H_2O$ bis zu ungefahr 215 °C gebildet wird; oberhalb 215 °C bildet sich dann $C_4A_3 \cdot 3H_2O$. Die entsprechenden hydratisierten Ferrite sind durch das metastabile $C_4F \cdot aq.$ und das $C_3F \cdot 6H_2O$ vertreten, und die letztgenannte Verbindung benötigt ein wenig Si oder Al oder beide, um ihre Struktur zu stabilisieren. Feste Lösungen, Verbindungen oder feste Lösungen mit Sulfate oder Chloride werden auch besprochen.

Paper III-3. Hydration of Calcium Aluminates and Ferrites*

F. E. Jones

Introduction

The purpose of the present paper is to review the knowledge of cement hydration with reference to the hydrated calcium aluminates and calcium ferrites which may now be taken as reasonably established, or on which research is still needed, and of certain of the more complex sulfo- and chloro-aluminates and ferrites which also play an important part.

Perhaps as useful a starting point as any is contained in two papers published in the Proceedings of the Second Symposium on the Chemistry of Cements held at Stockholm in 1938, one by Bessey [1][1] on the calcium aluminate and silicate hydrates, only the first part of which now concerns us, and the other by the present author [2] on the calcium aluminate complex salts. A selected list of references up to that time is given at the end of these two papers.

The most important methods which have been used in the determination of and study of these compounds include phase-rule studies of various systems, and attempts to elucidate the crystal structure of various compounds and "solid solutions." The term "solid solution" is retained in this paper as a convenient one. It covers the possibilities of mutual replacement of various atoms or groups of atoms or ions such as Al or Fe, Si, Cl, or SO_4 within relevant crystal lattices under defined conditions of temperature and environment which modify the relative stability of different possible lattice structures.

Structural Considerations

It seems essential to a discussion of hydrated calcium aluminates and ferrites to base this on their context in relation to the wider concept of structural possibilities in the cement-water system. Apart from the structure of calcium silicate hydrates, there appear to be at least three basic crystal lattice structures in hydrated cement compounds or solid solutions. These structures are:

(1) A "hexagonal" lattice typified by such compounds as $C_3A{\cdot}Ca(OH)_2{\cdot}aq.$, $C_3A{\cdot}CaCl_2{\cdot}aq.$, $C_3A{\cdot}CaSO_4{\cdot}aq.$, etc., and including also hexagonal or pseudo-hexagonal structures of compounds, $C_2A{\cdot}8H_2O$, $CA{\cdot}10H_2O$ and $C_2AS{\cdot}8(?)H_2O$.

(2) A "hexagonal" lattice typified by such compounds as $C_3A{\cdot}3Ca(OH)_2{\cdot}aq.$, $C_3A{\cdot}3CaCl_2{\cdot}aq.$, $C_3A{\cdot}3CaSO_4{\cdot}aq.$, etc.

(3) A cubic lattice typified by $C_3A{\cdot}6H_2O$.

It is well known that structure (1) is generally found (when sufficiently well-formed crystals are produced) as very thin hexagonal-shaped plates, which give a silken sheen in suspension in the mother-liquor, (2) as needles, often long and thin, of hexagonal cross section, and (3) as cubic crystals or various modifications based on a cubic lattice.

One point of interest in connection with structure is the difference in habit, as typically plates or needles, in structures (1) and (2) respectively. It may be noted too that Budnikov and Gorshkov [3] have recently demonstrated the splitting of needles of $C_3A{\cdot}3CaSO_4{\cdot}aq.$ (and $C_3F{\cdot}3CaSO_4{\cdot}aq.$) of structure (2) by passing through freezing cycles (−17 °C to +20 °C). It was found that the needles split along planes of cleavage parallel to the long (*c*) axis, giving smaller needles. The writer has long since observed a tendency for longitudinal splitting to occur on heating the high-sulfate calcium sulfoaluminate needles to 110 °C. There is this difference however. On heating, there is a loss of water ($32H_2O \rightarrow 8H_2O$, at 110 °C) with a consequent rise in refractive indices, whereas on freezing, water is retained, and there is no change in the properties of the solid phase.

Another paper of some interest, dealing with the crystalline habits of calcium aluminate hydrates is that of Sersale [4], summarizing to a large degree two earlier papers [5, 6]. This author has recently carried out experiments on the change of the metastable hexagonal calcium aluminate hydrates (structure (1)) to $C_3A{\cdot}6H_2O$ under the influence of various factors, including temperature, CaO/Al_2O_3 ratio in mother-liquor, *p*H, etc. Tests were carried out at 20°, 50°, and 80 °C. Confirming Koyanagi's results, it was found that hexagonal plates converted first into icositetrahedra, then into rhombododecahedra, and finally into cubes. As is well known, it was found that the rate of change increases with temperature. From the initial mixes of metastable lime and alumina solutions mixed with lime solution, it appears in the light of recent work by Jones and Roberts [7], that Sersale's initially precipitated phases were either $C_4A{\cdot}19H_2O$ or this compound together with its solid solution with α_1–$C_2A{\cdot}8H_2O$ (see later). It would seem, therefore, that the development of structure (3) from

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Building Research Station, Department of Scientific and Industrial Research, Watford, England. (Owing to the untimely death of the author in 1960, this paper was presented at the Symposium by M. H. Roberts.)

[1] Figures in brackets indicate the literature references at the end of this paper.

structure (1), leading to the variety of habits indicated, may perhaps provide useful supporting evidence for the precise structure of $C_4A{\cdot}19H_2O$ ($C\,A{\cdot}Ca(OH)_2{\cdot}18H_2O$).

Within the above structures, it is possible to replace the aluminum cation by iron, in greater or less degree, giving an increase in the size of the lattice owing to the spatial demands of the larger iron cation. In the cubic lattice it is also possible to replace $2H_2O$ by SiO_2 (i.e., $4H^+$ by Si^{4+}), resulting in a shrinkage of the lattice as the replacement proceeds completely to a compound C_3AS_3. In both hexagonal lattices (1) and (2) it is also possible to substitute various equivalent anionic groupings [2].

Thus, depending on considerations of stability and of elements involved, it may or may not be possible to produce compositions based on these three lattices which are sufficiently near end members of the possible solid-solution series to be termed compounds.

It is important however to realize that although solid solutions are formed, it does not follow that there is necessarily complete replacement of one ion by another throughout a theoretically conceivable range from one "compound" to another; e.g., it does not appear possible stably to replace Al by Fe completely in $C_3A{\cdot}6H_2O$, and a pure $C_3F{\cdot}6H_2O$ seems to be formed only exceptionally, as an unstable phase. Fundamentally, this replacement appears to be governed only by the size of the Fe ion. Thus it appears that room can be made for a 100 percent replacement of Al by Fe, by at the same time replacing 4H by Si to a limited extent, since less room is required by Si than 4H, and so space is made available for more Fe.

There are several possibilities for solid-solution formation. Thus in structures (1) and (2), the replacement of Al^{3+} by Fe^{3+} and of 2 OH^- by $2Cl^-$ or SO_4^{2-} (with any consequential change in H_2O) implies the possibility of a variety of solid-solution structures involving any or all of these ions, so that solid solutions of varying degrees of complexity are possible. In structure (3), where it appears that such ions as Cl^- or SO_4^{2-} do not enter, solid solution is correspondingly limited. However, the entry of silica into structure (3) as a replacement for some of the H_2O introduces a further complication, while silica may also enter into structures (1) and (2).

Solid solution of the kind shown between $C_3A{\cdot}Ca(OH)_2{\cdot}18\ H_2O$ and $C_2A{\cdot}8H_2O$ [7] is another variant.

Finally, the possibilities for different hydrates of the same compound may be noted. An example of this occurs in the hydrates of the tetracalcium aluminate, only one of which exists in the aqueous system $CaO\text{-}Al_2O_3\text{-}H_2O$. It may be noted that Turriziani and Schippa [8] (1954–55) consider that there are three hydrates of $C_3A{\cdot}CaSO_4{\cdot}$aq. since, depending on the drying conditions, they obtained compounds which, after X-ray powder-pattern examination, they characterized by the basal spacings as:

α_2 (moist solid); basal spacings d=10.39, 5.15 A.

α_1 (dried at 94 percent R.H.); basal spacings d=9.50, 4.79 A (13–14 H_2O).

α (dried at 55 percent R.H.); basal spacings d=8.99, 4.48 A (11–12 H_2O).

Schippa [9] (1958) has also concluded that there are two hydrated monosulfoferrites:

Moist solid; basal spacings d=10.45, 5.15 A

Dried at 55 percent R.H. and also over $CaCl_2$ & KOH; basal spacings d=9, 4.45 A.

It appears to be too early as yet to assess the significance of these alleged different hydrates of monosulfoaluminate and ferrite.

Reference should be made to table 1 for some X-ray data on compounds relevant to the lattice structures now discussed.

TABLE 1. *X-ray data on some relevant compounds*

$CA{\cdot}10H_2O$ [a]		$C_2AS{\cdot}8?H_2O$ [b]		$C_3A{\cdot}3CaSO_4{\cdot}32H_2O$ [c]		$C_3F{\cdot}3CaSO_4{\cdot}32H_2O$ [d]	
d(A)	*I*	*d(A)*	*I*	*d(A)*	*I*	*d(A)*	*I*
14.3	10	12.7	VS	9.8	10	9.8	10
7.16	10	6.30	S	5.7	8	8.9	2
5.39	4	4.20	VS	4.9	6	5.6	7
4.75	4	3.22	VW	4.67	7	5.0	3
4.52	3	2.89	M	4.34	2	4.81	4
4.16	3	2.62	M	3.87	8	4.06	1
3.93	1	2.51	M	3.60	3	3.95	8
3.72	5	2.41	W	3.45	6	3.65	4
3.56	7	2.38	MW	3.26	4	3.49	4
3.26	6	2.09	MW	3.02	3	3.24	3
3.10	5	1.90	M	2.79	9	3.07	2
2.88	6	1.83	M	2.67	3	2.80	7
2.69	5	1.66	MW	2.57	8	2.60	7
2.55	7	1.55	W	2.43	3	2.50	1
2.47	5	1.43	W	2.36	1	2.47	1
2.36	6			2.20	8	2.42	3
2.26	6			2.14	6	2.23	5
2.18	6			2.06	3	2.18	3
2.11	4			1.94	3	2.13	1
2.06	4			1.89	2	2.07	1
1.94	5			1.84	4	1.94	2
1.87	1			1.80	1	1.89	2
1.83	3			1.75	4	1.84	1
1.79	4			1.70	4	1.82	1
1.75	1			1.66	6	1.81	1
1.71	3			1.62	2	1.77	2
1.64	5			1.57	4	1.71	2
1.60	6			1.54	2	1.68	2
1.56	1			1.50	4		
1.52	2			1.45	3		
1.47	3			1.34	3		
1.40	2			1.30	3		
1.38	4						
1.27	1						
1.24	2						
1.18	2						
1.07	2						

[a] $CA{\cdot}10H_2O$. Midgley [18]. On preparation described by Jones and Roberts [7].

[b] $C_2AS{\cdot}8(?)H_2O$. Fratini and Turriziani [21]. Calculated from values for 2θ given by the authors. Fratini and Turriziani give hexagonal cell with a=8.85±0.05 A, c=12.66 A ±0.07 A.

[c] $C_3A{\cdot}3CaSO_4{\cdot}32H_2O$. Midgley [18] quoted by Lea [26]. Hexagonal cell, a=11.10 A, c=21.58 A.

[d] $C_3F{\cdot}3CaSO_4{\cdot}31\text{-}33H_2O$. Aruja and Rosaman [15]. On preparation by Jones [27]. Aruja and Rosaman give hexagonal cell, with a=11.23 A, c=22.14 A.

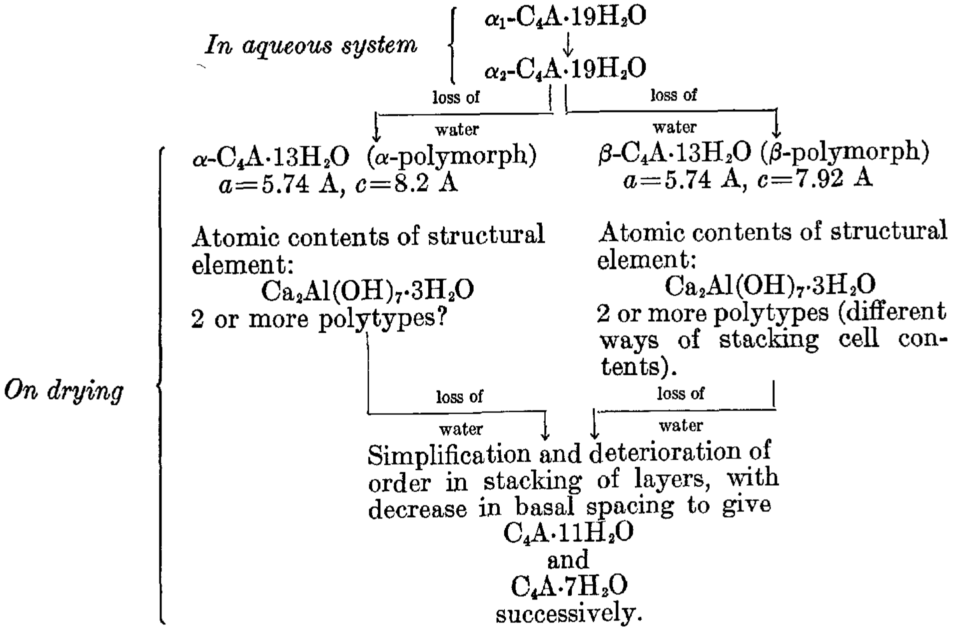
An attempt has been made to prepare, in a number of tables, X-ray powder-pattern data on as many compounds or solid solutions as possible relevant to these structures. It has however been concluded that the best available data are in many cases not sufficiently complete, or not always on pure phases or preparations of precisely known chemical composition, to justify at present their inclusion. Such tables must await further precise experimental work. It appears desirable to emphasize the importance of examining pure phases, free from carbonation, of precisely known chemical composition, including water content. It has been noted also that at least four different methods of recording intensities of lines in the patterns are in use in the literature, while the accuracy appears to vary. This variation is combined with slight differences in spacings and in numbers of lines recorded, etc., depending on the kind of camera used and slightly varying techniques. It is hoped that more precise tables may be published later.

(a) The Hexagonal Layer Lattice Typified by $C_3A\cdot Ca(OH)_2\cdot aq$.

The most recent attempt to solve the problem of the structure of the crystal lattice of "hexagonal" tetracalcium aluminate hydrate appears to be that of Buttler, Dent Glasser, and Taylor [10] (1959). It seems clear from recent papers by Roberts [11] and Jones and Roberts [7] that in the work of Buttler, Dent Glasser, and Taylor, which dealt with both $4CaO\cdot Al_2O_3\cdot 13H_2O$ and the natural mineral hydrocalumite, containing 1.8 percent CO_2, only one form, beta (c=7.9A) of $4CaO\cdot Al_2O_3\cdot 13H_2O$ was studied. Furthermore, this is a form obtained only after drying the $\alpha_1 \rightarrow \alpha_2$ forms of $C_4A\cdot 19H_2O$; i.e., the fully hydrated variety which exists in the aqueous equilibria of the system $CaO-Al_2O_3-H_2O$. Nevertheless the paper makes a valuable contribution to our understanding of the lattice structure of this group as a whole. The relationship between the fully hydrated forms and the structures obtained on drying to various stages of water content is conveniently summarized in table 2.

This is not the place for a detailed consideration of the structure, nor is the writer sufficiently experienced in experimental crystal-structure techniques to undertake it. However, the conclusions reached by the authors are very important. Previously it has been generally accepted that the structure is based on alternate layers of $Ca(OH)_2$ and $Al(OH)_3$ (Brandenberger [12] (1933)), a view supported by the work of Tilley (with Megaw and Hey) [13] (1934) on hydrocalumite. The structure proposed by the latter authors for synthetic $4CaO\cdot Al_2O_3\cdot 13H_2O$, based on their study of hydrocalumite, was of $Ca(OH)_2$ layers (one Ca^{2+} ion in three replaced by H_2O) alternating with layers of Al^{3+} and the remaining H_2O and OH^-. For various reasons, Buttler, Dent Glasser, and Taylor consider this arrangement unsatisfactory and although not able to determine the exact structure of the compound, they suggest that six of the OH^- ions in the "structural element" $Ca_2Al(OH)_7\cdot 3H_2O$ occur in an octahedral layer, and the seventh, outside, closely associated with H_2O molecules (presumably in a separate layer). Furthermore, it is indicated that the structural element is only one octahedral layer thick (though this does not seem to accord with the suggestion above, that the seventh OH^- is outside the octahedral layer and closely associated with H_2O) and that the three octahedral sites in the structural element are occupied by 2 Ca^{2+} and 1 Al^{3+} in "ordered" positions. The octahedral groups formed (Al^{3+} or Ca^{2+} at centers of the octahedra and OH^- at the 6 corners) then share OH^- at the corners along two edges to form a layer containing both Ca^{2+} and Al^{3+}. The alternate layers, according to the views of the authors, therefore appear to contain the remaining OH^- (outside the octahedral layer) and associated H_2O

TABLE 2. *Tetracalcium aluminate hydrates*



In aqueous system

α_1-$C_4A\cdot 19H_2O$

↓

α_2-$C_4A\cdot 19H_2O$

loss of water

On drying

α-$C_4A\cdot 13H_2O$ (α-polymorph)
a=5.74 A, c=8.2 A

Atomic contents of structural element:
$Ca_2Al(OH)_7\cdot 3H_2O$
2 or more polytypes?

β-$C_4A\cdot 13H_2O$ (β-polymorph)
a=5.74 A, c=7.92 A

Atomic contents of structural element:
$Ca_2Al(OH)_7\cdot 3H_2O$
2 or more polytypes (different ways of stacking cell contents).

loss of water

Simplification and deterioration of order in stacking of layers, with decrease in basal spacing to give
$C_4A\cdot 11H_2O$
and
$C_4A\cdot 7H_2O$
successively.

molecules. The actual structure in this layer is not discussed.

A complicating conclusion reached by Buttler, Dent Glasser, and Taylor is that the structural elements in the layers "appear to be stacked in a complex way, so that the 'true structure' only repeats after a large number of layers" giving "polytypes" (varieties with different systems of stacking). References are given to this type of structure in other compounds. For the present purpose it appears that such variations in stacking can be ignored, except for their effect in modifying a hexagonal lattice to a monoclinic one.

The relationship of $4CaO{\cdot}Al_2O_3{\cdot}13H_2O$ and hydrocalumite is however important since the differences between the two structures appear to be significant, in particular in relation to carbonation of $C_4A{\cdot}13H_2O$ and the structure of such compounds as $C_3A{\cdot}CaCl_2{\cdot}$aq., $C_3A{\cdot}CaSO_4{\cdot}$aq., $C_3A{\cdot}CaCO_3{\cdot}$aq., etc. It merits therefore a brief description.

The authors state, "The unit cell of hydrocalumite (a=9.9 A, b=11.4 A, c=16.84 A, β=111°) is closely related to that of $4CaO{\cdot}Al_2O_3{\cdot}13H_2O$. If the systematically weak groups of reflections are ignored, a pseudocell is obtained that contains two identical structural elements related by a pseudo glide plane. These structural elements are hexagonal with a=5.7 A, c=7.86 A. and are thus almost identical in size with those in $4CaO{\cdot}Al_2O_3{\cdot}13H_2O$. They are stacked differently in the two cases: in hydrocalumite the stacking is such as to make the crystal monoclinic, and some of the structural elements must contain carbonate ions. The true unit cells and the powder patterns therefore differ."

Although it would appear that differences in stacking alone may lead as suggested to a monoclinic structure in hydrocalumite, it is not clear to the writer why emphasis should necessarily be placed here. From Buttler, Dent Glasser, and Taylor's work, it would appear that it is the seventh OH^- of $4CaO{\cdot}Al_2O_3{\cdot}13H_2O$ ($Ca_2Al(OH)_7{\cdot}3H_2O$) outside the octahedral layer, that is involved in replacement by other ions. According to the authors, also, in hydrocalumite one in eight structural elements contains CO_3^{2-} replacing $2OH^-+3H_2O$. It seems possible that the fundamental difference between hydrocalumite and $4CaO{\cdot}Al_2O_3{\cdot}13H_2O$ may lie in the structural elements, those containing CO_3^{2-} conforming to a monoclinic lattice as opposed to a hexagonal lattice for the OH^- of $4CaO{\cdot}Al_2O_3{\cdot}13H_2O$. (Although the authors refer to the structural elements in hydrocalumite as hexagonal, they do not discriminate between those not containing and those containing carbonate ions.) It appears therefore to be a possibility that in hydrocalumite there is a mixture of hexagonal and monoclinic structural elements, making the structure as a whole monoclinic, and that this may be of greater importance than stacking differences.

Brief reference is made to synthetic compounds of the type $C_3A{\cdot}CaX_2{\cdot}$aq., and $C_3A{\cdot}CaY{\cdot}$aq. as being formed by complete replacement of the OH^- group outside the octahedral layer, while, depending on the size of the anion X or Y and the number of water molecules displaced by it, the thickness of the structural element can either increase or decrease.

Presumably the structures so produced may strictly be monoclinic rather than hexagonal.

It may be noted that Buttler, Dent Glasser, and Taylor do not discuss the possibility of other carboaluminate compositions besides that of natural hydrocalumite. It is not clear whether they regard it as a unique compound or as a stage in a solid-solution series $C_3A{\cdot}Ca(OH)_2{\cdot}$aq.-$C_3A{\cdot}CaCO_3{\cdot}$aq. although on the whole the latter seems to be inferred. There appears however to be no clear evidence of such a solid solution at present. Carlson [14] has recently commented in his work on the system CaO-Al_2O_3-H_2O at 1 °C, that in X-ray patterns obtained by him, the carboaluminate $3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}11H_2O$ and $4CaO{\cdot}Al_2O_3{\cdot}13H_2O$ appeared to exist side by side, with no evidence of solid solution. A similar observation has been made in investigations at the Building Research Station [15]. Although the monocarboaluminate is not directly involved in the system CaO-Al_2O_3-H_2O it is important as a possible contaminant. Since Bessey [1] first prepared "low" and "high" forms of carboaluminate, little work has been published, though reference is made by Carlson [14] and a paper has been published by Turriziani and Schippa [16].

Returning to the general consideration of the hexagonal layer lattice structure, several instances are known where Al is replaceable by Fe. They include the compounds "$C_3F{\cdot}Ca(OH)_2{\cdot}11$–$13H_2O$", "$C_3F{\cdot}CaCl_2{\cdot}xH_2O$", "$C_3F{\cdot}CaSO_4{\cdot}xH_2O$", or solid solutions, which will be discussed later. The existence of carboferrites must also be visualized, though no preparation appears to have been recorded. One such preparation has however been made at the Building Research Station and X-ray data obtained. (Roberts [15].)

In addition to compounds of the above general lattice type, we have also to consider the structures of $C_4A{\cdot}19H_2O$ (from which $C_4A{\cdot}13H_2O$ is presumably derived by loss of H_2O), of $C_2A{\cdot}8H_2O$, of $CA{\cdot}10H_2O$, and of $C_2AS{\cdot}8(?)H_2O$.

Accepting the proposal of Buttler, Dent Glasser, and Taylor on the structure of $C_4A{\cdot}13H_2O$, the additional $6H_2O$ of the $C_4A{\cdot}19H_2O$ hydrate may tentatively be assigned to the intermediate layers containing OH^- and H_2O only, possibly constituting in effect a separate H_2O layer.

The $C_2A{\cdot}8H_2O$ structure may then be derived from that of $C_4A{\cdot}19H_2O$ by substitution of $Al(OH)_3$ for $3H_2O$ in these layers, thus:

$$C_4A{\cdot}19H_2O+A-3H_2O \rightarrow C_4A_2{\cdot}16H_2O\ (C_2A{\cdot}8H_2O)$$

or

$$Ca_2Al(OH)_7{\cdot}6H_2O+Al(OH)_3 - 3H_2O \rightarrow Ca_2Al_2(OH)_{10}{\cdot}3H_2O.$$

Possible layer relationships may be indicated as

$$[Ca_2Al(OH)_6][(OH)\cdot 6H_2O]+Al(OH)_3-3H_2O \rightarrow [Ca_2Al(OH)_6][Al(OH)_4\cdot 3H_2O]$$

$\tfrac{1}{2}C_4AH_{19}$ $\qquad$ C_2AH_8 $\qquad$ or

$$[Ca_2Al(OH)_6][(OH)\cdot 3H_2O][3H_2O]+Al(OH)_3 -3H_2O \rightarrow [Ca_2Al(OH)_6][Al(OH)_4][3H_2O]$$

or $\qquad$ $[Ca_2Al(OH)_6][(OH)\cdot 3H_2O][Al(OH)_3]$

The very similar dimensions of the unit cells of α_2-$C_4A\cdot 19H_2O$ and α_2-$C_2A\cdot 8H_2O$ (Jones and Roberts [7]), which can be satisfactorily indexed (reference [7] and Aruja [15]) on unit cells of dimensions $a=5.77$ A, $c=21.37$ A and $a=5.80$ A, $c=21.59$ A respectively, support the indications from the phase-rule equilibrium studies by Jones and Roberts that a solid solution may be formed between these two compounds. The hexagonal plate solid solution of composition $C_{2-2.4}A\cdot 8-10.2H_2O$ appears to be formed in a crystal lattice which is virtually that of α_1-$C_2A\cdot 8H_2O$. Thus the X-ray patterns are indistinguishable. Tentatively we may write:

$$6C_2A\cdot 8H_2O=12Ca(OH)_2\cdot 12Al(OH)_3\cdot 18H_2O =C_{12}A_6\cdot 48H_2O$$

$$3C_4A\cdot 19H_2O=12Ca(OH)_2\cdot 6Al(OH)_3\cdot 36H_2O =C_{12}A_3\cdot 57H_2O$$

$$5C_{2.4}A\cdot 10.2H_2O=12Ca(OH)_2\cdot 10Al(OH)_3\cdot 24H_2O =C_{12}A_5\cdot 51H_2O$$

It may be that this solid solution is formed by replacement of up to one-sixth of $Al(OH)_3$ in the $C_2A\cdot 8H_2O$ by H_2O ($Al(OH)_3 \equiv 3H_2O$) without significant change in structure other than removal of some Al^{3+} and consequent replacement of equivalent $3OH^-$ by $3H_2O$ in the structure, and that further replacement results in a slight modification of structure to that of the $C_4A\cdot 19H_2O$ lattice. Since the unit-cell dimensions are practically identical, it would appear that the slight requisite rearrangement is wholly in the layers containing only $Al^{3+}+OH^-+H_2O$.

From the cell dimensions and densities of α_2-$C_2A\cdot 8H_2O$ and α_2-$C_4A\cdot 19H_2O$, it may be calculated that for a cell for α_2-$C_2A\cdot 8H_2O$ of $a=5.80$ A, $c=21.59$ A, with density 1.95, there are present 2 molecules of $C_2A\cdot 8H_2O$, corresponding to $4Ca(OH)_2\cdot 4Al(OH)_3\cdot 6H_2O$, and for a cell for α_2-$C_4A\cdot 19H_2O$ of $a=5.77$ A, $c=21.37$ A with density 1.81, there is present 1 molecule of $C_4A\cdot 19H_2O$, corresponding to $4Ca(OH)_2\cdot 2Al(OH)_3\cdot 12H_2O$. This does not accord with the suggestion implicit above that the unit cells may contain 6 and 3 molecules respectively to accord with $12Ca(OH)_2\cdot 12Al(OH)_3\cdot 18H_2O$ and $12Ca(OH)_2\cdot 6Al(OH)_3\cdot 36H_2O$ and with the solid solution indicated experimentally. The unit cells may however be based on multiples or submultiples of the dimensions given. Dimensions corresponding to found maximum solid solution are respectively α_2-$C_2A\cdot 8H_2O$, $a=5.80$ A, $c=64.8$ A, α_2-$C_4A\cdot 19H_2O$, $a=5.77$ A, $c=64.1$ A.

The pattern of $CA\cdot 10H_2O$ (table 1) is markedly different from that of $C_2A\cdot 8H_2O$. Carlson [17] has obtained it as weakly birefringent hexagonal prisms, with a mean refractive index of 1.471. This author gives the X-ray pattern together with that of an analogous monostrontium aluminate. A pattern has also been published by Midgley [18]. Brocard [19] had already indicated in 1948 that a product of hydration of CA obtained by him had an X-ray pattern which he assigned to a hexagonal lattice with $a=9.45$ A, $c=14.6$ A. From later work the pattern appears to be that of $CA\cdot 10H_2O$. It seems likely that there is an appreciable difference between the structures of $C_2A\cdot 8H_2O$ and $CA\cdot 10H_2O$, but the mode of transition and the relationship between the two structures is still not clear.

Finally, in the case of a compound C_2AS·aq., zur Strassen [20] writes the formula as C_2ASH_8. It appears from the literature that it crystallizes as hexagonal plates. Fratini and Turriziani [21] had previously given an X-ray pattern (table 1) and stated that they had indexed it satisfactorily on a hexagonal cell, with $a=8.85\pm 0.05$ A, $c=12.66\pm 0.07$ A. These values may be compared with those given previously by Wells, Clarke, and McMurdie [22] for $C_4A\cdot 13H_2O$ and $C_2A\cdot 8H_2O$; i.e., $a=8.8$ A, $c=8.2$ A (apparently for α-$C_4A\cdot 13H_2O$) and $a=8.8$ A, $c=10.6$ A, respectively. There appears thus to be a close similarity between all these structures. The parameters given by these authors are not necessarily the true parameters of the cell, though they will be simply related to them.

(b) The Hexagonal Layer Lattice Typified by $C_3A\cdot 3Ca(OH)_2$·aq., $C_3A\cdot 3CaCl_2$·aq., $C_3A\cdot 3CaSO_4$·aq., etc.

Of the three "type" compounds given, one, $C_3A\cdot 3Ca(OH)_2$·aq., appears to be formed only under conditions of exceptionally high lime concentrations, which do not occur in the cement-water system. Thus Flint and Wells [23] (1944) prepared it by mixing a metastable monocalcium aluminate solution with a strong solution of lime in a sugar solution. Again, the corresponding $C_3A\cdot 3CaCl_2$·aq. compound has been prepared by Serb-Serbina, Savvina, and Zhurina [24] (1956), by hydration of C_3A in a 23 percent $CaCl_2$ solution at −10 °C. (The authors state that the preparation of this compound below 0 °C was first reported by V. E. Leirikh.) At +20°C the "low" chloroaluminate was obtained ($3CaO\cdot Al_2O_3\cdot CaCl_2\cdot 10H_2O$), but the "high" form was also stated to be obtained at this temperature with a high solution/C_3A ratio. The formation of the "high" chloroaluminate appears to be partly dependent on temperature and partly on $CaCl_2$ concentration in solution. It would not be formed under normal practical conditions in hydrated cement, but the possibility at sufficiently low temperatures must be borne in mind.

The only structure of this type which appears to have been examined is that for $C_3A{\cdot}3CaSO_4{\cdot}aq.$ as the mineral ettringite, by Bannister [25] (1936), referred to most recently by Lea [26]. The latter states: "The hexagonal unit cell of ettringite contains two molecules of $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31H_2O$ and has $a_0=b_0=11.10$ A, $c_0=21.58$ A. The space group is $C\overline{3}1c$. Four close-packed layers of O or OH ions make up the structure, with embedded Ca, S, and Al. The latter form $Al(OH)_6$ groups in octahedral coordination and the sulfur is present as SO_4 tetrahedra. Four of the Ca ions have sevenfold coordination and eight sixfold. Forty-eight water molecules are located in channels parallel to the c axis and two are more closely built into the structure. The structural formula thus becomes $Ca_{12}Al_4(OH)_{24}(SO_4)_6{\cdot}50H_2O$. On dehydration at about 100–110 °C the 48 interstitial water molecules are lost and the lattice shrinks so that $a_0=8.4$ A and $c_0=10.21$ $(=\frac{1}{2}\,20.42)$ A."

It is noteworthy that the length of the c axis is very close to that of $C_4A{\cdot}19H_2O$, $a=5.77$ A, $c=21.37$ A and of $C_2A{\cdot}8H_2O$, $a=5.80$ A, $c=21.59$ A [7].

Few instances are known of replacement of Al by iron in structures of this type. They include $C_3F{\cdot}3CaSO_4{\cdot}aq.$ and solid solutions (stated to be only partial) between $C_3A{\cdot}3CaSO_4{\cdot}aq.$ and $C_3F{\cdot}3CaSO_4{\cdot}aq.$ Both Jones [27] and Budnikov and Gorshkov [3] have claimed the preparation of a pure $C_3F{\cdot}3CaSO_4{\cdot}aq.$ Cirilli [28] had concluded that it was not possible to obtain it by addition of ferric sulfate solution to saturated lime-calcium sulfate solution, but concluded that a partial mixed solid-solution series could be formed in this way. There is not necessarily any conflict of evidence here. An X-ray powder pattern obtained by E. Aruja and D. Rosaman at the Building Research Station on the preparation by Jones [27] is given in table 1. It will be seen that it is closely similar to that of $C_3A{\cdot}3CaSO_4{\cdot}32H_2O$. Aruja and Rosaman indexed the data on a hexagonal unit cell with $a=11.23$ A, $c=22.14$ A, only very slightly larger than that for $C_3A{\cdot}3CaSO_4{\cdot}32H_2O$ ($a=11.10$ A, $c=21.58$ A).

(c) The Cubic Lattice Typified by $C_3A{\cdot}6H_2O$

Lea [26] has quoted Brandenberger [29] and states that $C_3A{\cdot}6H_2O$ is "cubic with $a=12.56$ A, body centered, space group Ia_3d; eight formula units are contained in the unit cell". As discussed later, an isomorphous series of solid solutions can be formed in which A is replaced by F and $2H_2O$ by SiO_2 giving the garnet-hydrogarnet series found by Flint, McMurdie, and Wells [30]. An important point here is how far Fe can replace Al in the structure without causing instability. This point is discussed.

With reference to this section of the paper as a whole, it appears to the author that the development of discussion of structural considerations in a unified sense, as incompletely attempted above, should lead to significant advances in the understanding of what calcium aluminates and ferrites, as well as related complex chloro- or sulfocompounds or solid solutions, are practically possible. The X-ray data obtained by various authors appear to be as yet incomplete and of unequal value as between those available for different compounds, or known compositions approximating to probable compound compositions. The importance of precise control over "H_2O" content has already been stressed among other difficulties of obtaining a pure single phase for examination. The importance of knowing the precise chemical composition of the solid phase examined is also emphasized by the close similarity in X-ray powder patterns shown by different compounds or their solid solutions; e.g., compounds $C_4A{\cdot}19H_2O$ and $C_2A{\cdot}8H_2O$ or $C_3F{\cdot}Ca(OH)_2{\cdot}aq.$ and $C_3F{\cdot}CaCl_2{\cdot}aq.$ There is much yet to be done, but there are clearly many interesting possibilities, not fully worked out here, of simple relations between the various lattice structures under review.

In the remaining parts of this paper, the systems $CaO\text{-}Al_2O_3\text{-}H_2O$ and $CaO\text{-}Fe_2O_3\text{-}H_2O$ are discussed in detail, the former in particular from the phase-rule point of view, in relation to the calcium aluminates or ferrites or solid solutions which can be formed.

The System Lime–Alumina–Water

(a) Introduction and Review of Phase-Rule Equilibrium Studies

In the study of this system, Bessey's [1] original warning about the difficulty of avoiding carbonation of phases in carrying out experiments is still apt, and it is strongly emphasized by the present author that the utmost care should be taken to exclude carbon dioxide at every stage. Carbonation is probably responsible for much erroneous interpretation in the past.

In this connection, it may be noted that in recent years several authors have used polyethylene vessels as an alternative to glass vessels in order to avoid attack of the glass. Carlson [14] has recently drawn attention to a paper by Myers, Rogers, Stannett, and Szwarc [31] which gives data on the permeability of polyethylene to gases, including carbon dioxide. It is not clear at present how much risk of carbonation is involved, but it is evident that in order to reduce or eliminate it, consideration needs to be given to this factor in relation to the temperature of use, the grade, density, and wall thickness of the polyethylene, or other protective measures.

Apart from carbonation, the vital importance of the control of water content of solid phases has been made clear by recent work of Jones and Roberts [7].

The list of artificially prepared hydrated calcium aluminates given by Bessey in his 1938 paper was increased to include $C_6A \cdot 33H_2O$ in Steinour's very full review of 1951 [32]. D'Ans and Eick [33] also gave a tabulated chronological survey of individual solid phases in their 1953 paper, which covers substantially the same list but gives in detail different water contents reported by various authors. Perhaps the time has come when we can dismiss such varying water contents as partly the result of slightly varying drying conditions and varying amounts of carbonation, and assign, on grounds of precise control of experimental conditions and appeal to structural concepts, precise values of "H_2O" in the normal "oxide" formulation, whether this "H_2O" is present as actual H_2O groupings or OH^- groupings or both.

Preliminary Brief Chronological Survey

(1) Bessey [1] (in Collaboration With Lea) at 25 °C (1938)

Bessey gave a statement of general relationships in the system at 25 °C (fig. 1) as concluded by him and Lea on the basis of previous investigations carried out by them and others. They considered that there had been established a stable solubility curve *OA* for Al_2O_3·aq., an invariant point *A* for Al_2O_3·aq.-$C_3A \cdot 6H_2O$ (also indicating congruent solubility of $C_3A \cdot 6H_2O$), a stable solubility curve *AB* for $C_3A \cdot 6H_2O$, an invariant point *B* which was either for $C_3A \cdot 6H_2O$-$C_4A \cdot 13H_2O$ or $C_3A \cdot 12H_2O$-$C_4A \cdot 13H_2O$, a solubility curve *BC* which was either a continuation of the solubility curve for $C_3A \cdot 6H_2O$, or the stable solubility curve for $C_4A \cdot 13H_2O$, and *C*, the solubility of calcium hydroxide in water. *OD* was then described as a metastable solubility curve for Al_2O_3·aq., either passing through *A*, or an entirely separate curve, "possibly of a different hydrate of alumina." *D* is stated to represent the approximate solubility of $C_2A \cdot 8H_2O$, apparently congruent, in water, and also a metastable invariant point $C_2A \cdot 8H_2O$-Al_2O_3·aq. Finally, it was considered that the metastable solubility curves for $C_4A \cdot 13H_2O$, $C_3A \cdot 12H_2O$, $C_2A \cdot 8H_2O$ and $C_3A \cdot 18H_2O$ lay within the area *DEB*.

(2) Wells, Clarke, and McMurdie [22] at 21 °C and 90 °C (1943)

At 21 °C these authors made a substantial step forward. In precipitation from mixtures of metastable calcium aluminate solutions and lime solutions, they obtained a "practical" curve *ABD* (fig. 2) for a hexagonal-plate solid phase in which the CaO/Al_2O_3 ratio varied from 2 to 4. They considered that either (a) there are overlapping solubility curves for $C_4A \cdot 13H_2O$ and $C_2A \cdot 8H_2O$ or (b) the curve is a solid solution curve throughout the entire range. They preferred the former interpretation and concluded that the ends of the experimental curve relate primarily to one or other of the two hydrates respectively, with a middle portion where the two aluminates markedly intercrystallize. They expressed the belief that "the hydrated dicalcium and tetracalcium aluminates, being of a very similar structure parallel to the *a* axis, can intercrystallize and give masses which are made up of the one compound so intimately mixed with layers of the other that average indices of refraction are obtained." In spite of this region of postulated intercrystallization, Wells, Clarke, and McMurdie suggested that a metastable invariant point $C_4A \cdot 13H_2O$-$C_2A \cdot 8H_2O$ existed at about 0.5 to 0.6 g CaO per liter and 0.10–0.15 g Al_2O_3 per liter. It was also concluded that the hitherto supposed compound $C_3A \cdot 12H_2O$ is a mixture of $C_2A \cdot 8H_2O$ and $C_4A \cdot 13H_2O$ intercrystallizing in equimolar proportions.

It may be observed that at this stage the conclusions on the precise significance of the curve *ABD* are still left in the realm of conjecture.

At 90 °C, hexagonal phases were so unstable that no attempt was made to study their solubility relationships. Only curves for stable phases were therefore determined, gibbsite, $C_3A \cdot 6H_2O$, and $Ca(OH)_2$. No other stable hydrated calcium aluminates were found.

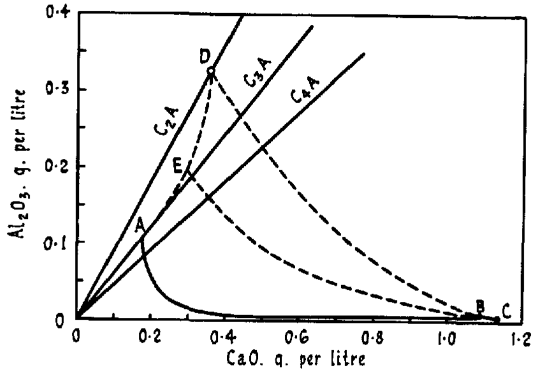


FIGURE 1. *Solubility relations in the system* CaO-Al_2O_3-H_2O *at 25 °C* (*Bessey* [*1*], *1938*).

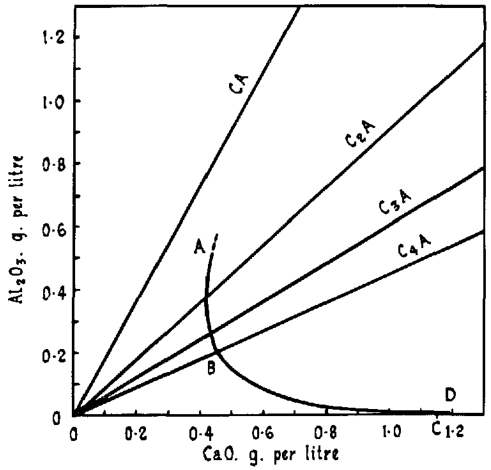


FIGURE 2. *System* CaO-Al_2O_3-H_2O *at 21 °C.*

Hexagonal plate "practical curve" from precipitation. (Wells, Clarke, and McMurdie [22], 1943.)

(3) D'Ans and Eick [33] at 20 °C (1953)

The solubility curves suggested by D'Ans and Eick are indicated in figure 3, which is based on their figure 4. From two series of mixtures of metastable calcium aluminate and lime solutions, D'Ans and Eick obtained precipitates which, following Wells, Clarke, and McMurdie, establish a "practical" equilibrium curve for metastable hexagonal plate phases. Certain of the mixtures are stated to precipitate immediately hexagonal mixed crystals. Filtration after two hours gave filtrates which yielded the solution compositions used to define a large part of the "practical" curve to the left of a deduced invariant point $C_2A{\cdot}8H_2O$-$C_4A{\cdot}13H_2O$. These mixed crystals are stated to consist mainly of crystals rich in α-$C_4A{\cdot}13H_2O$ with a little rich in $C_2A{\cdot}8H_2O$ and a little or some $C_3A{\cdot}12H_2O$. There was slow conversion to $C_2A{\cdot}8H_2O$. Two mixes (*D* and *E*) were also stated to give $C_3A{\cdot}18H_2O$, $C_3A{\cdot}12H_2O$, or $Al(OH)_3$. D'Ans and Eick refer specifically to the hexagonal-plate phases precipitated as having no uniform composition, and of being a mixture of plates, but state that pure compounds are rare and that there is a strong tendency toward the formation of anomalous "mixed-crystals." There seems little reason to doubt that the "practical" curve obtained is essentially similar to that of Wells, Clarke, and McMurdie, though it is not coincident with it.

Apart from this "practical" curve, D'Ans and Eick have concluded, on the basis of data which appear to be open to criticism as discussed later, that two distinct curves for $C_2A{\cdot}8H_2O$ and α-$C_4A{\cdot}13H_2O$ exist, each throughout a long range of solution concentrations, intersecting in an invariant point *Y* at 0.610g CaO per liter, 0.095 g Al_2O_3 per liter, that a solubility curve for a β-$C_4A{\cdot}13$-$14H_2O$ exists, extending into regions of low lime and low alumina concentrations, and that there are solubility curves for $C_3A{\cdot}12H_2O$ and $C_3A{\cdot}18H_2O$ situated between what are termed the "limit curves" for α-$C_4A{\cdot}13H_2O$ and $C_2A{\cdot}8H_2O$. Apart from the "practical" curve, none of the conclusions listed above seem to be built on very sure foundations.

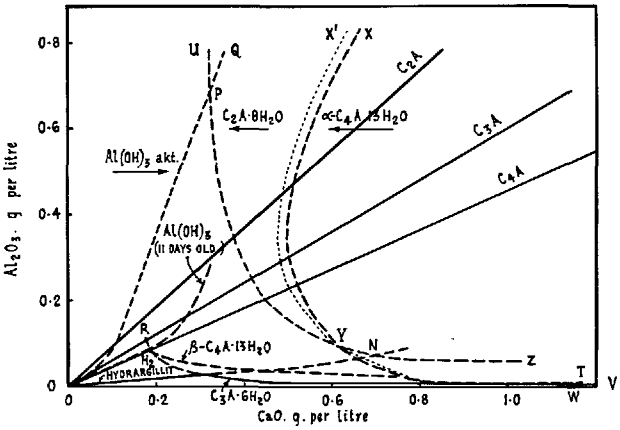


FIGURE 3. *System* CaO-Al_2O_3-H_2O *at 20 °C (D'Ans and Eick* [33], *1953).*
(Used by permission, Zement-Kalk-Gips.)

(4) Peppler and Wells [34] at 50 °C to 250 °C (1954)

Examination was made at 50 °, 120 °, 150 °, 200 °, and 250 °C at pressures from 1 to 39 atmospheres. The only new hydrated calcium aluminate phase formed was a compound $4CaO{\cdot}3Al_2O_3{\cdot}3H_2O$ (first prepared by Harris, Schneider, and Thorvaldson [35] (1943)), stable above 215 °C. Below this temperature the cubic $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ remains the stable hydrated calcium aluminate phase. The compound $C_4A_3{\cdot}3H_2O$ [34] "was prepared by heating a lime-alumina clinker for seven days at 278 °C. The resulting product was found to be homogeneous when examined microscopically. It consisted of rectangular plates having low birefringence with indices very close to 1.627". Properties had been given previously by Johnson and Thorvaldson [36] (1943) who stated that it crystallized in colorless elongated rectangular plates with parallel extinction, positive elongation, and low birefringence, of average R.I.=1.627, $d_{20\,°C}=2.71$, probably orthorhombic.

(5) Majumdar and Roy [37] at 100° to 1,000 °C (1955)

These authors state that the X-ray powder pattern they obtained of the compound $4CaO{\cdot}3Al_2O_3{\cdot}3H_2O$ varied from that reported by Johnson and Thorvaldson [36].

(6) Schippa and Turriziani [38] at 15°, 18°, 20 °C (1957)

Schippa and Turriziani carried out precipitation experiments from supersaturated solutions. Their data fall on a curve roughly coincident with that obtained by Wells, Clarke, and McMurdie at 21 °C, but again with no clear indication of an invariant point. X-ray examination of moist solids of CaO/Al_2O_3 ratio near to 4 yielded spacings similar to those for $C_2A{\cdot}8H_2O$, but which could not relate to this compound. This matter was not however cleared up.

(7) Buttler and Taylor [39] at 5 °C (1958)

The main feature of the behavior at 5 °C as compared with that at higher temperatures investigated by previous authors is the formation of the $CA{\cdot}10H_2O$ phase (see fig. 4, after Buttler and Taylor's fig. 2). This compound was originally prepared by Assarsson [40]. The establishment of an equilibrium curve for this compound appears however to be difficult because of the unstable or highly metastable nature of the equilibria, the formation of unstable hydrated alumina, and the apparent difficulty of obtaining equilibria from undersaturation. From undersaturation it appears that at 5 °C an equilibrium curve (*HC* in Buttler and Taylor's fig. 2) falls well below that for the hexagonal plate phase. There is, however, an apparent conflict of evidence from supersaturation and undersaturation, and it seems open to question whether in fact the curve *HC* concluded by Buttler and Taylor as that for $CA{\cdot}10H_2O$ can be taken as established in the position assigned to it.

(8) Carlson [14] at 1 °C (1958)

The general scheme of this work was again to approach equilibrium from supersaturation (by mixing calcium aluminate solutions and saturated limewater) and from undersaturation (by treating various prepared solid phases with water or lime solutions). The solid phases found in the system were stable $Ca(OH)_2$ and $C_3A{\cdot}6H_2O$ and metastable $CA{\cdot}10H_2O$, $C_2A{\cdot}8H_2O$ and $C_4A{\cdot}13H_2O$ (fig. 5).

(9) Percival and Taylor [41] at 21 °C (1959)

In a recently published note, these authors consider that they have established a curve for $CA{\cdot}10H_2O$ in the system at 21 °C, obtained by shaking $CA{\cdot}10H_2O$ with water or lime solutions. They could not however establish such a curve by precipitation from supersaturation, nor was any curve obtained by shaking $CA{\cdot}10H_2O$ with water or lime solutions at 50 °C. Further, in their precipitation tests from supersaturation at 21 °C, they always obtained $C_2A{\cdot}8H_2O$ (fig. 6).

(10) Buttler and Taylor [42] at 5 °C (1959)

This paper is restricted to the behavior of CA, CA_2, and mixtures of these when treated with water or lime solution in dilute suspension.

(11) Jones and Roberts [7] at 25 °C (1955–60)

The results of a re-examination of the system CaO-Al_2O_3-H_2O at 25 °C (to be published) show that the hydrates α- and β-$C_4A{\cdot}13H_2O$ previously thought to exist in the aqueous system, are formed only on drying a $C_4A{\cdot}19H_2O$ hydrate which is the only tetracalcium aluminate hydrate in the system. This hydrate can, however, exist in two forms, one of which is relatively unstable with respect to the other. The latter can be satisfactorily indexed on a hexagonal unit cell. In addition, a solid solution of composition range $C_{2-2.4}A{\cdot}8$–$10.2H_2O$, is formed, and also two $C_2A{\cdot}8H_2O$ hydrates of closely similar structures, one of which is unstable with respect to the other. The more stable of the two, when passed through a dehydration and rehydration cycle, converts to a form of $C_2A{\cdot}8H_2O$ which appears to conform strictly to a hexagonal lattice. The results give a substantial clarification of previous work on the system. Figure 7 shows the solubility relationships and curves for various solid phases as given by these authors.

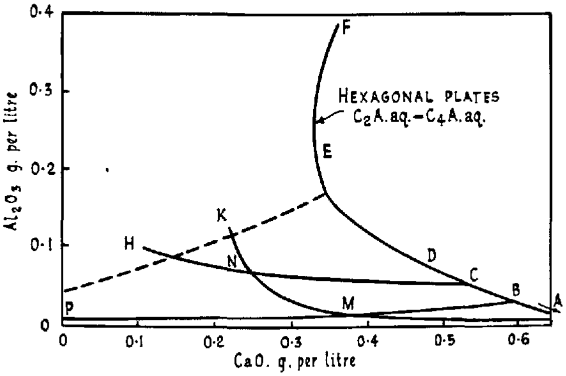


FIGURE 4. *System* CaO-Al_2O_3-H_2O *at 5 °C (Buttler and Taylor [39], 1958).*

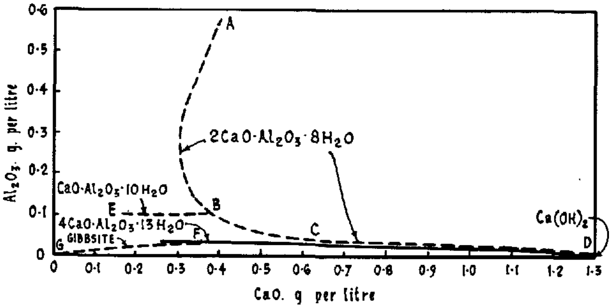


FIGURE 5. *System* CaO-Al_2O_3-H_2O *at 1 °C (Carlson [14], 1958).*

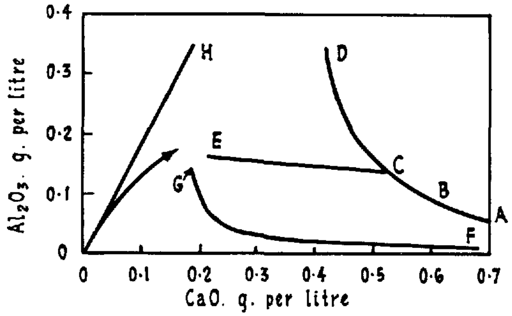


FIGURE 6. *System* CaO-Al_2O_3-H_2O *at 21 °C (Percival and Taylor [41], 1959).*

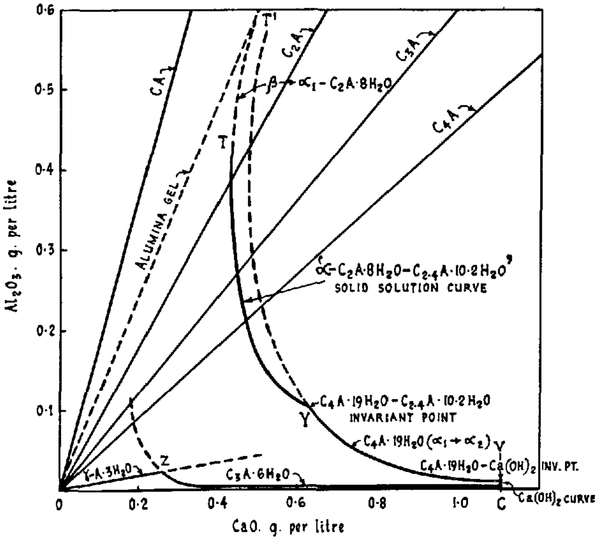


FIGURE 7. *System* CaO-Al_2O_3-H_2O *at 25 °C (Jones and Roberts [7], 1960).*

Review of Other Studies in the Light of Jones and Roberts' Work at 25 °C

It appears that the results and conclusions of Jones and Roberts may be used to reinterpret results previously obtained by other workers, and it is proposed to test this in the following discussion.

Jones and Roberts have concluded that at 25 °C:

(1) As previously recognized the only stable solid phases are crystalline $C_3A\cdot6H_2O$, $Ca(OH)_2$, and gibbsite (γ-$Al_2O_3\cdot3H_2O$).

(2) Hydrated (or hydrous) alumina, $Al_2O_3\cdot aq.$, can exist in the system in various unstable→stable states, ranging from a highly gelatinous hydrous alumina, through γ-$Al_2O_3\cdot H_2O$ (boehmite) and α-$Al_2O_3\cdot3H_2O$ (bayerite) to γ-$Al_2O_3\cdot3H_2O$ (gibbsite).

(3) Metastable hexagonal-plate phases can exist based on $C_4A\cdot aq.$ and $C_2A\cdot aq.$ structures as follows:

(a) *α_1- and α_2-$C_4A\cdot19H_2O$.* These are modifications of a new hydrate $C_4A\cdot19H_2O$.

The α_1-form is considered to possess an unstable or "disordered" layer structure. Where formed in the aqueous equilibria, it is unstable with respect to the α_2- structure and converts to it.

The α_2- form is basically the only C_4A hydrate which has a more than transient existence. The X-ray pattern is simpler than for the α_1- form and can be satisfactorily indexed on a hexagonal unit cell of dimensions $a=5.77$ A, $c=21.37$ A.

(b) *Solid solution $C_{2-2.4}A\cdot8$–$10.2H_2O$.* A metastable phase of varying CaO/Al_2O_3 ratio between 2 and 2.4, and varying H_2O/Al_2O_3 ratio between 8 and 10.2. It appears to be formed between α_1- or α_2-$C_4A\cdot19H_2O$ and α_1-$C_2A\cdot8H_2O$ (below).

(c) *α_1-$C_2A\cdot8H_2O$.* The previously known metastable $C_2A\cdot8H_2O$.

The X-ray pattern of this compound cannot be satisfactorily indexed on a hexagonal unit cell, apparently because of a "disordered" layer structure. In this respect it is similar to α_1-$C_4A\cdot19H_2O$. It does not transform to a more stable structure in solution (so far as observations have at present gone), but it can be so converted (to α_2-$C_2A\cdot8H_2O$ (below)) by passing through a dehydration and rehydration cycle.

(d) *β-$C_2A\cdot8H_2O$.* A new metastable hydrate, less stable than α_1-$C_2A\cdot8H_2O$ (above), into which it gradually converts in the aqueous system; i.e., in contact with solution. It cannot be satisfactorily indexed on a hexagonal unit cell, also apparently because of a "disordered" layer structure, which now, however, involves a slight decrease in the basal spacings (longest basal spacing 10.7 to 10.5 A).

(4) $C_4A\cdot19H_2O$ (α_1 or α_2) is the only tetracalcium aluminate hydrate which exists in the aqueous system (i.e., in contact with solution) and the α- and β-$C_4A\cdot13H_2O$ hydrates previously thought to be present in the aqueous equilibria are formed only as a result of dehydration of the $C_4A\cdot19H_2O$ hydrates according to the equation:

$$C_4A\cdot19H_2O-6H_2O\rightarrow C_4A\cdot13H_2O.$$

It follows that no "solubility" curves for α- or β-$C_4A\cdot13H_2O$ can exist in the aqueous equilibria, and that what have hitherto been interpreted as curves for these compounds are really curves for α_1- and α_2-$C_4A\cdot19H_2O$, or are not truly "solubility" curves.

(5) No hexagonal-plate form of tricalcium aluminate hydrate $C_3A\cdot12H_2O$ exists in the aqueous system. A solid hydrated hexagonal phase of C/A ratio=3 must at equilibrium consist of a mixture of $C_4A\cdot19H_2O$ and solid solution of composition $C_{2.4}A\cdot10.2H_2O$.

(6) Monocalcium aluminate hydrate does not form in the aqueous system at 25 °C except as a transient stage which passes into α_1-$C_2A\cdot8H_2O$.

(7) There is a transition temperature at approximately 22 °C at which $CA\cdot10H_2O$ and $C_2A\cdot8H_2O$ are relatively unstable with respect to one another in the aqueous phase, $CA\cdot10H_2O$ being relatively stable below, and $C_2A\cdot8H_2O$ relatively stable above that temperature.

$$2CA\cdot10H_2O \overset{22\ ^{\circ}C}{\rightleftharpoons} C_2A\cdot8H_2O+A\cdot aq.$$

In addition, there has been found

(8) *α_2-$C_2A\cdot8H_2O$.* A new metastable hexagonal plate hydrate, not so far found in the aqueous system in contact with solution, but into which α_1-$C_2A\cdot8H_2O$ converts on dehydration to the $5H_2O$ hydrate, followed by rehydration. This compound has the most stable structure of the different forms of $C_2A\cdot8H_2O$, one which can be satisfactorily indexed on a hexagonal unit cell of dimensions $a=5.80$, A, $c=21.59$ A. These dimensions are practically the same as those for α_2-$C_4A\cdot19H_2O$.

Since the most significant range of temperature for portland and high-alumina cement hydration is contained within the limits of 0 °C and 100 °C, we may exclude from immediate consideration the studies by Peppler and Wells and Majumdar and Roy in the higher range of temperature. Accepting as a basis the work of Jones and Roberts at 25 °C, it is proposed to consider first various studies, in order of decreasing temperature down to 1 °C (table 3), and then such work as has been done between 25 °C and 100 °C, leaving for final consideration work above 100 °C.

Range 25 °C to 1 °C

The investigations of Bessey (and Lea) at 25 °C, prior to 1938, have already been briefly referred to. Little information was given as to experimental detail. Only an alumina-gel phase, other than various hydrated calcium aluminates, was mentioned, while compounds $C_4A\cdot13H_2O$ and $C_3A\cdot12H_2O$ were then accepted as existing in the system. The last two compounds we now know do not exist in the aqueous system.

Jones [43] at 25 °C briefly considered the system CaO-Al_2O_3-H_2O as part of the quaternary system CaO-Al_2O_3-$CaSO_4$-H_2O and has described a little relevant experimental work. Special emphasis was laid on the equilibrium relations of hydrated alumina, separating out initially as a gel and changing both in crystal form and crystal size on aging, thus:

$$Al_2O_3\cdot aq.\ (\text{gel } \gamma\text{-}Al_2O_3\cdot H_2O)\rightarrow \alpha\text{-}Al_2O_3\cdot 3H_2O \rightarrow \gamma\text{-}Al_2O_3\cdot 3H_2O.$$

It was considered that the solubility "curve" must be regarded as unstable, sweeping out an area as its position changes with age, until a final stable position for γ-$Al_2O_3\cdot 3H_2O$ is reached.

The position of a solubility curve for a crystalline $A\cdot 3H_2O$ near to γ-$Al_2O_3\cdot 3H_2O$ was determined by Jones at 25 °C by shaking a preparation of $Al_2O_3\cdot 3H_2O$ with lime solutions of increasing concentrations for 7 or 28 days. This curve, combined with Bessey's curve for $C_3A\cdot 6H_2O$ at 25 °C, was accepted as defining with sufficient accuracy the stable equilibria for gibbsite, $C_3A\cdot 6H_2O$, and $Ca(OH)_2$ at 25 °C. No other work was done at this period in the ternary system, although it was clear that Jones' curve *SW* in the quaternary system CaO-Al_2O_3-$CaSO_4$-H_2O at 25 °C (his fig. 6) (considered at the time as a solid solution curve—conveniently then written as "$C_3A\cdot 12H_2O + C_3A\cdot CaSO_4\cdot 12H_2O + C_3A\cdot Ca(OH)_2\cdot 12H_2O + Ca(OH)_2$") corresponded to a similar curve in the ternary system. This in turn was to be identified with the solubility curve or curves within Bessey's area *DEB*.

Shortly before Jones' publication, Wells, Clarke, and McMurdie had published their study of the system CaO-Al_2O_3-H_2O at 21 °C. This fortunately presents a satisfactory amount of experimental data, which from supersaturation yielded their "practical" curve *ABD*. This, however, they found difficult to interpret satisfactorily. It seems evident now, in the light of Jones and Roberts' work, that this curve is really made up of a well-defined curve for the new $C_4A\cdot 19H_2O$ hydrate and a solid solution curve of composition range in the solid of $C_{2-2.4}A\cdot 8$–$10.2H_2O$. Data from undersaturation confirmed the practical curve *ABD*.

Wells, Clarke, and McMurdie had considered the problem of determining the exact water content of the various hexagonal-plate phases. However, they state that these hydrates "were, for the most part, washed with alcohol (and ether), and then were dried at room temperature in a desiccator containing $CaCl_2$". It has been shown by Roberts [11] that these procedures result in loss of water from the $C_4A\cdot 19H_2O$ hydrate to give $13H_2O$ and $11H_2O$ hydrates, respectively, and that although washing with alcohol does not affect the water content of $C_2A\cdot 8H_2O$, drying over anhydrous $CaCl_2$ results in a loss to $C_2A\cdot 5H_2O$. From this result it is clear that Wells, Clarke, and McMurdie could not detect the $C_4A\cdot 19H_2O$ hydrates in these dried products. In some instances, however, the samples were not dried over $CaCl_2$.

X-ray diffraction patterns on freshly-prepared samples (assumed washed with alcohol and ether, but not dried over $CaCl_2$) with CaO/Al_2O_3 ratios varying between 2.04 and 3.88, and H_2O/Al_2O_3 ratios varying between 7.92 and 12.60 were obtained by these authors. It was found that the extreme compositions gave the lines of

TABLE 3. *Studies of the system* CaO-Al_2O_3-H_2O *in range 25 °C–1 °C*

	Authors	Temperature °C	General procedure
1	Bessey (with Lea)	25 °C	
2	Wells, Clarke, and McMurdie	21 °C±1°	Precipitation from mixtures of supersaturated monocalcium aluminate solutions and lime solutions. The mixtures were contained in tightly stoppered flasks in a room at 21±1 °C. Approach to equilibrium from undersaturation by placing solid phases C_2A aq and C_4A aq in calcium hydroxide solutions of various concentrations. Phases examined by chemical analysis, optical examination, and to some extent X-ray diffraction. Solid phases dried, prior to examination, over $CaCl_2$.
3	D'Ans and Eick	20 °C±?	Precipitation from mixtures of supersaturated monocalcium aluminate solutions and lime solutions. Not apparently shaken, and precise condition of storage not given. Approach to equilibrium from undersaturation by shaking a preparation of $C_2A\cdot 8H_2O$ (of actual composition 2.25 CaO : 1 Al_2O_3 : 7.7 H_2O) with limewater of various concentrations. Phases examined by chemical analysis, but solids almost wholly by optical examination. No X-ray examination.
4	Buttler and Taylor	5 °C±0.5°	Precipitation from mixtures of supersaturated monocalcium aluminate solution and solid CaO shaken continuously for at least a week and then at least daily. Polyethylene bottles. Approach to equilibrium from undersaturation by adding solid phases $CA\cdot 10H_2O$, $C_3A\cdot 6H_2O$ and hydrated alumina to water or lime solutions in polyethylene bottles and shaking at least part of time. Phases examined by chemical analysis and X-ray diffraction.
5	Carlson	1 °C±1 °C	Precipitation from mixtures of supersaturated monocalcium aluminate solution and lime solutions and from undersaturation by treating various prepared solid phases with water and lime solutions. The mixes were stored in polyethylene bottles, with occasional shaking, in a refrigerator at 1 °C. Solid phases usually dried over $CaCl_2$. Identification by microscopic examination was stated to be often impossible and reliance was placed on X-ray examination.
6	Jones and Roberts	25 °C±1 °C	Precipitation from mixtures of supersaturated monocalcium aluminate solution and solid $Ca(OH)_2$, solid CaO, or lime solutions. Polyethylene vessels with very few exceptions. Continuous shaking. Solid phases examined in either moist solid condition or after controlled drying at definite relative humidities. Microscopic and X ray examinations.

$C_2A{\cdot}8H_2O$ and $C_4A{\cdot}13H_3O$ hydrates, while intermediate compositions gave the lines of both, in appropriate proportions. In particular, a sample with $CaO/Al_2O_3=3.15$ gave a pattern in which the two 001 lines were of almost equal intensity. On these grounds the authors concluded that the so-called hexagonal tricalcium aluminate hydrate is in reality "a mixture of hexagonal hydrated dicalcium and tetracalcium aluminates in equal molecular proportions." From Jones and Roberts' work, it would appear that such a composition is, in the highly hydrated state, as present in the aqueous equilibria, a mixture of $C_4A{\cdot}19H_2O$ and "solid solution" of composition $C_{2.4}A{\cdot}10.2H_2O$ in appropriate proportions, and is, after drying, a mixture of $C_4A{\cdot}aq.$ and $C_2A{\cdot}aq.$ in conditions determined by the intensity of the drying procedure.

One interesting matter raised by Wells, Clarke, and McMurdie was their conclusion that in the dry state $C_2A{\cdot}8H_2O$ decomposes to give $C_4A{\cdot}13H_2O$ and $Al(OH)_3$. This conclusion was not confirmed by Jones and Roberts. It is of course not directly significant as regards compounds present in the aqueous equilibria, though Bessey has stated that the conversion also occurs when $C_2A{\cdot}8H_2O$ is kept in contact with the saturated equilibrium solution in water. The latter statement is explicable on the basis of the relations in the aqueous equilibria as found by Jones and Roberts. Thus $C_2A{\cdot}8H_2O$ in contact with its saturated solution is at the point *T* of Jones and Roberts' figure 1. Since this compound represents a highly metastable equilibrium, it will tend to change along Jones and Roberts' curve *TYV*, $Al(OH)_3$ separating out and gradually changing to a more crystalline and stable state, tending finally to gibbsite, while the composition of the equilibrium hexagonal-plate phase changes through the solid-solution range and finally converts to $C_4A{\cdot}19H_2O$.

It is difficult to explain the conclusion reached by Wells, Clarke, and McMurdie. However, drying conditions were intense enough to give $C_2A{\cdot}5H_2O$, the X-ray powder pattern of which may have been confused with that of $C_4A{\cdot}13H_2O$.

Returning to the aqueous equilibria, it may be noted that Wells, Clarke, and McMurdie in 1943 had approached close to the definite conclusions reached by Jones and Roberts, in the former's tentative interpretation of their practical curve *ABD*. Thus the part of the curve which they concluded "applies primarily to the dicalcium aluminate hydrate" together with the "region where the two aluminates markedly inter-crystallize because of the close similarity of their crystal structures" clearly correspond to the solid solution curve *TY* of Jones and Roberts, and the part of the curve "pertaining mainly to the solubility of the hexagonal tetracalcium aluminate hydrate" to the definite solubility curve for $C_4A{\cdot}19H_2O$ now established.

Consideration was also given by Wells, Clarke, and McMurdie to the precipitation of hydrated alumina in the system. Since the region in which this can occur is also one in which the compound $CA{\cdot}10H_2O$ may be found, and the temperature (21 °C) is approximately or slightly below that of the stability limit of this compound with respect to $C_2A{\cdot}8H_2O$, it is desirable to discuss the findings of these authors. They make no reference to $CA{\cdot}10H_2O$. Later it may be noted that Percival and Taylor [41] could not establish a curve for $CA{\cdot}10H_2O$ by precipitation at this temperature. Wells, Clarke, and McMurdie found that either mixtures of hydrated alumina and hexagonal plate phases were formed, with solution concentrations along the *AB* portion of their curve *ABD*, or that hydrated alumina alone was precipitated over an area which is within the general area where alumina gel in various stages of crystallization may be formed. These areas clearly correspond with the unstable invariant point curve for aging alumina gel and solid solution concluded by Jones and Roberts and the area swept through for an aging alumina gel curve. It may be noted however that the alumina gel precipitated in Wells, Clarke, and McMurdie's experiments as an apparent single solid phase contained some lime ($CaO/Al_2O_3=0.07$ to 0.36).

E. T. Carlson [17] (1957) later expressed surprise that Wells, Clarke, and McMurdie had not found any $CA{\cdot}10H_2O$ compound at 21 °C. This apparent absence is however not so surprising in view of the closeness of the temperature to the transition point. However, Jones and Roberts obtained this phase at 20 °C together with hydrated alumina.

Wells, Clarke, and McMurdie's data, as indicated above, show that the hydrated alumina phase tends to become increasingly rich in lime with increase in lime concentration of the solution from which precipitation occurs. The question arises therefore as to the precise way in which this lime is linked with the hydrated alumina. The authors state that the hydrated alumina when first formed had a refractive index of about 1.50 (variable) increasing with age, more rapidly near the surface. This observation does not suggest any formation of $CA{\cdot}10H_2O$, which has a refractive index of about 1.47. The surface index is stated to have increased eventually to from 1.56 to 1.58, the interior index being definitely less. Although increase in index might be due to aging of hydrated alumina to gibbsite (R.I. 1.56 to 1.59), the observation was also made that the increase in index near the surface was linked with increase in lime content. The possibility of formation of $C_3A{\cdot}6H_2O$ was considered, although it was pointed out that it had not gone far enough to raise the external index to 1.605, the value for $C_3A{\cdot}6H_2O$. Wells, Clarke, and McMurdie draw attention to similar results of Assarsson [40]. They found that X-ray diffraction patterns of aged hydrated alumina showed the presence of gibbsite, increasing with age, that the H_2O/Al_2O_3 ratio was often greater than 3 and increased with the CaO/Al_2O_3 ratio. No lines of the pattern of $C_3A{\cdot}6H_2O$ were detected (possibly because the amount was too small). Thus if the lime present exists as a surface skin of $C_3A{\cdot}6H_2O$, this fact could not be established. The weight of evidence points to a change to gibbsite near the surface as explaining the rise in surface index. It remains a possibility that some $CA{\cdot}10H_2O$ was present.

A curve which was accepted (reasonably so) as the solubility curve for gibbsite at 21 °C was drawn through maximum solubility values for a gibbsite preparation allowed to stand in contact with lime solutions of different concentrations for periods of up to more than 2 yr.

Following Wells, Clarke, and McMurdie's work, no further comprehensive investigation of the system was published until that of D'Ans and Eick in 1953. As previously indicated, it seems to the writer that some of their conclusions are open to criticism. They state categorically that they determined at 20 °C the solubility curves of stable $C_3A{\cdot}6H_2O$, hydrargillite (i.e., gibbsite), and $Ca(OH)_2$; and metastable "active hydroxides of aluminum," $C_2A{\cdot}8H_2O$, α-$C_4A{\cdot}13H_2O$ and β-$C_4A{\cdot}13$–$14H_2O$.

As in the case of Wells, Clarke, and McMurdie the existence of $C_4A{\cdot}19H_2O$ rather than $C_4A{\cdot}13H_2O$ as the hydrated tetracalcium hydrate in the aqueous phase was not then realized, and their conclusions therefore need revision in the light of Jones and Roberts' work.

The "practical" curve obtained for hexagonal-plate phases by plotting data from supersaturation is given by D'Ans and Eick in their figure 4 (fig. 3 of this paper). The curve lies somewhat to the right of the similar curve obtained by Wells, Clarke, and McMurdie under very similar conditions of mixing metastable monocalcium aluminate solutions and lime solutions. The reason for the higher solution concentrations of D'Ans and Eick's curve is not clear. In the writer's experience, approach to equilibrium in the mixing of two such solutions and consequent precipitation is *on shaking* quite rapid, and there is no significant difference in the position of the curve for data obtained after two hours or up to 60 to 80 days. However there is little doubt that both curves have the same practical significance.

Of more immediate interest is the statement by D'Ans and Eick, based apparently only on optical evidence, that: (as the CaO/Al_2O_3 ratio of the initial mixed solution decreased) their mix *C* included, amongst other hexagonal-plate phases, small amounts of $C_3A{\cdot}12H_2O$; mix *D* included first a little $C_3A{\cdot}12H_2O$, then $C_3A{\cdot}18H_2O$; and mix *E* included (together with $Al(OH)_3$) $C_3A{\cdot}18H_2O$ of indices $\alpha=1.475$, $\gamma=1.495$, as well as $C_2A{\cdot}8H_2O$ and $C_3A{\cdot}12H_2O$. Again, their mix C_4 developed $C_3A{\cdot}18H_2O$.

It is believed that D'Ans and Eick were mistaken in their assumption that compounds $C_3A{\cdot}12H_2O$ or $C_3A{\cdot}18H_2O$ exist at all in the aqueous system. They do however say that $C_3A{\cdot}12H_2O$ may be $C_2A{\cdot}8H_2O$ crystals with a higher lime content, or mixed crystals of $C_2A{\cdot}8H_2O$ and $C_4A{\cdot}13H_2O$. Both Wells, Clarke, and McMurdie, and Jones and Roberts have concluded that $C_3A{\cdot}12H_2O$ does not exist in the system.

The position of the alleged $C_3A{\cdot}18H_2O$ is of some interest. Bessey included this compound in his 1938 list as consisting, according to Mylius [44] of long needles with refractive indices $\alpha=1.479$, $\beta=1.489$, $\alpha=1.495$, but comments that it had only been observed in precipitation experiments in which ions other than those of the calcium aluminates were present. It seems unlikely that such a compound exists in the CaO–Al_2O_3–H_2O, system. It seems possible that this alleged compound may have been confused with $CA{\cdot}10H_2O$ precipitation of which is possible at 20 °C in the precipitation regions concerned. The monocalcium aluminate hydrate can occur as prismatic needles and has a refractive index of about 1.47, rising on drying ($CA{\cdot}10H_2O \rightarrow CA{\cdot}7H_2O$) to $\omega=1.477$, $\epsilon=1.480$ [17].

With regard to Schippa and Turriziani's experiments at 20 °C, 18 °C, and 15 °C, it will be observed that they have also carried out moist solid examinations, but did not pursue the investigations to the conclusions reached by Jones and Roberts. No new hydrates were identified, and their experiments did not include mixes where the compound $CA{\cdot}10H_2O$ is a likely or possible solid phase.

It has been shown by Jones and Roberts that the hydrated calcium aluminate phase precipitated with hydrated alumina from monocalcium aluminate solutions of $CaO/Al_2O_3=1$ is $C_2A{\cdot}8H_2O$ above 22 °C and $CA{\cdot}10H_2O$ below this temperature, though $CA{\cdot}10H_2O$ may be formed occasionally in minor amounts above 22 °C and $C_2A{\cdot}8H_2O$ may also be formed initially at 20 °C, but transforming into $CA{\cdot}10H_2O$ with longer times of shaking. It was concluded that a transition temperature exists at 22 °C below which the $C_2A{\cdot}8H_2O$ structure is unstable with respect to $CA{\cdot}10H_2O$ within certain solution concentration limits. It follows that at the temperature of 21 °C or below, $CA{\cdot}10H_2O$ is to be expected from supersaturation. Percival and Taylor carried out some work from supersaturation at 21 °C but state that it was not found possible to define the curve (for $CA{\cdot}10H_2O$). They state that they did succeed in defining a curve by shaking $CA{\cdot}10H_2O$ with water or lime solutions. It will be further discussed following consideration of the results of Buttler and Taylor at 5 °C.

Considering the data obtained by Buttler and Taylor from supersaturation at 5 °C, it is clear that their curve *A B C D E F* is similar to the general form of the curves *VY*, *YT* obtained in the investigation of Jones and Roberts at 25 °C, but is displaced to the left; i.e., to solution concentrations with less lime and alumina. The authors were not able to distinguish separate solubility curves. However, their own data seem to provide clear evidence of an invariant point similar to that of *Y* in the present work. Using data

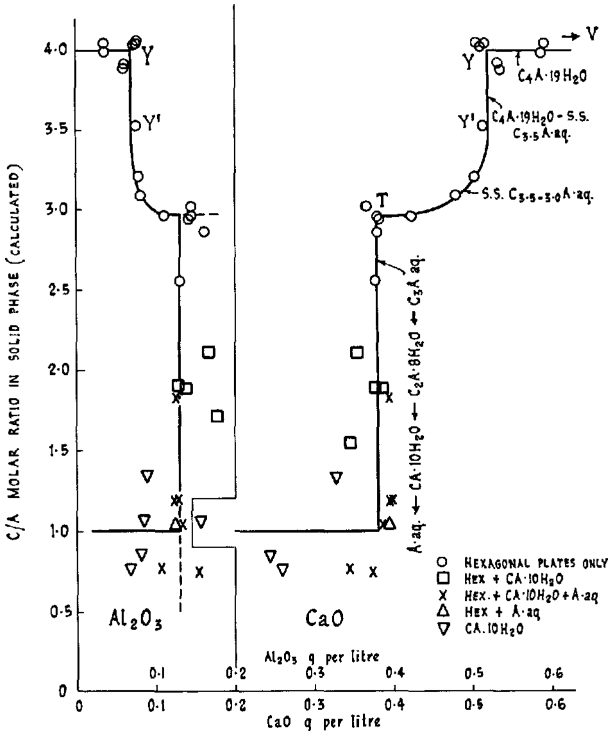


FIGURE 8. *System* CaO-Al_2O_3-H_2O *at 5 °C.*

Variation of C/A ratio in solid phase with solution composition. From supersaturation. Data of F. G. Buttler and H. F. W. Taylor [39].

obtained by Buttler and Taylor with mixes of total initial CaO/Al_2O_3 ratio greater than 1.6 (table 4), the CaO/Al_2O_3 ratio in the final solid phases is plotted against the lime and alumina concentrations in solution in figure 8. This figure is comparable to figure 2 of Jones and Roberts. Data obtained from some series of mixes (21, 22, and 23) have not been plotted at shorter times than 99 days. A number show a transition with time from the hexagonal-plate phase into $CA·10H_2O$ or $CA·10H_2O$ plus $A·H_3$.

Although Buttler and Taylor have not adopted the procedure of direct analysis of the solid phases, and their data suggest that the calculated CaO/Al_2O_3 ratios may therefore be subject to error, the results are neverthless of considerable interest. The first thing to be noted is that there is a clear break in the equilibria data at a point *Y* corresponding to a solution concentration of 0.52 g CaO per liter, 0.07 g Al_2O_3 per liter. This break evidently relates to an invariant point for mixtures of $C_4A·19H_2O$ and a second hexagonal plate phase. The corresponding phase at 25 °C has been concluded by Jones and Roberts to be a solid solution of composition $C_{2.4}A·10·2H_2O$. At 5 °C, the X-ray data of Buttler and Taylor, obtained only from solids dried at 34 percent rh at room temperature, indicate the presence of mixtures of $C_4A·13H_2O$ and $C_2A·8H_2O$ in these dried solids as the solution

TABLE 4. *System* CaO–Al_2O_3–H_2O *at 5° C*

(Selected data of F. G. Buttler and H. F. W. Taylor)
Equilibria from supersaturation

Mix No.[a]	Age	Total composition of initial mix, g/liter			Composition of filtrate, g/liter		C/A in solid (calculated)	Solid phases found in X-ray examination of solids dried over saturated $CaCl_2$ solution at room temperature
		CaO	Al_2O_3	C/A	CaO	Al_2O_3		
	Days							
6E	256	0.652	0.960	1.23	0.243	0.082	0.85	CAH_{10}
9C	574	.475	.593	1.46	.258	.068	.75	CAH_{10}
C5 (undersaturation)	*94*	----------	----------	----------	*.157*	*.085*	*1.05*	CAH_{10}
13B	137	.569	.638	1.62	.372	.155	0.74	$C_2AH_8+CAH_{10}+AH_3$
13C	574	.569	.638	1.62	.346	.108	.76	$AH_3+C_4AH_{13}+CAH_{10}$
16D	100	.976	1.016	1.75	.394	.127	1.19	$C_2AH_8+CAH_{10}+AH_3$
16E	212	.974	1.016	1.74	.397	.124	1.18	Do.
18D	99	.744	.768	1.76	.385	.134	1.03	$AH_3+CAH_{10}+C_2AH_8$
18E	212	.767	.768	1.79	.392	.125	1.03	$AH_3+C_2AH_8$
21B	136	.676	.566	2.17	.346	.176	1.54	$CAH_{10}+C_2AH_8$
21C	577	.676	.666	2.17	.327	.089	1.33	CAH_{10}
22D	100	1.342	1.016	2.40	.354	.166	2.11	$C_2AH_8+CAH_{10}+$tr. C_4AH_{13}
22E	213	1.312	1.016	2.35	.387	.128	1.89	$CAH_{10}+C_2AH_8$
23D	99	1.025	.768	2.43	.374	.137	1.88	$C_2AH_8+CAH_{10}+$tr. C_4AH_{13}
23E	214	1.042	.768	2.47	.394	.125	1.83	$C_2AH_8+CA+AH_3$
28A	124	.570	.268	3.87	.377	.131	2.56	C_2AH_8
28B	578	.570	.268	3.87	.366	.145	3.02	$C_2AH_8+C_4AH_{13}$
24	20	1.657	.974	3.09	.379	.162	2.86	$C_2AH_8+C_4AH_{13}$
25A	7	1.795	1.016	3.21	.384	.142	2.94	Do.
25B	223	1.795	1.016	3.21	.379	.147	2.96	Do.
26	36	1.825	0.974	3.41	.422	.111	2.96	Do.
27	22	2.010	.974	3.75	.478	.081	3.09	Do.
29	36	2.087	.974	3.90	.502	.077	3.21	Do.
30	23	2.259	.974	4.22	.512	.074	3.53	Do.
31A	4	2.054	.768	4.86	.515	.076	4.04	$C_4AH_{13}+C_2AH_8$
31B	13	2.054	.768	4.86	.506	.068	4.02	Do.
31C	214	2.052	.768	4.83	.503	.077	4.05	Do.
32A	109	0.853	.208	7.46	.535	.059	3.88	C_4AH_{13}
32B	353	.853	.208	7.46	.532	.059	3.92	Do.
33A	109	.909	.183	9.03	.589	.034	4.04	Do.
33B	567	.909	.183	9.03	.585	.035	3.98	Do.

---

[a] For mixes giving final solid phases containing CAH_{10}, only mixes of 99 days or older are included owing to the apparent slowness in attainment of equilibrium. In mixes not developing CAH_{10} equilibrium appears to be attained within a very short time and accordingly short period mixes are here included.

concentrations change from that at *Y* to that at *T* (i.e., to 0.38g CaO per liter, 0.13 g Al_2O_3 per liter). From the work of Jones and Roberts it is concluded that the actual $C_4A \cdot aq.$ phase present in the corresponding moist solid before drying, and therefore in the aqueous system, is probably $C_4A \cdot 19H_2O$ (as at 25 °C) and that the $C_2A \cdot 8H_2O$ phase at 5 °C is a solid solution. We have also to consider the fact that the $C_2A \cdot 8H_2O$ is unstable with respect to $CA \cdot 10H_2O$ below 22 °C in regions where $C_2A \cdot 8H_2O$ would otherwise form, though it appears however to be a possibility that a solid solution based on the $C_2A \cdot 8H_2O$ and $C_4A \cdot 19H_2O$ structures may still remain a metastable phase within a range of compositions before suffering breakdown in the direction

$$C_4A \cdot 19H_2O \rightarrow C_2A \cdot 8H_2O \rightarrow CA \cdot 10H_2O \rightarrow A \cdot 3H_2O.$$

In figure 8, the extent of the vertical drop *YY′* at constant solution composition in the portion *YY′T* suggests that a solid solution of composition $C_{3.5}A \cdot aq.$ is first formed on decomposition of the compound $C_4A \cdot 19H_2O$ and that these two phases at first coexist at the invariant point *Y*. The composition $C_{3.5}A \cdot aq.$ corresponds to 3 moles of $C_4A \cdot aq.$ and 1 mole of $C_2A \cdot aq.$, and one would therefore expect the X-ray pattern to be dominantly that of $C_4A \cdot 19H_2O$. However, Buttler and Taylor's X-ray examinations were made on solids dried over saturated $CaCl_2$ solution (34 percent rh) at room temperature, and the result of this treatment has to be considered. Under these conditions, a solid solution would be expected to dehydrate to α- and β-$C_4A \cdot 13H_2O$ and $C_2A \cdot 8H_2O$ (Buttler and Taylor did not distinguish between different forms of $C_4A \cdot 13H_2O$ or $C_2A \cdot 8H_2O$). Following conversion of $C_4A \cdot 19H_2O$ to the solid solution of maximum CaO/Al_2O_3 ratio of 3.5, the CaO/Al_2O_3 ratio is indicated in figure 8 to fall gradually to 3, the solution compositions changing gradually to another sharp break at *T* corresponding to 0.38 g CaO per liter, 0.13 g Al_2O_3 per liter. It appears reasonable to infer (on this data) that a solid solution is therefore formed of composition range $C_{3.5-3.0}A \cdot aq.$, in equilibrium with solutions along the curve *Y′T* (see also fig. 13). At *T*, the data (fig. 8) indicate a progressive breakdown in the structure from the solid solution through $C_2A \cdot 8H_2O$ to $CA \cdot 10H_2O$ and eventually to $A \cdot 3H_2O$ at a more or less constant solution composition. The sequence of X-ray patterns obtained by Buttler and Taylor is limited to $C_4A \cdot 13H_2O$ (derived partly from $C_4A \cdot 19H_2O$ and partly the solid solution, according to Jones and Roberts), $C_2A \cdot 8H_2O$, $CA \cdot 10H_2O$ and $A \cdot aq.$ Along *YT* the line intensities in the X-ray patterns of the dried solids indicated that $C_2A \cdot 8H_2O$ increased in amount with respect to $C_4A \cdot 13H_2O$, while from *T*, accompanying the rapid fall in CaO/Al_2O_3 ratios in the solid phase at the approximately constant solution composition, they indicated conversion to $C_2A \cdot 8H_2O$, $CA \cdot 10H_2O$ and $A \cdot 3H_2O$ respectively in order. It should be noted that since the $C_2A \cdot 8H_2O$ observed in the X-ray patterns of Buttler and Taylor obtained on dried solids could be derived from solid solution by dehydration and decomposition on drying, it is possible that there is direct breakdown of solid-solution phase to $CA \cdot 10H_2O$ and hydrated alumina with no actual intermediate formation of $C_2A \cdot 8H_2O$, which is unstable at this temperature.

The above appears to be consistent with the conclusion that in the aqueous system at 5 °C, the following sequence of curves and invariant points occur along the curve *A B C D E F* obtained by Buttler and Taylor.

Using the lettering of Jones and Roberts:

CV$=Ca(OH)_2$
YV$=C_4A \cdot 19H_2O$
YY′$=C_4A \cdot 19H_2O$ and ss $C_{3.5}$ A·aq.
Y′T=ss $C_{3.5-3}$ A·aq.
T=Invariant point ss $C_3A \cdot aq.-CA \cdot 10H_2O$
TT′=Metastable or unstable prolongation of ss curve *Y′T*.

Although, because of uncertainty in Buttler and Taylor's calculated data, the actual composition of the solid solution is somewhat in doubt, it

TABLE 5. *System* $CaO-Al_2O_3-H_2O$ *at 5 °C*

(Selected data of F. G. Buttler and H. F. W. Taylor). Equilibria from undersaturation

Mix No.[a]	Age	Wt. CA·aq.	Volume solution	CaO, g/liter	Composition of filtrate, g/liter		C/A in solid (calculated)	Solid phases found in X-ray examination of solids dried over saturated $CaCl_2$ solution at room temperature.
					CaO	Al_2O_3		
	days	*g*	*ml*					
C2	131	0.654	393	0	0.145	0.091	0.62	$CAH_{10}+AH_3$
C3	160	.818	394	0	.143	.080	.68	Do.
C5	94	.385	441.6	0.124	.157	.085	1.05	CAH_{10}
C7	31	.595	431.7	.224	.247	.064	1.00	$CAH_{10}+AH_3$
C9	50	.486	422.2	.252	.286	.072	.97	Do.
C11	35	.462	425.7	.440	.438	.062	1.12	CAH_{10}
C12	117	.347	420.2	.440	.430	.062	1.29	$CAH_{10}+AH_3$
C14	44	.327	398.7	.874	.604	.030	2.96	$C_4AH_{13}+C_3AH_6+AH_3$
C15	106	.404	409.2	.874	.565	.043	2.93	Do.
C16	28	.157	412.0	1.174	.994	.002	3.23	C_4AH_{13}
C17	131	.168	404.6	1.174	.960	.003	3.48	Do.

[a] Only mixes with longer periods of contact are included in the above table from Buttler and Taylor's data, since it is assumed that in the presence of CA H_{10} and A H_3 in the solid phase these relatively long period mixes are more likely to have reached an appropriate metastable (or unstable) equilibrium..

would appear on this interpretation that a solubility curve for $CA{\cdot}10H_2O$ should start from *T* and proceed to intersect an unstable hydrated alumina curve. Such a curve *TZ*, based on Buttler and Taylor's data, from both supersaturation and undersaturation, is drawn in figure 9, which gives suggested possible metastable and unstable equilibrium curves.

Selected data obtained by Buttler and Taylor from undersaturation are given in table 5. They were obtained by shaking $CA{\cdot}10H_2O$ with water or lime solutions, and are plotted on figure 10. This figure includes the curve *HC* drawn by Buttler and Taylor as the $CA{\cdot}10H_2O$ curve in the system. The position assigned by Buttler and Taylor was based mainly on the data obtained from undersaturation (table 5). The difference between the position assigned by Buttler and Taylor for the $CA{\cdot}10H_2O$ curve and that which seems to be suggested by their data in the present discussion is difficult to reconcile. Note also that in figure 8, the position for a $CA{\cdot}10H_2O$ curve assigned by Buttler and Taylor would imply a vertical drop from a point on the curve *YV* and an invariant point $C_4A{\cdot}19H_2O$-$CA{\cdot}10H_2O$. This hardly fits the data.

It may be relevant to note that the mixes were not continuously shaken throughout the duration of the test. The authors considered that continuous shaking for some indeterminate time above a week, followed by a daily shake (presumably brief hand shaking in the storage room) was sufficient. This assumption may not be correct, especially for the approach from undersaturation. It may also be noted that many of Buttler and Taylor's relatively short-period mixes from supersaturation, starting below an initial CaO/Al_2O_3 ratio of 1.5 and falling in many cases to final CaO/Al_2O_3 con-

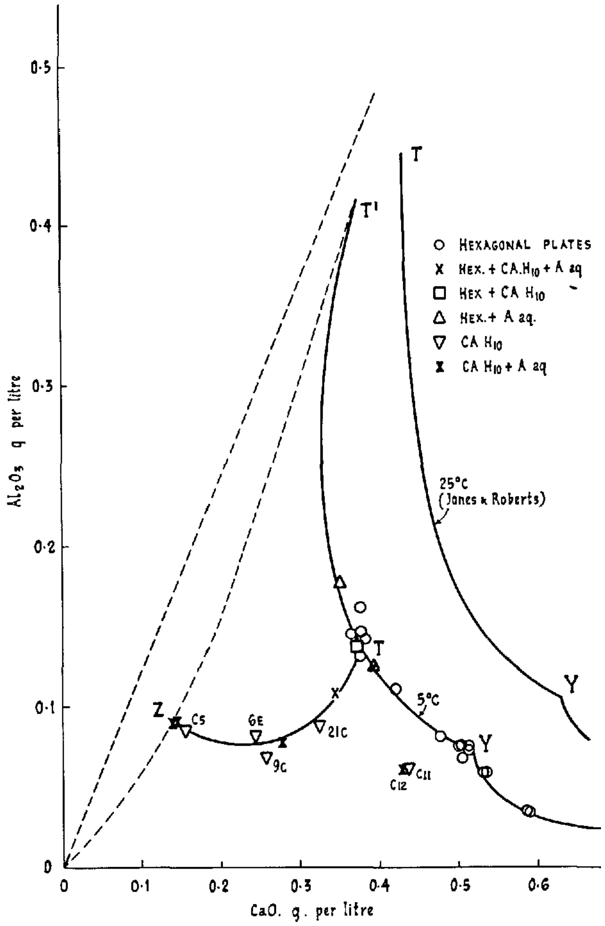


FIGURE 9. *System* CaO-Al_2O_3-H_2O *at 5 °C.*

Suggested metastable and unstable equilibria. Data (from supersaturation and undersaturation) of Buttler and Taylor [39].

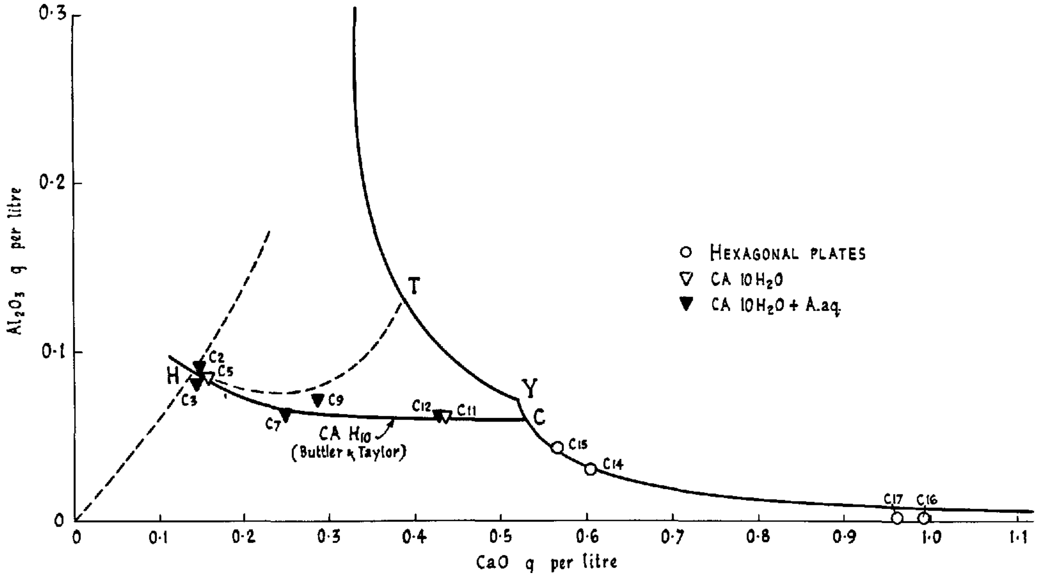


FIGURE 10. *System* CaO-Al_2O_3-H_2O *at 5 °C.*

Selected longer period data from undersaturation in relation to the position for a $CA{\cdot}H_{10}$ curve (F. G. Buttler and H. F. W. Taylor as concluded by them [39]).

centrations below those of curve *C D E F*, had final CaO/Al_2O_3 ratios in the solid phase well below unity. Also they were generally indicated, from X-ray data, to contain varying amounts of $CA \cdot 10H_2O$ and hydrated alumina, the latter generally increasing as the initial CaO/Al_2O_3 ratio decreased. From undersaturation also, alumina gel is present in most of the solid phases obtained by shaking $CA \cdot 10H_2O$ in water or lime solution. It seems possible therefore that either unstable invariant points $CA \cdot 10H_2O$–hydrated alumina may be obtained, the position of which will vary with the state of the hydrated alumina, or the latter phase may be dominant, as a protective layer, in determining the equilibrium solution.

Such a behavior is suggested by the solution compositions obtained in some experiments at the Building Research Station (Roberts [15]) in which monocalcium aluminate solutions were allowed to precipitate at 1 °C. For a series of 10 mixes, it was observed that the CaO concentrations were in the range 0.14 to 0.23 g CaO per liter and the Al_2O_3 concentrations in the range 0.1 to 0.24 g Al_2O_3 per liter, with a tendency for the latter to decrease with age. X-ray examination indicated that only $CA \cdot 10H_2O$ was precipitated. However, analysis of the solid phase usually showed CaO/Al_2O_3 ratios slightly less than 1 (0.89–1.01) indicating the possible presence of alumina gel.

A further paper relevant to the present discussion has very recently been published by Buttler and Taylor [42] (1959). This paper deals with the action of water and lime solutions on anhydrous calcium aluminates at 5 °C. It is chiefly noted here in so far as it considers the hydration of CA_2 and the possibility of a hydrated $CA_2 \cdot aq.$ compound. Reference is made to the work of Cocco [45]. The latter author found that pastes made from CA_2 were slow to set, but after about a month had a strength at least equal to that of ones made from CA. He deduced, but without any X-ray evidence, that a new hydrate $CA_2 \cdot xH_2O$ was formed. Buttler and Taylor found that CA_2 with relatively strong lime solutions, reacts at a rate comparable with that of CA under similar conditions (though they point out that in their experiments the CA_2 was more finely ground). Reaction with water was however very slow and incomplete. The authors state that "The only hydrated compounds formed with water at 5 °C were CAH_{10} and hydrated alumina, no evidence was obtained for a hydrate of CA_2." It seems most probable that Cocco's original deduction is erroneous. It may be worth noting that in Buttler and Taylor's paper figure 1 should be figure 2 and vice versa.

Returning to Percival and Taylor's determination, from undersaturation, of a curve for $CA \cdot 10H_2O$ at 21 °C [41], it will be seen (fig. 6) that the position assigned to the curve indicates that it meets the hexagonal-plate curve to the left of the position assigned by Jones and Roberts as most probable from the data of Wells, Clarke, and McMurdie for an invariant point $C_4A \cdot 19H_2O$-solid solution at 21 °C; i.e., 0.600 g CaO per liter, 0.100 g Al_2O_3 per liter. While this position seems more likely than one in which it meets the hexagonal-plate curve to the right of the invariant point, as assumed by Buttler and Taylor at 5 °C, with the implied invariant point (on Jones and Roberts' conclusion) of $C_4A \cdot 19H_2O$–$CA \cdot 10H_2O$, the actual point of intersection at 0.52 g CaO per liter and 0.14 g Al_2O_3 per liter (at 21 °C) does not accord well with the solid solution range of compositions which appear most probable at 21 °C.

The remaining investigation of the system CaO-Al_2O_3-H_2O in the range 25 °C to 1 °C is that by Carlson at 1 °C [14]. The general scheme of the work was again to approach equilibrium from supersaturation (by mixing calcium aluminate solutions and saturated limewater) and from undersaturation (by treating various prepared solid phases with water or lime solutions). The mixes were stored in polyethylene bottles, with occasional shaking, in a refrigerator at 1 °C. The solid phases were usually dried over $CaCl_2$ before examination, or by washing with alcohol and ether. It is stated that "With certain precipitates containing $2\,CaO \cdot Al_2O_3 \cdot 8H_2O$ it was found essential to obtain the X-ray pattern while the material was still damp, as important phase changes occurred on drying."

It may be noted here that some confusion and misinterpretation in identification appears to have arisen in Carlson's work owing to the nonrecognition at that time of the pattern of $C_4A \cdot 19H_2O$. This pattern may have been confused with that of $C_2A \cdot 8H_2O$. Thus Carlson states that precipitates consisting of mixtures of di- and tetra-calcium aluminate hydrates, after drying over $CaCl_2$, often gave patterns showing only the lines of $4CaO \cdot Al_2O_3 . 13\ H_2O$. This effect was not reversible, and it was concluded that $C_2A \cdot 8H_2O$ had undergone decomposition to the tetracalcium compound and alumina. Accordingly, Carlson determined the X-ray patterns for such mixtures in the moist condition. From the work of Jones and Roberts, however, it appears that the correct explanation is that Carlson really obtained an unrecognized $C_4A \cdot 19H_2O$ in several moist mixes, and mistook this for $C_2A \cdot 8H_2O$, while some of the $C_4A \cdot 19H_2O$ decomposed to $C_4A \cdot 13H_2O$ and was identified as such. Such misidentification may have, e.g., arisen with mix 8 (11 days and 11 mo) and mix 9 at 11 days, in Carlson's table 2, and mixes 9, 10, 11, 12, and 13, in his table 3, all of which probably do not actually contain $C_2A \cdot 8H_2O$.

Carlson does not attempt to plot CaO/Al_2O_3 ratios in solid phases against solution concentrations. This is done however in figure 11, which is comparable with figure 2 of Jones and Roberts' paper at 25 °C and with figure 8 of the present paper for Buttler and Taylor's investigation at 5 °C. Based on the conclusions developed at 25 °C, the same kind of curves may be drawn. These appear reasonably to fit the data. It is assumed that the $C_4A \cdot 13H_2O$ found in the dried solid is equivalent, as at 25 °C, to $C_4A \cdot 19H_2O$ in equilibrium with the aqueous phase, and that the carboaluminate identified is the result of accidental carbonation, and has no significant bearing on results. A suggested interpretation of the data (table 6), as plotted in figure 11 and figure 12, is that they are consistent with an invariant point *Y:* $C_4A \cdot 19H_2O$–solid solution "$C_{2 \cdot 4}A \cdot$aq." at a solution composition CaO=0.50 g per litre, Al_2O_3= 0.075 g per liter, a solid solution curve *Y′T* ("$C_{2.4-2.1}A \cdot$aq.") with metastable prolongation *TT′*, and invariant point *T:* "solid solution $C_{2.1}A \cdot$aq."-$CA \cdot 10H_2O$, and a curve *T(T″)Z* for $CA \cdot 10H_2O$. *Z* is an invariant point $CA \cdot 10H_2O$–$A \cdot$aq., while the curve *OT′* in figure 12 is a tentative position for a "most unstable" hydrated alumina curve. The unstable invariant point *T′* for alumina gel and a solid phase along any prolongation *TT′* of the curve *YT* is probably not realizable in practice.

It will be seen therefore that much of Carlson's data at 1 °C can be applied to a series of curves similar to those established at 25 °C by Jones and Roberts, and in addition indicate a $CA \cdot 10H_2O$ curve starting from an invariant point *T* similar to that which can be deduced from Buttler and Taylor's data at 5 °C.

Carlson has drawn his relevant equilibrium curves to correspond with data obtained from undersaturation, but because of their apparent difficulty in reaching a true equilibrium in this way, owing to the formation of protective films, the present author prefers to place greater reliance on data obtained from supersaturation. Accordingly, the curves of figure 12 are drawn to fit the latter.

The present author's interpretation places reliance on the recent detailed work of Jones and Roberts at 25 °C and what appears to be a reasonable "extrapolation" to 1 °C, bearing in mind the similarly interpreted work of Wells, Clarke, and McMurdie at 21 °C, that of Buttler and Taylor at 5 °C, and the further additional work of Percival and Taylor at 21 °C and Jones and Roberts at 25 °C.

Carlson interprets his work as indicating that tetracalcium aluminate hydrate is stable with respect to $C_3A \cdot 6H_2O$ at 1 °C and that there are two curves *ACD* and *FCD* (fig. 5) for $C_2A \cdot 8H_2O$ and $C_4A \cdot 13H_2O$ respectively which are practically coincident with one another along the portion *CD*. (Note that the scale of CaO in solution along the abscissa of Carlson's figure 2 is incorrect in that it starts at 0.1 instead of zero.)

The present author feels however that the evidence for a curve for $C_4A \cdot$aq. along *FC* is probably misleading. It depends on points obtained by placing water in contact with increasing amounts of a preparation of $C_4A \cdot 13H_2O$ containing $Ca(OH)_2$. Thus the final lime concentration varied in the "equilibrium" solutions by virtue of the fact that increasing amounts of $Ca(OH)_2$ were added in with the $C_4A \cdot 13H_2O$ at the start. The small amount of alumina dissolved can only arise by decomposition of some of the $C_4A \cdot$aq. and, on the basis of the present interpretation, possibly some hydrated alumina. This could form a protective coating giving therefore the equilibrium for hydrated alumina rather than for $C_4A \cdot$aq. With higher concentrations of lime initially, no formation of hydrated alumina would occur, and equilibrium solution concentrations would therefore be expected to fall, as they do, along the curve *CD*.

TABLE 6. *System* CaO–Al_2O_3–H_2O *at 1°C*

(Selected data of E. T. Carlson)
Equilibria from supersaturation

Mix no.	Age	Total composition of initial mix, g/liter			Composition of filtrate, g/liter		C/A in solid (calculated)	Solid phases found in X-ray examination of solids
		CaO	Al_2O_3	C/A	CaO	Al_2O_3		
1	13 mo	0.833	1.278	1.18	0.152	0.112	1.06	CAH_{10}, probably little A·aq., trace C_2AH_8.
11	7 mo	.970	1.310	1.35	.260	.092	1.06	CAH_{10}
2	75 days	*.879*	*1.150*	*1.39*	*.300*	*.104*	*1.01*	CAH_{10}, *trace* C_2A H_8, *trace* $C_3A \cdot CaCO_3 \cdot H_{11}$.
3	13 mo	.925	1.022	1.64	.388	.112	1.07	C_2AH_8, CAH_{10}, $C_3A \cdot CaCO_3 \cdot H_{11}$
4	15 mo	.970	.895	1.97	.394	.120	1.35	C_2AH_8, CAH_{10}, $C_3A \cdot CaCO_3 \cdot H_{11}$
12	10 mo	1.066	.916	2.12	.372	.153	1.65	C_2AH_8, CAH_{11}
5	9 mo	1.014	.767	2.40	.366	.203	2.09	C_2AH_8, tr. $C_3A \cdot CaCO_3 \cdot H_{11}$
6	9 mo	1.058	.639	3.01	.384	.085	2.21	C_2AH_8, $C_3A \cdot CaCO_3 \cdot H_{11}$
7	11 mo	1.108	.511	3.94	.503	.078	2.54	C_2AH_8, C_4AH_{13}
8	11 mo	1.154	.383	5.47	.499	.072	3.83	C_4AH_{13}, C_2AH_8,[b] $C_3A \cdot CaCO_3 \cdot H_{11}$
9	11 mo	1.191	.256	8.45	.695	.016	3.76	C_4AH_{13}, $C_3A \cdot CaCO_3 \cdot H_{11}$
10	9 mo	1.246	.128	17.7	.963	.004	4.15	C_4AH_{13}
CA157 [c]	11 days (shaker)	1.744	.997	3.18	.464	.075	[a] 2.47	*Moist solid* Much α_1-C_2AH_8(+trace α_1-C_4AH_{19}?) *Dried over* $(NH_4)_2SO_4$ Much α_1-C_2AH_8, little α-C_4AH_{13}
CA158 [c]	11 days (shaker)	2.134	.997	3.89	.478	.077	[a] 3.26	*Moist solid* Much α_1-C_4AH_{19}, little α_1-C_2AH_8 *Dried over* $(NH_4)_2SO_4$ Some α-C_4AH_{13}, some β-C_4AH_{13}, some α_1-C_2AH_8.

[a] By analysis.
[b] *Probably not* C_2AH_8 *but* C_4AH_{19}.
[c] Mixes prepared by Jones and Roberts.

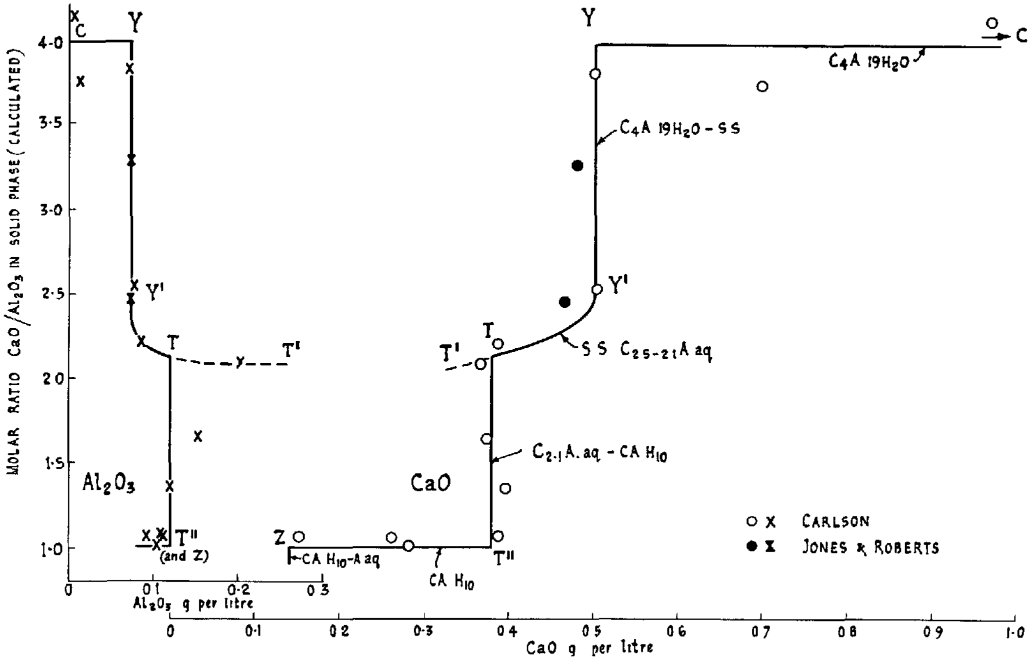


FIGURE 11. *System* $CaO\text{-}Al_2O_3\text{-}H_2O$ *at 1 °C.*

Variation of lime/alumina ratio in solid phase with equilibrium solution composition. From data of E. T. Carlson [14].

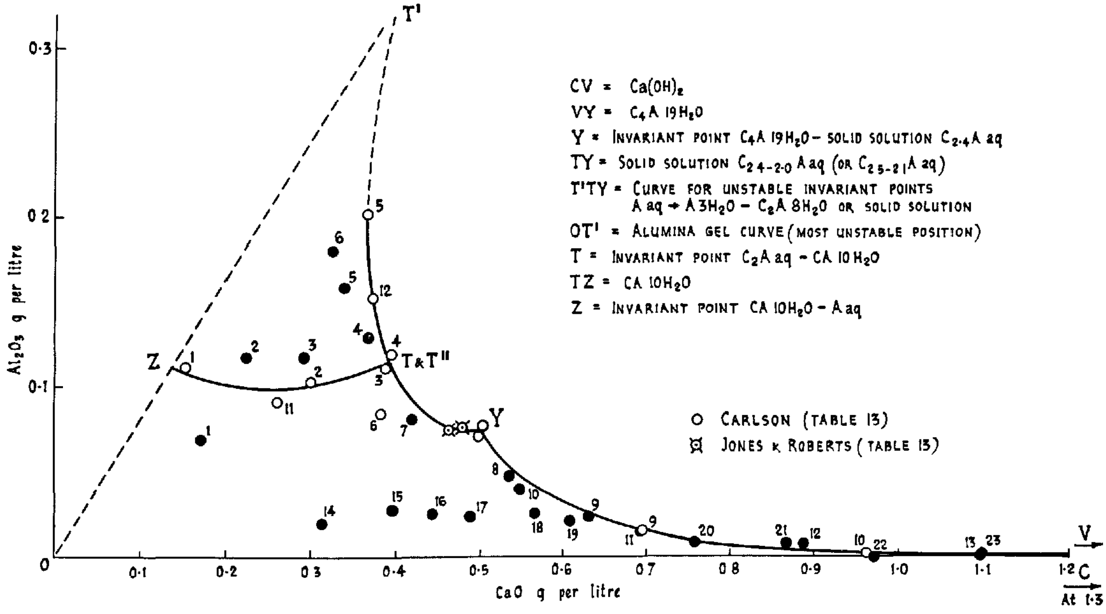


FIGURE 12. *System* $CaO\text{-}Al_2O_3\text{-}H_2O$ *at 1 °C.*

Suggested metastable and unstable equilibria. Data (from supersaturation ○ and undersaturation ●) of E. T. Carlson [14].

Before proceeding to a general tentative interpretation of the equilibria in this range of temperatures, it is necessary to consider a point of difference which is apparent from Buttler and Taylor's data at 5 °C as compared with data at 25 °C, 21 °C, and 1 °C. From figures 2 of Jones and Roberts and 8 and 11 of this paper it will be seen that the indicated solid solution composition range along respective curves *YT* is 2.4–2.0 at 25 °C, 3.5–3.0 at 5 °C, and 2.5–2.1 at 1 °C. (Data at 21 °C do not give a satisfactory indication of composition range.) The reason for the higher range in Buttler and Taylor's data is not clear. Although the molar ratios both in Buttler and Taylor's and in Carlson's investigations are calculated ratios and subject therefore to the likelihood of increased error as compared to the ratios obtained by direct analysis of the solid phase in the work at 25 °C, the curve *Y'T* based on Buttler and Taylor's data appears to be well defined, whilst Carlson's data at 1 °C, which fit the curve *YY'T* as drawn in figure 11, is supported by two mixes examined in the course of the work by Jones and Roberts. These were designed to repeat two of Buttler and Taylor's mixes (Nos. 25 and 29 of table 3), though at 1 °C, not 5 °C. The monocalcium aluminate solution used required dilution to give approximately the same initial Al_2O_3 concentration as the solution used by Buttler and Taylor. The relevant data are given with Carlson's data in table 6 and are plotted in figures 11 and 12. It will be seen *that they support the curves drawn through* Carlson's data from supersaturation. Further, the results of X-ray examination of moist and dry solids supports the expectation from solution analyses that the solid phases consist of $C_4A \cdot 19H_2O$ and solid solution in mix CA 158 and solid solution alone in mix CA 157.

Apart from this difference which calls for further work with careful direct analysis of solid phases, it seems possible to suggest tentatively a reasonably satisfactory picture of compound formation and equilibria in the system in the range 25 °C to 1 °C.

Relevant curves are given together in figure 13, the actual curves for hexagonal plate phases being those of the different authors, but drawn to include an invariant point *Y* as concluded by Jones and Roberts. At 20 °C and below, curves for $CA \cdot 10H_2O$ are drawn as deduced in the present discussion from a consideration of the various data.

It appears that at 20 °C or below, the equilibria include the following curves or invariant points.

OZ: Unstable alumina gel curve
Z: Unstable invariant point for A·aq.–$CA \cdot 10H_2O$
ZT: Unstable or metastable curve for $CA \cdot 10H_2O$
T: Unstable or metastable invariant point for $CA \cdot 10H_2O$–solid solution at minimum CaO/Al_2O ratio of its composition range
TY: Metastable solid solution of varying composition
Y: Metastable invariant point for solid solution at maximum CaO/Al_2O_3 ratio of its composition range–$C_4A \cdot 19H_2O$
YV: Metastable curve for $C_4A \cdot 19H_2O$
V: Metastable invariant point $C_4A \cdot 19H_2O$–$Ca(OH)_2$
VC: Metastable curve for $Ca(OH)_2$
C: Solubility of $Ca(OH)_2$

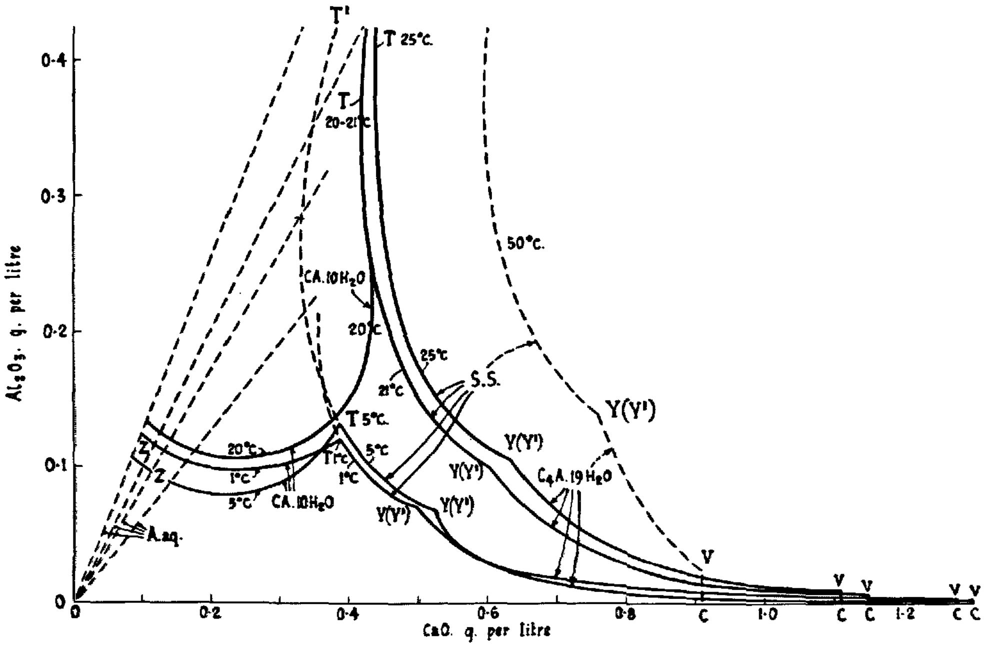


Figure 13. *System* CaO-Al_2O_3-H_2O *at various temperatures.*

Additionally, there are the stable curves for gibbsite (γ-A·3H_2O), $C_3A \cdot 6H_2O$, $Ca(OH)_2$ and stable invariant points for γ-A·3H_2O–$C_3A \cdot 6H_2O$ and $C_3A \cdot 6H_2O$–$Ca(OH)_2$.

Solution compositions for the invariant point *Y* at the various temperatures investigated appear to be: 25 °C, 0.630 g and 0.105 g per liter of CaO and Al_2O_3 respectively; 21 °C, 0.600 and 0.100; 5 °C, 0.520 and 0.07; 1 °C, 0.500 and 0.075.

Above about 22 °C, CA·10H_2O is no longer formed in the system, the curve for CA·10H_2O disappears, and the phase in metastable equilibrium with hydrated alumina may be $C_2A \cdot 8H_2O$, a solid solution, or ultimately $C_4A \cdot 19H_2O$, depending on the condition of the hydrated alumina.

Range 25 °C to 100 °C

The work of Peppler and Wells at 50 °C and of Wells, Clarke, and McMurdie at 90 °C will be considered again in the light of Jones and Roberts' work at 25 °C.

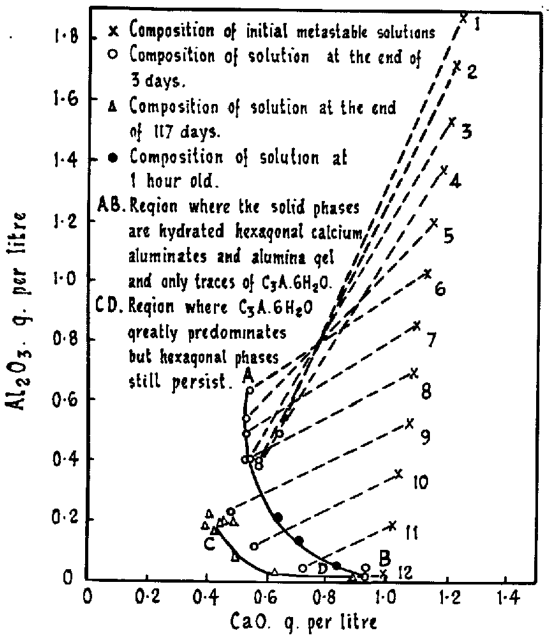


FIGURE 14. *System* CaO-Al_2O_3-H_2O *at 50 °C (Peppler and Wells [34], 1954).*

At 50 °C, Peppler and Wells [34] obtained a hexagonal-plate curve (fig. 14) the position for which was drawn through "equilibrium" solution concentrations for a number of 3-day mixes and for 3 1-hr mixes. As in previous work, an approach was made to equilibrium from supersaturation, starting with mixtures of calcium aluminate solutions and limewater. Final solids, however, included other, as well as hexagonal phases. For 3-day periods it was stated that mixes 1 to 8 of figure 14 contained alumina gel and hexagonal phases with only a very little $C_3A \cdot 6H_2O$. Mixes 9 to 11 after three days showed no hydrated alumina, and a predominating amount of $C_3A \cdot 6H_2O$ together with hexagonal phases. The reason for this behavior may lie in the composition of the final solid hexagonal phases which are to be expected prior to conversion to the cubic $C_3A \cdot 6H_2O$. The investigations at 25 °C suggest that along the more vertical portion of the curve, precipitation of $C_2A \cdot 8H_2O$ or solid solution is to be expected, the composition range of the solid solution at 25 °C being $C_{2-2.4}A$·8–10.2H_2O, while above an invariant point *Y* for solid solution and $C_4A \cdot 19H_2O$ (if this exists as such at 50 °C), $C_4A \cdot 19H_2O$ is to be expected. Actually, some tests at the Building Research Station have shown that at 50 °C and still more so at 90 °C, $C_4A \cdot 19H_2O$ originally formed in mixes at 25 °C is, on raising the temperature to 50 °C or 90 °C, rapidly converted into $C_3A \cdot 6H_2O$ and $Ca(OH)_2$, although some $C_4A \cdot 19H_2O$ was still present after 4 hr at 50 °C, and a trace of $C_4A \cdot 13H_2O$ remained after 1 hr or 20 hr at 90 °C. Accordingly, therefore, $C_3A \cdot 6H_2O$ could only arise by decomposition of $C_2A \cdot 8H_2O$, solid solution or $C_4A \cdot 19H_2O$. In the first two cases, this involves liberation of hydrated alumina to give an invariant point, probably yielding a protective film (in contact with the precipitating and changing hexagonal solid phases) which may retard the conversion. Where C_4A·aq. however is the expected final metastable solid phase, conversion to $C_3A \cdot 6H_2O$ involves only liberation of lime from the solid, and no protective film is to be expected. The reason for the absence of hydrated alumina in mixes 9 to 11 at three days appears simply to be that we are now concerned with mixes from which alumina gel is theoretically not expected to precipitate. So far as the hexagonal-plate curve is concerned, it appears that since from mixes 1 to 8 only a little $C_3A \cdot 6H_2O$ has been precipitated after three days, and the unstable invariant point curve A·aq.–$C_2A \cdot 8H_2O$ or solid solution is expected to be coincident with the hexagonal plate curve, the 3-day points for these mixes may provide an approximation to the correct position of the latter curve. Owing however to the more rapid conversion for mixes 9 to 11, shorter periods of contact must be employed. The one-hr mixes are therefore a compromise (though note that Al_2O_3 gel, as well as hexagonal phases, is also stated to be present), and the curve drawn by Peppler and Wells is therefore probably too low to accord with the true position in the complete absence of $C_3A \cdot 6H_2O$. An approximate location for the true position is given in figure 13. First a position for the expected invariant point *Y* is made by a straight line extrapolation of the similar invariant points suggested at 1 °C, 5 °C, 21 °C, and 25 °C, and a curve similar to that at 25 °C is then drawn, based on this invariant point. It will be seen that the curve given by Peppler and Wells falls somewhat below this.

Owing to the presence of other phases in the final solids besides hexagonal plates, a plot of CaO/Al_2O_3 ratios in solids against CaO and Al_2O_3 concentrations of solutions is of little or no value

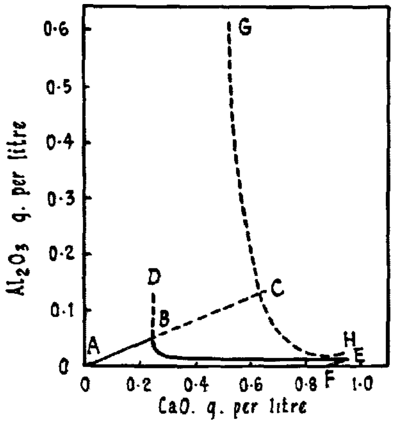


FIGURE 15. *System* $CaO\text{-}Al_2O_3\text{-}H_2O$ *at 50 °C (Peppler and Wells* [*34*]*, 1954).*

in throwing light on the equilibria. Peppler and Wells incidentally discuss the possibility of the hexagonal phases being stable with respect to the cubic $C_3A{\cdot}6H_2O$ at high lime concentrations. The discussion of their relevant mixes is however not clear to the author, and he is of the opinion that the hexagonal-plate phase at the high lime end of the curve is a tetracalcium aluminate hydrate and that this is always metastable with respect to cubic $C_3A{\cdot}6H_2O$. Finally, Peppler and Wells quote values of interplanar spacings in the hexagonal plate phases obtained by them, as determined from X-ray diffraction patterns. It must be borne in mind that, as shown in the work of Jones and Roberts, spacings are dependent on the water content to which the various compounds are dried, and this depends on precise control. The limited spacings reported by these authors could very well fall within the range for the structures of hydrated di- and tetracalcium aluminates possible, following the drying technique (not stated) used by Peppler and Wells.

However, the X-ray pattern of the hexagonal phases at 50 °C given by Peppler and Wells does not appear to correspond to any of the hydrates of $C_4A{\cdot}aq.$ or $C_2A{\cdot}aq.$, whether fully hydrated or in various stages of dehydration, given by Roberts [11]. It may be noted that, apart from spacings at 5.15 A (strong) and 1.680 A (strong) ($C_3A{\cdot}6H_2O$?) the spacings quoted are very similar or almost identical to those of $C_3A{\cdot}CaCO_3{\cdot}aq.$ The authors do not appear to have obtained the hexagonal-plate phases alone, free from alumina gel or $C_3A{\cdot}6H_2O$. Thus it seems probable that not only was some $C_3A{\cdot}6H_2O$ present in the sample or samples X-rayed (these are not indicated) but that carbonation has occurred. As previously noted, it has been pointed out by Carlson [14] that Myers, Rogers, Stannett, and Szwarc [31] have reported that polyethylene is somewhat permeable to carbon dioxide, and Peppler and Wells themselves refer to leakage of carbon dioxide through rubber stoppers.

In the light of the above discussion, there appears to be no conflict in the data of Peppler and Wells with the general interpretation of the metastable-plate phase equilibria in their paper.

Stable equilibria were also determined by Peppler and Wells at 50 °C. It is stated that "although the conversion of the hexagonal phase to the isometric phase is more rapid at 50 °C than at 21 °C, it is too slow to try to define the position of the stable isometric $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ curve from supersaturation". The closest approach to this curve is shown in their figure 4 (fig. 14 of this paper) at the end of 117 days. Peppler and Wells base their curve for $C_3A{\cdot}6H_2O$ at 50 °C on data obtained from undersaturation (as at 21 °C and 90 °C) by shaking $C_3A{\cdot}6H_2O$ with lime solution in polyethylene bottles. Similarly a stable curve for gibbsite was determined. These authors' conclusions as to the positions for the gibbsite, $C_3A{\cdot}6H_2O$, and $Ca(OH)_2$ curves are given in figure 15.

An investigation of the system at 90 °C had previously been published by Wells, Clarke, and McMurdie [22]. They had considered that so far as metastable hexagonal-plate phases were concerned, these would have too brief an existence to warrant investigation. However, some work was done later by Peppler and Wells [34]. They held a series of mixed calcium aluminate and lime solutions at 90 °C for one hr, before filtration and analysis. The time taken to raise the temperature to 90 °C was not stated. The solid phases contained alumina gel and hexagonal phases together with larger amounts of $C_3A{\cdot}6H_2O$. The authors state that the curve defined by the solution data "is considered to represent a metastable region rather than to define a metastable equilibrium. The metastable hexagonal hydrate equilibrium curve would lie above this curve and to the right of it". If one compares the position of the curve after 1 hr at 90 °C with that for the curves for 50 °C and lower temperatures as drawn in figure 13 of the present paper, it will be seen that it falls even below those for 25 °C or 21 °C. This is apparently due to a more rapid approach to the stable equilibrium at 90 °C. The actual position for a hexagonal plate-phase curve at 90 °C, if it could be determined at very short periods, must of course be to the right of and above the curve for 50 °C in figure 13.

Wells, Clarke, and McMurdie, in their investigations, did not find it feasible to determine equilibria at 90 °C by an approach from supersaturation, in spite of the more rapid approach noted above, because of persistence of some of the hexagonal phase. They therefore determined the stable equilibria by heating, on a steam bath for 4 to 5 days, mixtures of lime solutions and $C_3A{\cdot}6H_2O$ or gibbsite at 90 °C. Glass vessels were used, and some silica was found in solution as a result of attack of the glass by lime at this temperature. How far this or entry of silica into the $C_3A{\cdot}6H_2O$ structure may have had an effect on the equilibria is uncertain. A further point which seems uncertain to the present author is the precise location of the invariant point

$Al_2O_3 \cdot 3H_2O$ (gibbsite)–$C_3A \cdot 6H_2O$. Wells, Clarke, and McMurdie drew their curve for solubility of gibbsite through only three points, and appear to have ignored a group of five points apparently defining the invariant point. Had these been considered, and, on their data, the curve been drawn with a curvature towards the Al_2O_3 axis, the position of the invariant point might well have been placed somewhat higher. However, the stable curves as concluded by Wells, Clarke, and McMurdie are included in figure 16, with some reservation by the present author as to the correctness of the precise location of invariant points.

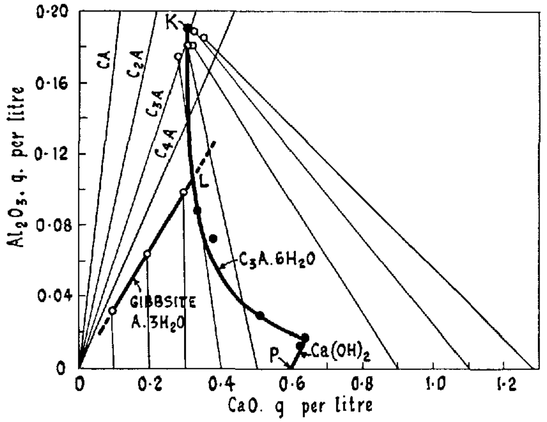


FIGURE 16. *System* CaO-Al_2O_3-H_2O *at 90 °C.*
Stable equilibria. (Wells, Clarke, and McMurdie [22], 1943.)

This survey of equilibria in the range 25 °C to 100 °C indicates that the stable phases are still gibbsite, $C_3A \cdot 6H_2O$ and $Ca(OH)_2$ and that unstable or metastable phases are still probably forms of hydrated alumina in the alumina gel→gibbsite range, $C_2A \cdot 8H_2O$, a limited solid solution between the C_2A·aq. and C_4A·aq. structures, and $C_4A \cdot 19H_2O$ (or possibly $C_4A \cdot 13H_2O$ at some higher temperature than 50 °C).

Range Above 100 °C

The system above 100 °C, involving pressures above atmospheric, has less interest for hydrated cement chemistry except in relation to steam curing, and will only be considered briefly.

From the present point of view, it is of chief interest for the preparation by Thorvaldson and coworkers of a calcium aluminate hydrate of formula $C_4A_3 \cdot 3H_2O$ [36]. As previously prepared by Harris, Schneider, and Thorvaldson [35] the exact composition was unknown, and the lime/alumina ratio was simply stated to be probably lower than 1.5. It was however found at 250 °C and above, when C_3A, $C_3A \cdot 6H_2O$, or "hexagonal C_3A·aq." were autoclaved at 250 °C, that rectangular, elongated, prismatic plates of low birefringence and R.I.=1.627 were formed. The compound was more precisely defined by Johnson and Thorvaldson by treating C_3A in saturated steam at 250 °C, and the formula $C_4A_3 \cdot 3H_2O$ was assigned, with a density of 2.71 at 20 °C. The crystals were described as probably orthorhombic. The water content was determined after drying over CaO. An older preparation of a $C_4A_3 \cdot 3H_2O$ compound is mentioned by the authors as that of Friedel, which may have been the same compound.

According to the work of Thorvaldson and coworkers also, a new hexagonal anisotropic calcium aluminate hydrate can be formed on autoclaving the lower calcium aluminates at 105–150 °C [46]. The average refractive index of this new hydrate was given as 1.58, or later, 1.576 with some grains of $\epsilon=1.589$, birefringence about 0.013, optically positive. The composition was not determined. Spangenberg [47] later considered the behavior of cement mortars during steam hardening at higher pressures with temperatures in the range 100–200 °C. Referring to the work of Thorvaldson, this author suggested that the hexagonal-plate phase possibly had a composition $C_2A \cdot H_3$, and wrote it as $2(Ca(OH)_2 \cdot AlO(OH))$, indicating a layer lattice in which boehmite layers occur instead of $Al(OH)_3$. This suggested composition was based on the fact that hydrargillite ($=2Al(OH)_3$) is converted on raising the temperature to boehmite ($=2AlO(OH)$). Spangenberg suggests that both the $Al(OH)_3$ layers of hexagonal hydrated calcium aluminate and isolated $Al(OH)_6$ groups in C_3AH_6 are unstable above 150 °C and pass into the boehmite layers of the new hexagonal phase or, above 250 °C, into $C_4A_3H_3$. For the latter phase, the formula $2CaO \cdot 3AlO(OH)$ was suggested. There is no space in this review to offer any detailed discussion of these suggestions, though the layer lattices appear to conflict with the views on the structure of the hexagonal-plate tetracalcium aluminate hydrate recently put forward by Buttler, Dent Glasser, and Taylor. However, reconsideration of the structural ideas of these various authors would help to clarify the problem.

Assuming, tentatively, that a high-temperature form of C_2A·aq. does exist, as indicated above, then there appear to be two high-temperature calcium aluminate hydrates, which we may write as $C_2A \cdot H_3$(?) and $C_4A_3 \cdot H_3$, the latter appearing at higher temperatures.

Peppler and Wells [34] have carried out work at 120°, 150°, 200°, and 250 °C, using stainless-steel pressure vessels. Representation of equilibria was as commonly used for low temperatures. It is possible here only to summarize their main conclusions.

At 120 °C, gibbsite was again the stable hydrated alumina phase, with a straight-line solubility curve, congruently soluble in limewater up to an invariant point with $C_3A \cdot 6H_2O$. The equilibrium curve for $C_3A \cdot 6H_2O$ (also a straight line) was determined up to the invariant point with $Ca(OH)_2$.

At 150 °C, boehmite ($Al_2O_3 \cdot H_2O$) was now the stable phase. Transformation of gibbsite to boehmite was very slow and it was found possible to determine a metastable curve for gibbsite.

At 200 °C there was rapid conversion of gibbsite to boehmite. Attack on the bomb was stated to be very severe, while the bomb absorbed lime from solution. Only approximate positions for solubility curves could be assigned. When $C_4A_3\cdot H_3$ was added to saturated limewater at 200 °C, $C_3A\cdot 6H_2O$ and boehmite were found as final phases; $C_3A\cdot 6H_2O$ was unchanged. In tests to locate the transition temperature $C_3A\cdot 6H_2O \rightarrow C_4A_3\cdot H_3$ in the range 200–250 °C, microscopically detectable amounts of $C_4A_3\cdot H_3$ were first found between 210 and 220 °C. At times, however, $C_3A\cdot 6H_2O$ persisted up to 250 °C below times of 4 days.

At 250 °C, $C_3A\cdot 6H_2O$ was quantitatively converted to $C_4A_3\cdot H_3$ at initial lime concentrations from 0.1 g per liter up to saturation. Lime solubility at 250 °C is actually given by the authors as approximately 0.02–0.03 g per liter (their solubility curve for $Ca(OH)_2$ at various temperatures).

Other work by Majumdar and Roy [37] lay in a range 100 °C to 1,000 °C, involving extremely high pressures. Results could be expressed as a series of compatibility triangles within triangular coordinates. There is no space to discuss this work in detail, but again it was concluded that only three stable hydrated phases are formed in the system, namely $Ca(OH)_2$, $3CaO\cdot Al_2O_3\cdot 6H_2O$ and $4CaO\cdot 3Al_2O_3\cdot 3H_2O$.

It may be noted here that Peppler and Wells have drawn a series of curves at different temperatures showing stable equilibria throughout the range they examined, somewhat parallel to those shown for metastable equilibria in figure 13.

(b) Compounds or Solid Solutions

The various hydrated compounds which can be formed in the system CaO-Al_2O_3-H_2O have been discussed fairly fully in the preceding, both in the light of phase-rule equilibria studies and of structural considerations. It is concluded that compound or solid-solution formation within the ternary system is restricted to those given in table 7. It should be particularly noted that

(a) It is concluded that no metastable hexagonal-plate tricalcium aluminate hydrate exists, while the existence of a needle-form $C_3A\cdot 18H_2O$ is doubtful.

(b) The only mutual solid solution amongst the calcium aluminate hydrates appears to be between $C_4A\cdot 19H_2O$ and $C_2A\cdot 8H_2O$. It is suggested that the solid solution may be derived from $C_2A\cdot 8H_2O$ by loss of Al_2O_3 and replacement by H_2O ($Al(OH)_3 \equiv 3H_2O$ or Al^{3+} replaced by $3H^+$) up to one-sixth of the A content, following which the $C_4A\cdot 19H_2O$ structure is formed.

(c) A compound $CA\cdot 10H_2O$ is formed only below about 22 °C. Above this temperature, the metastable structure formed is that of $C_2A\cdot 8H_2O$.

(d) Although $C_2A\cdot 8H_2O$ or its solid solution with $C_4A\cdot 19H_2O$ is formed above 22 °C, it is metastable with respect to $C_3A\cdot 6H_2O$.

(e) A possible lower hydrate of dicalcium aluminate of formula $C_2A\cdot 3H_2O$ may be formed above about 100 °C, in which Al is linked with O and OH as in the boehmite structure.

(f) $C_3A\cdot 6H_2O$ is fundamentally stable up to over 215 °C.

(g) $C_4A_3\cdot 3H_2O$ is formed at over 215 °C.

TABLE 7. *Hydrated calcium aluminates*

(a) Aqueous equilibria up to 100 °C	
α_1-$C_4A\cdot 19H_2O$ [a] $\downarrow$	Unstable or "disordered" layer structure. Formed from supersaturation and converts to α_2-$C_4A\cdot 19H_2O$
α_2-$C_4A\cdot 19H_2O$ [a]	Layer structure, satisfactorily indexed on hexagonal unit cell: $a=5.77$ A, $c=21.37$ A.
Solid solution $C_{2-2.4}A\cdot 8-10.2H_2O$	
β-$C_2A\cdot 8H_2O$ $\downarrow$	A new form of $C_2A\cdot 8H_2O$ formed from supersaturation as an unstable or "disordered" layer structure which converts to $\alpha_1 = C_2A\cdot 8H_2O$.
α_1-$C_2A\cdot 8H_2O$ $\downarrow$	The previously known $C_2A\cdot 8H_2O$. Unstable, when passed through a dehydration and rehydration cycle, with respect to a new $\alpha_2 = C_2A\cdot 8H_2O$.
α_2-$C_2A\cdot 8H_2O$	Not so far found in the aqueous equilibria but may be formed after long periods. Most stable structure of the three $C_2A\cdot 8H_2O$ structures, and one which can be satisfactorily indexed on a hexagonal unit cell; $a=5.80$ A, $c=21.59$ A.
It is concluded that no hexagonal tricalcium aluminate hydrate $C_3A\cdot 12H_2O$ exists. A form $C_3A\cdot 18H_2O$ which has occasionally been reported as occurring in long needles may possibly have a fleeting existence.	
$CA\cdot 10H_2O$	Formed below 22 °C, above which $C_2A\cdot 8H_2O$ is formed. 22 °C is a transition temperature for the change $2\,CA\cdot 10H_2O \rightleftarrows C_2A\cdot 8H_2O + A\cdot aq$. Hexagonal(?) crystal structure. Brocard's work suggests may have $a=9.45$A(?), $c=14.6$ A(?).
$C_3A\cdot 6H_2O$	The only stable phase. Cubic crystal structure $a=12.56-12.59$ A.
(b) At high temperatures (>100 °C) and pressures	
$C_2A\cdot 3H_2O$?	Formed at 105–150 °C (Thorvaldson). Spangenberg suggested the composition C_2AH_3 with a layer lattice structure in which Al is linked with O and OH as in the boehmite structure.
$C_4A_3\cdot 3H_2O$	Formed only at high temperatures (over 215 °C) and pressures. Not relevant therefore in cement-water system up to 100 °C. Probably orthorhombic (Johnson and Thorvaldson).
(c) After dehydration	
Various. Not relevant to aqueous system, but their study may throw light on structure of the fully hydrated compounds and on behavior of cement pastes mortars, and concrete on drying.	

[a] Observed only up to 50 °C.

When consideration of hydrated aluminates is extended to the effect of gypsum, added as retarder, or calcium chloride, added to accelerate hardening, structures based on the metastable lattice (1) or (2) may be obtained, depending on the nature and amount of the additional anions present, and the temperature. The present position is summarized in table 8.

So far as appears to be known at present, no substitution in the stable cubic lattice by such ions as SO_4^{2-}, Cl^-, etc., appears to be possible. Thus when a metastable structure such as the low form of chloro- or sulfoaluminate reverts to a cubic $C_3A\cdot 6H_2O$ lattice, chloride or sulfate should be freed. This release may be important; e.g., in considering the effect of calcium chloride additions to concrete on possible corrosion of reinforcement. Thus calcium chloride originally taken up into a solid solution and so originally removed as a factor in possible corrosion may, if a stable cubic lattice structure is subsequently formed, be freed again.

TABLE 8. *Hydrated calcium sulfo- and chloroaluminates and ferrites*

Sulfoaluminates	Sulfoferrites
$C_3A\cdot 3CaSO_4\cdot 32H_2O$	$C_3F\cdot 3CaSO_4\cdot 32H_2O$
Hexagonal needles. Slight birefringence. Uniaxial negative, $\omega=1.464$, $\epsilon=1.458$	"Hexagonal" needles: Slight birefringence. Mean R.I=1.49. Uniaxial positive?, $\omega=1.486$, $\epsilon=1.490$
$C_3A\cdot CaSO_4\cdot 12H_2O$	$C_3F\cdot CaSO_4\cdot 12H_2O$
"Hexagonal" plates, uniaxial negative. $\omega=1.504$, $\epsilon=1.488$	Uniaxial negative, $\omega=1.564$, $\epsilon=1.539$.

Solid solution—$C_3A(F)\cdot 3\ CaSO_4\cdot 32H_2O$ in limited degree (up to ¼A and ¾F approx). May be more extensive.
Solid solution—$C_3A(F)\cdot CaSO_4\cdot 12H_2O$. Little evidence in literature for such a solid solution, but it appears likely, and one typical solid solution of this general composition with A/F=2 has been prepared at Building Research Station with $\omega=1.520$, $\epsilon=1.505$.

Chloroaluminates	Chloroferrites
$C_3A\cdot 3CaCl_2\cdot 30H_2O$	$C_3F\cdot 3CaCl_2\cdot xH_2O$
Formed preferentially below 0 °C by hydration of C_3A in 23% $CaCl_2$ solution.	Existence not yet established.
$C_3A\cdot CaCl_2\cdot 10H_2O$	$C_3F\cdot CaCl_2\cdot 10H_2O$
Hexagonal plates $\omega=1.550$, $\epsilon=1.535$. Uniaxial negative.	Biaxial negative, $\alpha=1.600$, $\gamma=1.605$

Solid solution—$C_3A(F)\cdot 3CaCl_2\cdot aq$. Presumably possible, but no evidence.
Solid solution—$C_3A(F)\cdot CaCl_2\cdot 10H_2O$. Stated to be obtained, but no details.

(c) Hydration of Anhydrous Compounds

A good deal of work has been done in the past on the behavior of various anhydrous aluminates when treated with water in various ways. It is however not proposed to examine this older work in detail. Space does not permit more than a brief reference, nor indeed does it appear for this system, where so much work has been done in phase-rule studies, to be essential to the present purpose. It is thought that the more recent knowledge of phase-rule equilibria will contribute to an understanding of many of the results described in the older literature. The position is reversed in considering the system $CaO\text{-}Fe_2O_3\text{-}H_2O$, where little has been possible as yet on a phase-rule approach, and results obtained on treating anhydrous iron compounds with water, or lime, etc., solutions are correspondingly more important.

The System $CaO–Fe_2O_3–H_2O$

(a) Introduction and Review of Phase-Rule Equilibria Possibilities

Malquori and Caruso [48] pointed out in 1938 the limited knowledge available of the system $CaO\text{-}Fe_2O_3\text{-}H_2O$ or related quaternary systems with calcium salts, and in this and later papers [49–52] described the preparation of such compounds as hexagonal $C_4F\cdot 14H_2O$ (after Hoffmann) cubic $C_3F\cdot 6H_2O$, hexagonal $C_3F\cdot CaSO_4\cdot 10H_2O$, and $C_3F\cdot CaCl_2\cdot 10H_2O$ and their solid solutions and also partial replacement of Al by Fe in $C_3A\cdot 3CaSO_4\cdot 31–33H_2O$.

It has been independently suggested by Jones [27] in 1945 that for this and related systems, equilibria somewhat similar to those found for Al_2O_3 may exist, though the possibilities of compound and solid-solution formation (of the type found in the $CaO–Al_2O_3–H_2O$ system) may be much more limited. This suggestion has received support from Steinour [32]. Very little work has been done on this system, partly owing to the need for further clarification of the more important $CaO–Al_2O_3–H_2O$ system and partly owing to the practical difficulties involved. Yet there seems little doubt that the variety of hydrated compounds containing iron, analogous to corresponding alumina compounds, and which can be formed in cement hydration, demands sooner or later a radical study of this system and of more complex quaternary and quinary systems involving additionally sulfate, chloride, and alkali (Na_2O and K_2O).

The main difficulty in studying the ternary system is the fact that an approach to equilibrium is difficult from supersaturation since no metastable calcium ferrite solutions are formed analogous to the metastable calcium aluminate solutions. However, it may be possible in the way adopted by Schippa [9] (1958) in his study of calcium sulfoferrite hydrates, using a ferric hydroxide sol prepared from ferric sulfate. Further, the solubilities of corresponding or related iron compounds appear to be very much less, only extremely small amounts of iron being found in solution. However, hydration of cement involves not only the intermediate formation of metastable supersaturated solutions of calcium aluminates from which metastable and ultimately stable solid phases may be formed in an approach to equilibrium, but also a hydration process in which substantially no intermediate metastable supersaturated solution is formed. The latter appears to be the case with the iron-containing compounds of portland cement, so far as the iron component is concerned. The reason for nonformation of a metastable supersaturated calcium ferrite solution cannot be clearly stated. That it is connected with the difference in properties of the Al and Fe atoms is obvious. It may perhaps be sufficient to say that this difference involves a very high instability of a postulated calcium ferrite solution or (saying the same thing in another way) that the hydrated calcium ferrites are very much less soluble than even the calcium aluminates. For a study of the system $CaO–Fe_2O_3–H_2O$ it appears that it is necessary in the first place to rely on an approach from undersaturation and on analogy with the compounds formed in the system $CaO–Al_2O_3–H_2O$ and other more complex systems.

A cubic $3CaO{\cdot}Fe_2O_3{\cdot}6H_2O$ (the precipitate was stated to contain some "calcium silicate") was prepared originally by Eiger [53] (1937). It is isomorphous with cubic $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$. Physical properties are given in table 9. At about 400 °C the hydrate loses $4.5H_2O$, showing similar behavior to that of the corresponding aluminate.

TABLE 9. *Hydrated calcium ferrites*

$C_4F{\cdot}14H_2O$	Hexagonal plate hydrated calcium ferrite analogous to $C_4A{\cdot}13H_2O$. No satisfactory evidence that this exists without some Si or Cl or both in the structure. Apparently lattice similar to $C_4A{\cdot}13H_2O$. $\omega=1.59$ A (Malquori & Cirilli [52] 1943). Feitknecht [62] (1942) proposed hexagonal or pseudo hexagonal parameters $a=3.42$, $c=8.0$ A, compared with (Feitknecht and Gerber [63] 1942) $a=3.36$, $c=7.9$ A for the corresponding $C_4A{\cdot}13H_2O$.
$C_2F{\cdot}aq$	No satisfactory evidence for the existence of a hexagonal layer structure corresponding to $C_2A{\cdot}8H_2O$.
$CF{\cdot}aq$	No satisfactory evidence for the existence of a structure corresponding to $CA{\cdot}10H_2O$.
$C_3F{\cdot}6H_2O$	May be formed as a pure phase, but difficult to prepare free from contamination with other phases, possibly due to formation of protective films, or to carbonation. Also, a pure $C_3F{\cdot}6H_2O$ may be an unstable structure with respect to a solid solution containing, e.g., Al or Si or both. $n=1.72$. Cubic cell, $a=12.76$ A

It appears therefore that we may expect stable equilibria in the system $CaO–Fe_2O_3–H_2O$ involving solubility curves for $Ca(OH)_2$, "$C_3F{\cdot}6H_2O$" (which may contain SiO_2), and hydrated ferric oxide with corresponding invariant points. We may expect solubilities of both "$C_3F{\cdot}6H_2O$" and hydrated ferric oxide to be much lower than for the corresponding alumina phases, but there appear to be no data available from which a precise diagram may be constructed. However, a theoretical scheme is given in figure 17, based on analogous equilibria in the $CaO–Al_2O_3–H_2O$ system. No trihydrates of ferric oxide similar to $Al_2O_3{\cdot}3H_2O$ appear to exist, and the stable ferric-oxide hydrate would seem to be either α-$Fe_2O_3{\cdot}H_2O$ (goethite) with a crystal structure similar to that of naturally occurring α-$Al_2O_3{\cdot}H_2O$ (diaspore), or γ-$Fe_2O_3{\cdot}H_2O$ (lepidocrocite) with a crystal structure similar

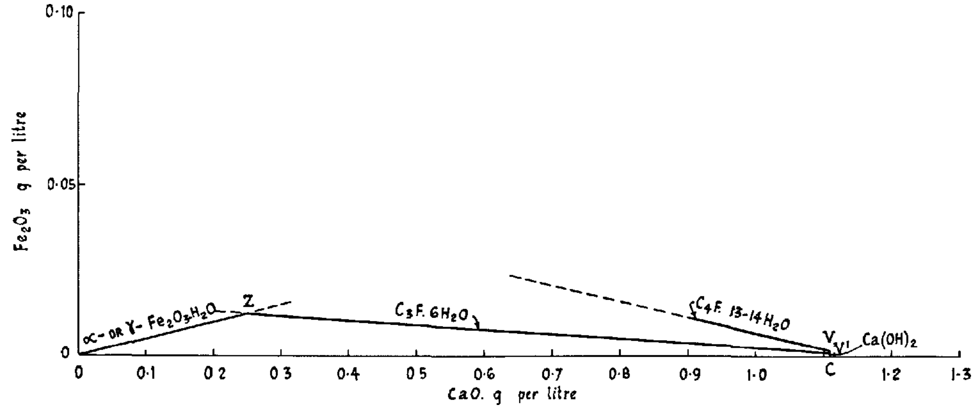


FIGURE 17. *Tentative approach to representation of system* $CaO–Fe_2O_3–H_2O$ *at room temperature, 25 °C.*

to that of $\gamma\text{-}Al_2O_3{\cdot}H_2O$ (boehmite). (An interesting point is that Hoffmann [54] states that $\gamma\text{-}Fe_2O_3{\cdot}H_2O$ easily changes to $\alpha\text{-}Fe_2O_3{\cdot}H_2O$ on crushing in an agate mortar.)

Besides the $C_3F{\cdot}6H_2O$ compound which now appears to be established as the "stable" analog of $C_3A{\cdot}6H_2O$, a hexagonal-plate tetracalcium ferrite hydrate is also formed. Following Pelouze [55] (1851), Hoffmann [54] (1935) prepared a hydrate which was assigned the formula $4CaO{\cdot}Fe_2O_3{\cdot}14H_2O$. This was also prepared by Malquori and Cirilli [49] (1940), who got a similar X-ray pattern. Hoffmann had also claimed the existence of a $4CaO{\cdot}Fe_2O_3{\cdot}7H_2O$ hydrate said to be formed at 50–60 °C, but Malquori and Cirilli did not confirm this, saying that the latter was really the cubic $C_3F{\cdot}6H_2O$ compound.

Eiger has stated that $C_3F{\cdot}6H_2O$ is not stable below a lime concentration of 0.25 g CaO per liter, but then changes to a dicalcium ferrite hydrate $2CaO{\cdot}Fe_2O_3{\cdot}5H_2O$, of orange color, which is stable down to a concentration of 0.15 g CaO per liter. This compound was stated to be further hydrolyzed to give "$Fe_2O_3{\cdot}3H_2O$".

Bogue and Lerch [56] and Yamauchi [57] have also considered that a hydrated dicalcium ferrite is formed, while the former authors also cite the possible formation of an amorphous hydrated monocalcium ferrite. The evidence for hydrated di- and monocalcium ferrites is however indecisive, as discussed later. If formed, it is possible that they are similar in structure to the hexagonal di- and monocalcium aluminates.

Brocard [19] (1948) concluded that in hydration of C_4AF with water at 15 °C there is first produced (besides hydrated hexagonal dicalcium aluminate hydrate and cubic $C_3A{\cdot}6H_2O$) an iron-containing amorphous gel which gradually decomposes into Fe_2O_3 and lime. At 50–100 °C, cubic $C_3A{\cdot}6H_2O$ was stated to be formed, together with a gel and Fe_2O_3. Malquori and Cirilli [52] (1943) found that by hydration of C_4AF in saturated lime solution at 0 °C, a solid solution of $C_4A{\cdot}aq.$ and $C_4F{\cdot}aq.$ with an Al_2O_3/Fe_2O_3 molar ratio of one is formed. At room temperature, the same phase appeared to have formed first and then to convert to a solid solution $C_3A{\cdot}6H_2O\text{–}C_3F{\cdot}6H_2O$.

Returning to figure 17, the schematic tentative indication of stable equilibria is based on corresponding equilibria in the $CaO\text{–}Al_2O_3\text{–}H_2O$ system. The solubility of lime at 25 °C is given at point *C*, while on the basis of a statement by Eiger, a possible invariant point for "$C_3F{\cdot}6H_2O$" with, it is thought, α- or $\gamma\text{-}Fe_2O_3{\cdot}H_2O$ rather than a compound $C_2F{\cdot}5H_2O$ is indicated at *Z*. The Fe_2O_3 concentration at *Z* is indicated quite arbitrarily (for want of a precise value) as half that for the $C_3A{\cdot}6H_2O\text{–}A{\cdot}3H_2O$ (gibbsite) invariant point at 25 °C. Eiger's statement of decomposition of $C_3F{\cdot}6H_2O$ at 0.25 g CaO per liter to give a $C_2F{\cdot}5H_2O$ compound, stable down to 0.15 g CaO per liter, is not supported by experimental detail. No statement is made as to crystal structure of the supposed $C_2F{\cdot}5H_2O$ compound. If, by analogy, it was a hexagonal-plate phase, it appears more probable that it forms part of metastable equilibria linked with a hexagonal "$C_4F{\cdot}14H_2O$" curve. On the whole, and on present inadequate evidence, it appears preferable to reject this supposed compound $C_2F{\cdot}5H_2O$ as part of the stable equilibria. It may however form part of metastable equilibria analogous to the $C_{2\text{-}2.4}A{\cdot}8\text{–}10.2H_2O{\rightarrow}C_4A{\cdot}19H_2O$ equilibria of the corresponding $CaO\text{–}Al_2O_3\text{–}H_2O$ system. In the light of this discussion, the establishment of the stable equilibria from undersaturation would seem to be reasonably practicable. No one so far appears, however, to have undertaken it, or if so, has been able to carry it to completion.

At present, also, work designed to clear up the existence and solubility relations and transformations of possible metastable hexagonal-plate phases in the system appears to be making very slow progress.

However, the preparation of a C_4F hydrate by Hoffmann indicates that we should expect a curve starting from a "$C_4F{\cdot}aq.$"–$Ca(OH)_2$ invariant point denoted by V in figure 17, at a lime concentration near the saturation concentration of lime. Theoretically, following a similar curve for $C_4A{\cdot}19H_2O$ in the $CaO\text{–}Al_2O_3\text{–}H_2O$ system a curve for "$C_4F{\cdot}aq.$" should proceed from this invariant point in the direction of lower lime and higher ferric oxide concentrations. This line presumably may terminate in an invariant point for a $C_4F{\cdot}aq.\text{-}C_{<4}F{\cdot}aq.$ structure.

To proceed with a study of the system $CaO\text{–}Fe_2O_3\text{–}H_2O$ from undersaturation it is first desirable to consider the preparation of $C_3F{\cdot}6H_2O$ or $C_4F{\cdot}aq.$, or if it exists, a $C_2F{\cdot}aq.$ in the pure state. It is to a consideration of this that we must now turn.

(b) Compounds or Solid Solutions

1. *Cubic $C_3F{\cdot}6H_2O$ or solid solutions.* As stated, $C_3F{\cdot}6H_2O$ was originally prepared by Eiger [53]. The method was to place a quantity of "colloidal iron hydrate" in a large volume of supersaturated lime solution at room temperature and shake several times a day. A clear brown deposit formed which in the course of some days showed a silky appearance similar to that of the aluminate observed by Hoffmann. At the end of 6 weeks, the residue, now become white, was separated by filtration and dried, first over calcium chloride and then at 100 °C. Eiger reports that it contained some calcium silicate "owing to the action of lime on the glass". After correcting for the silica (how is not stated, but it is here assumed that it was considered to be present as a second phase $CS{\cdot}aq.$), the composition was stated to be $3.01CaO{\cdot}Fe_2O_3{\cdot}6H_2O$. Optical examination of Eiger's preparation by Lea and Bessey (see ref. [53]) showed that it consisted of cubes of R.I. = 1.710, and birefringent hexagonal plates of indexes 1.61–1.66. There is little doubt, in the light of further experience, that the first result of interaction was to produce a $C_4F{\cdot}aq.$

hydrate as a hexagonal plate phase, giving the silky appearance noted, followed later by its partial transformation to cubic $C_3F{\cdot}6H_2O$. This transformation was evidently not entirely complete. Furthermore, later work by others indicates that silica can enter the crystal structure of $C_3F{\cdot}6H_2O$ and may therefore not have been present as a separate CS·aq. phase, but as part of the lattice structure of $C_3F{\cdot}6H_2O$ and possibly $C_4F{\cdot}aq$.

Malquori and Cirilli [49] (1940) reported preparation (apparently in glass vessels) by precipitating a mixed solution of $CaCl_2$ and $FeCl_3$ in the molar proportions of 3 to 1, by sodium hydroxide. The precipitate was left in contact with the markedly alkaline mother-liquor for about a month at 50–60 °C, when it was observed that the preparation appeared to consist entirely of octahedral crystals of R.I. very nearly 1.72. The water retained after drying *in vacuo* over $CaCl_2$ or P_2O_5 corresponded to $6H_2O$. X-ray examination showed a pattern similar to that of $C_3A{\cdot}6H_2O$, while the dehydration curves of the two hydrates were also similar. No examination appears to have been made for SiO_2.

Flint, McMurdie, and Wells [30] (1941) included tests in which mixtures of dilute acidified iron and aluminum chloride were added very slowly to a large volume of boiling lime solution in a glass flask. The resultant crystals were filtered at room temperature, washed with alcohol and ether, and dried over $CaCl_2$. It was found that they consisted of a series of solid solutions between $C_3A{\cdot}6H_2O$ and $C_3F{\cdot}6H_2O$ and they all contained SiO_2 (usually about 5 to 6 percent). Attempts were made to avoid SiO_2, using copper and iron vessels and a silver-lined glass flask. In these experiments, however, the products were all badly contaminated with hydrous iron oxide. It was concluded that SiO_2 helps to stabilize the calcium aluminoferrite hydrates.

Burdese and Gallo [58] (1952) reported a "similar" method of preparation, though actually the details were not identical. Thus it is stated that ferric chloride solution in amount sufficient to produce 4 g of $C_3F{\cdot}6H_2O$ was slowly added to 6 liters of a saturated lime solution. The solution, contained in a "Pyrex" glass vessel, was kept at 80 °C for 3 to 4 days, and the precipitate then filtered off, washed with alcohol and ether, and dried over $CaCl_2$. Analysis showed the presence of SiO_2, though this was considerably less than found by Flint, McMurdie, and Wells, 0.1–0.15 mole instead of 0.4–0.5 mole. Similar preparations, using a platinum vessel of 2 liters capacity (to yield about one gram $C_3F{\cdot}6H_2O$), gave preparations near the theoretical composition, with no SiO_2. From these authors' experiments therefore it appears to be practicable to obtain a $C_3F{\cdot}6H_2O$ free from SiO_2, with refractive index 1.74. They do not however report any examination for chloride.

The reason why Burdese and Gallo were able to get the cubic compound pure and free from SiO_2 is not at first sight clear. Thus it might perhaps lie in the different temperatures used and the difference in the mechanisms involved. These are actually quite distinct. Flint, McMurdie, and Wells used boiling saturated lime solution, the concentration of lime therefore being 0.53 g CaO per liter, and the temperature 100 °C, while the dropwise addition of ferric chloride solution (or mixed ferric and aluminum chlorides) means that the temperature is maintained at 100 °C, and the product or products expected are those in stable equilibrium at 100 °C. These could well be therefore, as found, a mixture of ferric hydroxide and $C_3F{\cdot}6H_2O$ at 100 °C. In Burdese and Gallo's preparation, the two solutions were first mixed cold. This procedure results in the formation of a hexagonal-plate phase which may be $C_3F{\cdot}CaCl_2{\cdot}10H_2O$ or a solid solution of this with $C_3F{\cdot}Ca(OH)_2{\cdot}aq$. The temperature was then raised to 80 °C, at which the lime solubility is 0.68 g CaO per liter. It might thus be that at 80 °C, $C_3F{\cdot}6H_2O$ produced by decomposition of the $C_3F{\cdot}CaCl_2{\cdot}10H_2O$ or solid solution is congruently soluble in the solution formed.

Flint, McMurdie, and Wells had in fact reported that when ferric chloride solution is added to limewater at room temperature, the compound $C_3F{\cdot}CaCl_2{\cdot}10H_2O$ is formed, and that, at room temperature, this changes slowly to $C_3F{\cdot}6H_2O$. Thus a sample kept at room temperature in contact with the solution was 50 percent changed and contained 0.83 percent SiO_2. Another preparation of chloroferrite with negligible silica (since it was filtered shortly after precipitation) was placed at 60 °C in contact with a lime solution containing 0.626 g CaO per liter (saturation concentration=0.84 g CaO per liter at 60 °C), with frequent shaking. After two weeks it was stated to have completely transformed to the isometric $C_3F{\cdot}6H_2O$, which however now contained 6.85 percent SiO_2 taken up from the glass container.

There is of course a close parallelism between Eiger's mixture of colloidal iron hydrate and lime solution at room temperature yielding hexagonal C_4F hydrate initially, followed by transformation to $C_3F{\cdot}6H_2O$ hydrate, and Flint, McMurdie, and Wells' mixtures of ferric chloride and lime solution, also at room temperature, yielding hexagonal $C_3F{\cdot}CaCl_2{\cdot}10H_2O$ followed by change to $C_3F{\cdot}6H_2O$. There is, for example, clearly an initial formation of the appropriate metastable hexagonal-plate structure, followed by transformation to the stable $C_3F{\cdot}6H_2O$. There is also a further parallelism to be drawn between the $CaO–Fe_2O_3–H_2O$ and $CaO–Al_2O_3–H_2O$ systems. In the latter, from metastable calcium aluminate solutions plus lime (cf., colloidal iron hydroxide plus lime), the metastable $C_4A{\cdot}aq$. hexagonal-plate phase is precipitated at higher lime concentration and slowly transforms to $C_3A{\cdot}6H_2O$.

Attempts have been made at the Building Research Station (M. H. Roberts [15]) using polyethylene vessels to obtain pure $C_3F{\cdot}6H_2O$ free from contamination with other material, so far without success, though it appears that in some cases the $C_3F{\cdot}6H_2O$ found in the admixtures produced is in itself a pure phase.

Only a brief indication of some of the tests made can be given here. Addition of ferric chloride solution, dropwise with continuous stirring, to saturated lime solution at 90 °C and at 50 °C produced brown material. At 50 °C some isotropic grains were found with R.I.=1.71. Modification of conditions by adding at room temperature, then heating at 50 °C, or by shaking cold for 2 days until white, and then heating at 60 °C, merely gave brown material in which no cubic grains could be detected, in one case up to 4 months.

Attempts were made to convert calcium chloroferrite to $C_3F{\cdot}6H_2O$. In lime solutions at 60 °C, only a deep red-brown solid phase was obtained. In *N* NaOH solution, however, at 60 °C, the solid was cream-colored after 3 days, and microscopic examination showed some cubic grains. After 5 months the mix was filtered. X-ray examination of the solid after washing with alcohol and ether and drying at 81 percent R.H. indicated the presence of much $C_3F{\cdot}6H_2O$ and much $C_4F{\cdot}aq.$—or more probably $C_4F{\cdot}aq.\text{-}C_3F{\cdot}CaCl_2{\cdot}aq.$ solid solution, plus a little $Ca(OH)_2$. The $C_3F{\cdot}6H_2O$ pattern gave $a=12.76$ A±.01 A, indicating a pure $C_3F{\cdot}6H_2O$.

Somewhat similar tests in stainless steel tubes at 50 °C and 90 °C have given either, at 50 °C, some conversion of calcium chloroferrite to $C_3F{\cdot}6H_2O$ or, at 90 °C, a brown phase indicating further decomposition with production of ferric oxide. The presence of $C_3F{\cdot}6H_2O$ was indicated by X-ray examination of moist solids. Visual comparison indicated identity of the patterns with that referred to above.

These results and those of Burdese and Gallo are at first sight rather contradictory, and it is not known clearly as yet why in Burdese and Gallo's work, a chloroferrite precipitate held with its mother-liquor at 80 °C should transform to $C_3F{\cdot}6H_2O$, while in the above work a similar precipitate held with its mother-liquor at 60 °C should decompose. Clearly work is required in particular on the system $CaO\text{-}Fe_2O_3\text{-}CaCl_2\text{-}H_2O$ to try and solve this problem, while the possibility of sufficient carbon dioxide penetration through the walls of polyethylene vessels to cause decomposition also needs further examination.

Flint, McMurdie, and Wells have however apparently already found that a pure $C_3F{\cdot}6H_2O$ structure may sometimes be obtained in the presence of other phases. Thus sample 10 of their table 10, in their series of precipitated solid solutions was prepared in a vessel of dense unglazed porcelain. No alumina appeared to be present, though it was not apparently analyzed for, so that apart from SiO_2 (and possibly alumina) taken up from the porcelain, only calcium ferrite hydrate was expected. The preparation actually contained 6.34 percent SiO_2. It was stated however to show "considerable contamination by fine-grained material of low birefringence, which may have been calcium silicate." Excess lime was present, since the molar ratio in the whole product was calculated to be $3.54CaO{\cdot}0.52SiO_2{\cdot}Fe_2O_3{\cdot}6.01H_2O$. It was concluded possible therefore that the silica was combined with the excess lime and that the $C_3F{\cdot}6H_2O$ was free from SiO_2. This conclusion received confirmation from the fact that the X-ray pattern indicated a cell size of 12.74 A, equal to that deduced by McMurdie in his discussion of the X-ray data obtained by him on the garnet-hydrogarnet series.

Thus it appears that a pure $C_3F{\cdot}6H_2O$ may sometimes be realized, though the precise conditions are not clearly known, and the structure seems to be unstable.

However it is also evident that the presence of silica in the structure of $C_3F{\cdot}6H_2O$ will stabilize it. Flint, McMurdie, and Wells concluded, in fact, that solid solutions could be formed between $C_3A{\cdot}6H_2O$, $C_3F{\cdot}6H_2O$, $C_3A{\cdot}3SiO_2$, and $C_3F{\cdot}3SiO_2$, each being capable of forming complete mixed crystals with the other three, Fe_2O_3 and Al_2O_3 (Fe^{3+} and Al^{3+}) being mutually replaceable, while one part of SiO_2 substitutes for two parts of H_2O (1 Si^{4+} for 4 H^+). They were unable to obtain $C_3F{\cdot}6H_2O$ free from SiO_2 except exceptionally, and concluded that $C_3F{\cdot}6H_2O$ or the aluminoferrite hydrates are unstable in the absence of a certain amount of SiO_2 in solid solution. This conclusion to a limited degree contradicts the statement of complete miscibility between each member of the solid solution series including $C_3A{\cdot}6H_2O$ and $C_3F{\cdot}6H_2O$.

Zur Strassen [20] (1958) has recently discussed work on the garnet-hydrogarnet series, including investigations by Dörr, Zeeh, and Schmitt. He concludes that a pure $C_3F{\cdot}6H_2O$ does not exist, and that there is not complete miscibility between $C_3A{\cdot}6H_2O$ and $C_3F{\cdot}6H_2O$. In other words, it is not possible to replace Al wholly by Fe. A point is reached when the structure becomes unstable.

Figure 18 shows a garnet-hydrogarnet solid-solution identification chart as given by zur Strassen. This was prepared on the basis of a repetition, to some extent, of the work of Flint, McMurdie, and Wells. The figure shows the mixed crystal system with the positions of prepared mixes plotted therein. The entire field could not be covered owing to various experimental difficulties. From the data obtained, a series of

TABLE 10. *Solid solutions of calcium aluminates and ferrites*

$C_3A{\cdot}6H_2O-C_3A{\cdot}3SiO_2$ $C_3F{\cdot}6H_2O-C_3F{\cdot}3SiO_2$	The garnet-hydrogarnet series. See also figure 18.
$C_4A{\cdot}aq-C_4F{\cdot}aq$	No definite evidence as yet that a *pure* $C_4F{\cdot}aq.$ structure exists.
$C_3A{\cdot}6H_2O-C_3F{\cdot}6H_2O$	Doubtful if can be formed stably entirely free from silica, at least at iron-rich end.

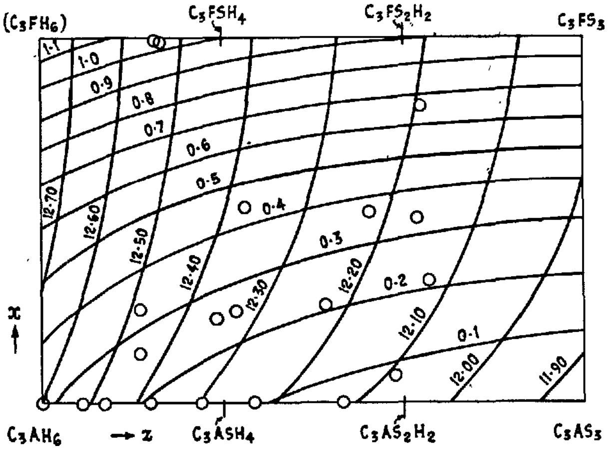


FIGURE 18. *The garnet-hydrogarpet solid solutions.*
(Identification chart—H. zur Strassen [20], 1958.) (Used by permission, Zement-Kalk-Gips.)

curves for constant cell dimensions, 11.90 A to 12.70 A, were drawn as the content of Al_2O_3 and Fe_2O_3, SiO_2 and H_2O, varied. A second value, necessary to determine the position of a solid solution in the series was based on the finding that the 220 reflection shows marked differences in intensity in relation to composition, whereas other reflections such as 611 are almost independent of composition. Thus the intensity ratio 220/611 can be used with the cell size to determine composition. Intensity-ratio curves from 0.1 to 1.1 are also plotted in the figure. It will be seen that according to the diagram a pure $C_3F{\cdot}6H_2O$ should have a=12.76 A, intensity ratio=1.2. The Building Research Station preparation of $C_3F{\cdot}6H_2O$ (Roberts) obtained from hexagonal chloroferrite in N NaOH solution at 60 °C had a=12.76 A, intensity ratio 1.3. It appears, therefore, that a pure $C_3F{\cdot}6H_2O$ can be obtained, although unstable. A high OH^- concentration in solution may assist in preventing breakdown. (Note that the ratio 1.3 was obtained [15] from measurements of intensities on a powder pattern obtained with an 18-cm-diam cylindrical camera. With a focusing camera the value obtained was 1.7. The discrepancy between these values and that given by zur Strassen (1.2) is probably due to differences in experimental technique.)

2. *Hexagonal $C_4F{\cdot}14H_2O$ or Solid Solutions.* As previously stated, Hoffmann claimed to have prepared a hydrate to which he assigned the formula "$4CaO{\cdot}Fe_2O_3{\cdot}14H_2O$". The method used was to add a mixed solution of calcium chloride and ferric chloride in the molar ratio CaO/Fe_2O_3=5 to a large volume of sodium hydroxide solution. Amounts were arranged so as to leave an $N/4$ NaOH solution after reaction. The filtered product was washed with methyl alcohol and ether, and dried *in vacuo* for several days over $CaCl_2$. Precipitates were obtained at 20 °C and 50–60 °C. In both cases it was noted that the initial precipitate contained a little free ferric hydroxide. At 20 °C, the precipitate soon became white, while at 50–60 °C, it remained very slightly brown. Analysis of the products indicated "$C_4F{\cdot}14H_2O$" at 20 °C and "$C_4F{\cdot}7H_2O$" at 50–60 °C. Hoffmann does not indicate whether silica or chloride was looked for. So far as can be ascertained, glass vessels were used, both in the actual preparation of the $C_4F{\cdot}$aq., and probably in the initial preparation of CO_2-free NaOH by allowing a saturated solution of NaOH to stand for some weeks. If this is the case, silica would be taken into solution, and as other work shows, may be expected in the precipitated $C_4F{\cdot}$aq. Chloride also may have been present, as found in later work at the Building Research Station. The accuracy of the analysis for a supposed $C_4F{\cdot}7H_2O$ also appears to be doubtful. As discussed later, the "$C_4F{\cdot}7H_2O$" was almost certainly cubic $C_3F{\cdot}6H_2O$ together with free $Ca(OH)_2$.

Malquori and Cirilli [49] (1940) also prepared $C_4F{\cdot}14H_2O$ in the same way and stated that for the degree of dilution used by Hoffmann, the resulting solid does not contain any chloroferrite, but that with higher concentrations, this forms as impurity. The authors do not say so, but it is presumed that glass vessels were also used, with at least the possibility of silica contamination. They indicate that their products did not contain chloroferrite. This result is contrary to later findings on similar preparations at the Building Research Station. The hydrated calcium ferrite is described as pure white in color, retaining $14H_2O$ when dried *in vacuo* over $CaCl_2$ and $12H_2O$ over P_2O_5. The X-ray pattern found was similar to that obtained by Hoffmann.

In another method of preparation, gradual addition of 20 ml $FeCl_3$ solution containing 0.04 g Fe_2O_3 per ml to 20 liters of saturated lime solution, hexagonal plates were obtained. Results of analysis were stated to point to the formula $C_4F{\cdot}$aq.

The authors draw attention to behavior similar to $C_4A{\cdot}12H_2O$ when the $C_4F{\cdot}14H_2O$ was dehydrated.

Early work at the Building Research Station (Roberts) [15] on the preparation of $C_4F{\cdot}$aq., using glass vessels, has confirmed Malquori and Cirilli's observation that with high concentration of reactants in Hoffmann's method of preparation, $C_3F{\cdot}CaCl_2{\cdot}$aq. is formed. In fact, with an initial chloride concentration in solution of about 8–9 g Cl per liter, the composition of the product approached very closely to that of $C_3F{\cdot}CaCl_2{\cdot}$aq. Even at much lower initial chloride concentration of about 1 g Cl per liter, as used by Hoffmann, there was still appreciable contamination with the chloroferrite, and the products were not white, but cream-colored, suggesting incomplete reaction and the presence of free ferric hydroxide. Further experiments were made, varying the CaO/Fe_2O_3 ratio in the mixed chloride solutions, and the amount of NaOH, to give varied final NaOH concentrations. The results indicated the NaOH concentration to be more important than the CaO/Fe_2O_3 ratio in the mixed chloride solutions in producing a white precipitate free from ferric hydroxide. However, as stated, these early experiments were carried out in glass vessels, and it was found that most of the products contained from 1 to 8 percent of SiO_2, depending upon the strength of the alkali solution and the time in contact with the glass. Further attempts were made in polyethylene bottles to avoid silica contamination. Also, in order to minimize contamination by chloride, the precipitate was extracted first with one liter of $N/10$ NaOH (to remove excess solid $Ca(OH)_2$) and then with two lots, each of one liter, of nearly saturated lime solution (1.10 g CaO per liter). However, even with a molar ratio $CaO/Fe_2O_3=5$ in the mixed chlorides and a final NNaOH concentration in solution, a deep cream or buff-colored precipitate was obtained containing 2.2 percent of Cl, equivalent to about 19 percent of $C_3F{\cdot}CaCl_2{\cdot}aq$. In order to reduce the Cl further, the initial chloride concentration was reduced from about 1.0 to about 0.05 g Cl per liter, giving products containing 1 to 5 percent of Cl. X-ray and microscopic examination indicated that the products consisted of a single solid phase of the solid solution series $C_4F{\cdot}aq.$-$C_3F{\cdot}CaCl_2{\cdot}aq$. An attempt to replace Cl^- by OH^- in the product obtained, by repeated extraction with one-liter lots of saturated lime solution, produced at best, after five extractions, a minimum content of 1.2 percent of Cl, corresponding to about 10 percent of $C_3F{\cdot}CaCl_2{\cdot}aq$.

From this later experimental evidence, therefore, the author cannot feel convinced that either Hoffmann or Malquori and Cirilli obtained a pure tetracalcium ferrite hydrate free from either silica or chloride or both. The possibility that the crystal lattice structure of the $C_4F{\cdot}aq.$ compound is not stable without the presence of silica is implicit in the findings of Flint, McMurdie, and Wells [30] (1941) with regard to the cubic $C_3F{\cdot}6H_2O$, which they could not prepare free from SiO_2 (with one possible exception). It seems possible also that the apparently strong tendency of Cl^- to substitute for OH^- in the structure "$C_4F{\cdot}aq.$" is partly bound up with spatial considerations concerned with the relative sizes of the ions involved. Thus it may be speculated that since the chloride ion is slightly larger than OH^-, it will partly conform to slight increase in size of Fe^{3+} substituting for Al^{3+} and result in less instability than where Fe^{3+} and OH^- are associated alone in the structure. There may however be other factors. Thus it seems possible that where two or more anions are available for entry into a crystal structure, that ion is preferred which confers greatest insolubility, or relative concentrations in solution may play some part. The factors at work and their relative importance in this structure are however not yet clear.

3. *$C_2F{\cdot}xH_2O$ or Solid Solutions.* Following the analogy of the hexagonal-plate hydrated calcium aluminates, it would seem possible at first sight that a hexagonal plate $C_2F{\cdot}xH_2O$ compound may exist. However, the apparent difficulty of preparing pure $C_4F{\cdot}aq.$ because of instability of structure when too much iron is present suggests that it may never be possible in a structure analogous to $C_2A{\cdot}8H_2O$. It seems more likely that a limited replacement of Al by Fe in the $C_2A{\cdot}8H_2O$ compound may occur before the structure becomes unstable.

There appears to be no reported preparation by a precipitation method. Nor has any satisfactory evidence been reported of preparation in any other way. As previously indicated, it is concluded that a dicalcium ferrite hydrate probably does not exist, though it must be accepted as a possibility.

(c) Hydration of Anhydrous Compounds

1. *Hydration of C_2F.* Besides precipitation experiments, Hoffmann examined the effect of shaking more or less finely crushed C_2F with water or lime solutions at 20 °C for various times (CF gave practically no reaction). In this first series he used C_2F crushed to pass a sieve of 10,000 meshes per sq cm in admixture with a standard sand (1 g C_2F with 10 g sand and 75 ml water or lime solution), shaking for periods up to 6 days. No iron was found in the filtrate. Depending on the initial concentration of lime, lime was either released from or taken up by the solid phase to give a final lime concentration of 1.06 g CaO per liter. (The sand appears to have been used in an attempt to prevent interference of protective films forming on the surface of the C_2F particles.)

Another series was carried out with a rather more coarsely crushed C_2F (2,500–4,900 meshes per sq cm; diam 88–120 μ). This was shaken (10 g C_2F with 20 g sand and 300 ml saturated or half-saturated limewater) at 20 °C for 150 days. It was stated that after the sand and (residual) C_2F had settled, the hydrated calcium ferrite was found as a rather heavy suspension of light brown color in the solution. This was white after a week (presumably due to further settling of the brown material). The white suspension was analyzed on a 50 ml sample, apparently including both solid and solution, while lime in solution was determined on a 25 ml sample of suspension after filtration. In this way, final lime concentrations were found to be 1.005 g CaO per liter, starting with 1.239 g CaO per liter, and 1.100 g CaO per liter, starting with 0.600 g CaO per liter. The CaO/Fe_2O_3 ratios in the calcium ferrite hydrate were stated to be 3.4 and 2.9, respectively.

From the above, Hoffmann concluded that two calcium ferrite hydrate phases, $C_4F{\cdot}aq.$ and another phase with a lower CaO/Fe_2O_3 ratio were present in equilibrium with a solution containing 1.06 g CaO per liter. This conclusion however appears open to question. Hoffmann compared the X-ray patterns of the product obtained with an initial half-saturated lime solution of final CaO/Fe_2O_3 molar ratio 2.9 and the compound "$C_4F{\cdot}7H_2O$" thought by Hoffmann to have been obtained by him by precipitation at 60 °C, and stated that they showed agreement. Malquori and Cirilli [49] however could not confirm the existence of such a compound. Repetition of

Hoffmann's experiments, at 50–60 °C, produced cubic $C_3F{\cdot}6H_2O$, and Malquori and Cirilli concluded that at this temperature there is fairly rapid conversion of $C_4F{\cdot}14H_2O$ to $C_3F{\cdot}6H_2O$. They point out too that the pattern given by Hoffmann for his supposed "$C_4F{\cdot}7H_2O$" is similar to that for $C_3F{\cdot}6H_2O$. On the whole, it seems very probable (and this is supported by later work) that Malquori and Cirilli are correct and that Hoffmann really got partial transformation of C_4F·aq. to $C_3F{\cdot}6H_2O$ at 50–60 °C, and also in the above shaking experiments at 20 °C. Thus it appears that Hoffmann, by hydration of C_2F, produced $C_3F{\cdot}6H_2O$, thus:

$$C_2F+C{\cdot}\text{aq.}\rightarrow C_3F{\cdot}6H_2O,$$

or

$$2C_2F+H_2O\rightarrow C_3F{\cdot}6H_2O+C+F.$$

Hoffmann, further, appears not to have considered the significance of the brown iron-rich solid phase present (apart from residual C_2F). If no lower hydrates than C_4F·aq. or $C_3F{\cdot}6H_2O$ were formed, this solid phase would be iron hydroxide (or Fe_2O_3). In this case it would appear that Hoffmann obtained an approximation to an invariant point for iron hydroxide–C_4F·aq. or iron hydroxide–$C_3F{\cdot}6H_2O$. This would suggest only a short curve for C_4F·aq. or $C_3F{\cdot}6H_2O$ in the system, since the apparent "equilibrium" lime concentration is 1.06 g CaO per liter compared with (at 20 °C) a saturation concentration of 1.24 g CaO per liter. Such speculations are of course subject to other possibilities for calcium ferrite hydrate formation yet to be discussed.

Bogue and Lerch [56] had previously attempted to hydrate C_2F. The compound was stated to require about 30 percent of water to form a plastic paste. No stiffening or temperature changes were observed. Hydration was found to be very slow, combined water amounting to only 7 percent by weight of C_2F after 2 years. It was stated that the hydrate formed was amorphous, with a refractive index of about 1.70. The authors suggested that it was a dicalcium ferrite hydrate, but no direct evidence was offered.

In the light of the evidence provided by later work (e.g., Eiger, Hoffmann, and Malquori and Cirilli), it would appear that treatment of C_2F with water results first in extraction of lime leaving an iron-rich surface residue, which later reacts with the lime solution producing $C_3F{\cdot}6H_2O$ (or possibly first C_4F·aq., this transforming to $C_3F{\cdot}6H_2O$), so producing, under the conditions used by Bogue and Lerch, a protective coating. The product of partial hydration may thus be an outer skin of $C_3F{\cdot}6H_2O$, over a shell from which some lime has been extracted, leaving a shell of composition $C_{<2}{\cdot}F$, and within this, unaffected C_2F. It has been shown by Malquori and Cirilli that dehydration of both $C_3F{\cdot}6H_2O$ and $C_4F{\cdot}14H_2O$ results eventually in breakdown to C_2F and lime, in agreement with Bogue and Lerch's assumption for the behavior of calcium ferrite hydrate with $C/F>2$. It will be seen that on the mechanism of hydration now suggested, not only is the amount of $C_3F{\cdot}6H_2O$ probably small, but free lime liberated on complete dehydration may react with the lime-poor shell to produce further C_2F. Thus, either no free lime may be left or it may be present in too small amount for detection. This may well explain the fact that Bogue and Lerch could not detect free lime in the dehydrated product.

Bogue and Lerch considered also the possible formation of a less basic hydrated compound such as CF·aq. This is at first sight in line with the fact that lime is extracted from the C_2F. However no $Ca(OH)_2$ could be found either by microscopic or by X-ray examination.

It seems clear that there is no evidence for either a di- or monocalcium ferrite hydrate in these experiments. It should be noted that at the time of Bogue and Lerch's experiments, neither $C_3F{\cdot}6H_2O$ nor $C_4F{\cdot}14H_2O$ was known, except, in the latter case, for the very old work (1851) by Pelouze [55].

The author regrets that the length of this paper precludes consideration of the relatively small amount of work relevant to hydration of C_2F by other authors at this time. It does not appear that such work modifies the conclusions now reached on the calcium ferrites which can be formed.

2. *Hydration of C_4AF.* Hydration of C_4AF, which later work has shown to be not a compound, but a solid solution of this composition in anhydrous cement, has been studied by several authors. Brief summaries have been published by Steinour [32], Bogue [59], and Lea [26]. The results of experimental studies are now described and discussed, not in chronological order, but in an order which seems best to explain behavior.

Malquori and Cirilli [52] (1943) found that on shaking C_4AF with "constantly saturated limewater" at about 0 °C (in order to prevent transformation to the cubic phase) a "perfectly white" product was obtained, consisting of hexagonal plates of refractive index 1.57, corresponding to that of a 50 percent solid solution between C_4A·aq. and C_4F·aq. The X-ray pattern was also stated to be similar to that of the product obtained by precipitation from solution when equimolar amounts of $AlCl_3$ and $FeCl_3$ were added to sodium hydroxide solution. At 20–25 °C, the same hexagonal-plate crystals plus cubic crystals of index 1.66–1.67 were obtained, corresponding to the 50–50 percent solid solution of $C_3A{\cdot}6H_2O$ and $C_3F{\cdot}6H_2O$.

These experiments appear to lead quite definitely to the conclusion that the hydration of C_4AF in limewater maintained in the saturated condition leads initially at lower temperatures to formation of a one-to-one molar solid solution of C_4A·aq. and C_4F·aq., this gradually transforming to the corresponding C_3A·aq.-C_3F·aq. solid solution at higher temperatures.

In Hoffmann's prior tests at 20 °C, for times up to 270 days, it had been found that, whether starting with saturated limewater, half-saturated limewater, or water, using initially 1 g C_4AF with 75 ml water or solution, the lime concentration, subject to some fluctuation, approached a final value of 0.63–0.64 g CaO per liter. The hydrated product produced was light brown in color, while a little unreacted C_4AF was stated to remain. Hoffmann argues that three hydrated phases must be formed in the hydration of C_4AF, either two hydrated calcium aluminate phases and one ferrite hydrate or vice versa. This conclusion would follow if the alumina and ferric oxide components behaved independently, but the mutual replacement of Al and Fe in solid solution suggests that the system $CaO–Al_2O_3–Fe_2O_3–H_2O$ may be effectively ternary in part. (The same conclusion may also be made where SiO_2 additionally forms part of the solid-solution equilibrium). Further, Hoffmann accepts an earlier conclusion by von Polheim on the $CaO–Al_2O_3–H_2O$ system that the solid phase in equilibrium in this system at a lime concentration of 0.64 g CaO per liter is C_3A·aq. This conclusion of course is in conflict with the results of later work. The argument developed by Hoffmann that the phases formed are C_3A·aq., iron hydroxide, and a mono- or more probably a dicalcium ferrite hydrate C_2F·aq. thus hardly seems valid. However, Hoffmann states that the hydrated products obtained with an initial saturated lime solution (final concentration, 0.64 g CaO per liter, nil Fe_2O_3) and water (final concentration 0.64 g CaO per liter, nil Fe_2O_3) gave on analysis compositions corresponding respectively to $7.26\ CaO \cdot 2.3Al_2O_3 \cdot 1\ Fe_2O_3$ and $6.93CaO \cdot 2.3Al_2O_3 \cdot 1Fe_2O_3$.

Flint, McMurdie, and Wells [30] hydrated C_4AF by shaking with water in the proportion of 100 g C_4AF to 2 liters water, presumably at room temperature, filtering after various times, and analyzing the filtrates. Only CaO and Al_2O_3 passed into solution, concentrations of about 0.55 g CaO and 0.32 g Al_2O_3 per liter being reached in about one-half hr, then decreasing slowly and asymptotically to about 0.45 and 0.05 g per liter respectively after about a week. The metastable solutions precipitated "silky" precipitates (indicating formation of a hexagonal-plate phase) on standing after various indicated times of shaking, ½, 1, 2, 4, 6, 24 hr; 3 and 7 days. After 3 months, mixtures of hexagonal calcium aluminate hydrate and $C_3A \cdot 6H_2O$ of R.I.=1.605 were formed. The residual iron-containing material after filtration was not further considered.

This method of experiment clearly separates the iron-containing residue from the metastable solution containing lime and alumina at an early stage, and the subsequent precipitation from the solution on standing may be expected to yield (from the work of Jones and Roberts) initially hexagonal plates of solid solution in the range $C_{2-2.4}A \cdot 8–10.2\ H_2O$, possibly accompanied by alumina gel. There appears then to be a further conversion to the stable cubic hexahydrate $C_3A \cdot 6H_2O$ and hydrated alumina at the invariant point $A \cdot 3H_2O–C_3A \cdot 6H_2O$. No iron would of course be expected in the solid phases under these conditions.

Another identical mix was allowed to stand for 10 yr at room temperature with occasional shaking. Under these conditions, several processes are or may be proceeding side by side or consecutively with overlapping:

1. Precipitation from the extracted solution of hexagonal-plate hydrated aluminates and possibly alumina gel as described above.
2. Removal of further lime from the iron-containing residue, leading to increase in lime concentration of the solution.
3. Formation of crystals of $C_3A \cdot 6H_2O–C_3F \cdot 6\ H_2O$ solid solution from the iron-containing residue, presumably preceded by a hexagonal-plate solid solution of C_4A·aq.–C_4F·aq.
4. Formation of a residue of iron hydroxide.

The above suggested mechanism appears to fit the description given by the authors, viz: "Analysis of this solution (i.e., after 10 yr) showed but a trace of alumina. The lime in solution was 1.087 g CaO per liter, slightly less than that of a saturated lime solution. This increase in concentration of lime was accompanied by the disappearance of the hexagonal forms of hydrated calcium aluminate, and of the anhydrous phase. The solid residue was a mixture of isometric crystals and finely divided reddish material. The bulk of the isometric crystals had the normal refractive index of $3CaO \cdot Al_2O_3 \cdot 6H_2O$. A relatively small proportion possessed a higher index of refraction with a maximum value of about 1.637."

In the present author's view, the results of this experiment may be reasonably interpreted on the basis that the initial extraction in effect produces two experiments proceeding side by side in the same reaction vessel, with relatively little mutual interaction:

(a) Precipitation from a metastable solution containing lime and alumina in molar ratio.

(b) Reaction of the partly hydrated solid phase from the extraction containing CaO, Al_2O_3, and Fe_2O_3 in molar ratio with a lime solution.

Thus (a) may be expected to give the equilibrium of the system $CaO–Al_2O_3–H_2O$ and (b), that of $CaO–Fe_2O_3–H_2O$, finally ending with, for (a), an invariant point $C_3A \cdot 6H_2O$-hydrated alumina, and for (b) an invariant point for a solid solution "$C_3F \cdot 6H_2O–C_3A \cdot 6H_2O$"–ferric hydrate. The final lime concentration appears to be common to both equilibria. It seems probable that the high degree of insolubility of ferric hydroxide (or oxide) prevents any attainment of equilibria between the $C_3A \cdot 6H_2O$ obtained by precipitation from supersaturation, and the solid solution "$C_3F \cdot 6H_2O–C_3A \cdot 6H_2O$" obtained from the iron-rich residual solid phase. If these conclusions are correct, no hydrated hexagonal calcium ferrite phase with a CaO/Fe_2O_3 ratio less than 3 could be expected in these experiments.

Flint, McMurdie, and Wells apparently used glass vessels. There is therefore a possibility that some silica was removed from the glass and entered into the structures of the hexagonal and cubic phases formed.

The authors finally examined behavior in a paste made from 10 g C_4AF and 5 g water, stored in a glass vessel for 6 days. There will be an appreciable evolution of heat in a paste of this composition and the temperature will therefore be somewhat above room for some time. We may however assume that the general form of the equilibria to be expected in extracted solution and residue will be as given above. Microscopic examination of the mixture "showed the presence of about 20 percent of unhydrated $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ with the alteration products consisting of a mixture of reddish amorphous material and of isometric crystals with index of 1.63 to 1.64." The authors concluded that the increase in index was due to the presence of Fe_2O_3 in solid solution. This is clearly so, while the fact that the observed crystals are now solid solution and not pure $C_3A \cdot 6H_2O$ appears to be due to the large solid-to-solution ratio, little lime-alumina solution being produced from which $C_4A \cdot aq. \rightarrow C_3A \cdot 6H_2O + C$ could precipitate. The intimate association of alumina and ferric oxide in the relatively large body of hydrating C_4AF then leads to solid-solution formation. For this paste therefore, under the conditions and for the time tested, it is concluded that the final solid phases, excluding unhydrated material, consisted of cubic solid solution $C_3A(F) \cdot 6H_2O$ and a mixture or possibly solid solution of ferric and alumina hydrates.

Work had been carried out previously by Bogue and Lerch [56] (1934). These authors stated that the anhydrous phase had disappeared after one month. The isotropic crystalline phase had an index of 1.640, as later confirmed by Flint, McMurdie, and Wells. Bogue and Lerch could not however at the time distinguish the X-ray pattern from that of $C_3A \cdot 6H_2O$. The reddish-brown amorphous phase was not identified. It was suggested as "probable" that it was a hydrated calcium ferrite, but in the light of the discussion given in the present paper, this suggestion seems untenable.

Brocard [19] (1948) carried out similar though not identical shaking tests, with analyses of solutions, to those of Flint, McMurdie, and Wells. Instead of using 100 g C_4AF to 2 liters of water, he used 30 g C_4AF, and instead of using separate mixes for each time period, filtering and analyzing, he withdrew 50 ml aliquots after various times, thus gradually decreasing the amount of liquid present by 450 ml in 9 withdrawals over a period of 3 days. He carried out tests at various temperatures also, 15°, 30°, 50°, 70°, and 100 °C. Considering his results at 15 °C in comparison with those of Flint, McMurdie, and Wells, the initial maximum content of CaO is much the same in both cases, but Brocard found a much higher content of alumina than did Flint, McMurdie, and Wells at their room temperature and therefore a much lower lime/alumina ratio. No iron was found in solution, confirming Flint, McMurdie, and Wells' finding. Hexagonal-plate crystals first precipitated, later converting into cubes. There was also left a brownish amorphous gel. X-ray examination of the hydrated product after 3 days indicated the presence of hexagonal "$C_2A \cdot 7H_2O$" and cubic $C_3A \cdot 6H_2O$. Brocard wrote the reaction as $2C_4AF + aq. \rightarrow C_3A \cdot 6H_2O + C_2A \cdot 7H_2O + 2C_xF$ and considered that an amorphous calcium ferrite gel was present.

When the reaction was allowed to proceed at room temperature (15°–18 °C), it was noted that the lime concentration reached a minimum of 0.29 g CaO per liter after 8 days, and then increased slowly, becoming 0.41 g at 6 months. X-ray examination at 6 months showed a preponderance of cubic aluminate.

In the light of the present discussion and of the work of Jones and Roberts, it seems clear that the lime-alumina solution of relatively low CaO/Al_2O_3 molar ratio obtained by Brocard can be expected to precipitate dicalcium aluminate hydrate, with possibly alumina gel, in contrast to higher calcium aluminate hydrates expected from Flint, McMurdie, and Wells' solution. The conversion to $C_3A \cdot 6H_2O$ can then be expected to follow, the final equilibria ending up as described above.

At higher temperatures, Brocard found precipitation of $C_2A \cdot 7H_2O$ followed by more and more rapid transition to cubic $C_3A \cdot 6H_2O$, while in X-ray examination the presence of hematite (α-Fe_2O_3) was evident. To the present author, this lends support to the view that the final products of hydration of C_4AF with water in the relative amounts used by Flint, McMurdie, and Wells, or Brocard, in their shaking tests, are those indicated above for the various conditions of experiment, with the evidence pointing to the iron being present partly as a solid solution "$C_3A \cdot 6H_2O$–$C_3F \cdot 6H_2O$" and partly as a hydrated (or hydrous) iron phase. There is no satisfactory evidence of a $C_2F \cdot aq.$ or $CF \cdot aq.$ compound.

There are two further points on which it seems desirable to comment. One is concerned with the actual constitution of the residual "amorphous" material produced in the process of hydration of C_4AF, the other with the formation of hematite.

As the present author sees it, when a particle of "C_4AF" is placed in contact with water, Ca and Al pass into solution from the crystal lattice, first from the surface layer, as "$Ca(OH)_2$" and "$Al(OH)_3$", with possibly some replacement by H_2O and the immediate formation of a more or less structureless "gel". This is a continuous process, as water penetrates into the crystal lattice of C_4AF, and the initially formed hydrated material remaining *in situ* will exercise a protective effect on the underlying residual unaffected C_4AF structure, as visualized by Brocard. In the present author's view, however, it is not possible at any stage to regard the external initially "gelatinous" residue as a definite calcium ferrite hydrate. Perhaps this is more a matter of words than anything else, and the author is otherwise in substantial agreement with Brocard's conclusions. It is not thought however that one can speak in too rigid terms about the change from the initially formed gel to "hematite". The whole is a gradual process in which the gradual extraction of lime and alumina from the C_4AF lattice and the increasing rapidity of building the residual disordered "micro-lattices of hematite" into larger units are essential features.

The second point is concerned with the structure of the final iron-containing phase. Although Brocard states that he found the lines of hematite (α-Fe_2O_3) in the X-ray powder patterns of the hydrated products, he nevertheless states in a footnote that the pattern of hematite is identical with that of hydrous or hydrated hematite "$Fe_2O_3 \cdot nH_2O$" and appears to conclude that the iron phase is really in a hydrated condition. There seems to be some doubt about this, since in work at the Building Research Station (Roberts), only α-Fe_2O_3 (hematite) has been identified on X-ray examination of mixes in which calcium chloroferrite, $C_3F \cdot CaCl_2 \cdot aq.$ was treated at 90 °C with water, saturated limewater, or 0.5 percent and 1.0 percent NaOH and KOH solutions saturated with lime. This result of course confirms Brocard's actual observations.

In view of these findings on the ferric oxide formed, and the bearing which the phase has in the CaO-Fe_2O_3-H_2O equilibria, it seems desirable to discuss very briefly the position with regard to anhydrous and hydrated oxides of iron insofar as this is relevant. Rooksby [60] has discussed these oxides (1951) and summarized the position at that time.

The only anhydrous oxides which need concern us here are α-Fe_2O_3, which occurs naturally as hematite, and γ-Fe_2O_3, found naturally as a comparatively rare mineral maghemite. The γ-Fe_2O_3 is metastable with respect to α-Fe_2O_3, rapid conversion occurring at about 400 °C, while the color changes with the change in structure from light brown to a "turkey-red".

Of the hydrates, α-, β-, and γ-$Fe_2O_3 \cdot H_2O$, only the α- and γ- forms occur naturally, as goethite and lepidocrocite respectively. The crystal structures of these two forms are similar to those of α-$Al_2O_3 \cdot H_2O$ (diaspore) and γ-$Al_2O_3 \cdot H_2O$ (boehmite), respectively. So-called limonite appears to be poorly crystallized goethite. The third form, β-$Fe_2O_3 \cdot H_2O$, can be obtained from ferric chloride as an orange-yellow precipitate by "heating a solution of moderate concentration to 60 °C for 45 min". Rooksby comments that in natural bauxite, in which the main constituent has the boehmite crystal structure, iron, if present, may replace the aluminum isomorphously. It may here further be remarked that this observation may also apply to the system CaO–Al_2O_3–H_2O, where initial precipitation of hydrated alumina may be as a boehmite structure.

The colors of the hydrated iron oxides are respectively yellow, orange, and brown, apparently related to the changes in structure. Both α- and γ-hydrated oxides are comparatively easily decomposed to the corresponding α- and γ-anhydrous oxides by heating in air for one hr at 300 °C. As stated, heating of the γ-Fe_2O_3 above 400 °C then causes transformation to α-Fe_2O_3. It is of interest to recall that Hoffmann [54] found a change of structure of γ-$Fe_2O_3 \cdot H_2O$ to α-$Fe_2O_3 \cdot H_2O$ on grinding in an agate mortar.

We can now return to Brocard's observation on the iron-oxide phase produced in the hydration of C_4AF. He states that the X-ray pattern of hematite is identical with that of hydrated hematite "$Fe_2O_3 \cdot nH_2O$." It is not clear precisely what this "$Fe_2O_3 \cdot nH_2O$" material was. From the data presented by Rooksby [60], the structure and X-ray pattern of hematite is substantially different from those of α-$Fe_2O_3 \cdot H_2O$ or the β- and γ- forms. If Brocard's material was really a limonite, assigned a formula such as $2Fe_2O_3 \cdot 3H_2O$, Rooksby comments that X-ray examination of "limonite" shows it to be generally composed of goethite, i.e., α-$Fe_2O_3 \cdot H_2O$. It is difficult to reconcile these apparently conflicting data about the identity of hematite and hydrated iron oxide.

Replacement of Al by Fe in Hydrated Calcium Aluminates, and Calcium Chloro- and Sulfoaluminates

Owing to the length of this paper, only a brief and somewhat incomplete discussion can be given here.

Following their experiments on the preparation of hexagonal $C_4F \cdot 14H_2O$ and cubic $C_3F \cdot 6H_2O$, Malquori and Cirilli [52] (1943) investigated the possibility of solid solution formation between these compounds and the corresponding aluminates.

For the hexagonal-plate structures the method used was still that of adding a mixed solution of chlorides to sodium hydroxide solution. The precipitate obtained under the conditions used, after drying over $CaCl_2$ and KOH, was stated to contain (as determined by analysis) a Cl content always below one percent, based on the anhydrous compound. It is evident from this statement that the product contained some chloroaluminate and/or chloroferrite in the hexagonal-plate solid solutions. It appears also that the authors worked throughout with glass vessels, so that the presence of silica in the structures is probable. Precipitates obtained in this way, with compositions (neglecting the possible presence of Si and of Cl) of $C_4A\cdot aq.$; $4CaO\cdot 0.33Fe_2O_3\cdot 0.67Al_2O_3\cdot aq.$; $4CaO\cdot 0.5Fe_2O_3\cdot 0.5Al_2O_3\cdot aq.$; $4CaO\cdot 0.67Fe_2O_3\cdot 0.33Al_2O_3\cdot aq.$; and $C_4F\cdot aq.$ showed X-ray patterns indicative of solid-solution formation. It appears that Malquori and Cirilli did not use in their mixed precipitates a higher proportion of Fe to Al than 2:1 (molar).

Tests were also carried out to investigate the possibility of solid solutions between $C_3A\cdot 6H_2O$ and $C_3F\cdot 6H_2O$, though it was stated that since the X-ray patterns and spacings are very similar, comparison of these is not a suitable criterion. Reliance was placed on refractive-index determinations. The method of preparation was to heat solid solutions of $C_4A\cdot aq.$ and $C_4F\cdot aq.$ in lime solutions at about 70 °C for several days. The cubes obtained, of composition $C_3A\cdot aq.$; $3CaO\cdot 0.25Fe_2O_3\cdot 0.75Al_2O_3\cdot aq.$; $3CaO\cdot 0.33Fe_2O_3\cdot 0.67Al_2O_3\cdot aq.$; $3CaO\cdot 0.5Fe_2O_3\cdot 0.5Al_2O_3\cdot aq.$; $3CaO\cdot 0.67Fe_2O_3\cdot 0.33Al_2O_3\cdot aq.$; and $C_3F\cdot aq.$ showed a continuous variation of index, indicating solid solution. Again it is to be noted that Malquori and Cirilli did not work with a higher molar proportion of Fe to Al than 2:1.

It seems possible therefore that silica was present in both the above cases, while some Cl was present in the $C_4A(F)\cdot aq.$ structure. While Cl would not be expected in the cubic $C_3A(F)\cdot aq.$ structure, analysis does not appear to have been carried out to confirm its absence.

The "low" form of calcium chloroaluminate has long been known. A corresponding ferrite compound was obtained by Malquori and Caruso [48] (1938). Malquori and Cirilli [61] (1952) state that solid solution of the two compounds can be obtained, but few details are given.

Only recently has there been evidence of a "high" chloride calcium chloroaluminate [24] (1956), and the existence of a corresponding ferrite or of solid solution with $C_3A\cdot 3CaCl_2\cdot aq.$ does not yet appear to have been established.

Corresponding to the "low" sulfoaluminate, the "low" sulfoferrite was prepared by Malquori and Caruso [48] (1938). Evidence for the existence of a $C_3A(F)\cdot CaSO_4\cdot aq.$ solid solution does not appear to be available in the literature. However, one solid solution within this general composition has been prepared at the Building Research Station (Roberts [15]). Analysis gave $2.99CaO\cdot 0.63Al_2O_3\cdot 0.37Fe_2O_3\cdot 0.94CaSO_4\cdot 13.7H_2O$, with refractive indices intermediate between those of $C_3A\cdot CaSO_4\cdot aq.$ and $C_3F\cdot CaSO_4\cdot aq.$

Limited solid solution between a "high" sulfoferrite and the corresponding high-sulfate sulfoaluminate was reported by Cirilli [28] (1943), up to about 75 percent Al_2O_3 being replaced by Fe_2O_3.

Malquori and Cirilli [61] (1952) have discussed the calcium aluminate complex salts and summarized the evidence obtained by them for the close analogy between hydrated calcium ferrites and aluminates and among the salts derived from them.

Generally, it appears likely that the existence of a complete series of corresponding "low" and "high" forms of chloro- and sulfoaluminates and ferrites will eventually be established and partial or full solid solution shown between corresponding structures, depending on the effect of replacement of Al by Fe in the particular type of structure concerned.

Conclusions

On the basis of the preceding discussions, it seems possible to attempt some unifying picture of at least one portion of the cement-hydration field, which, however inadequate, may serve to stimulate discussion helpful to further investigation. The picture thus drawn must inevitably be a mixture of what is proven and what is more or less conjectural.

The simplest conception, on present evidence, appears to be that hydrated calcium aluminates formed within the portland cement-water system, before any dehydration occurs, are restricted, within the range 22 °C–100 °C, to $C_4A\cdot 19H_2O$ and $C_2A\cdot 8H_2O$, metastable however with respect to $C_3A\cdot 6H_2O$, while below 22 °C, $C_2A\cdot 8H_2O$ is replaced by $CA\cdot 10H_2O$. Above about 100 °C, the metastable $C_4A\cdot 19H_2O$ and $C_2A\cdot 8H_2O$ may have only a short life or not be formed at all, or possibly a lower hydrate of dicalcium aluminate of formula $C_2A\cdot 3H_2O$ may be formed. Apart from these, the only compounds formed in the high-pressure steam-curing range are $C_3A\cdot 6H_2O$ and, above about 215 °C, the compound $C_4A_3\cdot 3H_2O$. The position with regard to $C_4A\cdot 19H_2O$ and $C_2A\cdot 8H_2O$ is complicated by the slightly different structural arrangements possible in precipitation from supersaturated solution, but this does not appear to affect the overall picture.

Corresponding hydrated ferrites are limited, on present evidence, to metastable $C_4F\cdot aq.$ (there being no satisfactory evidence of a hexagonal $C_2F\cdot aq.$) and "unstable" $C_3F\cdot 6H_2O$. In the latter case, experimental evidence and structural considerations suggest that a pure $C_3F\cdot 6H_2O$ structure is unstable and that the Al of $C_3A\cdot 6H_2O$ can only be replaced fully by Fe if room is made in the crystal lattice by replacing $2H_2O$ by SiO_2 ($4H^+$ by Si^{4+}). The experimental evidence seems at present not sufficiently decisive to say definitely whether similar spatial considerations apply in the case of $C_4F\cdot aq.$ Nor is there evidence which gives definitely the H_2O content of $C_4F\cdot aq.$ or indicates whether a possible hydrate $C_3F\cdot Ca(OH)_2\cdot 18H_2O$ exists parallel to $C_3A\cdot Ca(OH)_2\cdot 18H_2O$ (i.e., $C_4A\cdot 19H_2O$), dehydrating to $C_3F\cdot Ca(OH)_2\cdot 12H_2O$.

Solid-solution series are formed both in hexagonal-plate and cubic structures in the systems $CaO–Al_2O_3–H_2O$ and $CaO–Fe_2O_3–H_2O$.

One form of solid solution is that exemplified between $C_4A{\cdot}19H_2O$ and $C_2A{\cdot}8H_2O$ in the system $CaO–Al_2O_3–H_2O$, where a limited solid solution is formed within the range $C_{2-2.4}A{\cdot}8–10{\cdot}2H_2O$.

Another form is that between C_4A·aq. and C_4F·aq. and between $C_3A{\cdot}6H_2O$ and $C_3F{\cdot}6H_2O$, where Al is replaced by Fe. Thus during hydration of cement compounds, when both aluminate and ferrite compounds are present together with sufficient lime, or both Al and Fe are present in the same compound, as in "C_4AF", hydration leads to a solid solution of the series C_4A·aq.–C_4F·aq., metastable with respect to the cubic solid solution series $C_3A{\cdot}6H_2O–C_3F{\cdot}6H_2O$, the latter however taking up silica from silicates present to a composition of the hydrogarnet type.

In the presence of sulfate, as in normal portland cements, sulfate will enter the structure of the hexagonal-plate lattice and produce either a solid solution of the hexagonal-plate type or the hexagonal-needle type depending on the relative amount of alumina, iron, and sulfate present. If such a solid solution reverts to the cubic structure, sulfate, but not iron, is liberated from the structure. Additionally, in the presence of chloride, Cl may also enter into the solid solution. It may be, however, that because of the relatively high solubility of alkali chlorides and $CaCl_2$, sulfate will be taken up preferentially into the structure.

This simplified picture appears to go as far as the present evidence and discussion permit. There is a need for further more exact experimental work to establish or refute the more conjectural aspects of the conclusions reached.

The importance of considering the problem in terms of the limited crystal lattice structures which appear to be possible may perhaps be stressed. There seems to be an obvious relationship between various compounds in the positions which they occupy in slight modifications of essentially the same lattice, and it seems clear that a further attack on structural aspects would give very valuable results. What is, for example, the exact structure of $C_2A{\cdot}8H_2O$ in relation to $C_4A{\cdot}19H_2O$, or of $CA{\cdot}10H_2O$ in relation to both? What of the compound $C_2AS{\cdot}8(?)H_2O$? This is apparently not resistant to attack by sulfates, whereas in the cubic lattice, replacement of $4H^+$ by Si^{4+} apparently confers sulfate resistance. It is hoped that what has been said will help to concentrate attention on these and other aspects of the problem, including the mutual interplay with calcium silicate hydrates also formed in cement hydration.

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Discussion

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On the Stability of C_3FH_6 and C_4FH_{14}

The authors [1, 2] have expressed the opinion that the C_3FH_6 phase would not exist in a pure state, but would only be formed in the presence of silica. If silica is not present, C_4FH_{14} would be formed instead. The experiments leading to this conclusion [1] are described here in a few words:

(1a) Freshly precipitated iron hydroxide is shaken with saturated lime solution and lime in excess, using polyethylene vessels. C_4FH_{14} is formed and still remains stable after a period of 39 weeks.

(1b) The same mixture in glass vessels yields hydrogarnet after 6 to 30 weeks, and contains 0.1 to 0.2 mole SiO_2 per mole Fe_2O_3.

(1c) The same mixture in polyethylene vessels with addition of highly reactive silica (aerosil) likewise yields hydrogarnet (silica-content: 0.23 to 0.28 mole SiO_2 per mole Fe_2O_3).

(2a) The hydration of C_2F with different excesses of lime yields C_4FH_{14} after a reaction time up to 26 weeks, eventually with additional $Ca(OH)_2$.

(2b) The same reaction in the presence of C_2S yields hydrogarnet with 0.17 to 0.20 mole SiO_2 per mole Fe_2O_3 and very small amounts of C_4FH_{14}.

The experiments mentioned in (2a) and (2b) were allowed to react up to a period of two years. With respect to (2b), the reaction product remains hydrogarnet. The mixtures under (2a), however, show partial decomposition of the original C_4FH_{14} to $Ca(OH)_2$, α-$Fe_2O_3 \cdot H_2O$ and a third substance not yet identified, with X-ray-lines at d=5.40 A and 4.29 A.

These results confirm the opinion that a stable C_3FH_6 does not exist in the system CaO-Fe_2O_3-H_2O. The C_4FH_{14} itself proves to be metastable and decomposes to iron hydroxide. Only the presence of small amounts of silica renders possible the formation of the very stable hydrogarnet phase.

Jones gives evidence that a C_3FH_6 free of silica could form from $C_3F \cdot CaCl_2 \cdot H_{10}$ by hydrolysis in NaOH-solution. This phase has not yet been prepared in a pure state and probably is completely unstable, as Jones himself emphasizes. According to our experiments the formation of a silica-containing hydrogarnet should be considered in all those cases in which an allegedly pure C_3FH_6 is said to be formed in the presence of calcium silicate hydrate.

Identification Chart of the Garnet-Hydrogarnet Solid Solution Series

Completely unobjectionable hydrogarnet phases can be obtained only if *dry* glasses of corresponding composition are allowed to react with water vapor, whereby a definite interval of temperature must be observed, dependent on the silica content of the glasses. The usual method of mixing the glasses with water and then putting them into the autoclave leads to initial reactions with a different tendency, which cannot be broken off, so that impure products are formed.

As a result of this, the identification chart is not completely exact and must be replaced by another. These investigations are not yet finished, so that the final identification chart cannot be presented at the moment.

On the Existence of the Compounds C_4ASH_{12} and $C_6AS_3H_{31}$

Flint and Wells [3] described the compounds $C_3A \cdot CS \cdot H_{12} (= C_4ASH_{12})$ and $C_3A \cdot (CS)_3 \cdot H_{31}$ $(= C_6AS_3H_{31})$. The first, isomorphous with $C_3A \cdot CaSO_4 \cdot H_{12}$, was said to be formed by mixing calcium silicate and calcium aluminate solutions. The second, isomorphous with $C_3A \cdot 3CaSO_4 \cdot H_{31}$, originated by transformation out of the first, the precipitate having been in contact with the solution for three years.

Dörr [4] was of the opinion that he had reproduced the compound C_4ASH_{12}, but later experiments [2] which had a reaction time of 1 and 2 years, respectively, showed only $Ca(OH)_2$, C_4AH_{13}, and calcium silicate hydrate. A repeated exhaustive control of the 2-yr samples showed in one case weak X-ray-lines (d=9.7 A, 5.6 A, 4.7 A), identical with the strongest lines of ettringite. The products, however, are free of sulfate and therefore they must be attributed to the $C_6AS_3H_{31}$ phase of Flint and Wells. In the other samples these lines were at least indicated.

The experiments are being continued, because the conditions of formation of the compound $C_6AS_3H_{31}$ are still obscure. It is remarkable that at this point hydrated silicate and aluminate phases coexist without formation of hydrogarnet [2]. Mohri [5, 6] also reported the compound $C_6AS_3H_{31}$.

References

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Discussion

C. H. Schmitt

With reference to the report submitted by Dr. Jones, there are submitted the following lines concerned with the substitution of aluminum by iron in gehlenite hydrate, C_2ASH_8. A detailed publication will be made elsewhere in the near future, as soon as investigations have been completed.

Gehlenite hydrate can be obtained in a pure form by treating a glass of gehlenite composition with half-saturated lime solution [1]. As starting materials glasses were used which had an increasing iron content ranging from C_2AS to $C_2A_{0.4}F_{0.6}S$ (table 1). Since the partial thermal decomposition of Fe_2O_3 during melting cannot be prevented, the finely ground glasses were subsequently carefully oxidized in an open electric furnace. The nonoccurrence of any crystallization was checked by X-ray diffraction. These glasses were shaken with half-saturated lime solution for 13 weeks; then the reaction products were washed with acetone and dried. The water content of the hydration products (table 1) did not increase during shaking over a longer period; i.e., the hydration process of the glasses thus could be considered as having come to an end. In all samples the X-ray test showed gehlenite hydrate as the newly formed hydrated phase (and very small amounts of calcium silicate hydrate, hydrogarnet and gibbsite).

Table 1. *Reaction of glasses $C_2A_{(1-x)}F_xS$ with half-saturated lime solution*

5.00 g glass+300 ml lime solution containing 63.6 mg CaO in 100 ml; reaction time 13 weeks.

(1) Analysis of the glasses				(2) Lime and water content after hydration		(3) Lattice constant A		(4) Refractive index
moles				*moles*		a (±0.01)	c (±0.02)	
C	A	F	S	C	H			
1.97	1.00	-------	1.00	2.07	7.97	9.96	12.56	1.512±0.003
1.99	0.90	0.10	1.00	2.09	8.01	10.00	12.56	------------
2.02	.80	.20	1.01	2.09	8.04	10.04	12.55	1.517±0.003
1.99	.70	.30	0.99	2.11	8.08	10.07	12.52	1.525±0.005
2.01	.60	.40	.99	2.13	7.76	10.08	12.54	1.525±0.005
2.00	.50	.50	1.00	2.11	6.85	10.08	12.55	1.525±0.005
2.00	.395	.605	1.00	2.08	5.30	--------	--------	------------

Table 2. *X-ray data of C_2ASH_8 (hydration product of the C_2AS-glass)*

I	d	hkl	I	d	hkl
s	12.58	001	m	2.367	303
m	6.28	002	vw	2.239	[d] 312
W	4.98	110	m	2.122	304
w	4.89	(a)	w	2.076	313
vw	4.39	(a)	w	2.047	[d] 106
w	4.28	200	m	1.8922	305
s	4.183	003	m-w	1.8602	206
w	3.534	202	vw	1.8363	(b)
vw	3.037	[b] (203)	vw	1.7637	(a)
vs	2.873	300	s	1.6623	330
vw	2.798	[b] (301)	m	1.6469	331
vw	2.718	(c)	m	1.6063	332
m	2.613	302	vw	1.5603	316
s	2.489	220	m	1.5440	333
w	2.438	(a)	m	1.4383	600
vw	2.404	(a)	w	1.3599	603
m	2.385	310			

[a] Possibly gibbsite.
[b] Possibly calcium silicate hydrate.
[c] Possibly hydrogarnet (C_3ASH_4).
[d] Possibly coincidence with gibbsite.

Up to an iron oxide content of 0.3 mole in the glasses, the hydrates formed were white or somewhat yellowish-white and contained 8 moles of H_2O after completed reaction, the lime content ranging from 2.07 to 2.11 moles per mole of R_2O_3. The hydration products of glasses containing 0.4 mole of iron oxide or more were of an increasingly brown color and no longer reached the water content of 8 moles.

From the X-ray diagrams of the hydrates, the conclusion must be drawn that the *a*-parameter of the hexagonal unit cell increases up to 0.3 mole of iron oxide in the glasses and remains constant at higher iron oxide contents (table 1). According to the results obtained hitherto, the *c*-parameter is not influenced by the entrance of iron.

Likewise, the refractive index of the hydrates increases up to an iron oxide content of 0.3 mole and remains constant at higher iron contents of the starting material.

All these results lead to the same conclusion that up to 0.3 mole or a value slightly exceeding this amount, aluminum in the gehlenite hydrate is replaceable by iron.

Comparing the dimensions of the unit cell of the gehlenite hydrate, $a=9.96\pm0.01$ A, $c=12.56\pm0.02$ A, with the values found by Fratini and Turriziani, $a=8.85$ A, $c=12.66$ A [2], it is obvious that the *a*-parameters are essentially different. The values given here have been calculated from the hk0- and 001-lines respectively according to the indices as listed in table 2.

References

[1] F. H. Dörr, Dissertation, Mainz 1954; H., zur Strassen, Zement-Kalk-Gips 11, 137 (1958).

[2] N. Fratini, and R. Turriziani, Ric. Sci. **24,** 1654 (1954).

Discussion

H. zur Strassen

In Jones' paper the close relationship between C_2ASH_8 and C_4AH_{13} is mentioned; both should have the same hexagonal layer structure. Schmitt [1], however, has found for C_2ASH_8 another value of the *a*-axis than that found by Fratini and Turriziani [2].

The single-crystal electron-diffraction patterns of the two substances are compared in figure 1. In both cases the reciprocal lattice shows the same lattice distance and the same reflection arrangement; only the distribution of intensities differs (as to the distribution of intensities the lattice of C_2ASH_8 has only monoclinic symmetry). The great similarity of both diagrams confirms the assumption that gehlenite hydrate should belong to the group of the hexagonal layer structure typified by $C_3A \cdot Ca(OH)_2 \cdot aq$.

Buttler, Dent Glasser, and Taylor [3] have found by X-ray determination for β-C_4AH_{13} the value $a=5.74$ A, which complies with the electron diffraction measurements. The a-axis of C_2ASH_8 as found by X-rays [1] is $a=9.96 \text{ A}=\sqrt{3}\times 5.75$ A; a few reflections of the X-ray powder diagram which are not contained in the electron diffraction pattern require a unit cell of triple size.

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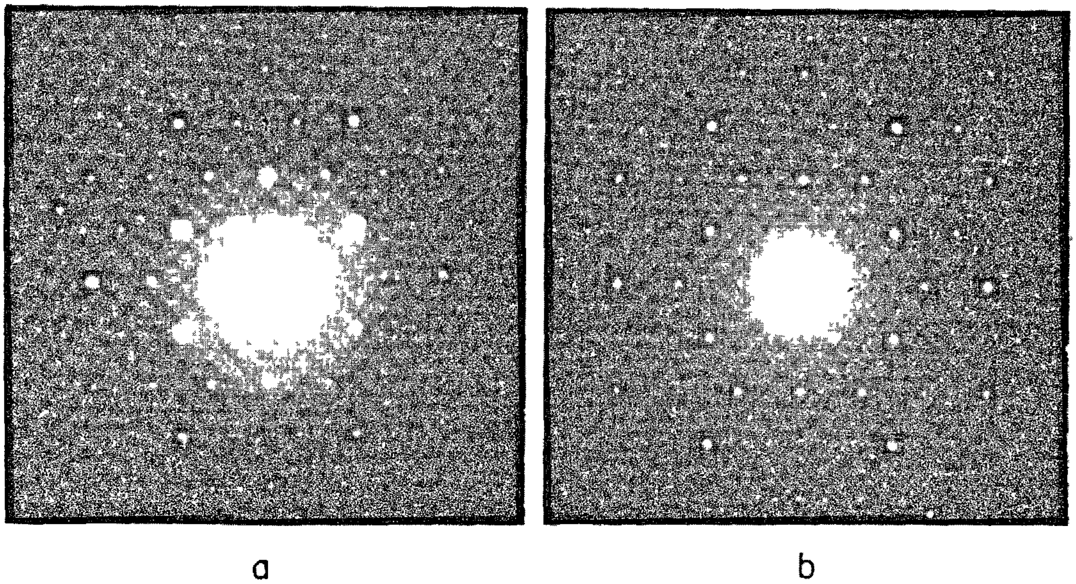

FIGURE 1. *Single-crystal electron diffraction patterns.*

(a) Gehlenite hydrate.
(b) β-C_4AH_{13}.

(Pictures by H. Grothe and G. Schimmel, Battelle Institute, Frankfurt a.M.)

Closure

M. H. Roberts

The contributions by zur Strassen and Schmitt to the discussion are of considerable interest and present new information.

The experiments on the stability of $C_3F \cdot 6H_2O$ and $C_4F \cdot 14H_2O$ show that while in the presence of silica a stable hydrogarnet phase is formed fairly readily, there appears to be no tendency for $C_4F \cdot 14H_2O$ in contact with saturated lime solution at room temperature to transform into $C_3F \cdot 6H_2O$ when silica is excluded. Nevertheless, it is still possible that the latter transformation may occur more readily at higher temperatures, as is the case for the conversion of $C_4A \cdot 19H_2O$ to $C_3A \cdot 6H_2O$. However, in one recent experiment at the Building Research Station it was observed that when a mix of $C_4F \cdot aq.$ in saturated lime solution was shaken in a stainless steel tube for 2 weeks at 50 °C the $C_4F \cdot aq.$ was unaffected. Since under similar conditions some conversion of $C_4A \cdot 19H_2O$ to $C_3A \cdot 6H_2O$ occurred in a few hours, there appears therefore to be a marked reluctance for $C_4F \cdot aq.$ to convert to $C_3F \cdot 6H_2O$ in the absence of silica. This result does not accord well with the previous experiments described in the principal paper in which some conversion of $C_3F \cdot CaCl_2 \cdot aq.$ to pure $C_3F \cdot 6H_2O$ was thought to have been obtained in NaOH solutions at 50° or 60 °C after only a few days. While it is possible that behavior in NaOH solutions is different from that in lime solutions, it must be noted, however, that there is now some doubt as to whether silica was completely excluded in the experiments using NaOH solutions. Recent analysis of the solid phase obtained by treating $C_3F{\cdot}CaCl_2{\cdot}aq.$ in *N* NaOH solution at 60 °C for 5 months showed that 0.3 percent SiO_2 was present. This small amount of silica contamination may have arisen from the brief contact of the NaOH solution with a glass burette during the course of preparation of the mix. Furthermore, the chloroferrite preparations used may have contained traces of silica, because they were prepared by adding a mixed $CaCl_2$-$FeCl_3$ solution to a NaOH solution which again may have been contaminated with traces of silica. On present evidence, therefore, it seems doubtful whether a $C_3F{\cdot}6H_2O$ preparation completely free from silica has yet been obtained, and it may well be, as concluded by zur Strassen and Schmitt, that the $C_3F{\cdot}6H_2O$ structure is not stable without the presence of some silica.

With regard to the silicoaluminate compounds, the conclusion that the existence of $C_3A{\cdot}CaSiO_3{\cdot}12H_2O$ is doubtful is supported by Carlson [1] in his discussion of another paper in this Symposium. Similarly, the compound $C_3A{\cdot}3CaSiO_3{\cdot}32H_2O$ does not yet appear to have been firmly established. Carlson and Berman [2] have indicated that it is unlikely that Mohri [3] obtained this compound, and furthermore showed that contamination with CO_2 may be a significant factor. This possibility requires further examination, and the results of further experiments on $C_3A{\cdot}3CaSiO_3{\cdot}32H_2O$ will be awaited with considerable interest. The remaining silicoaluminate, $C_2AS{\cdot}8H_2O$, appears now to be well established, and the new results showing limited substitution of up to about 0.3 mole of aluminum by iron in this compound are of interest in that they emphasize again that although solid solutions are formed there is not necessarily complete replacement of one ion by another. The assumption that $C_2AS{\cdot}8H_2O$ belongs to the group of basic crystal lattice structures typified by such compounds as $C_3A{\cdot}Ca(OH)_2{\cdot}aq.$, $C_3A{\cdot}CaCl_2{\cdot}aq.$, $C_3A{\cdot}CaSO_4{\cdot}aq.$, etc., is confirmed by zur Strassen's observation of a close similarity between the single crystal electron diffraction patterns of $C_2AS{\cdot}8H_2O$ and $C_4A{\cdot}13H_2O$. It seems that the value of the *a*-axis is almost the same for the compounds of this group, while the *c*-axis varies depending upon the space requirements of the anion and the water present. The limited single crystal X-ray and electron diffraction observations which have been made support the *a*-axis value of 5.75 A (or $\sqrt{3}\times 5.75=9.96$ A) rather than the value of about 8.8 A which has also been reported for some of these compounds. There is, however, a need for further work to establish these structures and the slight modifications brought about by changes in the states of hydration.

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Paper III-S1. Heat of Formation of Calcium Trisulfoaluminate at 25 °C*

H. A. Berman and E. S. Newman

Synopsis

Determinations were made of the heats of solution of $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31\text{–}33H_2O$ and of less completely hydrated samples of the same compound in $2N$ HCl. The preparations containing $2\text{–}8H_2O$ showed a continuous decrease in the heat of solution from -180 to -145 kilocalories per mole as the water content increased. A break occurred in the neighborhood of $8H_2O$, followed by a continuous decrease between 8 and $33H_2O$ from -145 to -74.9 kilocalories per mole at $31H_2O$ and -72.4 kilocalories at $32H_2O$. The rate of change of the heat of solution with increase in H_2O content in the $31\text{–}33H_2O$ region is 2.49 kilocalories per mole per mole H_2O. From these values and from the heats of solution of $3CaO \cdot Al_2O_3 \cdot 6H_2O$ and $CaSO_4 \cdot 2H_2O$ in the same acid solution, the heat of formation of the hydrated calcium trisulfoaluminate from these compounds was calculated to be -46.11 kilocalories per mole for a hydrate containing $31H_2O$ and -48.62 for one containing $32H_2O$. The heat of formation of the hydrated trisulfoaluminate from the elements was calculated to be -4122 kilocalories per mole for $31H_2O$ and -4193 for $32H_2O$. A possible tendency for CO_2 to enter the crystal structure of the hydrated calcium trisulfoaluminate in a manner similar to that of H_2O is discussed.

Résumé

On a fait des déterminations de la chaleur de dissolution en $2N$ HCl de $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31-33H_2O$ et d'échantillons de la même composition de moindre teneur en H_2O. Les préparations contenant $2-8H_2O$ ont montré une décroissement continue de la chaleur de dissolution de -180 à -145 kilocalories par mole lorsque la teneur en H_2O s'est augmentée. Il y eut une discontinuité environ de $8H_2O$, suivie d'une décroissement continue entre 8 et $33H_2O$ de -145 à -74.9 kilocalories par mole à $31H_2O$ et à -72.4 kilocalories à $32H_2O$. La vitesse de changement de la chaleur de dissolution contre l'augmentation de la teneur en H_2O dans la région $31-33H_2O$ est de 2.49 kilocalories par mole par mole H_2O. A partir de ces valeurs et des chaleurs de dissolution de $3CaO \cdot Al_2O_3 \cdot 6H_2O$ et de $CaSO_4 \cdot 2H_2O$ dans la même solution acide, on a calculé pour la chaleur de formation du trisulfoaluminate de chaux hydraté à partir de ces composés -46.11 kilocalories par mole pour un hydrate de $31H_2O$ et -48.62 pour un hydrate de $32H_2O$. On a calculé pour la chaleur de formation du trisulfoaluminate à partir des éléments -4122 kilocalories par mole pour un hydrate de $31H_2O$ et -4193 pour un hydrate de $32H_2O$. On envisage la possibilité que le CO_2 entre dans la structure du cristal du trisulfoaluminate de chaux hydraté d'une façon analogue à celle de l'eau.

Zusammenfassung

Die Lösungswärme von $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31-33H_2O$ und von weniger wasserhaltigen Proben derselben Komposition wurden in $2N$ HCl bestimmt. Die Lösungswärme der $2-8H_2O$ enthaltenden Präparate verminderte sich von -180 zu -145 Kilokalorien pro Mol (Kkal/Mol) mit zunehmendem Wassergehalt. Ein Knick in der Kurve tritt bei ca. $8H_2O$ auf; zwischen 8 und 33 H_2O, erfolgt ein kontinuierlicher Abfall von -145 Kkal/Mol, sodaß bei $31H_2O$ ein Wert von -74.9 Kkal/Mol und bei $32H_2O$ ein Wert von -72.4 Kkal/Mol erreicht wird. Die Abhängigkeit der Lösungswärme von der Wassergehaltszunahme zwischen 31 und $33H_2O$ ist 2.49 Kkal/Mol pro Mol H_2O. Von diesen Resultaten und den Lösungswärmen für $3CaO \cdot Al_2O_3 \cdot 6H_2O$ und $CaSO_4 \cdot 2H_2O$ in derselben Salzsäurelösung wurde die Formationswärme für das $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31-33H_2O$ aus diesen Verbindungen berechnet. Sie beträgt -46.11 Kkal/Mol für ein Hydrat mit $31H_2O$ und -48.62 für eins mit $32H_2O$. Die Formationswärme des Kalziumtrisulfoaluminathydrats aus den Elementen wurde berechnet und beträgt -4122 Kkal/Mol für $31H_2O$ und -4193 für $32H_2O$. Die Möglichkeit daß CO_2 eine ähnliche Tendenz hat, wie Wasser, in die Kristallstruktur des Kalziumtrisulfoaluminathydrats einzudringen, wird diskutiert.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the National Bureau of Standards, Washington.

Introduction

Calcium trisulfoaluminate, $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31-33H_2O$ [1],[1] is formed by the aggressive action of sulfate waters on portland cement concrete and is a reaction product of the hydration of the slag-calcium sulfate cements used extensively in Europe [2] because of their resistance to such waters. Lerch's value of 149 calories per gram of SO_3 [3] for the heat of the reaction

$$3CaO \cdot Al_2O_3 \cdot 6H_2O + 3(CaSO_4 \cdot 2H_2O) + 19H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O \qquad (1)$$

appears to be the only thermochemical data for the trisulfoaluminate in the literature. In the present work, the heat of formation of calcium trisulfoaluminate was calculated from measurements of its heat of solution in $HCl \cdot 26.61H_2O$ (2.00*N* HCl at 25 °C.) and similar values obtained by measurement or calculation for the reactants in the above equation. The heats of formation of the reactants were taken from Circular 500 [4] of NBS.

The water content of this compound is variously reported as $30H_2O$ [5], $31H_2O$ [1, 3, 6], $31.5H_2O$ [7], $32H_2O$ [8], and $31-33H_2O$ [9]. According to Lefol [5], the water between 8 and $30H_2O$ is loosely bound, and changes in water content are reversible, depending on ambient water vapor pressure. Electron microscope studies by Astreeva and Lopatnikova [6] show that part of the water of crystallization may be driven off without destroying the crystal structure but with the formation of intracrystalline voids. A study of this compound must consider the variability of water content. Calculations of the heat of formation have therefore been made for the hydrate at two compositions $31H_2O$ and $32H_2O$.

It is appropriate at this point to consider briefly the nomenclature of this compound and related compounds. The terms sulfoaluminate, chloroaluminate, carboaluminate, etc., are subject to question because they do not correctly represent the relationship of the various atoms involved. Although our knowledge of the crystal structure is incomplete, it seems clear that the "sulfoaluminates" might more correctly be called "aluminate sulfates". In particular, the "hydrated calcium trisulfoaluminate" might be more correctly called "hexacalcium aluminate trisulfate hydrate". The term "sulfoaluminate", however, has become firmly established through many years of usage and will be employed in this symposium paper in preference to the more cumbersome exact terminology.

Materials, Apparatus, and Procedure

Preparation of the Sulfoaluminate

Ten samples of the calcium trisulfoaluminate were prepared. Their properties and details of their preparation are listed in table 1. Two general methods were used to prepare them: (a) The reaction between calcium sulfate solution and a solution of calcium aluminate obtained by shaking a high-alumina cement[2] with water; (b) the reaction between solutions of calcium hydroxide and aluminum sulfate, sometimes in the presence of calcium sulfate solution. With the exception of the high-alumina cement, analytical reagents were used in all the preparations. In the case of samples *A* and *F*, precautions were taken to exclude atmospheric carbon dioxide during every step of the process. The distilled water used to dissolve the reagents was boiled to expel dissolved gases. The flask was closed, while cooling the boiled water, with a stopper containing an inlet tube equipped with a CO_2-absorption bulb. The solutions were prepared and the samples were precipitated, digested, filtered, and conditioned in closed systems protected from the laboratory air. "CO_2-free" air[3] was used to flush all containers and to transfer water, solutions, or slurries into the stoppered containers under pressure. For sample *B*, these precautions were taken only during the filtration and conditioning.

In general, the solutions shown in table 1 were added alternately in small quantities or simultaneously in approximately stoichiometric ratios. The reaction mixture was stirred magnetically during the addition of the reagents and with a current of "CO_2-free" air for several minutes afterwards. The precipitates formed were digested in the stoppered reaction flasks for various periods (from 8 days for sample *H* to 9 months for sample *B*), filtered on a Buchner funnel, and dried by several methods: (a) Washing with alcohol and ether, (b) conditioning over calcium chloride in an evacuated desiccator (sample *H*), (c) conditioning over saturated $MgCl_2 \cdot 6H_2O$ in a closed desiccator or in a desiccator through which a stream of "CO_2-free" air previously bubbled through saturated $MgCl_2 \cdot 6H_2O$ was passed (samples *A*, *B*, *F*). Samples *A*, *B*, and *F* were conditioned until their ignition loss at 1,000 °C. was constant, a process which required about 2 to 2½ months. Before and after removing a portion of the sample

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[1] Figures in brackets indicate the literature references at the end of this paper.

[2] The high-alumina cement had been heated overnight in air at 950 °C to oxidize the sulfides present to sulfates.

[3] Compressed air passed through moisture- and CO_2-absorbents. The actual CO_2 content of this air may vary, depending on the rate of flow and the history of the absorbent. In one case, where the "CO_2-free" air was passed through the absorption tube of a CO_2-determination train overnight, the tube showed no gain in weight. When CO_2-determinations were run on sulfoaluminate samples, blank determinations prior to the runs showed gains of 0.0 to 1.0 mg in 1 hr., possibly from CO_2 in the water and acid used in the determination. When the water was not boiled in advance, but taken directly from the distilled-water supply, the blank determination occasionally showed a pickup of as much as 2.0 mg of CO_2.

TABLE 1. *Preparations of* $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 30\text{–}33H_2O$

Sample Designation	A	B	C	D	E	F	G	H	J	K
Method of preparation [a]	1	2	3	4	3	5	6	7	6	8
Heat of solution, $-\Delta H$, calories per gram	58.1408 58.2680 58.4099 58.3354 57.8739 58.7516 58.2407	58.704 59.533 58.549 57.885 58.655	59.14 59.39	61.06 60.84 61.96 61.67 60.01	59.62 59.00 58.55	58.0685 57.1606 56.6756 57.5242 57.6190 57.1509 56.1170 57.6998 57.7546 58.0854	58.65 58.37 59.53	60.45 62.43 62.41 62.76 61.53	57.47 56.32	49.19 49.04
Average	58.289	58.665	59.26	61.11	59.06	57.387	58.85	61.92	56.90	49.12
Standard deviation of average	.120	.262	0.13	0.34	0.31	0.197	0.35	0.42	0.57	0.07
Analysis, wt. percent CaO	26.96 ±0.02	26.70 ±0.02	27.17	26.63	27.16	27.28	26.71	27.06	26.83	27.54
Al_2O_3	8.23 ±0.02	8.09 ±0.017	8.27	8.09	8.20	8.63	8.12	8.54	7.96	7.26
SO_3	19.11 ±0.08	18.81 ±0.09	19.38	19.32	18.97	19.10	18.66	19.16	19.60	21.21
CO_2	0.207 ±0.014	0.24 ±0.014	1.15	0.29	0.91	0.46	1.53	1.49	0.76	2.12
H_2O	45.44	45.82	44.12	45.36	44.78	44.66	45.88	43.86	45.18	41.84
SiO_2	0.00	0.15 ±0.00	-------	-------	-------	0.00	-------	-------	-------	-------
Mole ratios, CaO/Al_2O_3	5.957 ±0.015	6.000 ±0.014	5.972	6.152	6.021	5.747	5.980	5.760	6.126	6.896
SO_3/Al_2O_3	2.958 ±0.014	2.960 ±0.016	2.984	3.057	2.945	2.819	2.927	2.857	3.135	3.719
CO_2/Al_2O_3	0.058 ±0.004	0.069 ±0.004	0.322	0.083	0.257	0.123	0.436	0.404	0.221	0.676
H_2O/Al_2O_3	31.255	32.053	30.185	31.726	30.900	29.287	31.972	29.062	32.114	32.609
Mole ratios of compounds (to Al_2O_3):										
$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot nH_2O$	0.986 ±0.005	0.987 ±0.005	0.995	1.000	0.982	0.940	0.976	0.952	0.997	1.000
where $n=$	31.656	32.425	30.322	31.600	31.466	30.965	32.758	30.376	31.913	31.171
$CaSO_4 \cdot 2H_2O$	-------	-------	-------	0.057	-------	-------	-------	-------	0.144	0.719
$CaCO_3$	0.041 ±0.032	0.069 ±0.004	0.004	0.083	0.131	0.109	0.126	0.046	-------	0.177
$Ca(OH)_2$	-------	0.011 $\begin{cases}+0.035\\-0.011\end{cases}$	-------	0.012	-------	-------	-------	-------	-------	-------
$Al_2O_3 \cdot 3H_2O$	0.014 ±0.005	0.013 ±0.005	0.005	-------	-------	0.060	-------	0.048	0.003	-------
CO_2	0.017 $\begin{cases}+0.032\\-0.017\end{cases}$	-------	0.318	-------	0.126	0.014	0.310	0.358	0.221	0.499
Weight percent purity	99.4	99.2	98.7	98.5	98.5	98.2	97.9	97.7	97.3	88.4
Heat of solution of $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot nH_2O$, $-\Delta H$:										
kcal. per mole	72.86_6	73.71_5	73.46_0	76.65_0	73.56_4	71.26_2	75.17_0	77.31_2	74.14_4	71.54_4
cal. per gram	58.34_3	58.37_4	59.97_2	61.42_2	59.06_3	57.63_2	59.24_5	63.06_7	59.14_7	57.68_8

[a] Method 1: Aluminum sulfate solution added to calcium hydroxide solution (alternate additions).
Method 2: Calcium aluminate solution added to calcium sulfate solution; calcium hydroxide solution added later.
Method 3: Aluminum sulfate—calcium sulfate solution added to calcium hydroxide solution.
Method 4: Calcium hydroxide and aluminum sulfate solutions added to calcium sulfate solution.
Method 5: Aluminum sulfate solution added to calcium hydroxide solution; calcium sulfate solution added to the mixture (alternate additions).
Method 6: Calcium aluminate solution added to gypsum-lime solution; calcium sulfate solution added later.
Method 7: Calcium hydroxide solution added to aluminum sulfate—calcium sulfate solution.
Method 8: Calcium aluminate solution added to gypsum-lime solution.

from the closed chamber for the purpose of determining ignition loss, the chamber was evacuated and refilled with "CO_2-free" air.

X-ray diffraction patterns of samples *A*, *B*, and *F* were obtained by the powder method on a Geiger-counter diffractometer with copper Kα radiation. The patterns are tabulated in table 2 and compared with data published by Fratini, Schippa, and Turriziani [8]. Since the preparations obtained showed more peaks than the published pattern, a series of possible *d*-spacings was calculated from the unit cell parameters proposed by these authors. The close correspondence between the observed and calculated *d*-spacings is a measure of the purity of the samples prepared and an indication of the impurities present in several instances where the correspondence was not as good. The X-ray data provide confirmation as well for the unit cell parameters calculated by these authors.

The oxide analysis in table 1 was obtained by duplicate or triplicate determinations for samples *A* and *B*, and the precision of the analysis and of the calculated mole ratios of the oxides (and of compounds calculated from the oxides) was determined. Duplicate or triplicate determinations of CO_2 content were made on all the samples. The standard deviation for each of the oxide analyses was obtained by pooling the variances of analyses for samples *A* and *B*. The designation and calculation of compounds present as impurities was based on the phase equilibrium studies of Jones [10] and of D'Ans and Eick [11] as discussed by Eitel [12], and on optical microscopic examination, chemical analysis, and X-ray diffraction patterns.

Preparation of the Gypsum

Fifty grams of plaster of Paris were dissolved in distilled water at room temperature, stirred 1 min, and quickly filtered. Crystallization of $CaSO_4 \cdot 2H_2O$ occurred in the filtrate about 15 min after the beginning of the filtration. The crystals were filtered, washed with alcohol and ether, and dried in the laboratory air. Chemical analysis gave the composition $CaSO_4 \cdot 2.018H_2O$.

Preparation of Hydrated Calcium Aluminate

Tricalcium aluminate hydrate, $3CaO \cdot Al_2O_3 \cdot 6H_2O$, was prepared by autoclaving $3CaO \cdot Al_2O_3$ at 150 °C for several days, according to the method of Thorvaldson, Brown, and Peaker [13]. The

TABLE 2. *X-Ray diffraction patterns of the* $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 31\text{–}33H_2O$ *samples*

Calculated [a]		Observed *d*-spacings, Angstrom units		
hkl	*d*, Angstrom units	*A*	*B*	*F*
100	9.734	9.774	9.817	9.861
101	8.864	8.853	8.972	9.092
				9.036
110	5,620	5.623	5.67	5.647
112	4.978	4.979	5.01	4.995
200	4,867	[b] 4.849	[b] 4.897	[b] 4.897
				4.870
104	4.697	4.694	4.729	4.721
203	4.024	4.020	4.046	4.053
				4.035
114	3.880	3.880	3.899	3.895
210	3.679	3.679	3.696	3.693
				3.682
204	3.604	3.601	----------	3.608
212	3.480	3.477	3.494	3.486
300	3.245	3.241	3.256	3.246
214	3.034	3.018	3.030	[c] 3.023
		3.015		
220	2.810	2.806	2.818	2.815
221	2.786	----------	2.788	2.783
304	2.776	2.776	----------	----------
310	2.700	2.696	2.706	2.706
				2.699
312	2.618	2.618	2.626	2.621
216	2.564	2.565	2.573	2.570
313	2.526	----------	2.533	----------
224	2.489	2.486	2.497	----------
401	2.418	----------	2.417	----------
314	2.411	2.410	----------	2.412
208	2.348	2.351	2.359	2.352
320	2.233	2.232	2.238	2.233
404	2.216	2.208	----------	2.212
322	2.186	2.184	2.191	2.194
				2.185
316	2.154	2.155	2.160	2.158
323	2.132	2.130	----------	----------
410	2.124	2.124	2.127	2.126
412	2.084	2.082	2.087	----------
324	2.061	2.062	2.066	2.064
414	1.975	1.975	1.979	1.979
500	1.947	1.946	1.951	1.947
415	1.904	1.903	1.906	----------
330	1.873	----------	1.878	----------
332	1.845	1.844	1.849	1.849
421	1.833	1.832	1.834	1.829
422	1.813	1.814	1.816	1.813
333	1.812	1.812	----------	----------

[a] Calculated from the unit cell parameters published by Fratini, Schippa and Turriziani [8].

[b] May be a line of $Al_2O_3\cdot 3H_2O$.

[c] May be a line of calcite, $CaCO_3$.

hydrated aluminate was dried over potassium hydroxide. Chemical analysis gave the composition $3CaO\cdot Al_2O_3\cdot 5.859H_2O$ (plus 0.007 mole $CaCO_3$ per mole as impurity). The anhydrous aluminate had been prepared by repeated heating of lime and alumina with intervening moistening of the material to aid in dispersing the CaO, as described by the same authors.

Heat of Solution Measurements

The heats of solution of the compounds were determined in $HCl\cdot 26.61_4H_2O$ (2.00*N* HCl at 25 °C). A precision-type calorimeter, described by Newman [14] was used. Since it was inconvenient to prepare the sulfoaluminate in large quantities, 1-g samples of this compound were used with the normal quantity of acid for the calorimeter, 600 g. In accordance with equation 1, 0.4-g samples of gypsum and 0.3-g samples of calcium aluminate hydrate were used with the same quantity of acid. Larger amounts of these compounds were also employed to determine whether the greater precision of a larger sample would be usable, in view of the theoretical loss of some heat of dilution due to the formation of a more concentrated solution. Although equation 5 below, used in calculating the heat of the reaction, specifies that the gypsum be introduced into the solution already obtained by dissolving the calcium aluminate hydrate in the acid, the gypsum was instead added directly to the fresh acid. The effect of the presence of calcium aluminate on the heat of solution of gypsum is negligible, as shown by the experiments of Newman with anhydrite [14, 15]. A heat of solution of $-\Delta H = -12.75 \pm 0.34$[4] calories per gram was obtained for $CaSO_4$ previously ignited at 1,000 °C and dissolved in fresh acid. When the same material was dissolved in acid to which calcium aluminate had been added, the heat of solution was -12.69 ± 0.14. Since the ions present are the same for anhydrite and gypsum once they are in solution, the heat of solution of gypsum should be unaffected by the presence or absence of calcium aluminate in the acid solution, to the extent that the interaction can be measured.

The heat effect of adding the 19 moles of water appearing in equation 1 (or 20 moles when the sulfoaluminate contains 32 moles of H_2O) was estimated as the partial molal heat content of water in 2*N* HCl [4], neglecting the contribution of the small amounts of other solutes present.

To determine the effect of the water content of the calcium sulfoaluminate, portions of sample *H* were dried by various means and their heats of solution determined. The drying methods used were: (a) Heating at 60 °C, 110 °C, 145 °C, and 200 °C; (b) drying over calcium chloride or sodium hydroxide; and (c) vacuum pumping with a dry-ice-acetone trap.

Results and Discussion

Heats of Solution of the Preparations

The heats of solution obtained on the sulfoaluminate samples are shown in table 1, as well as the heats of solution and water contents of the pure $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot nH_2O$ calculated from the chemical composition of the sample itself. The samples are listed in descending order of purity.

The heats of solution and water contents obtained on the dried portions of sample *H* are shown in table 3, together with similarly calculated heats of solution and water content of the pure $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot nH_2O$.

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[4] The estimates of standard deviation quoted in this paper represent the standard deviation of the average, using $n-1$ degrees of freedom.

TABLE 3. *Preparations of* $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 0\text{–}20H_2O$

(Dried preparations of sample H)

Sample Designation	H-1	H-2	H-3	H-4	H-5	H-6	H-7	H-8	H-9	H-10	H-11
Method of drying: Heated at (°C)						(a)	60°	110°			
Conditioned over	$CaCl_2$	NaOH	Suction								
Treatment time	34 days	34 days	2 days	3 days	7 days	8 days	13 days	1 hr.	2 hr.	13 days	35 days
Heat of solution, −ΔH, calories per gram	77.26	110.95	178.48	182.51	182.74	143.56	102.53	116.25	150.17	171.69	168.28
n = Molecules of H_2O per molecule $3CaO \cdot Al_2O_3 \cdot 3CaSO_4$	25.756	17.737	7.880	7.655	7.693	7.436	19.066	16.825	11.170	7.794	7.715
Heat of solution of $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot nH_2O$, −ΔH kcal. per mole	90.21_7	113.58_8	151.27_5	153.95_9	154.27_9	120.45_0	107.39_1	117.12_3	136.11_6	145.23_3	142.10_5
cal. per gram	78.95_5	113.79_6	184.34_9	188.55_3	188.78_6	142.10_5	105.06_8	119.30_1	154.70_2	177.32_7	173.80_5

Sample Designation	H-12	H-13	H-14	H-15	H-16	H-17	H-18	H-19	H-20	H-21	H-22
Method of drying: Heated at (°C)	145°							200°			
Treatment time	45 min.	45 min.	1 hr.	1 hr.	1 hr.	20 hr.	1 hr.	1½ hr.	2 hr.	5 days	13 days
Heat of solution, −ΔH, calories per gram	168.66	177.73	182.07	188.67	183.62	191.06	219.39	223.18	226.18	248.89	238.53
n = Molecules of H_2O per molecule $3CaO \cdot Al_2O_3 \cdot 3CaSO_4$	7.605	7.445	5.329	6.105	6.938	6.140	4.246	3.846	3.805	2.068	2.561
Heat of solution of $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot nH_2O$, −ΔH kcal. per mole	141.78_6	148.92_1	145.77_5	153.55_8	152.19_3	155.62_9	171.28_0	172.63_7	174.79_5	184.59_9	179.01_6
cal. per gram	173.83_7	183.23_1	187.99_0	194.72_0	189.38_5	197.18_9	226.82_5	230.82_5	233.94_3	257.86_3	247.00_1

[a] Temperature unknown.

TABLE 4. *Calorimeter calibrations*

Calibration	1	2	3
Date	March 1956	November 1956	April 1959
Heat capacity of calorimeter, calories per ohm	5857.4 5861.8 5860.9 5855.9 5856.4 5861.9	5851.47 5846.27 5852.77 5859.16 5856.46 5847.47 5842.17	5838.23 5842.17 5840.69 5839.07 5840.63 5838.56 5842.13
Average	5859.05	5850.82	5840.21
Standard deviation of the average	1.01	2.25	0.61
Samples determined	C, D, E, G, H, J, K, and H-1 to H-22	B $CaSO_4 \cdot 2H_2O$ $3CaO \cdot Al_2O_3 \cdot 6H_2O$	A, F

TABLE 5. *Reactants*

	$C_3A.6H_2O$	$CaSO_4.2H_2O$
Heat of solution, −ΔH calories per gram	371.33 370.40 369.33 368.18 369.54 370.13 369.86 370.33 368.44	−32.84 −33.24 −32.93 −32.28 −32.91 −33.53
Average	369.73	−32.955
Standard deviation of average	0.33	0.17
Analysis, wt. percent CaO	44.52	------------
Al_2O_3	26.93	------------
CO_2	0.11	------------
H_2O	27.88	21.08
$CaSO_4$	------------	78.92
Mole ratios, CaO/Al_2O_3	3.007	------------
CO_2/Al_2O_3	0.009	------------
H_2O/Al_2O_3	5.859	------------
$H_2O/CaSO_4$	------------	2.018
Mole ratios of compounds (to Al_2O_3):		
$3CaO \cdot Al_2O_3 \cdot 5.859H_2O$	1.000	------------
$CaCO_3$	0.007	------------
CO_2	.002	------------
Heat of solution of the reactant, −ΔH kcal. per mole	139.16_3±0.12	−5.685±0.03
cal. per gram	370.35_1±0.33	-32.95_5±0.17

In figure 1, the heats of solution of both series of samples are plotted against the water contents. The inset in figure 1 is an enlargement of the 30 to 33 H_2O portion of the main curve.

The heat capacities obtained in the calorimeter calibrations are listed in table 4.

The heats of solution of the reactants, $3CaO \cdot Al_2O_3 \cdot 5.859H_2O$ and $CaSO_4 \cdot 2.018H_2O$, are shown in table 5.

Correction for Impurities

The calculated water contents and heats of solution were obtained on the assumption that the impurities present were calcium hydroxide, calcite, gypsum ($CaSO_4 \cdot 2H_2O$), and hydrated alumina ($Al_2O_3 \cdot 3H_2O$). These assumptions are based on the equilibrium studies of Jones and of D'Ans and Eick [10, 11, 12] and the following additional observations.

The microscope showed small quantities of calcite in samples *A*, *B*, and *F*, roughly in proportion to the relative quantities calculated by chemical analysis. It was particularly noted that the visibility of the needles of calcium trisulfoaluminate under crossed Nicols was also roughly proportional to the $CaCO_3$ calculated from chemical analysis, and appeared to be caused by the entrapment of minute particles of calcite in the needle clusters or possibly by the growth of these clusters on the calcite grains. The strong calcite line at 3.035 A was observed in the X-ray patterns.

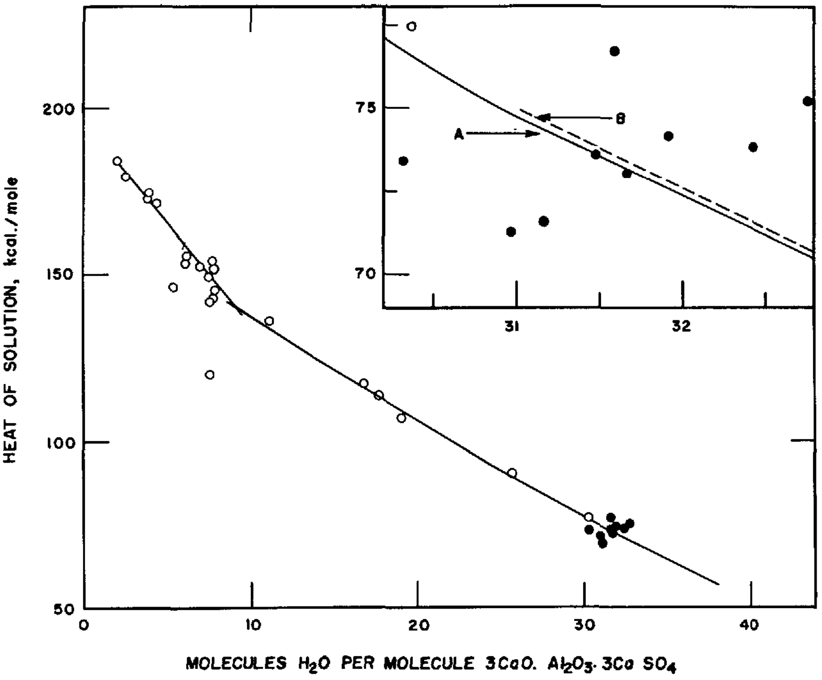

FIGURE 1. *Variation of the heat of solution of* $3CaO·Al_2O_3·3CaSO_4·nH_2O$ *with its water content,* n.

The inset is a representation of 30–33H_2O area on an expanded scale, with the same units as in the large figure.
● Closed circles represent all the preparations containing 30–33H_2O except sample H.
○ Open circles represent sample H and the dried samples obtained from sample H.

Although it could have been a possible sulfoaluminate line at 3.034 A, the deviation of this line in each pattern from 3.034 A was greater (or in the opposite direction from) the deviation of the rest of the observed pattern from the calculated lines. The presence of calcium monocarboaluminate, $3CaO·Al_2O_3·CaCO_3·11H_2O$, had been suspected, but the main lines of this compound (reported by Turriziani and Schippa at 7.74 and 3.79 A [16] and by one of the authors of this paper at 7.57 and 3.78 A [17]) were not stronger than the pattern background and no plates or edge views of the monocarboaluminate were visible in the microscope. Mixed samples of the trisulfoaluminate and the monocarboaluminate were prepared in which no tendency to form solid solution was observed, although the possibility of solid solution to a small extent is not precluded.

Although $Al_2O_3·3H_2O$ was not identified in the microscope except possibly as small, irregular, opaque particles, the X-ray line at 4.85 to 4.90 A in the various patterns was a poor fit with the rest of the sulfoaluminate pattern (as compared with the calculated pattern), and is considered to be a line of hydrated alumina [10]. In the heat-of-solution experiments, an opalescent undissolved residue was observed in those samples in which the analysis indicated free alumina, roughly proportional to the quantity calculated. The residue from one heat-of-solution determination of sample *F* was filtered and ignited, and found to be close to the weight expected from ignition of the quantity of $Al_2O_3·3H_2O$ calculated as an impurity in the sample.

The X-ray line at about 8.85 to 9.09 A in the three patterns could be attributed to the presence of calcium monosulfoaluminate, $3CaO·Al_2O_3·CaSO_4·12H_2O$, which has a strong line at 8.99 A [8]. It has been attributed instead to the 101 plane of the trisulfoaluminate, calculated as 8.86 A from Fratini's unit cell parameters. The strong line of the monosulfoaluminate at 4.48 A is absent from the patterns and the presence of this compound is doubtful.

In the two instances where the CO_2 content of the sample was insufficient to account for all the excess CaO (samples *B* and *D*), the latter was calculated to $Ca(OH)_2$. When excess SO_3 and CaO was present (samples *D*, *J*, and *K*), $CaSO_4·2H_2O$ was assumed to be present. Although no X-ray or optical evidence was found for these two compounds (their major X-ray lines conflict with those of the sulfoaluminate), both assumptions are in accordance with phase equilibrium data.

Carbon dioxide in excess of the quantity required to form $CaCO_3$ was taken as free CO_2. This assumption is discussed later in connection with speculation on the possible constitution of the sulfoaluminate hydrate.

The small quantity of SiO_2 in sample *B* (0.03 mole per mole Al_2O_3) is probably due to the long period of digestion of the precipitate and alkaline mother liquor in a glass container (9 mo). Some of the CaO in this sample, which has been attributed to $CaCO_3$ and $Ca(OH)_2$, may be present as a calcium silicate. Inasmuch as there are many possible compositions for calcium silicate hydrates, the correction in this case would be uncertain. A calculation based on the simple composition $CaO \cdot SiO_2 \cdot H_2O$ shows that the change in the corrected heat of solution would be small, only 0.09 calories per gram or 0.13 kilocalories per mole of sulfoaluminate.

It should be noted that the calculated standard deviation for the molar content of minor impurities is obtained from the standard deviation of the content of major oxides. For this reason, the calculated quantity of a minor constituent is on occasion less than its standard deviation.

The calculation of the composition of a sample and of the heat of solution of the pure sulfoaluminate present in a sample is shown in the appendix, with sample *A* as the example.

Heat of Solution of the Trisulfoaluminate

It is evident from table 1 and figures 1 and 2 that there is considerable scatter both in the heat of solution and in the water content of the various preparations, even after correction for the impurities. This scatter is evident in individual determinations on each sample as well. The following sources of scatter may be summarized:

(a) Variations in chemical composition and water content within each sample. This source was evident in the chemical analysis, particularly in SO_3 determinations.

(b) Variations in chemical composition between samples. The correction for impurities may be incomplete, particularly for interaction between impurities and for the effect of CO_2 in those samples which contained an appreciable quantity. Figure 2, in which the corrected heat of solution in calories per gram has been plotted against the weight percent purity, shows that even after correction there is a residual scatter which seems to decrease as 100 percent purity is approached.

(c) The small heat of solution of the compound, which produces a rise of only 0.1 °C in the calorimeter. Although the temperatures can be read to the nearest 0.00004 °C, the accumulation of experimental errors in the calculation of corrected temperature rise is capable of producing uncertainties of 0.5 percent for the 0.1 °C rise.

(d) A residual variation, even among samples low in impurities and especially low in CO_2, as in samples *A*, *B*, *D*, and *F*, which is difficult to explain.

Figure 1 indicates that, for one sample (*H*), the heat of solution decreases in a continuous manner with increase in the H_2O content in the 2 to $8H_2O$ range. There appears to be a discontinuity at about $8H_2O$ and then a continuous decrease in the 9 to $33H_2O$ range. The 7 to $9H_2O$ region is where most investigators postulate the appearance of a definite hydrate, the structure of which differs from that of the 30 to $33H_2O$ compound. Forsén's hydrate [7] is at $7.5H_2O$, obtained by drying over P_2O_5. Lefol's [5] is at 6.5 to $8H_2O$, depending on ambient water vapor pressure. With the electron microscope Astreeva and Lopatnikova [6] have observed the delayed change in structure with removal of water, but do not state the water content at which it occurs. Drying experiments made in this laboratory resulted in a drop in water content to about $20H_2O$ for 60 °C, $8H_2O$ for 110 °C, $6H_2O$ for 145 °C, 2 to $3.5H_2O$ for 200 °C, in general agreement with Lefol's data. The X-ray diffraction pattern for a sample containing $23.0H_2O$ was almost identical to the pattern for the $32H_2O$ sample except for an increase in the intensity of the line in the vicinity of 3.49 A. Patterns for samples at 11.3 and $8.3H_2O$ were different, however. The intense 9.8 A and 5.6 A lines had disappeared and new lines appeared at 7.7 A and 6.1 A. For samples containing 6.6 and $5.3H_2O$, the largest *d*-spacing dropped still farther to $7.4H_2O$. These results agree well with Lefol's concept of a definite hydrate at 6.5 to $8H_2O$ and also with his suggestion of an intermediate hydrate between 8 and $30H_2O$. Samples ignited to $0H_2O$ showed their most intense line at 3.5 A, probably indicating $CaSO_4$ (anhydrite), and included no lines above 5 A.

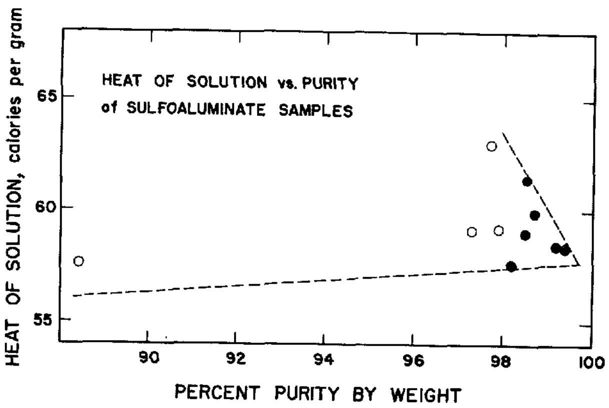

FIGURE 2. *Relationship between heat of solution of the preparations and purity.*

● Closed circles represent samples included in the average.
○ Open circles represent samples not included in the average.

The inset in figure 1, which is an expansion of the main part of the figure in the 30 to $33H_2O$ region, shows no readily apparent trend for the heat of solution versus nH_2O in that range. The scatter among the preparations, however, is probably responsible for this condition. From the main portion of the figure, the slope of the curve for sample *H* in the 31 to $33H_2O$ range is -2.49 kilocalories per mole per mole H_2O. Line *A* in the inset represents this slope and the position of the curve for sample *H* transferred to the expanded figure. It is reasonable to suppose that the slope for each preparation is the same as for sample *H*, but that the curve is displaced vertically in each case. For this reason, the average heat of solution and the average H_2O content of the preparations have been calculated, and from this pair of values a curve of heat of solution versus nH_2O has been drawn with the same slope as for sample *H*.

To eliminate a major source of error, only the results for the purest preparations have been included in the average. As already stated, there is still a residual dependence of the heat of solution on purity. The uncertainty of the CO_2 correction (see the calculation in the appendix) also made it desirable to include all the samples with low CO_2 content in the average. Two pairs of averages were calculated, one set for the four preparations low in CO_2 (samples *A*, *B*, *D*, and *F*), and one set which includes two additional samples of equally high purity by weight (samples *C* and *E*). The averages for the first set are 73.62 ± 1.13 kilocalories per mole and 31.66 moles H_2O; for the second set 73.59 ± 0.72 and 31.41. (For all ten samples, the averages are 73.86 ± 0.62 and 31.46.) The value $-\Delta H = 73.60$ kilocalories per mole at 31.54 moles H_2O was assigned to the sulfoaluminate, with a slope of -2.49 kilocalories per mole per mole change in H_2O content in the 31 to $33H_2O$ range. Line *B* in the inset of figure 1 represents this slope and average for the heat of solution versus nH_2O.

The heat of solution of $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$ is then $-\Delta H = 74.94$ kilocalories per mole, and the figure for $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ is 72.45 kilocalories per mole.

Heat of Formation of the Product From the Reactants

The heat of the reaction

$$3CaO \cdot Al_2O_3 \cdot 5.859H_2O + 3(CaSO_4 \cdot 2.018H_2O) + 19.087H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O \quad (2)$$

or

$$3CaO \cdot Al_2O_3 \cdot 5.859H_2O + 3(CaSO_4 \cdot 2.018H_2O) + 20.087H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \quad (3)$$

is calculated from the heats of solution of the reactants and product as follows:

For equation (2):

$$3CaO \cdot Al_2O_3 \cdot 5.859H_2O + 1438.666(HCl \cdot 26.614H_2O) \rightarrow 3CaCl_2 + 2AlCl_3 + 1426.666(HCl \cdot 26.846H_2O) \quad -\Delta H = +139.163 \text{ kilocalories} \quad (4)$$

$$3(CaSO_4 \cdot 2.018H_2O) + 1426.666(HCl \cdot 26.846H_2O) \rightarrow 3CaSO_4 + 1426.666(HCl \cdot 26.850412H_2O) \quad -\Delta H = -17.054 \text{ kilocalories} \quad (5)$$

$$3CaCl_2 + 2AlCl_3 + 3CaSO_4 + 1426.666(HCl \cdot 26.863791H_2O) \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O + 1438.666(HCl \cdot 26.614H_2O) \quad -\Delta H = -74.94 \text{ kilocalories} \quad (6)$$

$$1426.666(HCl \cdot 26.850412H_2O) + 19.087H_2O \rightarrow 1426.666(HCl \cdot 26.863791H_2O) \quad -\Delta H = +0.303 \text{ kilocalorie} \quad (7)$$

The heat of formation is the sum of the heat effects of eqs (4), (5), (6), and (7), or $-\Delta H = 47.472$ kilocalories per mole $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$.

By a similar calculation, the heat of formation in eq (3) is $-\Delta H = 49.978$ kilocalories per mole $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$.

Correction for the Water Content of the $3CaO \cdot Al_2O_3 \cdot 5.859H_2O$ and the $CaSO_4 \cdot 2.018H_2O$

These corrections are found by adding to the heat of reaction for eqs (2) or (3) the heat of the following reactions:

$$3CaO \cdot Al_2O_3 \cdot 6H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 5.859H_2O + 0.141H_2O \quad (8)$$

$$3(CaSO_4 \cdot 2H_2O) + 0.054H_2O \rightarrow 3(CaSO_4 \cdot 2.018H_2O). \quad (9)$$

These are very small corrections, approaching the precision of the measurements. The error in the heat of eq (8) will be small if the heat of the reaction is assumed to be 0.141/6.00 times the heat of hydration of anhydrous $3CaO \cdot Al_2O_3$ to the hexahydrate.

Thorvaldson, Brown, and Peaker [13] have reported the heat of this hydration to be $-\Delta H = 214$ calories per gram (or 57.8 kilocalories per mole) of $3CaO \cdot Al_2O_3$ at 20 °C. In the absence of data indicating a difference in the heat capacities of the hydrate and anhydrous $3CaO \cdot Al_2O_3$, the effect of transforming this value from 20 to 25 °C and from 20° calories to thermochemical calories may be considered negligible. The calculated correction is therefore $-57.8 \times 0.141/6.00$ or -1.36 kilocalories per mole $3CaO \cdot Al_2O_3$.

Assuming the analysis of the gypsum to be accurate, the correction for gypsum may be calculated from its heat of solution in water. The correction for eq (9) calculated on this basis is negligible, only -0.0009 kilocalorie.

If these corrections are applied, the heat of formation of $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$ from $3CaO \cdot Al_2O_3 \cdot 6H_2O$, $CaSO_4 \cdot 2H_2O$, and additional H_2O (eq 1) is $-\Delta H = 47.472 - 1.36$ or 46.11 kilocalories per mole. For $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$, the corrected value is 48.62 kilocalories per mole.

Heat of Formation

The heat of formation of the calcium sulfoaluminate is the sum of the heat effect of eq (1) and the heats of formation of the reactants in that equation [4], and is calculated as follows:

ΔH_f° $3CaO \cdot Al_2O_3 \cdot 6H_2O$ $= -1329.$[5] kilocalories
ΔH_f° $3(CaSO_4 \cdot 2H_2O)$ $= -1449.18$ kilocalories
ΔH_f° $19H_2O$ $= -1298.03$ kilocalories
ΔH $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$ from these reactants $= -46.11$ kilocalories

ΔH_f° $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$ $= -4122.$ kilocalories per mole.

By a similar calculation, the heat of formation of $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ is $\Delta H_f^\circ = -4193$ kilocalories per mole. The calculated uncertainty of each of these results, based on a standard deviation for the heat of solution of 0.72 kilocalorie per mole for the sulfoaluminate, 0.12 for the $3CaO \cdot Al_2O_3 \cdot 5.859H_2O$, and 0.09 for the $CaSO_4 \cdot 2.018H_2O$, is 0.74 kilocalorie per mole. This value does not include the uncertainty in the heat of formation of the reactants, which is certainly of the order of 1 kilocalorie per mole for the hydrated calcium aluminate, nor the uncertainties due to the chemical analyses.

Role of Carbon Dioxide

Several of the preparations contained more CO_2 by chemical analysis than that equivalent to the CaO available to form $CaCO_3$, unless a lower percentage of $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot nH_2O$ and large quantities of hydrated alumina and gypsum were assumed to be present. The oxide ratios, however, were in all cases close enough to the stoichiometric ratios for calcium trisulfoaluminate to make assumption of free CO_2 more reasonable. Microscopic examination generally indicated the preponderance of the sulfoaluminate needles.

The presence of more CO_2 in complex calcium compounds than can be accounted for as $CaCO_3$ is not unusual. Gaze and Robertson report the same observation in calcium silicate hydrate (tobermorite) [18] and express the opinion that CO_2 may enter the inter-layer spacings in the crystal structure. The variation in the water content of the trisulfoaluminate without change in structure as reported by different authors [5, 6, 7] and observed in this work shows that this structure can accommodate additional molecules. It is possible that CO_2 may play a role similar to that of H_2O. The related compound, $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$, shows some tendency for the sum of H_2O and free CO_2 to be constant, although such a tendency was not observed in these sulfoaluminate preparations.

If it is assumed that the free CO_2 found in the preparations is part of the molecule rather than an impurity, there is no change in the calculated heat of solution in terms of kilocalories per mole. There is a change, however, in the heat of solution in terms of calories per gram and in the relative purity of the preparations. The effect of purity on heat of solution in this instance is shown in figure 3. The heats of solution tend to congregate about the limiting lines of the diagram, instead of spreading more or less uniformly between them as in figure 2. If the six purest preparations in figure 3 (samples *C*,

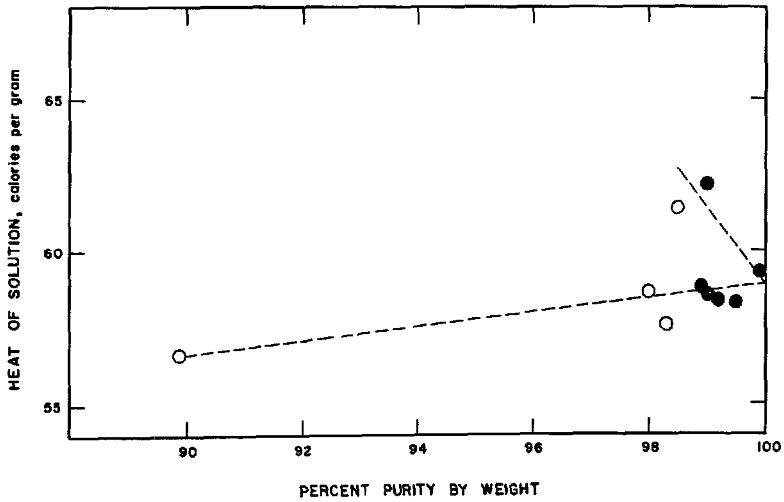

FIGURE 3. *The same plot as in figure 2, but with residual CO_2 included in the sulfoaluminate molecule.*

The samples, and their corresponding purities based on this calculation, are:

C—99.9%
A—99.5
B—99.2
G—99.0 (58.60 cal/g)
H—99.0 (62.23 cal/g)
E—98.9%
D—98.5
F—98.3
J—98.0
K—89.9

● Closed circles represent samples included in the average for this calculation.
○ Open circles represent samples not included in the average.

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[5] In accordance with established practice, exothermic heats of formation are negative. For convenience of tabulation, exothermic heats of solution and reaction were considered positive in the earlier portion of this paper.

A, *B*, *G*, *H*, and *E*, in descending order of purity) are used to calculate the average heat of solution, the result is 74.35 kilocalories per mole and 31.69 molecules of combined H_2O and CO_2. It is not certain whether these results or the arrangement of figure 3 are significant, but it appears that more investigation concerning the role of CO_2 in the complex calcium aluminate salts is desirable. Regardless of the effect of CO_2, however, the heat of solution of 73.60 kilocalories per mole for the 31.54 H_2O hydrate calculated above, as well as the heats of formation obtained from this value, should be considered more representative of the pure compound because it was obtained largely from compounds low in CO_2 content.

Appendix

Calculation of the Impurities, H_2O Content, and Heat of Solution of a Preparation of Calcium Trisulfoaluminate

Sample A

From the mole ratios of the oxides (table 1), the mole ratio of $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}nH_2O$ to Al_2O_3 is taken (in this case) as ⅓ the mole ratio SO_3/Al_2O_3, or 0.986, of which the equivalent CaO is 5.916 and the equivalent Al_2O_3 is 0.986. The excess CaO (5.957 − 5.916=0.041) is calculated to 0.041 mole $CaCO_3$, which accounts for 0.041 mole CO_2. The remaining CO_2 (0.017) is taken as free CO_2. The remaining Al_2O_3 (0.014) is assigned to $Al_2O_3{\cdot}3H_2O$. The H_2O in the $Al_2O_3{\cdot}3H_2O$ (0.042 mole) is subtracted from the total H_2O to obtain 31.213 moles H_2O per mole Al_2O_3 or 31.213/0.986=*n*=31.656 moles H_2O per mole $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4$.

The heat of solution of each impurity is multiplied by its weight per mole Al_2O_3, the total subtracted from the product of the heat of solution of the sample and the total weight of the sample per mole Al_2O_3. This result divided by the mole ratio of sulfoaluminate to Al_2O_3 is the heat of solution of the sulfoaluminate present in calories per mole; if this quotient is further divided by the formula weight of the sulfoaluminate, the heat of solution is obtained in calories per gram. Thus, for sample *A*:

0.986 mole $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31.656H_2O$ ×1248.93=1231.445 grams
0.041 mole $CaCO_3$ × 100.09= 4.104 grams
0.014 mole $Al_2O_3{\cdot}3H_2O$ × 156.01= 2.184 grams
0.017 mole CO_2 × 44.01= 0.748 gram

Total weight of sample per mole Al_2O_3 =1238.481 grams
Total heat of solution per mole Al_2O_3 = 58.289 cal/g×1238.481 =72,189.8 calories
Heat of solution of $CaCO_3$=4.104g× 83.72 cal/g = 343.6 calories
Heat of solution of $Al_2O_3{\cdot}3H_2O$ and of CO_2 = 0.0 calorie

Net heat of solution of sulfoaluminate per mole Al_2O_3 =71,846.2 calories
Net heat of solution per mole sulfoaluminate

$$=\frac{71{,}846.2}{0.986}=72{,}866 \text{ calories}$$

Heat of solution of the sulfoaluminate per gram

$$=\frac{71{,}846.2}{1231.445}=58.343 \text{ calories}$$

The heat of solution of the $Al_2O_3 \cdot 3H_2O$ was taken as zero because it did not go into solution. The physical and chemical state of the CO_2 is uncertain and no heat of solution is therefore included, but its weight is taken into account. If it escapes into the air, its heat contribution is minor; but if it dissolves, the contribution is about 57 calories per gram, a correction which, in the case of sample *A*, amounts to only 0.04 kilocalorie per mole and is within the precision limits of the heat-of-solution determination. The heat of solution of $Ca(OH)_2$ was taken from the work of Wells and Taylor [19], corrected for the fact that their figures were in calories per gram CaO. The value used for the heat of solution of $CaCO_3$ is the result of a recent redetermination of this quantity in this laboratory, to be reported more fully in a pending publication [20].

The authors acknowledge with thanks the help of Howard E. Swanson and coworkers, who made the X-ray diffraction measurements, and R. M. Senior, who performed much of the early calorimetric work and prepared the dehydrated samples.

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Paper III–S2. The Composition of Ettringite in Set Portland Cement*

H. G. Midgley and D. Rosaman

Synopsis

X-ray powder diffraction patterns and differential thermograms of synthetic calcium sulfo- and hydroxyaluminate hydrates of known chemical composition were recorded and compared with the X-ray spacings and peak temperatures of the "ettringite" phase in set portland cement.

Using the calibration curves for X-ray spacing and normalized peak temperature obtained from the synthetic compounds, the composition of the "ettringite" phase in setting portland cements has been determined.

For three cements it was found that the phase first precipitated was very near to the pure calcium sulfoaluminate hydrate composition, but as the cements were stored for longer periods the composition changed, the solid solution containing more of the calcium hydroxyaluminate hydrate.

Résumé

L'exposé présente des diagrammes de diffraction des rayons X à travers de la poudre et des thermogrammes différentiels d'hydrates synthétiques de sulfo- et hydroxy-aluminate de calcium de composition chimique connue. Ils sont ensuite comparés aux espacements des rayons X et aux températures des crochets des courbes pour la phase "ettringite" dans le ciment Portland pris.

La composition de la phase "ettringite" dans des ciments Portlands en train de prendre est déterminée par des courbes d'étalonnage pour l'espacement des rayons X et la température normalisée du crochet obtenue à partir des composés synthétiques.

On trouva que pour trois ciments la phase précipitée d'abord était très proche de la composition du sulfo-aluminate de calcium hydraté pur. Mais à mesure que les ciments étaient conservés pendant de plus longues périodes, la composition changeait et la solution solide contenait une plus forte proportion d'hydrate d'hydroxy-aluminate de calcium.

Zusammenfassung

Röntgendiagramme von Pulvern und Differentialthermogramme der synthetischen Kalzium-Sulfo- und Hydroxyaluminathydrate bekannter chemischer Zusammensetzung wurden aufgezeichnet und mit den Röntgenbeugungslinien und den Spitztemperaturen für die sogenannte Ettringitphase im abgebundenen Portlandzement verglichen.

Bei Anwendung der Eichkurven für die Röntgenbeugungslinien und der normalisierten Spitztemperaturen der synthetischen Verbindungen war man in der Lage, die Zusammensetzung der sogenannten Ettringitphase im abbindenden Portlandzement zu bestimmen.

In drei Zementen wurde gefunden, daß die zuerst präzipitierende Phase beinahe die Zusammensetzung des reinen Hydrats des Kalziumsulfoaluminats hat, daß aber, wenn die Zemente für längere Zeiten abgelagert wurden, die Zusammensetzung sich verändern würde, sodaß die feste Lösung mehr Hydrat des Kalziumhydroxylaluminat enthält.

Introduction

The mineral ettringite occurs in set portland cement as a result of the reaction between the hydrating calcium aluminates and the calcium sulfate. It was first observed by Candlot, and since it is formed in large quantities during the destructive attack of sulfate solutions on cement mortars and concretes it has been called the "cement bacillus." The usually accepted formula for ettringite is $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32H_2O$, although Kalousek [1][1] has suggested that there is a solid solution between $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot aq.$ and $3CaO\cdot Al_2O_3\cdot 3Ca(OH)_2\cdot aq.$ and a solid solution between the "low sulfate" sulfo-aluminate $3CaO\cdot Al_2O_3\cdot CaSO_4\cdot aq.$ and $3CaO\cdot Al_2O_3\cdot Ca(OH)_2\cdot aq\cdot$

Of these compounds $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot aq.$, $3CaO\cdot Al_2O_3\cdot CaSO_4\cdot aq.$, and $3CaO\cdot Al_2O_3\cdot Ca(OH)_2\cdot aq\cdot$ are well established. $3CaO\cdot Al_2O_3\cdot 3Ca(OH)_2\cdot aq.$ was first described by Flint and Wells, [2] who did not give any X-ray powder data but described it as having a pattern indistinguishable from that given by $3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot aq.$

It had been noticed by the present authors that the X-ray pattern given by the ettringite phase in set portland cement mortars and concretes had *d* values a little lower than those for the pure calcium sulfoaluminate hydrate, and also the temperature of the differential-thermal-analysis peak was higher than for the pure compound.

This paper is a report on the investigations undertaken to find an explanation for these differences.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Building Research Station, Department of Scientific and Industrial Research, Watford, England.

[1] Figures in brackets indicate the literature references at the end of this paper.

Methods

The two methods used in this investigation were X-ray powder diffraction and differential thermal analysis (DTA). The X-ray analyses were carried out with cylindrical Debye-Scherrer cameras, diameter 10 cm. or 11.4 cm.; the radiation used was Cobalt K alpha filtered with iron foil. The long spacing at about 9.7 A was found to be of most use.

The differential thermal analyses were carried out with ceramic crucibles, chromel-alumel thermocouples, alpha alumina as the inert substance, and a heating rate of 10±1 °C/min.

Thermograms for some of the compounds likely to be met with in this investigation are given in figure 1. The problem of specifying the temperature of the peak for each of the substances was solved in the following manner. Samples of the pure compounds were diluted with alpha-alumina, a known weight was placed in the DTA crucible and the analysis was carried out. From the thermograms it was discovered that for any one substance the following relationship between the peak area and the peak temperature existed; $T=a+b \ln A$, where T is peak temperature in °C, a and b are two arbitrary constants, and A is the area of the peak. This means that peak temperatures may be compared in relation to some arbitrary area; for this investigation 1,000 sq mm was used, and the corresponding temperature is called the normalized peak temperature. The results for the compounds met with in this investigation are given in figure 2, from which it may be seen that an unknown substance present in a mixture at an unknown concentration may be identified by finding on which of the curves it lies.

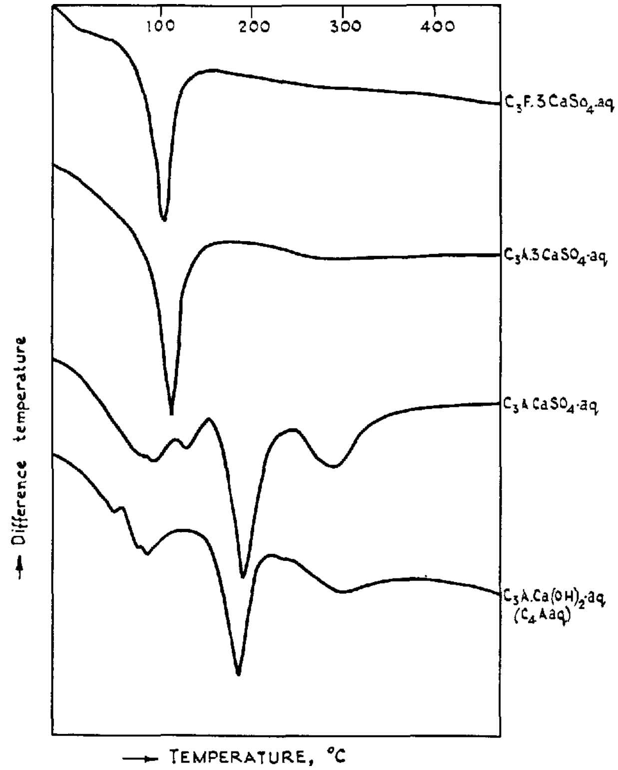

FIGURE 1. *Differential thermograms of pure calcium aluminate salt hydrates*

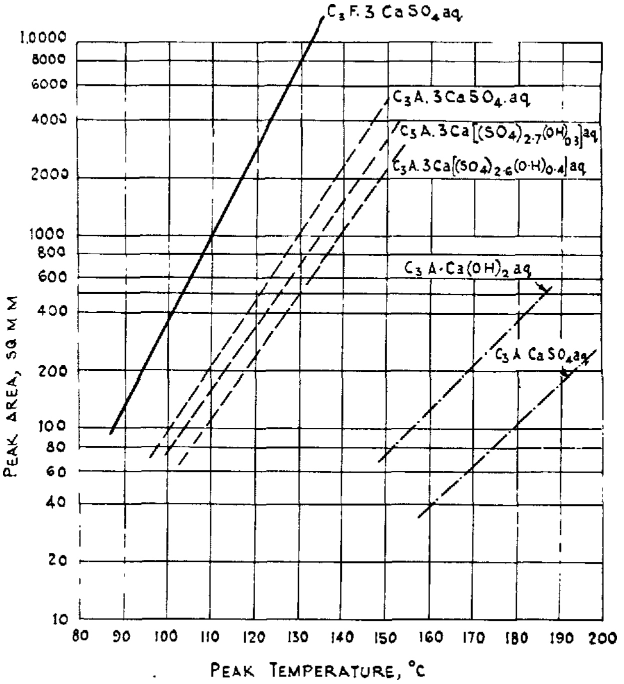

FIGURE 2. *Peak area and peak temperature for calcium sulfo- and hydroxyaluminate hydrates*

Portland Cements

TABLE 1. *Normalized peak temperature and d value of long spacing of ettringite phase in set portland cement cured at 18 °C in water*

Age	1 day	7 days	14 days	28 days	3 mo.	6 mo.
Normalized peak T °C	136	144	149	152	156	156
d A	9.75	9.75	9.73	9.67	9.65	9.63

A series of DTA and X-ray examinations of a set portland cement of different ages was carried out. From a series of DTA's of different dilutions, the set of curves given in figure 3 was obtained.

The normalized peak temperatures of ettringite for a series of set portland cements stored at 18 °C in water are given in table 1.

The normalized peak temperature of ettringite is shown to increase with age of storage. This change in peak temperature could be caused by two factors: by a change in the grain size of the ettringite crystals, or by a change in the composition of the ettringite phase. X-ray powder-diffraction analyses of the same cements gave the *d* values for the longest spacing as in table 1. This result would seem to support the view that there is a change in composition of the ettringite solid solution. It has not been possible to separate the ettringite phase from the cement, so analysis was impossible. An attempt was therefore made to discover the identity of the solid solution responsible for the change in the X-ray pattern. The compounds investigated included $C_3F{\cdot}3CaSO_4{\cdot}aq.$, $C_3A{\cdot}CaSO_4{\cdot}aq.$, and $C_4A{\cdot}aq.$ The normalized peak temperature (from figure 2) and the *d* values are given in table 2.

TABLE 2

Compound	Normalized peak temperature	*d*
	°*C*	*A*
$C_3F{\cdot}3CaSO_4{\cdot}32H_2O$	111	9.78
$C_3A{\cdot}CaSO_4{\cdot}12H_2O$	224	8.95
$\beta C_3A{\cdot}Ca(OH)_2{\cdot}12H_2O$	200	7.94

None of these compounds fitted the data given by the ettringite solid solutions in set portland cement.

Another possible compound is $C_6A{\cdot}aq.$ (or $C_3A{\cdot}3Ca(OH)_2{\cdot}aq.$) which may be regarded as ettringite having all its sulfate ions replaced by hydroxyl ions. This compound was first described by Flint and Wells [2] who said that its X-ray pattern was almost indistinguishable from that of ettringite, although they gave no detailed X-ray or DTA data.

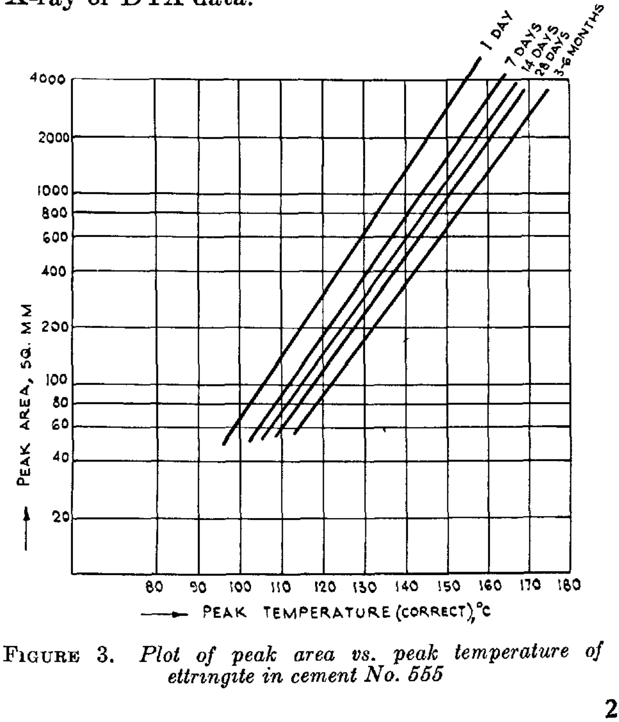

FIGURE 3. *Plot of peak area vs. peak temperature of ettringite in cement No. 555*

All attempts by the present authors to prepare this compound were unsuccessful.

Attempts were also made to prepare members of the solid solution $C_3A{\cdot}3CaSO_4{\cdot}aq.$-$C_3A{\cdot}3Ca(OH)_2{\cdot}aq.$ by preparing a lime-sugar solution containing 16.6 g CaO/l, adding 1.45 g and 0.38 g of gypsum respectively to two separate 450-ml portions and then adding 450 ml of calcium aluminate solution to each. The calcium aluminate solution was prepared by shaking 10 g of "Secar 250" white high-alumina cement with 1 liter of air-free distilled water for 24 hrs at 25 °C. The filtered solution gave the following analysis; 1.026 g CaO/l and 1.815 g Al_2O_3/l. After shaking the reactants in polyethylene bottles for 7 days, the white precipitate was filtered off and chemically analyzed. Differential thermograms and X-ray powder-diffraction patterns of each solid were recorded after the solids had been stored over saturated ammonium sulfate (R.H. 81 percent) for one week. The two compounds E and F produced the following data: (table 3).

TABLE 3

Component	Molar ratios		
	E	F	Ettringite (theoretical)
CaO	5.50	5.96	6.0
Al_2O_3	1.00	1.00	1.0
SO_3	2.58	2.72	3.0
X-ray diffraction, *d*A			
	9.70	9.75	9.75
Normalized peak temperature, °C			
	140	135	130

These results indicate that there is a solid solution, at least part of the way, between $C_3A{\cdot}3CaSO_4{\cdot}aq.$ and $C_3A{\cdot}3Ca(OH)_2{\cdot}aq.$

A relationship between the normalized peak temperatures and composition of these pure compounds can be obtained, figure 4. From this relationship the formula of a solid solution of unknown composition may be inferred from the differential thermogram. To check the validity of this assumption, the composition of six "ettringites" in a setting portland cements were obtained in this manner; the values of the long spacing on the X-ray diffraction pattern were also obtained. The results of change in X-ray *d* value and composition are given in figure 5 and are in reasonable agreement, indicating that the composition given by DTA cannot be very far out.

This method of obtaining the compositions of the "ettringite" phase in setting portland cement has been carried out on three cement types; a) normal 545, b) rapid hardening 549, and c) sulfate resisting 555. The results of this composition determination in relation to the age of the set cement are given in figure 6.

All samples show the same trend; the ettringite first produced is nearest to the pure sulfate end member, but with increasing time of hydration the ettringite phase becomes more substituted by hydroxy end member.

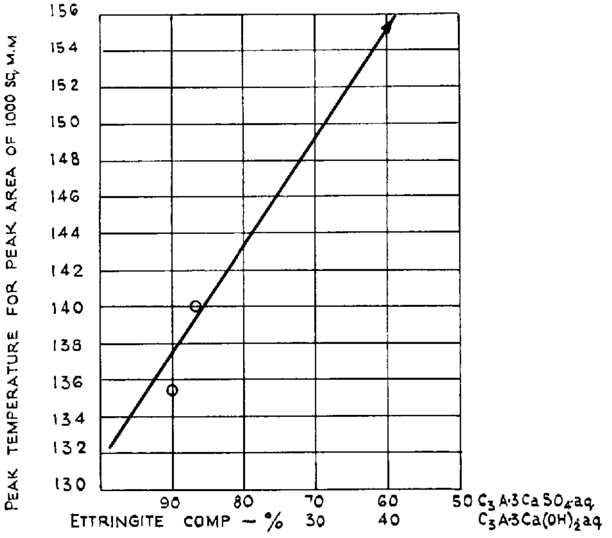

FIGURE 4. *Relationship between normalized peak temperature of endotherm and composition of ettringite solid solution.*

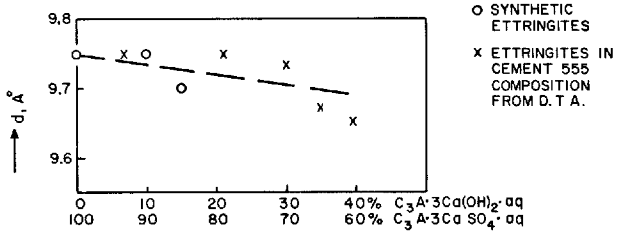

FIGURE 5. *Relation of d value for longest spacing of ettringite solid solutions to composition.*

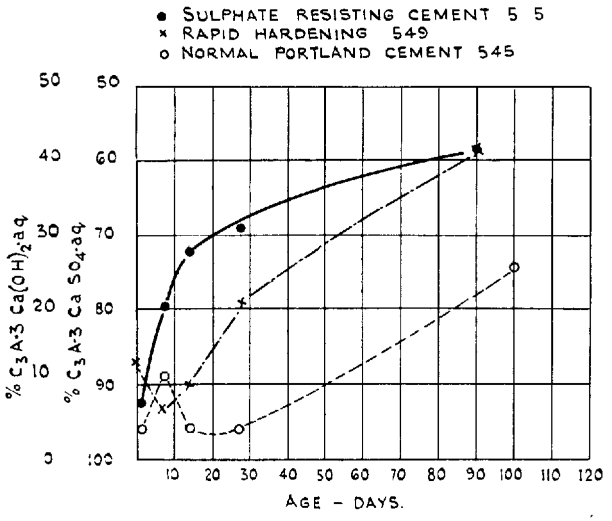

FIGURE 6. *Change in composition of ettringite composition with age of set portland cements.*

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Paper III–S3. The Temperature Coefficient of the Rate of Hydration of β-Dicalcium Silicate*

John H. Taplin

Synopsis

A synthetic preparation of β-C_2S was hydrated at 25 and 43 °C. Possible rate-determining processes are discussed by using the particle-size distribution and assuming spheres. It is found that, except for the initial part of the reaction, a rate-determining process involving the transport of material through the hydration products is more consistent with the observed kinetics than is a process at the β-C_2S surface. The apparent activation energy is 18 kcal/mole.

Résumé

On a procédé à l'hydration à 25 et 43 °C d'une préparation synthétique de β-C_2S. Discussion est faite des méthodes possibles pour déterminer la vitesse, au moyen de la distribution par dimensions des particules et en supposant qu'elles soient sphériques. Il en résulte que, exception faite pour la partie initiale de la réaction, une méthode de détermination de la vitesse impliquant le transport de matériaux à travers les produits d'hydration est plus logique par rapport à la cinétique observée que ne l'est une méthode à la surface de β-C_2S. L'activation apparente de l'énergie est de 18 kcal/mole.

Zusammenfassung

Ein synthetisch hergestelltes β-C_2S wurde bei 25 und bei 43 °C hydratisiert. Die Prozesse, die möglicherweise die Geschwindigkeit bestimmen, werden an Hand von Teilchengrößenbestimmungen besprochen, wobei es angenommen wird, daß die Teilchen kugelförmig sind. Es wurde gefunden, daß, mit Ausnahme des Reaktionsbeginnes, ein geschwindigkeits-bestimmender Prozeß, bei welchem ein Materialtransport durch die Hydratisierungsprodukte angenommen ist, den beobachteten kinetischen Verhältnissen besser entspricht, als ein Vorgang an der Oberfläche des β-C_2S. Die scheinbare Aktivierungsenergie ist 18 Kal/Mol.

Introduction

Brunauer and Greenberg [1][1] have discussed the temperature coefficient of the rate of hydration of C_3S and β-C_2S. The apparent activation energies of about 2 kcal/mole which they quote are much less than those obtained by us. This paper describes an experiment with a preparation of β-C_2S, which illustrates the evidence for higher temperature coefficients.

Experimental

Materials

The β-C_2S was prepared by repeated firing to 1400 °C of a stoichiometric mixture of calcium carbonate and precipitated silica, together with 0.5 percent of boric oxide. The preparation gave a negative result when tested for free lime by White's reagent. At least 95 percent of the preparation had a refractive index above 1.698.

The sand was an 18-to-25 B.S.S. mesh, washed-quartz sand from Leighton Buzzard, England.

Particle-Size Distribution

The β-C_2S was ground in a ball mill and then subjected to air elutriation and the coarse material removed. The remainder was used to make the specimens. The particle-size distribution of this material was determined microscopically using Feret's diameter [4] as the criteria of classification.

The particle-size distribution was determined in two stages. Particles less than 0.5 μ were neglected. In the first stage particles were classified into groups which had a range of 1.0 μ, starting from 0.5 μ. In this manner it was established that 1.1 percent of the material by weight had a diameter less than 2.5 μ. In the second stage particles were classified into groups with a range of 2.0 μ starting from 2.5 μ. The results of the two counts were combined, with the following result:

Mean diameter (μ)	1.5	3.5	5.5	7.5	9.5	11.5	13.5	15.5	17.5
Weight percent	1.1	8.3	17.8	20.9	12.7	13.2	8.5	13.0	4.6

The major uncertainty in this size distribution resides with the large particles. By scanning additional fields it was estimated that the 17.5 μ fraction was, if anything, overestimated.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Cement and Refractories Section, Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia.

[1] Figures in brackets indicate the literature references at the end of this paper.

Specimens

All specimens were right rectangular prisms having dimensions $4\times\frac{1}{2}\times\frac{1}{2}$ in., formed from 1:1 mortars of β-C_2S and sand. The specimens with a water/C_2S ratio of 0.27 were produced by tamping [2], and those with a water/C_2S ratio of 0.474 by casting in a steel mold.

The specimens were cured in individual stoppered tubes to which excess curing water was added as soon as the specimens started to harden. The specimens reached their curing temperature within an hour of mixing.

Strength

The compressive strength was measured by a method which has been described [3]. These strengths are quoted in units of force because the area stressed is uncertain although it is constant.

Hydration

The extent of the hydration reaction was estimated as follows. The larger fragments from the strength test were dried under vacuum and placed in a test tube. The mouth of the tube was drawn out to form a short capillary tube in order to minimize the rate of reabsorption of moisture on cooling. The tube and contents were heated to 120 °C for 22 hr and, after cooling and weighing, to 650 °C for several hours. The weight loss per gram of C_2S was corrected for the weight loss of the unhydrated C_2S (0.0059) and taken as a measure of the amount of C_2S hydrated. This measure is designated h/C. (It should not be confused with the similar but different measure, H/C, described in reference [3]).

Rate-Determining Processes

It is instructive to consider some of the possible rate-determining processes. The paste hydrations of C_3S and β-C_2S are heterogeneous reactions characterized by solid reactants which are particulate and by reaction products which form a cohesive network and occupy a greater volume than the clinker minerals. Those products which are inside or outside the original boundaries of the clinker mineral particles have been designated inner and outer products respectively [3]. The following three types of process may control the rate at some stage of the reaction: (a) the rate of transport of some substance through the inner products, (b) the rate of transport of some substance through the outer products, and (c) the rate of a reaction at the clinker-mineral surface. In each case it will be assumed that the concentrations in solution remain constant.

Resistance to Flow Through the Hydration Products

It is convenient to treat (a) and (b) type processes together for they are, perhaps, better regarded as extreme examples of a single type of process in which the rate is controlled by the rate of transport of clinker material outwards or of water inwards. In general, the specific resistance of the inner products will differ from that of the outer products, either because they are formed at different concentrations of the substance whose flow is rate-determining, or because only the inner products are formed on the clinker-mineral surface, which might influence their structure.

A mathematical treatment for an isolated spherical particle is indicated below.

r = the radius of the spherical particle.
F = the fraction of the particle reacted.
t = the curing time.
i = the specific resistance of the inner products.
o = the specific resistance of the outer products.
c = the concentration or pressure difference which drives the transport process.
η = the resistance.
ν = the ratio of the volume of the outer products to that of the inner products.

At the appropriate stages of the analysis the equations for type (a) and (b) processes will be obtained by introducing the conditions $i \gg o$ and $i \ll o$ respectively.

From the geometry of a sphere

thickness of inner products $= r[1-(1-F)^{1/3}]$

thickness of outer products $= r[(1+\nu F)^{1/3}-1]$

For a small amount of further reaction dF

increase in thickness of inner products $= r\,dF/3(1-F)^{2/3}$

increase in thickness of outer products $= \nu r\,dF/3(1+\nu F)^{2/3}$

the new layer of inner products has an area $4\pi r^2(1-F)^{2/3}$

the new layer of outer products has an area $4\pi r^2(1+\nu F)^{2/3}$.

The increase in resistance of the inner products due to the extra reaction dF is

$$d\eta_i = i r\,dF/3(1-F)^{2/3}\cdot 4\pi r^2(1-F)^{2/3}.$$

After simplifying and integrating from O to F

$$\eta_i = i[1-(1-F)^{1/3}]/4\pi r(1-F)^{1/3}$$

and similarly for the outer products

$$\eta_o = o[(1+\nu F)^{1/3}-1]/4\pi r(1+\nu F)^{1/3}.$$

The total resistance $\eta = \eta_i + \eta_o$.

The rate of reaction per unit original volume of particle is

$$dF/dt = 3c/\eta 4\pi r^3.$$

Now, the condition for process (a) amounts to $\eta \approx \eta_i$ so that for the rate controlled by the resistance of the inner products

$$dF/dt=3c(1-F)^{1/3}/ir^2\,[1-(1-F)^{1/3}] \qquad (1)$$

and similarly for the rate controlled by the resistance of the outer products

$$dF/dt=3c(1+\nu F)^{1/3}/or^2[(1+\nu F)^{1/3}-1]. \qquad (3)$$

Rearranging the full expression for dF/dt

$$(\eta_i+\eta_o)dF=3cdt/4\pi r^3$$

and after integrating (assuming $F=0$ when $t=0$)

$$i[1-(1-F)^{2/3}-2F/3]+(o/\nu)[1+2\nu F/3 \\ -(1+\nu F)^{2/3}]=2\,c\,t/r^2.$$

After again applying our conditions for processes (a) and (b) for the rate controlled by the resistance of the inner products

$$1-(1-F)^{2/3}-2F/3=2ct/ir^2 \qquad (2)$$

and for the rate controlled by the resistance of the outer products

$$1+2\nu F/3-(1+\nu F)^{2/3}=2\nu ct/or^2. \qquad (4)$$

If the particle is not isolated so that the outer products merge with the outer products of other particles, then the situation is more complicated. However, the resistance of the inner products is not affected, and provided the particles are not packed too closely the kinetics will not be very different from eq (4). For uniform spheres in cubical packing (octahedral coordination) it can be shown that, for $\nu=1$, the following relation holds approximately in place of eq (4)

$$F^2 \propto t/r^2.$$

This relation corresponds to behavior intermediate between eqs (2) and (4) and is in fact the relation applicable to a plane surface.

A Process at the Clinker Mineral Surface

If the rate depends on some process at the surface of the clinker mineral, so that the rate is proportional to the surface area, then the reaction will penetrate into particles at a constant rate.

For a sphere, if the penetration rate is K

$$dF/dt=3K(1-F)^{2/3}/r \qquad (5)$$

and

$$1-(1-F)^{2/3}=Kt/r. \qquad (6)$$

Because eqs (1) and (3) predict an infinite rate at $F=0$ we see that a surface reaction will be slower at the very beginning of the reaction and, because of the different dependence of the rate on the radius, it will remain as the slower process for a greater fraction of the reaction if the particles are smaller.

Results and Discussion

Figure 1 is a plot of compressive strength against h/C for the water/C_2S ratio of 0.27. It is assumed that essentially the same reaction occurs at 25 and 43 °C, because the hydration products develop the same strength.

Figure 2 shows the hypothetical reaction relations for the three rate-determining processes discussed above; i.e., the rate is limited by a process at the C_2S interface, by the flow of material through the inner products, or by the flow of material through the outer products. The curves are obtained by summing the contribution of each size fraction at a particular time. It is assumed that the particles are spheres with the experimental particle-size distribution. In applying eq(4) it is assumed that $V=1$.

The curve for the rate limited by a process at the interface will plot as a straight line in the form log $(1-F)$ against penetration distance (and consequently against time). Figure 3 is a plot of this kind. A straight line is obtained for the data at a water/C_2S ratio of 0.474 if h/C at complete hydration is assumed to be 0.20. This result can be interpreted as a penetration rate of 6×10^{-4} μ per hr at 25 °C. In order to obtain straight lines for the data at a water/C_2S ratio of 0.27, it is necessary to assume h/C at complete hydration is 0.17. However this rate-determining process cannot explain the influence of water/C_2S ratio.

The points in figure 2 corresponding to the rate limited by the flow of material through the outer products are close to the relationship, F^2 proportional to time. The hydration data are tested against this relationship in figure 4. A better fit is obtained by assuming an induction period of 250 hr at 25 °C. This assumption is reasonable in view of the very obvious induction periods obtained with other preparations of β-C_2S [1, 5]. Thus it appears likely that the flow of material through the hydration products does determine the rate, except at the beginning.

The apparent activation energy calculated from figure 3 or figure 4 is 18 kcal/mole. This is much greater than the 2 kcal/mole quoted by Brunauer and Greenberg [1] but more consistent with the value of 10 kcal/mole obtained by us [5] for portland cement paste. It may be significant that a value of about 10 kcal/mole is obtained by extrapolating the permeability activation energy data of Powers [6] to the porosity of cement gel (0.28).

Activation energies of above 10 kcal/mole have been obtained in this laboratory for two more preparations of β-C_2S. Two preparations of C_3S (alite composition) behaved in different ways. The temperature coefficient for the first preparation was initially very large but decreased as the reaction proceeded, eventually becoming negative. The second preparation gave a more constant temperature coefficient corresponding to an activation energy of about 10 kcal/mole.

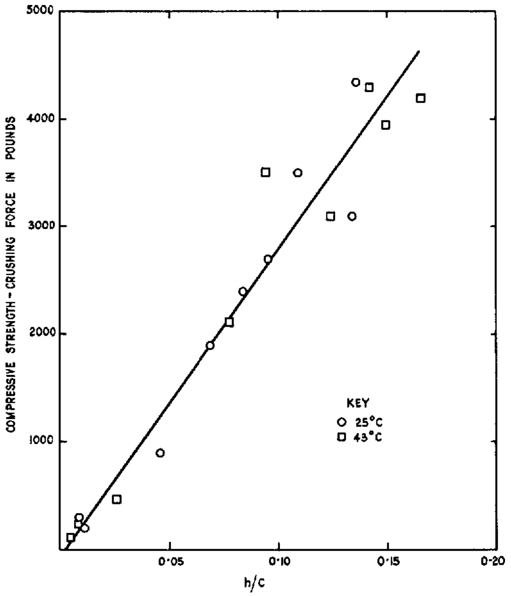

FIGURE 1. *Data for a water/C_2S ratio of 0.27 showing that the relationship between compressive strength and hydration is not affected by curing temperature.*

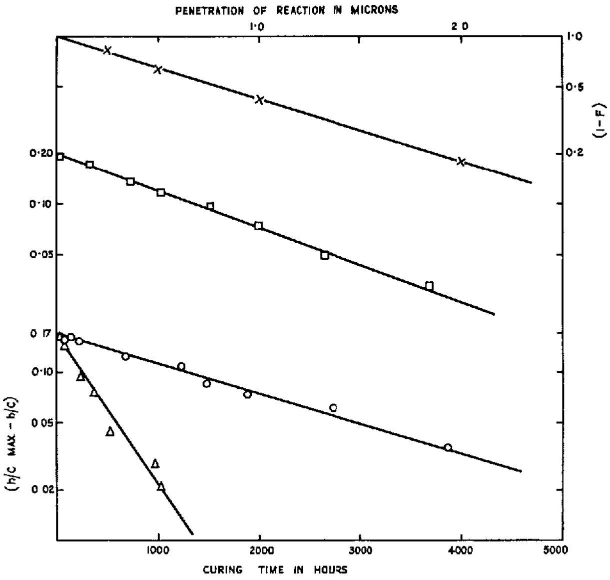

FIGURE 3. *Plots to test the empirical relation: log fraction not reacted, proportional to penetration distance, proportional to time.*

X=Fraction not reacted, calculated for the rate controlled by a process at the surface, assuming spherical particles with the observed size distribution.

□ Log (0.20 – h/C) versus curing time for water/C_2S = 0.474 and 25 °C
○ Log (0.17 – h/C) versus curing time for water/C_2S = 0.27 and 25 °C
△ Log (0.17 – h/C) versus curing time for water/C_2S = 0.27 and 25 °C

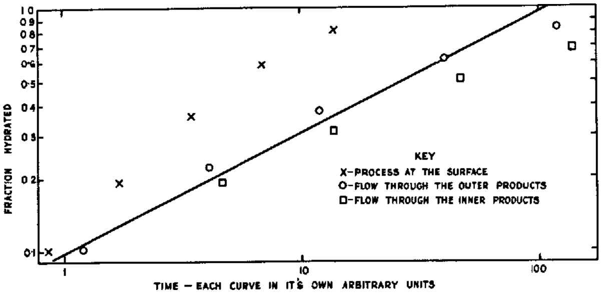

FIGURE 2. *A plot of log fraction reacted against log curing time.*

The fraction reacted is calculated for various hypothetical rate-controlling processes assuming spherical particles with the experimental size distribution. The straight line represents the relation: square of fraction reacted proportional to time.

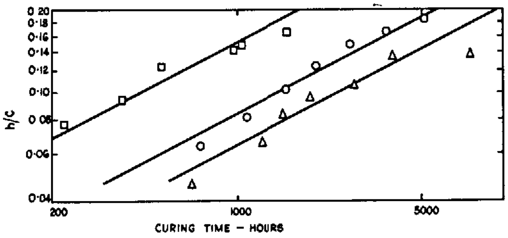

FIGURE 4. *The experimental data tested against the relation: square of the fraction reacted proportional to time, by plotting log h/C versus log time.*

△ Water/C_2S ratio of 0.474, 25 °C
○ Water/C_2S ratio of 0.27, 25 °C
□ Water/C_2S ratio of 0.27, 43 °C

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Paper III–S4. Hydraulic Properties and Hydration of Glasses of the System CaO-Al_2O_3-SiO_2*

F. W. Locher

Synopsis

In the ternary system CaO-Al_2O_3-SiO_2 some 45 glasses were melted with CaO contents between 36 and 52 percent, Al_2O_3 contents between 9 and 56 percent, and SiO_2 contents between 3 and 55 percent. Some of these glasses contained in addition 5 percent of MgO. The glasses, which had been ground to a uniform specific surface of 4000 cm^2/g, were activated with portland cement clinker (blast-furnace cement), with anhydrite (slag-sulfate cement) and with calcium hydroxide (lime-slag cement), and tested in the form of small mortar bars.

The hydraulic strengths rise with an increasing Al_2O_3 content, reach a maximum, fall sharply with a further increase in the Al_2O_3 content, and then rise again with a still higher Al_2O_3 content to a second maximum. Beyond this second maximum follows a second minimum and, in fields with less than 10 percent of SiO_2, the maximum alumina cement hardening.

The X-ray diffraction determinations of the hydrate phases showed that in glasses with medium Al_2O_3 contents gehlenite hydrate, $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 8H_2O$, occurs as a strength-forming hydrate phase. The three maxima of hydraulic strength occurring in the ternary system CaO-Al_2O_3-SiO_2 are caused, therefore, by the formation of calcium silicate hydrate in the field of high SiO_2 and lower Al_2O_3 contents, of calcium aluminate hydrate in the field with low SiO_2 and high Al_2O_3 contents, and of calcium silicoaluminate hydrate (gehlenite hydrate) in the field of medium SiO_2 and Al_2O_3 contents.

In the hardened cements gehlenite hydrate is not stable but is transformed while absorbing CaO into a hydrogarnet whose composition approximately conforms to the formula $3CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 4H_2O$. The MgO content promotes this transformation.

In the hardened glasses with Al_2O_3 contents of less than 18 percent the X-ray pattern revealed only very little gehlenite hydrate in addition to slight amounts of calcium aluminate hydrate. As the lime content of the glasses is not adequate to form aluminate hydrates rich in lime it must be assumed that, irrespective of the kind of activation, the Al_2O_3 content of the glasses poorer in alumina is also bound in the gehlenite hydrate and that the errors in the determinations by the X-ray diffraction method must be attributed to the poor lattice arrangement of the gehlenite hydrate. The assumption of the formation of gehlenite hydrate in the hardening glasses and technical slags tallies with the practical behavior of the slag-bearing cements towards sulfate solutions. It could be demonstrated that gehlenite hydrate is resistant to sodium sulfate and calcium sulfate solutions, but that it disintegrates in lime-rich sulfate solutions while forming ettringite. Gehlenite hydrate is also nonresistant to magnesium sulfate solutions.

According to the results of the investigations, the effect of the activators is to contribute to the formation of a liquid phase of favorable composition out of which the dissolved constituents of the slag can be precipitated again in the form of strength-forming hydrates of various kinds. Due to the precipitation of the hydrate phases, the solvent effect of the liquid phase is retained.

Résumé

Environ 45 verres du système ternaire CaO-Al_2O_3-SiO_2 furent fondus, les teneurs en CaO variant de 36% à 52%, les teneurs en Al_2O_3 variant de 9% à 56%, et les teneurs en SiO_2 variant de 3% à 55%. Certains de ces verres contenaient de plus 5% de MgO. Les verres, qui avaient été pulverisés en une surface specifique uniforme de 4000 cm_2/g, furent activés avec du clinker de ciment Portland (ciment de haut-fourneau), avec de l'anhydrite (ciment de laitier sulfaté) et avec de l'hydroxide de calcium (ciment de laitier à la chaux).

La résistance hydraulique s'elève avec une augmentation de la teneur en Al_2O_3, atteint un maximum, tombe brusquement avec une augmentation supplémentaire de la teneur en Al_2O_3, et puis s'élève de nouveau à un second maximum avec une teneur encore plus forte en Al_2O_3. Au delà de ce second maximum fait suite un second minimum et, quand on a moins de 10% de SiO_2, le durcissement maximum du ciment alumineux.

Les déterminations des phases d'hydrate par diffraction des rayons X indiquèrent que dans les verres avec une teneur moyenne en Al_2O_3 un hydrate de gehlenite, $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 8H_2O$, se produit sous forme de phase d'hydrate générative de résistance. Les trois maxima de résistance hydraulique qui se produisent dans le système ternaire CaO-Al_2O_3-SiO_2 sont donc causés par la formation d'hydrate de silicate de calcium quand on a une forte teneur en SiO_2 et une faible teneur en Al_2O_3, d'hydrate d'aluminate de calcium avec une faible teneur en SiO_2 et une forte teneur en Al_2O_3, et d'hydrate de silico-aluminate de calcium (hydrate de gehlénite) avec des teneurs moyennes en SiO_2 et en Al_2O_3.

Dans les ciments durcis, l'hydrate de gehlénite n'est pas stable mais se transforme, tandis qu'il absorbe CaO, en un hydrogrenat dont la composition répond approximativement à la formule $3CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 4H_2O$. La teneur en MgO contribue à cette transformation.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from Forschungsinstitut der Zementindustrie, Düsseldorf, Germany.

Dans les verres durcis à teneur en Al_2O_3 inférieure à 18% la diagramme aux rayons X ne révélait que très peu d'hydrate gehlénite en plus d'une légère quantité d'hydrate d'aluminate de calcium. Comme la teneur en chaux des verres n'est pas suffisante pour former des hydrates d'aluminate riches en chaux, il faut supposer que, indépendamment du genre d'activation, la teneur en Al_2O_3 des verres les plus pauvres en alumine est également trouvé dans l'hydrate de gehlénite et que les erreurs de détermination par la méthode de diffraction des rayons X doivent être attribuées a l'arrangement imparfait du réseau de l'hydrate de gehlénite. La supposition de la formation de l'hydrate de gehlénite dans les verres et laitiers techniques en train de durcir concorde avec le comportement pratique des ciments de laitier dans des solutions de sulfate. On pourrait démontrer que l'hydrate de gehlénite est résistant aux solutions de sulfate de sodium et de sulfate de calcium, mais qu'il se désintègre dans les solutions de sulfate riches en chaux, formant alors de l'ettringite. L'hydrate de gehlénite n'est pas résistant non plus aux solutions de sulfate de magnésium.

Suivant les résultats des expériences, l'effet des activateurs est de contribuer à la formation d'une phase liquide de composition favorable hors de laquelle les constituents dissous du laitier peuvent être précipités de nouveau sous forme d'hydrates de différentes sortes et générateurs de résistance. A cause de la précipitation des phases d'hydrate, l'effet dissolvant de la phase liquide est maintenu.

Zusammenfassung

Im Dreistoffsystem $CaO-Al_2O_3-SiO_2$ wurden etwa 45 Gläser erschmolzen mit CaO-Gehalten zwischen 36 und 52%, Al_2O_3-Gehalten zwischen 9 und 56% und SiO_2-Gehalten zwischen 3 und 55%. Einige dieser Gläser enthielten zusätzlich 5% MgO. Außerdem wurden 4 technische Hochofenschlacken in die Versuche einbezogen. Die auf eine einheitliche spez. Oberfläche von 4000 cm^2/g gemahlenen Gläser und Schlacken wurden angeregt mit Portlandzementklinker (Hochofenzement), mit Anhydrit (Sulfathüttenzement) und mit Calciumhydroxyd (Kalkschlackenzement). Die hydraulischen Festigkeiten steigen an mit zunehmendem Al_2O_3-Gehalt, erreichen ein Maximum, fallen mit weiter steigendem Al_2O_3-Gehalt schroff ab, um bei noch höheren Al_2O_3-Gehalten zu einem zweiten Maximum anzusteigen. Jenseits dieses zweiten Maximums folgt ein zweites Minimum und in Bereichen mit weniger als 10% SiO_2 das Maximum der Tonerdezementerhärtung.

Röntgenographische Bestimmungen der Hydratphasen zeigten, daß in Gläsern mit mittleren Al_2O_3-Gehalten Gehlenithydrat, $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 8H_2O$, als festigkeitsbildende Hydratphase entsteht. Die drei im Dreistoffsystem $CaO-Al_2O_3-SiO_2$ auftretenden Maxima der hydraulischen Festigkeit werden also hervorgerufen durch die Bildung von Calciumsilikathydrat im Bereich hoher SiO_2- und geringerer Al_2O_3-Gehalte, von Calciumaluminathydrat im Gebiet mit geringen SiO_2- und hohen Al_2O_3-Gehalten und von Calciumsilicoaluminathydrat (Gehlenithydrat) im Bereich mittlerer SiO_2- und Al_2O_3-Gehalte.

In den erhärteten Zementen ist Gehlenithydrat nicht beständig, sondern wandelt sich unter Aufnahme von CaO in einen Hydrogranat um, dessen Zusammensetzung ungefähr der Formel $3CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 4H_2O$ entspricht. Der MgO-Gehalt fördert diese Umwandlung.

In erhärteten Gläsern mit Al_2O_3-Gehalten unter 18% war röntgenographisch nur sehr wenig Gehlenithydrat neben geringen Mengen Calciumaluminathydrat nachzuweisen. Da zur Bildung kalkreicher Aluminathydrate der Kalkgehalt der Gläser nicht ausreicht, muß angenommen werden daß auch der Al_2O_3-Gehalt der tonerdeärmeren Gläser unabhängig von der Art der Anregung im Gehlenithydrat gebunden wird und daß die Fehler der röntgenographischen Bestimmung auf die schlechte Gitterordnung des Gehlenithydrats zurückzuführen sind. Die Annahme der Gehlenithydratbildung in den erhärtenden Gläsern und technischen Schlacken steht im Einklang mit dem praktischen Verhalten schlackenhaltiger Zemente gegenüber Sulfatlösungen. Es konnte gezeigt werden, daß Gehlenithydrat gegenüber Natriumsulfat- und Calciumsulfatlösungen beständig ist, daß es sich jedoch in kalkreichen Sulfatlösungen unter Ettringitbildung zersetzt. In Magnesiumsulfatlösungen ist Gehlenithydrat ebenfalls instabil.

Nach den Untersuchungsergebnissen wirken die Anregerstoffe in der Weise, daß sie zur Bildung einer günstig zusammengesetzten flüssigen Phasen beitragen, aus der die gelösten Bestandteile der Schlacken möglichst schnell in Form von erhärtungsfähigen Hydraten verschiedener Art wieder ausgeschieden werden können. Durch das Ausfällen der Hydratphasen bleibt die lösende Wirkung der flüssigen Phase erhalten.

Introduction

Simply composed glasses of the ternary system $CaO-Al_2O_3-SiO_2$ have often been used to find a connection between the chemical composition of blast-furnace slags and their hydraulic properties. Mention may here be made of the works of F. Keil and F. Gille [1], T. Tanaka, I. Sakai, and J. Yamane [2] and S. Solacolu [3][1]. As these investigations had been exclusively concerned with the hardenability of the glasses, it was now intended to establish the reactions which produce the hydraulic properties.

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[1] Figures in brackets indicate the literature references at the end of this paper.

Hydraulic Properties

Preparation of the Glasses

The glasses were melted in the manner indicated by W. Dyckerhoff [4] with an acetylene-oxygen flame from mixtures of reagent-grade basic substances, and the drops of the melt were quenched in water. The glass sand thus obtained was dried and ground to a specific surface of 4,000 cm^2/g.

Figure 1 shows the chemical composition of these 33 glasses in their position in the ternary system CaO-Al_2O_3-SiO_2. The melts are arranged in four series according to their CaO content, i.e., Series 10 with a CaO content of 52.5 percent, Series 10a with 50 percent of CaO, Series 20 with 44 percent of CaO, and Series 30 with 36 percent of CaO. Between these series lie a number of other glasses which were used only for the strength investigations. To investigate the influence of the magnesia content of the glass on the hydraulic properties, fifteen additional glasses, designated M in figure 1, were melted with an MgO content of 5 percent, the constituents CaO, Al_2O_3 and SiO_2 being proportionately reduced.

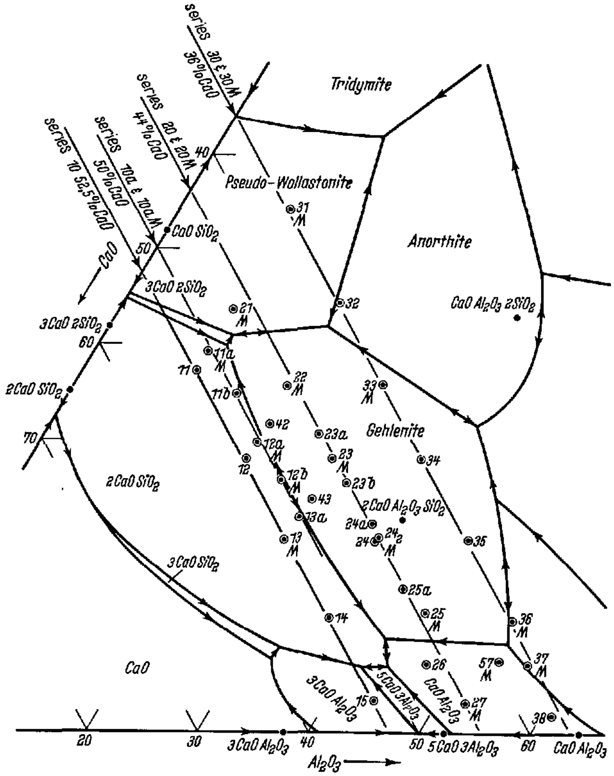


FIGURE 1. *Chemical compositions of the synthetic glasses presented in the ternary system CaO-Al_2O_3-SiO_2.*

Activation of the Glasses

The ground glasses were activated in three different ways:

1. with 18 percent of portland cement clinker and 5 percent of gypsum (blast-furnace-slag cement),
2. with 15 percent of anhydrite and 2 percent of portland cement clinker (slag-sulfate cement),
3. with 10 percent of $Ca(OH)_2$ (lime-slag cement).

Hydraulic Properties

The properties were tested by the small-scale testing method described by F. Keil and F. Gille [5] on small mortar bars (1×1×6 cm). The findings of these investigations have already been published [6].

Figure 2 shows the results of the strength tests of the glasses activated with clinker, in the form of lines of similar compressive strength. It is seen that between the area of the silicatic hardening of blast-furnace cement with SiO_2 contents of about 30 percent and the area of the aluminatic hardening of glasses poor in silica, there lies a third area of high strength with SiO_2 contents of about 20 percent and Al_2O_3 contents of about 37 percent.

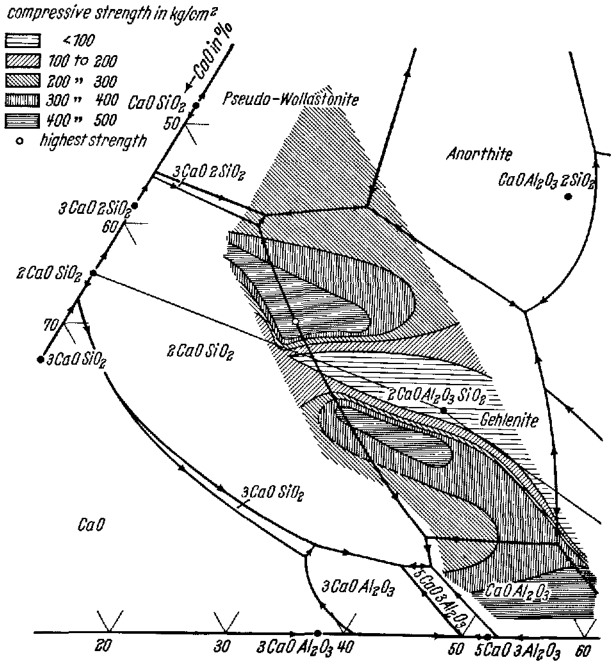


FIGURE 2. *28-day values of the compressive strengths of glasses of the ternary system CaO-Al_2O_3-SiO_2, activated with portland cement clinker.*

Figure 3 represents the strength behavior of all the glasses with 44 percent of CaO, i.e., without MgO, at the top, and with an MgO content of 5 percent below. In the top part of the figure the curve clearly shows the three high-strength areas and the very poor hardenability of glasses 23, 23b and 24a with about 27 to 34 percent of Al_2O_3. It can also be recognized that these glasses show considerably higher strengths where activation is accomplished with $Ca(OH)_2$ than with clinker

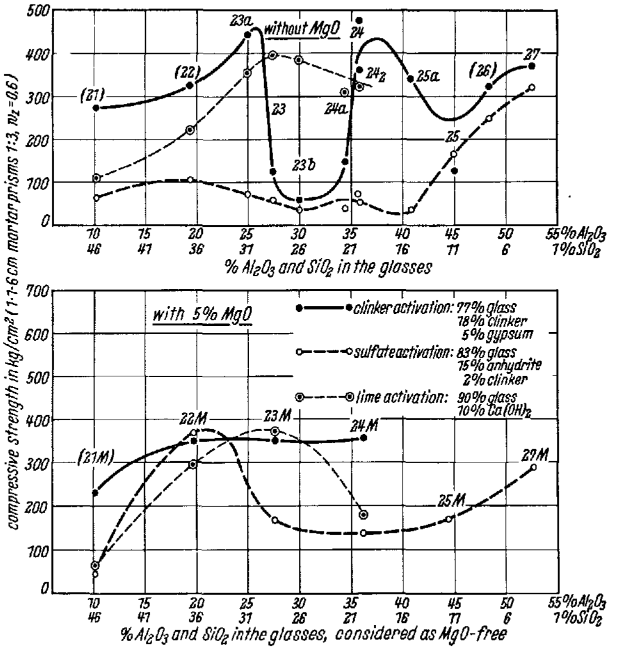


FIGURE 3. *Compressive strengths of the glasses with 44 percent of CaO after 28 days' curing in water, with clinker, sulfate, and $Ca(OH)_2$ activation.*

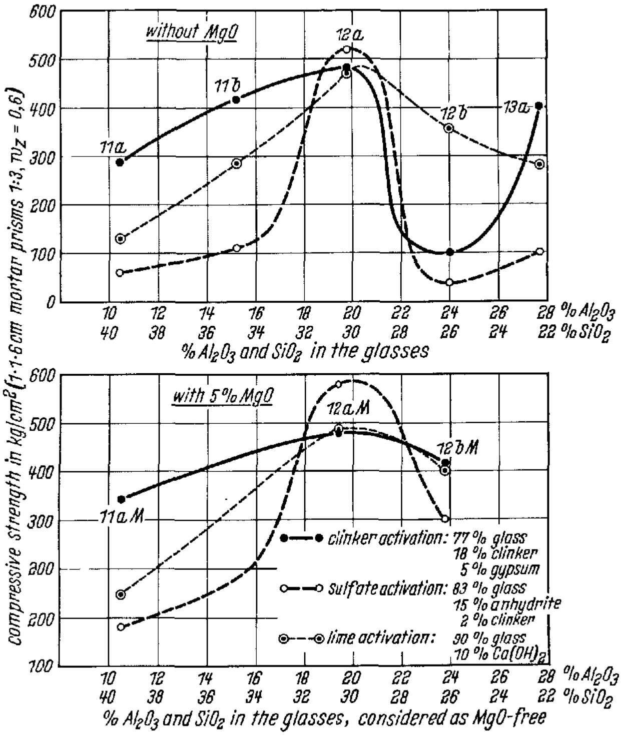


FIGURE 4. *Compressive strengths of the glasses with 50 percent of CaO after 28 days' curing in water, with clinker, sulfate, and $Ca(OH)_2$ activation.*

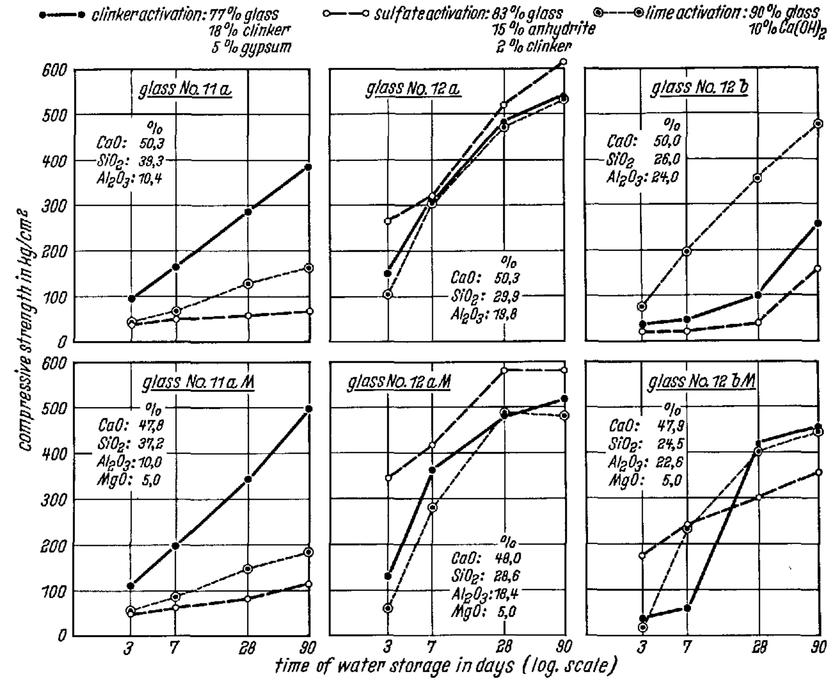


FIGURE 5. *Development of the compressive strength of glasses with 50 percent of CaO with clinker, sulfate, and $Ca(OH)_2$ activation.*

activation. Similarly favorable effects in this area are obtained with an MgO content of 5 percent. With sulfate activation these glasses, comparatively poor in lime, i.e., with 44 percent of CaO, achieve only low strengths. An MgO content of 5 percent improves the hydraulic properties, particularly in glass 22M.

Figure 4 indicates the strengths of the glasses with 50 percent of CaO. One recognizes the very high strengths of glass 12a with 20 percent of Al_2O_3 and 30 percent of SiO_2 and the low strengths of glass 12b with 24 percent of Al_2O_3 and 26 percent of SiO_2. As in the case of the glasses with poor hardenability, 23, 23b, and 24a with 44 percent of CaO, the hydraulic properties are also improved in glass 12b when it is activated with $Ca(OH)_2$, or when the glass contains 5 percent of MgO. In the lime-rich glasses with 50 percent of CaO, sulfate activation also produces very high strengths.

It is seen from the strength development (fig. 5) that glass 12b from the field of low strengths also possesses hydraulic properties, but that it hardens only very slowly when activated with clinker, while activation with $Ca(OH)_2$ results in rapid hardening and produces very high strengths. Furthermore, the figure reveals that the strength development of this glass is greatly accelerated by an MgO content of 5 percent.

The results of the present investigations indicated a "most favorable" glass composition for all kinds of activation of 50 percent of CaO, 31 percent of SiO_2, and 19 percent of Al_2O_3. Similar results have already been published by T. Tanaka, I. Sakai, and J. Yamane [2].

Possible Explanations of the Hardening Behavior

The strength investigations revealed that in certain areas of the chemical composition there are abrupt changes in the hydraulic properties of the glasses. In order to clarify the causes of this behavior, the investigation started from the following conceptions of hydraulic hardening: The capacity of certain compounds to harden hydraulically presupposes that these compounds react with water or with hydrous solutions and form strength-giving hydrates. Here it is essential that the anhydrous compounds dissolve and that the hydrates separate again out of this solution.

Assuming such a reaction there are the following two possibilities of explaining the afore-mentioned abrupt changes of the hydraulic properties. Either the dissolution behavior of the glass changes erratically or erratic changes will be established in the formation of the hydrate phases. These two possibilities were investigated.

Behavior of the Glasses in Basic Ammonium Citrate Solution

To investigate the dissolution behavior, a number of glasses with particularly good and with very poor hydraulic properties were agitated in a ten-percent basic ammonium citrate solution according to the method described by F. Keil and F. Gille [7]. At fixed intervals they were filtered, and CaO, Al_2O_3 and SiO_2 were determined in the filtrate. The residue was suspended in a fresh solution and agitated again. The investigations showed that the solubility of the glasses changes continuously and not erratically if SiO_2 is replaced by Al_2O_3. Consequently, there is no connection between the behavior of the glasses in ammonium citrate solutions and their hydraulic properties.

Formation of the Hydrate Phases

Investigations

It followed, therefore, that the explanation for the hydraulic behavior of the glasses was to be found in the formation of the hydrate phases. For this reason it was necessary to determine the hydrate phases in hardened neat mixtures of glass and activators by the X-ray diffraction method. The neat mixtures hardened both in pastes ($W/C=0.4$) and also suspended in calcium hydroxide solutions, and these suspensions contained 10 g of the glass-activator mixture in 150 ml $Ca(OH)_2$ solution. The phases present in the hydrated mixtures were first qualitatively determined. No calcium silicate hydrate could be found. Only the X-ray lines of ettringite were revealed, which was formed from the gypsum added in clinker activation, and the lines of tetracalcium aluminate hydrate, gehlenite hydrate, hydrogarnet, and calcium hydroxide. Ettringite and gehlenite hydrate were then determined quantitatively by the X-ray diffraction method, with fluorspar as an internal standard. In the same way the portion of the activators which had not yet taken part in the reactions was also determined.

Results of the X-ray Diffraction Investigations

The patterns of the X-ray determinations showed that with activation with clinker and calcium hydroxide first of all tetracalcium aluminate hydrate occurs, and that it is formed in greater amounts when activation is with calcium hydroxide than with clinker activation. It apparently occurs predominantly in the glasses rich in lime and poor in alumina.

Gehlenite hydrate ($2CaO{\cdot}Al_2O_3{\cdot}SiO_2{\cdot}nH_2O$) forms primarily in the alumina-rich glasses whose chemical composition approaches that of gehlenite. The quantitative determinations showed that in the glasses containing MgO, considerably less gehlenite hydrate was formed than in the MgO-free glasses.

Hydrogarnet could be ascertained mainly in the glasses which also contained a large amount of gehlenite. The hydrogarnets which occurred in the hydration of these iron-free glasses are phases from the solid-solution series

$$3CaO{\cdot}Al_2O_3{\cdot}6H_2O \text{———} 3CaO{\cdot}Al_2O_3{\cdot}3SiO_2$$

$$Ca_3Al_2(H_{12}O_{12}) \text{———} Ca_3Al_2(Si_3O_{12}).$$

In such solid-solution series, the interatomic distances in the crystal lattice change continuously with the chemical composition, and these can be measured by the X-ray diffraction method. The connection between the lattice spaces and the SiO_2 content of hydrogarnet was determined by H. zur Strassen [8]. For the hydrogarnet occurring here, a chemical composition was determined corresponding to the formula: $3CaO{\cdot}Al_2O_3{\cdot}SiO_2{\cdot}4H_2O$. A comparison with the formula of gehlenite hydrate, $2CaO{\cdot}Al_2O_3{\cdot}SiO_2{\cdot}8H_2O$ shows that the two formulas only differ in the CaO content, if the water content is disregarded. It might be assumed, therefore, that the hydrogarnet was formed from the gehlenite hydrate while absorbing CaO, that is to say, that in the presence of CaO gehlenite hydrate is not stable. A similar result was obtained by the investigations of H. zur Strassen [8] who showed that when shaken in saturated calcium hydroxide solution gehlenite hydrate disappears and hydrogarnet occurs.

The Silicoaluminatic Hardening

In order to be able to assess the content of hydrogarnet, various mixtures were prepared from gehlenite hydrate and a hydrogarnet which contained 1 mole SiO_2 per formula unit. Figure 6 shows the hydrogarnet lines in the mixtures in comparison with the same lines in the hardened test specimens. It is seen that the glasses 24 and 24M, activated with calcium hydroxide, contain about 60 and 80 percent respectively of hydrogarnet after 90 days hydration. The X-ray diffraction determination of the gehlenite hydrate content for these two glasses gives values of 21 and 5 percent (glass 24M); that is to say, both samples consist of more than 80 percent of gehlenite hydrate or a hydrogarnet which was a secondary formation from gehlenite hydrate. As these two phases contain all the available SiO_2, the hydraulic strength cannot be attributed in this case to the formation of calcium silicate hydrate. In these glasses, therefore, gehlenite hydrate is the strength-forming phase.

This result of the investigation leads to the following conclusion: The results of the strength investigations, as presented in figure 2, reveal three fields of high compressive strength. We know that in the glasses that contain a large amount of silica and little alumina the hydraulic hardening is due to the formation of the calcium silicate hydrate. It is also known that in the field of alumina cement the hardening is due to the formation of calcium aluminate hydrates poor in lime.

The present investigations now show that the high strengths obtained by the glasses with medium contents of silica and alumina were caused by gehlenite hydrate. Between the areas of the "silicatic" and the "aluminatic" hardening, therefore, lies the field of the "silicoaluminatic" hardening. Gehlenite hydrate is not stable in the presence of calcium hydroxide, but changes into hydrogarnet while absorbing lime. It may be assumed that the strength of the hardened cement is reduced by this transformation. This change probably accounts for the decrease in strength which can be observed particularly clearly for glass 24M, i.e., for the glass in which an extremely high content of hydrogarnet was determined.

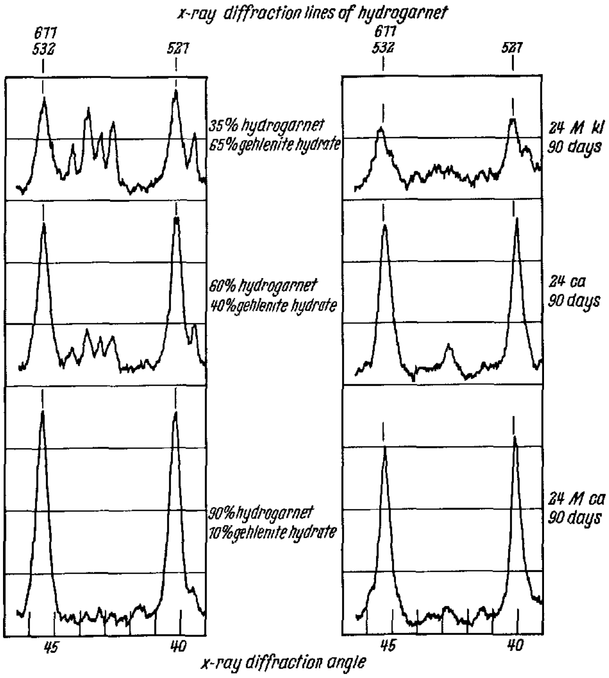


FIGURE 6. *Hydrogarnet lines in the X-ray diagrams of a number of hydrated samples and in mixtures of gehlenite hydrate and hydrogarnet of the composition $3CaO{\cdot}Al_2O_3{\cdot}SiO_2{\cdot}4H_2O$.*

Sample 24Mca with 5 percent of MgO contains less gehlenite hydrate and more hydrogarnet than the MgO-free sample 24ca with an otherwise similar chemical composition.

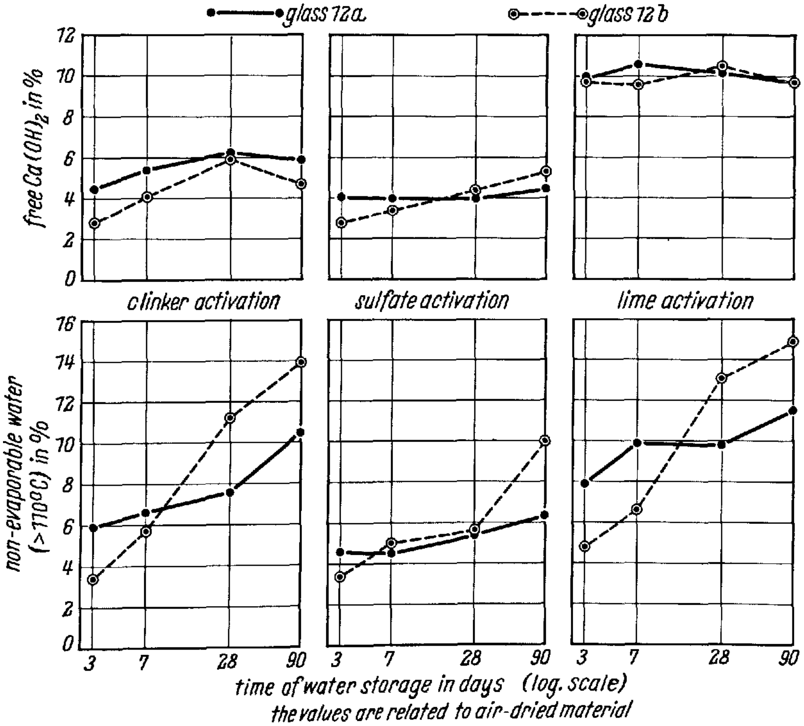
The Aluminate Phase in the Hardened Glasses Poorer in Alumina

In the paste hardening of the glasses poorer in alumina, gehlenite hydrate occurs only in very small amounts, up to about 3 percent. With clinker activation it could be found only after 28 days, while with anhydrite activation it was not found at all. If the mixtures of glass and activators was hydrated in suspension, that is to say, with a high excess of water, gehlenite hydrate was formed in every case, also with sulfate activation. For this reason it is assumed that in the hydration of the glasses poorer in alumina the major portion of the alumina is also bound in the gehlenite hydrate, though the latter crystallizes so badly that it can only be established in small amounts in the X-ray pattern.

This assumption is supported by the following finding: The content of free calcium hydroxide, which was determined in the hardened glasses and slags after curing in water for 3, 7, 28, and 90 days, changes only slightly with progressive hydration. Thus the diagrams in figure 7, for instance, show that in the hardened glasses 12a with the maximum strengths and 12b with very poor hydraulic properties the content of free calcium hydroxide remains approximately the same, while the content of nonevaporable water (water that escapes above 110 °C) increases, that is to say, hydration progresses. Figure 7 shows furthermore that with lime activation the content of free calcium hydroxide varies only slightly around 10 percent. As 10 percent of calcium hydroxide was added to the anhydrous glass, there has been no decrease in the content of free calcium hydroxide.

These investigations show that in the hardening of the glasses the lime of the activator is not used to form the hydrate phases. In all hydrate phases, therefore, only so much lime can be bound as was available in the glass alone. Glass 12a, which yielded the maximum strengths, contains 1.8 mole CaO per mole of SiO_2. In the calcium silicate hydrate phase which is formed with the hydration of these silica-rich glasses, the molecular ratio CaO/SiO_2 is very probably about 1.5. Only a very small amount of lime, therefore, would be available for the binding of the alumina. It might be assumed, therefore, that part of the silica is bound not only to lime but, together with alumina and lime, forms gehlenite hydrate. These considerations are valid both for activation with clinker and also for lime and anhydrite activation.

It may be reckoned that part of the alumina is taken up into the calcium silicate hydrate phase, in the form of mixed-layer crystal structures of calcium silicate and gehlenite hydrate layers. Similar mixed-layer crystal structures are possessed by numerous clay minerals. The absence of X-ray lines of aluminate hydrate phases might be explained in this way.



the values are related to air-dried material

FIGURE 7. *Content of free $Ca(OH)_2$ and of non-evaporable water in the hardened glasses 12a and 12b with clinker, anhydrite, and lime activation.*

The Behavior of Gehlenite Hydrate in Sulfate-Bearing Solutions

According to investigations carried out by G. Malquori and V. Cirilli [9, 10], gehlenite hydrate is not stable in lime-saturated gypsum solutions and forms ettringite. This finding was confirmed by H. zur Strassen [8]. If it is assumed that gehlenite hydrate occurs in major amounts not only in the hydration of the glasses used here but also in the hardening of slag-bearing cements, these cements must be expected to have only a very low resistance to sulfate. However, as the practical behavior reveals just the opposite, it might be concluded that no gehlenite hydrate is formed in these cements. As G. Malquori and V. Cirilli investigated the behavior of gehlenite hydrate only in a lime-saturated gypsum solution, similar experiments were made with a saturated gypsum solution, a solution saturated with calcium hydroxide and gypsum, a 0.15-molar Na_2SO_4 solution, and a 0.15-molar $MgSO_4$ solution, 3g of gehlenite hydrate being agitated for 4 weeks in 1 liter of solution.

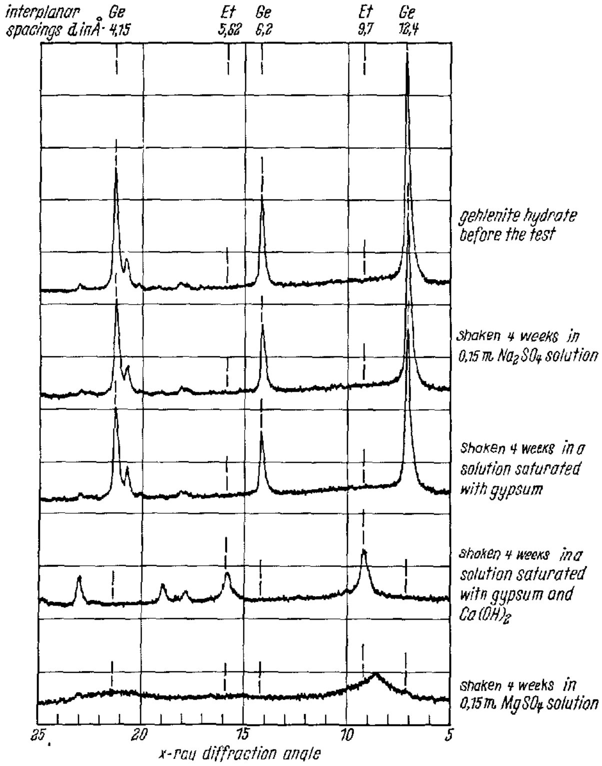


FIGURE 8. *Sections from the X-ray diagrams of an untreated gehlenite hydrate sample and of gehlenite hydrate samples which were agitated for 4 weeks in* Na_2SO_4 *solution, saturated gypsum solution, lime-saturated gypsum solution, and* $MgSO_4$ *solution.*

The X-ray pattern of the investigation (fig. 8) revealed that the gehlenite hydrate was transformed into ettringite in the solution saturated with gypsum and calcium hydroxide and disintegrated in the $MgSO_4$ solution, but that it was stable in the gypsum solution and in the Na_2SO_4 solution. Applying this information to practical conditions, one would arrive at the following conclusions: If gehlenite hydrate is the sole aluminate phase in the hardened blast-furnace cements, these cements are stable in sulfate solutions if the solutions are poor in lime and free from $MgSO_4$ and if the hardened cement contains little free calcium hydroxide. Furthermore, it follows that the resistance of the blast-furnace cement to sulfate is influenced very largely by the amount of the clinker content and only to a secondary degree by the Al_2O_3 content of the slag.

The Progress of Reaction in the Hardening of the Glasses

Activation of the Glasses

The high strengths in three different fields of the ternary system CaO-Al_2O_3-SiO_2 were attributed to the formation of calcium silicate hydrate, gehlenite hydrate, and calcium aluminate hydrate. In these fields the afore-mentioned phases were primarily formed during hydration. The probable explanation is that in the field between the "silicatic" and the "silicoaluminatic" hardening, neither the calcium silicate hydrate nor the gehlenite hydrate can form rapidly and that the glass therefore hydrates slowly.

The effect of the activators can be similarly explained. Glasses and slags alone do not hydrate and harden, or if at all, only slowly, that is to say, they do produce a solution, in which, however, strength-forming hydrate phases cannot form quickly enough. By the addition of an activator the chemical composition of the solution is so changed that the substances dissolved out of the slag can rapidly form strength-producing hydrate phases.

The Progress of Hardening of Slag-Containing Binding Agents

The following pattern emerges for the progress of the hardening: The reactions of cement hardening proceed in a system that contains a large amount of cement and very little water. The water, in which parts of the cement are dissolved, coats all the particles of the system, that is to say, also the yet unhydrated particles of the cement, with a very thin liquid film, the so-called intergranular film. Hydration reactions of the yet unhydrated cement and the formation of the hydrate phases proceed in the intergranular film, that is to say, in the immediate vicinity of the original cement grains. The solution which forms the liquid film is not saturated in respect to the anhydrous cement but is supersaturated in respect to the hydrate phases. The more rapidly the hydrate phases are precipitated, and the lower, therefore, the concentration of the substances to be dissolved, the more rapid is the dissolution of the anhydrous cement. If no hydrate phases are precipitated, the concentration increases in the solution phase, and hydration of the anhydrous cement ceases. The activators of latent hydraulic binders have therefore only the task of adjusting the concentration conditions in the solution in such a manner that the dissolved substances can be precipitated again as quickly as possible in the form of strength-forming hydrates.

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Discussion

H.-G. Smolczyk

The excellent paper of Dr. Locher has been of great interest for the Forschungsinstitut für Hochofenschlacke at Rheinhausen, for it is a valuable development towards basic problems of the hydration of portland blast furnace slag cements. But it must be taken into account that our technical blast furnace slags cannot entirely be compared with the high-alumina melts of chemically pure components mentioned by Dr. Locher. I must refer to this, for otherwise one might get a wrong impression of the behavior of blast furnace slag cements. Thus, at the annual German cement meeting at Salzburg (1960), Dr. zur Strassen stated—and he was fully agreed with by Professor Schwiete—that blast furnace slag cements of various types did not show any X-ray diffraction pattern of hydrogarnets even after having been cured in water for years. (We have never observed any hydrogarnet peaks either, after water curing under normal conditions.) These observations are in accordance with Dr. Locher's statement that there had been only very weak peaks of gehlenite hydrate in hydrated technical blast furnace slags. Furthermore I want to state that we have tested X-ray diagrams of at least 100 blast furnace slag cements at different stages of hydration, and in only one or two specimens with very high alumina content have we found a very weak peak of gehlenite hydrate at a very early stage of hydration. This peak, however, disappeared after 28 days of water curing.

Another difference for the chemically pure glass melts is the decrease of the $Ca(OH)_2$ content in good blast furnace slag cements. After 7 days of water curing the $Ca(OH)_2$ content in the low-clinkered type of these cements would be reduced to a very small amount. The $Ca(OH)_2$ content of special blast furnace slag cements, as well as that of supersulfated cements would be brought down almost to zero.

This phenomenon is one of the causes for the well-known resistance of these cements to various aggressive fluids. As for a concrete using these cements as matrix, there will certainly not be any disintegration in contact with an $MgSO_4$ solution either.

Closure

F. W. Locher

The results of H.-G. Smolczyk show that, as a rule, no gehlenite hydrate can be established in hydrated blast furnace slags and slag cements, and our own findings tally with these results. It must then be explained, however, in what hydrated phases the alumina is present in hardened slag-sulfate cements. Our own X-ray diffraction investigations showed that only a small portion of the alumina forms aluminates rich in lime. The lime content of low-clinker blast furnace cements is not sufficient to bind all the alumina of the slag in this form. It may be expected, therefore, that aluminate hydrate phases poorer in lime are formed. When mixtures of glass or slag with various activators were shaken in diluted and saturated calcium hydroxide solutions, gehlenite hydrate occurred in every case and it was therefore assumed that gehlenite hydrate was also formed in the paste during hydration of these mixtures. The non-occurrence of X-ray interferences might be attributed to the fact that the gehlenite hydrate in the paste is as ill-crystallized as the calcium silicate hydrate.

H.-G. Smolczyk established that the calcium hydroxide content decreases in the course of hardening and that practically no calcium hydroxide is contained in the hardened special blast furnace cements and slag-sulfate cements. The results of our own investigations do not agree with this finding. As in the hydration of the pure glasses, in the hydration of four technical blast furnace slags of various compositions a definite content of calcium hydroxide occurred which showed little change with progressive hardening. This behavior did not depend on the kind of activation. With an activation with anhydrite also, a calcium hydroxide content of about 4 to 5 percent was observed in the cement.

Paper III–S5. The Precipitation of $CaO \cdot Al_2O_3 \cdot 10H_2O$ From Supersaturated Calcium Aluminate Solutions at 21 °C*

A. Percival, F. G. Buttler, and H. F. W. Taylor

Synopsis

Deposition from clear, supersaturated solutions, made by shaking anhydrous calcium aluminates with water has been studied at 21 °C. Alkali-free solutions containing initially more than 0.85 g CaO, 1.46 g Al_2O_3/l yield C_2AH_8, CAH_{10}, and AH_3; after sufficiently long times, only CAH_{10} and AH_3 are found. With weaker solutions, down to 0.48 g CaO, 0.81 g Al_2O_3/l, the usual products are C_2AH_8 and AH_3; CAH_{10} appears irreproducibly. With still weaker solutions, only AH_3 is found. The effect of using NaOH instead of water to prepare the supersaturated solution has been studied. One thousandth molar NaOH solution behaves no differently from water; M/100 NaOH alters the concentrations but not the general course of precipitation; M/10 NaOH yields solutions, very weak in CaO, which did not precipitate within 28 days.

The results obtained using water or M/1000 NaOH support the metastable solubility curve for CAH_{10} previously reported by Percival and Taylor and not the modified curve proposed by Jones and Roberts. Reasons are also advanced for preferring the 5 °C curve for CAH_{10} determined by Buttler and Taylor to that proposed by Jones.

Résumé

On a etudié les precipités formés dans des solutions claires et sursaturées, préparées d'aluminates de calcium anhydre agités dans l'eau à 21 °C. Les solutons sans alcali et contenant originellement plus de 0.85 g de CaO, 1.46 g de Al_2O_3/l donnent C_2AH_8, CAH_{10}, et AH_3; après des périodes suffisamment longues on ne trouve que CAH_{10} et AH_3. Avec des solutions plus faibles descendant jusqu'à 0.48 g de CaO, 0.81 g de Al_2O_3/l, C_2AH_8 et AH_3 sont habituellement produits; CAH_{10} apparaît quelquefois. Avec des solutions encore plus faibles, on ne trouve que AH_3. L'effet de l'utilisation de NaOH au lieu d'eau dans la préparation des solutions sursaturées est étudié. M/1000 NaOH se comporte de façon semblable à l'eau; M/100 NaOH modifie les concentrations mais pas le cours général de précipitation; M/10 NaOH donne des solutions, très faibles en CaO, qui ne précipitaient pas pendant 28 jours.

Les résultats obtenus, si l'on utilise ou l'eau ou M/1000 NaOH, supportent la courbe métastable de solubilité présentée précédemment par Percival et Taylor et non pas la courbe modifiée proposée par Jones et Roberts. Les raisons pour préférer la courbe 5 °C pour CAH_{10} déterminée par Buttler et Taylor à celle proposée par Jones sont également présentées.

Zusammenfassung

Die Ausfällung der klaren, übersättigten Lösungen, die durch das Schütteln des wasserfreien Kalziumaluminats mit Wasser erhalten wurden, wurde bei 27 °C studiert. Alkalifreie Lösungen, die ursprünglich mehr als 0.85 g CaO und 1.46 g Al_2O_3/l enthalten, liefern C_2AH_8, CAH_{10} und AH_3; nach einer genügend langen Zeit werden nur noch CAH_{10} und AH_3 beobachtet. Wenn die Lösungun verdünnter sind, bis zu 0.48 g CaO und 0.81 g Al_2O_3/l, wird meistens C_2AH_8 und AH_3 erhalten; CAH_{10} entsteht manchmal, aber es ist nicht reproduzierbar. Bei weiterer verdünnter Lösungen wird nur AH_3 beobachtet. Es wurde auch untersucht, wie sich die Benutzung von NaOH an Stelle des Wassers für die Bereitung der übersättigten Lösung auswirkt. M/1000 NaOH zeigt dieselben Wirkungen wie Wasser; M/100 NaOH verändert die Konzentrationen, aber hat keinen Einfluß auf den Gang der Niederschlagsprozesse; M/10 NaOH liefert Lösungen, die wenig CaO enthalten und die während 28 Tagen keinen Niederschlag ausfallen lassen.

Die mit Wasser oder M/1000 NaOH erhaltenen Ergebnisse zeigen, daß die metastabile Löslichkeitskurve, die Percival und Taylor früher für CAH_{10} beschrieben haben, richtig ist, und nicht die abgeänderte Kurve, die von Jones und Roberts in Vorschlag gebracht wurde. Gründe werden auch angegeben, warum die 5°-Kurve für CAH_{10}, die von Buttler und Taylor bestimmt wurde, der Kurve, die Jones vorgeschlagen hat, vorzuziehen ist.

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Introduction

It is generally agreed that the hydration of either CA or aluminous cement in pastes at 21 °C gives CAH_{10} as a major product. In contrast, most of the investigators who have studied deposition from clear, supersaturated solutions at or near this temperature have not reported formation of CAH_{10}. Jones and Roberts [1][1], however, recently obtained CAH_{10} from such solutions at 20 °C. They also obtained it, though irreproducibly, at 25 °C, and in some unthermostatted experiments at 19 to 23 °C.

The present work was done to find whether CAH_{10} is reproducibly obtainable from clear, supersaturated solutions at 21 °C, and if so to define the conditions of its formation. The influence of alkali was also studied. The results provide further evidence about the position of the metastable solubility curve for CAH_{10}.

Experimental

Precipitation From Alkali-Free Solutions

The solutions were made by shaking weighed amounts (20 to 100 g) of "Secar 250" (a white high-alumina cement made from commercial calcined alumina, and consisting of CA, CA_2 and corundum) with boiled distilled water (1 liter) in a large, stoppered polythene bottle for 1 to 4 hours. The resulting suspensions were filtered in CO_2-free air immediately after shaking, and the filtrates transfered to 500-ml polythene bottles. These were immediately closed with polyvinylchloride gasketed screw stoppers, and placed in a 21 °C thermostat. Portions of the clear filtrates were analyzed for CaO and Al_2O_3. By varying the shaking time and the amount of cement used, a range of supersaturated solutions of differing concentrations was obtained. It was extended to concentrations below 0.4 g CaO/l by diluting the filtrates with water.

After varying times, bottles containing initially clear solutions of different concentrations were removed from the thermostat. The precipitated solids were filtered off under CO_2-free conditions, dried over saturated $CaCl_2$ solution, and X-ray powder photographs taken. The filtrates were analyzed for CaO and Al_2O_3. The $CaO:Al_2O_3$ ratios in the solids were calculated from the changes in the solution compositions.

The principal phases deposited were C_2AH_8, CAH_{10}, and hydrous alumina which gave diffuse X-ray patterns approximating in varying degrees that of gibbsite. In a few cases, small amounts of C_4AH_{13} or of $C_3A{\cdot}CaCO_3{\cdot}12H_2O$ were also detected. Some precipitates in which only AH_3 was detected by X-rays had calculated C/A ratios as high as 0.4. These high ratios can probably be attributed mainly to adsorption of Ca ions or their incorporation into the poorly crystallized structure; traces of $C_3A{\cdot}CaCO_3{\cdot}12H_2O$ may also have been present.

Experiments Using NaOH Solutions

The above procedure was followed, but the "Secar 250" was shaken with dilute solutions of NaOH instead of with water. When M/1000 or M/100 NaOH was used, precipitates were formed, and the experimental procedure was completed as with water. With M/10 NaOH, no precipitation occurred, at least in periods of up to 3 weeks.

Results

The results are given here in abbreviated form; full tables of data may be obtained on request to the authors.

Alkali-Free Solutions

Figure 1 shows the initial concentrations, times in the thermostat to approach equilibrium, and phases detected in the precipitates using X-rays. It also gives an indication of the molar C/A ratios of the precipitates. Only one variable is needed to express the initial concentration, because all the initial solutions had the same molar C/A ratio (1.07±0.01).

Figure 2 shows the paths followed by the solution compositions in some typical cases, with the experimental points for most of the runs of over 120 days duration. Variation of CaO and Al_2O_3 concentrations with time is shown in more detail in figure 3 for the runs where high initial concentrations were used.

The phases detected by X-rays varied with both initial solution composition and time. Three ranges of initial solution composition can be distinguished:

Range 1—At high initial concentrations (above about 0.85 g CaO, 1.46 g Al_2O_3/l) and short times, CAH_{10}, C_2AH_8, and AH_3 are usually all observed. The C_2AH_8 lines gradually become weaker in the X-ray pattern, and after a few months usually only CAH_{10} and AH_3 can be detected. The decrease in the proportion of C_2AH_8 is also shown by a fall in the C/A ratio of the precipitate. The variation in solution composition with time (fig. 3) was substantially the same for all the initial concentrations within this range. The concentrations drop within

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[1] Figures in brackets indicate the literature references at the end of this paper.

1 day to about 0.45 g CaO, 0.60 g Al_2O_3/l. The concentration of CaO falls to a minimum at 5 to 14 days and afterwards rises again; that of Al_2O_3 continues to decrease for at least six months. After eight months the concentration of Al_2O_3 has become almost constant at about 0.15 g/l, but that of CaO is still increasing slowly. This rise in CaO concentration provides incidental confirmation that no appreciable CO_2 contamination is occurring; its significance is discussed later. Closely similar data were obtained by Wells and Carlson [2] and by Jones and Roberts [1] some of whose results are included in figure 3. Wells and Carlson considered the final concentrations to be 0.46 g CaO, 0.16 g Al_2O_3/l, but the present results suggest that the final CaO concentration may be above 0.46 g/l.

Range 2—At moderate initial solution compositions (down to about 0.48 g CaO, 0.81 g Al_2O_3/l) the usual combination of phases found by X-rays is C_2AH_8 and AH_3 (fig. 1). Particularly at the lower initial solution concentrations in this range, AH_3 was the dominant phase in the X-ray pattern; the lines of C_2AH_8 and of CAH_{10}, when it occurred, were relatively weak. Sometimes CAH_{10} was observed, and it was present in two out of the three runs of over 150 days duration, but its occurrence in this range was irreproducible, at any rate in quantities detectable with X-rays. Some of the supersaturated solutions gave it readily, while others of similar concentration did not, although they had been prepared by a seemingly identical method. As in the previous range, the C/A ratio of the precipitate falls with time, though less markedly. The paths followed by the solution compositions (fig. 2) were similar to those noted for Range 1, but the CaO concentrations tended to be less as the initial concentration decreased. There were no significant differences as regards solution compositions between the runs in which CAH_{10} was detected in the precipitate and those in which it was not.

Range 3—At low initial solution concentrations (below about 0.48 g CaO, 0.81 g Al_2O_3/l), X-ray

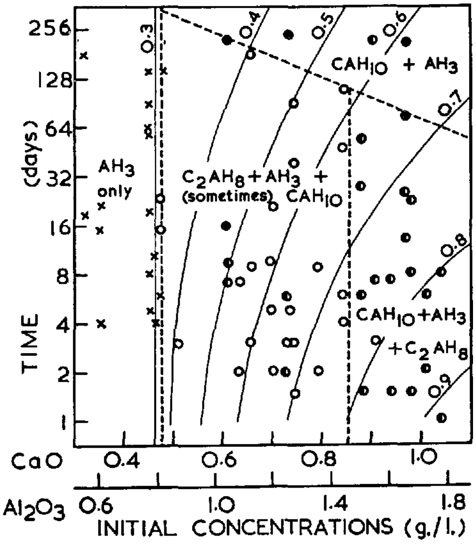

FIGURE 1. *Initial solution compositions, times, and principal solid phases detected by X-rays in alkali-free runs.*

Principal solid phases:
O, C_2AH_8, AH_3. ◑, $C_2AH_8+CAH_{10}+AH_3$. ●, $CAH_{10}+AH_3$. ×, AH_3. *Thin full lines give a general indication of molar C/A ratios of precipitates.* Broken lines define fields in which different combinations of solid phases usually occur.

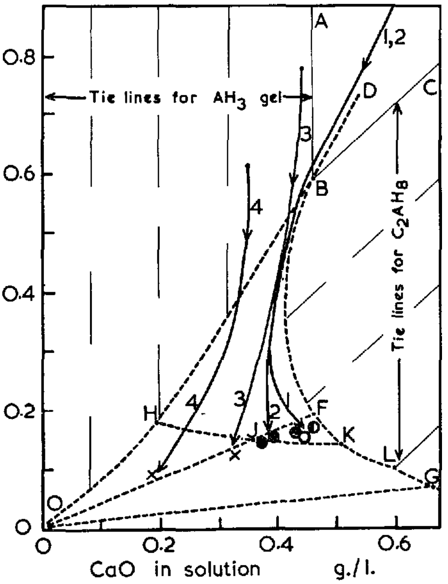

FIGURE 2. *Typical paths (full lines) followed by solution compositions in alkali-free runs.*

[Curves 1–4 are for initial CaO concentrations of 0.88–1.04, 0.61, 0.45, and 0.32–0.35 g/l respectively. Heavy broken lines represent stable or metastable solubility curves (*DBFKL*–C_2AH_8, *LG*–C_4AH_{19}, *HJK*–CAH_{10}, *OHB*–AH_3 gel, *OJH*–microcrystalline AH_3, *OG*–gibbsite). Experimental points are given only for long term runs, and have the same significance as in figure 1.]

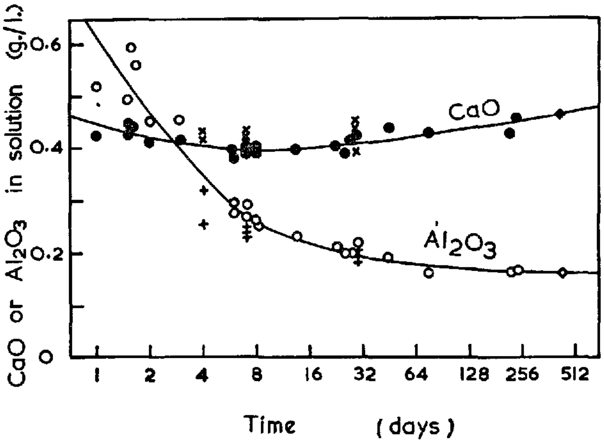

FIGURE 3. *Variation with time in the concentrations of* CaO *and* Al_2O_3 *for all alkali-free runs with initial* CaO *concentrations* ≥ 0.88 g/l ($Al_2O_3 \geq 1.53$ g/l).

[●, CaO; ○, Al_2O_3 (this investigation, 21 °C.) ×, CaO; +, Al_2O_3 (Jones and Roberts, 20 °C). ♦, CaO; ◇ Al_2O_3 (Wells and Carlson, 21 °C). The curves are drawn through the points at 21 °C.]

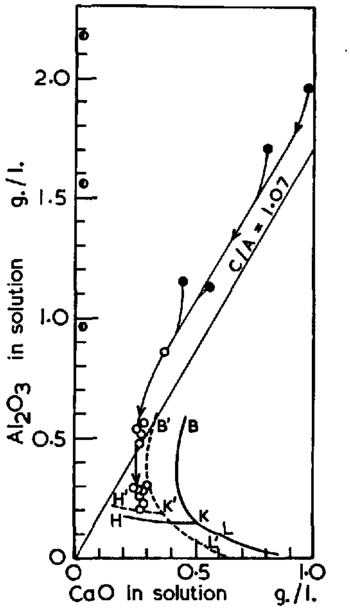

FIGURE 4. *Results of runs using M/10 or M/100* NaOH.

◑, ●, initial solution composition using M/10 and M/100 NaOH respectively. ○, final solution compositions using M/100 NaOH. Heavy full lines represent metastable solubility curves in absence of alkali for C_2AH_8 (*BKL*) and CAH_{10} (*HK*). Broken lines represent positions of these curves in M/100 NaOH.

examination of the precipitates showed only AH_3, apart from traces of $C_3A{\cdot}CaCO_3{\cdot}12H_2O$ in some cases. The results agreed closely with those obtained in a similar study by Wells and Carlson [2] and will therefore not be reported or discussed in detail.

Solutions Containing Alkali

Eighteen runs were made using M/1000 NaOH; the initial CaO concentrations were 0.539—1.09 g/l, and the times were 0.5—143 days. The results did not differ significantly from those obtained using water. The results with M/10 and M/100 NaOH are shown briefly in figure 4. The solutions made with M/10 NaOH did not precipitate. Those made with M/100 NaOH precipitated, and 12 runs were made with times of 1 to 92 days. The two more concentrated solutions ($CaO \geq 0.8$ g/l, $Al_2O_3 \geq 1.7$ g/l) gave C_2AH_8, CAH_{10}, and AH_3 at all ages studied. With the two weaker ones ($CaO \leq 0.55$ g/l, $Al_2O_3 \leq 1.15$ g/l) only C_2AH_8 and AH_3 were detected. The approximate rates of precipitation, and the course followed by the solution compositions, were similar to those found with water or M/1000 NaOH, but the CaO concentrations were consistently lower.

Discussion

Precipitation of CAH_{10} From Alkali-Free Solutions

The results show that CAH_{10} is precipitated at 21 °C from supersaturated solutions to which no additional lime has been added, provided the concentration immediately after filtration is high enough. This observation is consistent with the known behavior of CA on paste hydration at 21 °C, where CAH_{10} is formed as the main product, though usually with some C_2AH_8 and AH_3. In a partly hydrated paste, the concentrations of CaO and Al_2O_3 in solution are presumably kept high by the presence of unreacted CA.

Range 1—Initial precipitation from solutions in this range is probably always of AH_3 and C_2AH_8. This conclusion can be correlated with the fact that the initial solution compositions lie in the field *ABC* (fig. 2) between the tie lines of these two phases. During the first 1 to 2 days, the solution composition therefore reaches the unstable triple point at *B*. In the present work, periods under 1 day were not studied, but Wells and Carlson's results suggest that AH_3 alone is precipitated at first; afterwards, AH_3 and C_2AH_8 are precipitated together, and the solution compositions move down the upper part *DB* of the C_2AH_8 metastable solubility curve towards the triple point.

The next stage in the precipitation may begin even before the first is complete and continues for some 6 to 12 months. It appears to involve three separate processes. Firstly, the C_2AH_8 is unstable and reacts with the solution, abstracting alumina to give CAH_{10}. Secondly, the crystallinity of the AH_3 gradually improves so that its effective solubility curve changes from ' *OB* ("AH_3 gel") to *OF* ("microcrystalline AH_3") (fig. 2). These are, of course, only two stages in a continuous sequence which continues beyond *OF* in the direction of fully crystalline gibbsite (curve *OG*). Thirdly, the CAH_{10} is probably also poorly crystalline at first (Buttler and Taylor, [3]), and its effective solubility curve may be supposed to fall gradually towards the limiting curve *HJK* for CAH_{10} of maximum crystallinity. The solution composition moves towards a triple point *J* between solution, CAH_{10}, and microcrystalline AH_3 (fig. 2). Its path can perhaps be regarded as the locus of the unstable triple point which occurs at the intersection of a constantly changing series of unstable solubility curves for AH_3 with a similar series of curves for CAH_{10}.

Towards the end of this stage of precipitation, the CaO concentration, which has passed through a minimum at 5 to 14 days, begins to increase. This is because the CAH_{10} has almost attained its maximum crystallinity, but that of the AH_3 is continuing to increase. CAH_{10} therefore begins to redissolve as the solution composition is now tending to move to the right along, or just above, the curve *JK*. Eventually, at the triple point *K*, C_2AH_8 may be expected to reprecipitate, but several years would probably be needed for this CaO concentration to be reached.

Range 2.—The behavior of the solutions in this range presents a difficulty in that CAH_{10} was detected in only a few of the solids, whereas the trends in solution and solid compositions closely resembled those found for Range 1. The most likely explanation is perhaps that CAH_{10} was formed in amounts sufficient to influence the solution compositions, but usually insufficient for detection by X-rays. The minimum proportion of CAH_{10} that can be so detected in the presence of larger amounts of AH_3 and C_2AH_8 is not known, but may be quite high, especially when the CAH_{10} is poorly crystallized. On this hypothesis, the sequence of reactions is essentially the same as for Range 1, but the formation of CAH_{10} at the expense of C_2AH_8 occurs less reproducibly. The rate at which this process occurs seems to depend on a number of factors that are not properly understood. The high concentrations in solution initially present in Range 1 seem to trigger off the process in some way. Some observations by Jones and Roberts [1] suggest that seeding with preformed CAH_{10} may also be effective. Lastly, the present results show that two clear, filtered solutions in Range 2 may have approximately the same concentrations and yet differ markedly in the ease or speed with which they yield CAH_{10}. This suggests that the properties of a supersaturated calcium aluminate solution are not uniquely determined by its composition. It is tempting to speculate on the possibility of differing degrees of condensation or molecular weight in the aluminate anion, but there are no satisfactory data on this subject.

Range 3.—The initial solution compositions lie in a region of AH_3 tie lines, at CaO concentrations too low for the precipitation of C_2AH_8 (fig. 2). Precipitation is therefore essentially of AH_3, the crystallinity of which gradually improves with time. The paths followed by the solution compositions cross the CAH_{10} curve *HJK*. After 6 to 12 months the solution compositions reach the curve *OF* for microcrystalline AH_3 which was established by Wells and Carlson.

The Influence of Alkali on the Precipitation of CAH_{10} at 21 °C

The present results show that NaOH in M/1000 concentration has negligible effect on the composition or behavior of the supersaturated solutions. One hundredth-molar NaOH solution lowers the CaO concentration for a given Al_2O_3 concentration, though not to an extent equivalent to the amount of NaOH added. Detectable amounts of CAH_{10} are formed if the initial solution is concentrated enough, as with water or M/1000 NaOH. Tenth-molar NaOH appears to inhibit the formation of hydrated calcium aluminates entirely. There do not appear to be any precise data regarding the alkali concentrations in setting pastes of commercial aluminous cements. The fact that these yield CAH_{10} under much the same conditions as does pure CA (Wells and Carlson, [2]; Schneider, [4]) suggests that the alkali concentrations probably do not exceed M/100.

The results using M/100 NaOH suggest tentative placings of the metastable solubility curves for C_2AH_8 and CAH_{10} in this medium at *B′K′L′* and *H′K′* respectively (fig. 4).

Metastable Solubility Curve for CAH_{10} at 21 °C

The present results cause us to alter our view (Percival and Taylor, [5]) that the CAH_{10} metastable solubility curve cannot be reached from supersaturation at 21 °C. The failure to reach this curve from supersaturation in the experiments reported earlier can be explained mainly by the fact that most of the initial solutions used were too dilute; in a few cases they were sufficiently concentrated, but carbonation was afterwards found to have occurred in the longer-term experiments, destroying the CAH_{10} that had been formed.

Jones [6] has suggested that the CAH_{10} curve does not follow the line *HK* proposed by Percival and Taylor [5], and used in the foregoing discussion, but the hypothetical line *PYQ* (fig. 5). He bases this view mainly on an analogy with the positions of similarly revised curves for CAH_{10} at 1° and at 5 °C, which in turn were derived from reinterpretations of the results of Carlson [7] and of Buttler and Taylor [3] respectively. It will therefore be necessary to consider the data for lower temperatures. First, however, the direct evidence at 21 °C for and against each of the two CAH_{10} curves will be considered.

Percival and Taylor obtained their curve from undersaturation. In lime solutions of medium concentration, the CAH_{10} dissolved congruently, giving solution compositions at a number of points along *HK*. With water or dilute lime solutions some AH_3 was formed, giving solution compositions at a metastable triple point *H;* with stronger lime solutions there was some formation of C_2AH_8, or C_4AH_{19}, or both, and the solution compositions were at or near the triple point *K* (fig. 5). The present results show that the lime-rich end of

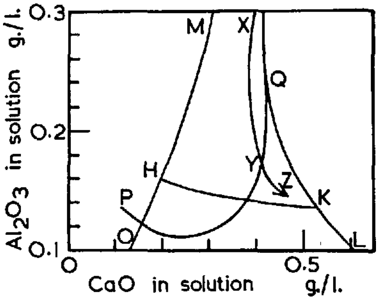

FIGURE 5. *Metastable solubility curves in the alkali-free system at 21 °C.*

QKL, C_2AH_8. *OHM,* AH_3 gel. *HK,* CAH_{10} according to Percival and Taylor. *PYQ,* CAH_{10} according to Jones. *XYZ:* path followed by solution compositions for supersaturated solutions in range 1.

the curve, near *K*, can also be reached, or closely approached, from supersaturation. Jones' curve *PYQ*, in contrast, explains neither the results obtained from undersaturation nor those obtained from supersaturation. He refers to experiments by Jones and Roberts [1] at 20 °C in which CAH_{10} was precipitated. These experiments were closely similar to some of those starting from Range 1 in the present investigation, and their durations were 1 to 28 days. The 28-day experiments gave solution compositions near the point *Y*, in close agreement with the present results and with those of Wells and Carlson [figs. 3 and 5]. This point happens to lie on the CAH_{10} curve proposed by Jones, but with longer times the solution compositions move off this curve towards that proposed by Percival and Taylor. The agreement with Jones' proposed curve therefore appears fortuitous.

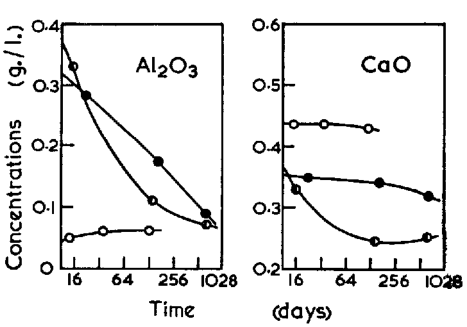

FIGURE 6. *Variation with time in* CaO *and* Al_2O_3 *concentrations for some typical groups of runs made by Buttler and Taylor (3).*

○, CAH_{10} treated with lime solution containing initially 0.440 g CaO/l. ◑, deposition from supersaturated solution containing initially 0.475 g CaO, 0.593 g Al_2O_3/l. ●, deposition from supersaturated solution containing initially 0.676 g CaO, 0.566 g Al_2O_3/l.

Metastable Solubility Curve for CAH_{10} at 5 °C

Figures 9 and 10 of Jones' paper show selected experimental points obtained by Buttler and Taylor [3], with the curve *HC* for CAH_{10} deduced by them from these data (fig. 10) and the somewhat different curve *ZT* (fig. 9) which Jones considered to explain the data more satisfactorily. His main grounds for this were as follows:

(1) All of Buttler and Taylor's runs yielding CAH_{10} from supersaturation gave final solution compositions approximately on, or else above *ZT*. None fell decisively between *ZT* and *HC*.

(2) The C/A ratios for the solid phases existing in contact with solutions whose compositions lay on the hexagonal plate curve are shown in Jones' figure 8. He argues that the sharp drop from 3 to approximately 1 at point *T* indicates that this is the triple point for CAH_{10} and C_2AH_8 with solution, and that the absence of any sharp drop at about 0.53 g CaO/l shows that there is not a triple point in the position suggested by Buttler and Taylor.

(3) Jones rejects the results of runs from undersaturation, such as C11 and C12 (his fig. 10) on the ground that equilibrium was not reached.

It must be admitted that the results at 5 °C are harder to interpret than are those at 21 °C. Carlson's curve for CAH_{10} at 1 °C [7] differs from Buttler and Taylor's at 5 °C by more than seems likely to be explained by the difference in temperature. Also, Carlson's results indicate the existence of a triple point CAH_{10}-C_2AH_8-solution, whereas Buttler and Taylor's demand instead a triple point CAH_{10}-C_4AH_{19}-solution. Further experimental work at low temperatures is needed to settle these points. Nevertheless, we consider that Buttler and Taylor's curve for CAH_{10} at 5 °C. fits the evidence at least as well as Jones' for the following reasons:

(1) The data do not support Jones' assertion that the runs from supersaturation reach equilibrium more readily than those from undersaturation. In figure 6, CaO and Al_2O_3 concentrations are plotted against time for three key groups of runs by Buttler and Taylor. Group 1, from undersaturation, includes points C11 and C12 which are on their curve but not on Jones' curve (his fig. 10). The results suggest that equilibrium is being reached. Group 2, from supersaturation, includes point 9C on Jones' figure 9, which is also close to Buttler and Taylor's curve; the results suggest a near approach to equilibrium. Group 3, also from supersaturation, includes point 21C on Jones' figure 9. This point lies on Jones' curve, but the results suggest that equilibrium has not been reached. An appreciable further decrease in Al_2O_3 concentration could be expected to occur.

(2) The data given in Jones' figure 8 can equally well be explained if the formation of CAH_{10} from supersaturated solutions at 5 °C follows a similar mechanism to that proposed here for its formation at 21 °C. The sharp change in the C/A ratios of the solids at point *T* can be attributed to the fact that the paths followed by the solution compositions in those runs where CAH_{10} is formed at the expense of C_2AH_8 or C_4AH_{19} diverge from the C_2AH_8 curve at or near this point. No sharp change in the observed C/A ratios of the solids would be expected to occur at the triple point C_4AH_{19}-CAH_{10}-solution, on the C_4AH_{19} curve, because the runs from which this curve was obtained were all ones in which CAH_{10} was not involved.

This work was carried out as part of a program of research on the system CaO-Al_2O_3-H_2O supported by the Lafarge Aluminous Cement Company Ltd., whose generous assistance is gratefully acknowledged.

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Paper III–S6. Steam Curing of Cement and Cement-Quartz Pastes*

A. Aitken and H. F. W. Taylor

Synopsis

Pastes of neat cement, and of finely divided quartz mixed with cement in weight ratios of 0.23–3.0, were cured at temperatures mostly between 75 and 200 °C. The phases existing in the products were investigated mainly by X-ray diffraction. Neat cements give poorly crystallized tobermorite minerals, $Ca(OH)_2$, tricalcium silicate hydrate, C_2S α-hydrate, and, at low temperatures only, hydrated aluminate or sulfoaluminate phases. Cement-quartz mixtures give poorly crystallized tobermorite minerals, $Ca(OH)_2$, tobermorite, xonotlite, C_2S α-hydrate, scawtite (presumably resulting from carbonation), and possibly a hydrogarnet. The conditions of temperature, time, and composition needed to give each of these phases are defined.

Résumé

Des pâtes de ciment pur, et de quartz finement divisé mélangé avec le ciment dans des rapports de poids de 0.23–3.0, ont été conservées à des températures variant pour la plupart entre 75 et 300 °C. Les phases existant dans les produits ont été examinées principalement par diffraction des rayons X. Les ciments purs donnent des minéraux tobermorites médiocrement cristallisés, $Ca(OH)_2$, hydrate de silicate tricalcique, C_2S α-hydrate, et, aux températures basses seulement, des phases d'aluminate hydraté ou de sulfoaluminate. Les mélanges ciment-quartz donnent des minéraux médiocrement cristallisés, $Ca(OH)_2$, tobermorite, xonotlite, C_2S α-hydrate, scawtite (qui résulte probablement de la carbonatation), et peut-être un hydrogrenat. Les conditions de température, de temps, et de composition nécessaires à l'obtention de chacune de ces phases sont définies.

Zusammenfassung

Purzementpasten und feingemahlener Quarz der mit Zement in Gewichtsverhältnissen 0.23–3.0 vermischt wurde, wurden bei Temperaturen zwischen 75 und 200 °C aushärten gelassen. Die in den Produkten existierenden Phasen wurden meistens mit Röntgenstrahlen untersucht. Purzemente liefern Tobermoritmineralien, die nicht zu gut kristallisieren, $Ca(OH)_2$, hydratisiertes Trikalziumsilikat, das α-Hydrat des C_2S, und bei niedrigen Temperaturen werden auch hydratisierte Aluminate oder Sulfoaluminatphasen beobachtet. Zement-Quarzmischungen liefern Tobermoritmineralien, die schlecht kristallisieren, $Ca(OH)_2$, Tobermorit, Xonotlit, das α-Hydrat des C_2S, Scawtit (welcher vermutlich durch Kohlensäureaufnahme entstanden ist), und vielleicht auch einen Hydrogranat. Die Temperatur-, Zeit- und Zusammensetzungsbedingungen, unter denen eine jede solche Phase entstehen kann, werden beschrieben.

Introduction and Experimental Methods

Previous work on the phases detectable in autoclaved cement and cement-quartz pastes is reviewed elsewhere in this symposium. This contribution describes some new results.

Materials Used

Cement—To reduce complications caused by the presence of iron- and alkali-bearing phases, a white cement low in alkali was used. Table 1 gives its analysis and potential phase composition: the latter was calculated assuming the small amount of iron to occur as C_4AF. X-ray powder photographs showed C_3S, β-C_2S, and C_3A. To obtain a more detailed qualitative idea of the phase composition, some of the cement was

TABLE 1. *Analysis and potential phase composition of the cement (Snowcrete; A.P.C.M. Ltd., England)*

Analysis	%	Potential phase composition	%
SiO_2	22.16	C_3S	48.5
Al_2O_3	4.62	β-C_2S	26.9
Fe_2O_3	0.41	C_3A	11.6
FeO	.02	C_4AF [a]	1.3
MgO	.20	$Ca(OH)_2$	6.3
MnO	.03	MgO	0.2
CaO	67.44	$CaSO_4 \cdot 2H_2O$	2.5
Na_2O+K_2O	0.34	$CaSO_4 \cdot \frac{1}{2}H_2O$	2.1
Insol. res.	.27	Na_2O K_2O MnO FeO Insol.	0.7
SO_3	2.34		
S^{2-}	Nil.		
Ignition loss	2.17		
	100.00		
Free CaO	4.76		
$Al_2O_3:Fe_2O_3$	11.27		

[a] Of doubtful occurrence: see text.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Department of Chemistry, University of Aberdeen, Scotland.

divided by successive specific gravity fractionations with methylene iodide-benzene mixtures into 25 fractions. The denser fractions consisted of C_3S and β-C_2S. They were dark, and therefore probably contained most of the iron, but no ferrite phase was detected optically or by X-rays. The middle fractions contained C_3S and C_3A. The least dense fractions contained C_3S, C_3A, $Ca(OH)_2$, gypsum, and hemihydrate. These results confirm that C_3S, β-C_2S, and C_3A are the main phases. The apparent absence of a ferrite phase suggests that the iron may occur in the silicates, though its presence there is not certain. The assignment of the free CaO and the SO_3 in table 1 is based on the observation that $Ca(OH)_2$, gypsum, and hemihydrate were all present. An attempt was made at quantitative X-ray determination of the phases, but the results were unconvincing, and it was decided that further experience with the method was needed before it could be considered reliable.

Silica—Three samples of fine quartz were used, two of them the same as, and all of them similar to, those used in the work on lime-quartz pastes (Aitken and Taylor, [1][1]). All passed completely through a 300-mesh sieve. One sample possibly reacted a little more slowly than the others, but no important differences between the samples were found.

Experimental Methods

The cement and quartz were intimately mixed in the required proportions, and the mixture transferred to a small silver test tube. Carbon dioxide-free distilled water was added to give a water: cement weight ratio of 0.4, and the paste mixed as quickly as possible to reduce contamination by atmospheric CO_2. The silver tube was placed immediately in either a stainless steel bomb, or a glass test tube which was then sealed off. In either case, the outer vessel contained also enough water to saturate the atmosphere at the temperature subsequently used. The vessel was placed in an oven regulated to ±1 °C for the desired time. The heating and cooling processes were probably each complete in less than 30 min. The products were equilibrated over saturated $CaCl_2$ before examination. All were examined with X-rays, using 11.46-cm-diam powder cameras with filtered copper radiation. Thermal weight-loss curves were obtained for some specimens, using a Stanton recording thermobalance. The conclusions regarding the phases present were based mainly on the X-ray results, supplemented in some cases by those obtained using the thermobalance.

Results and Discussion

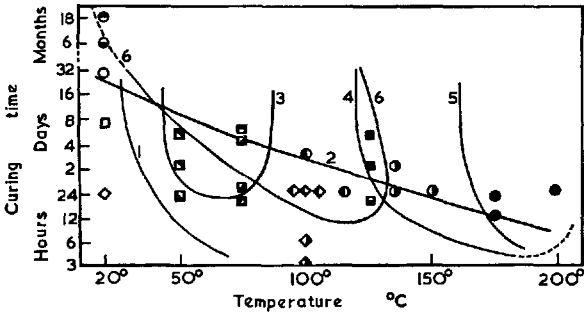

FIGURE 1. *Phases detected in neat cement pastes.*

Curve 1: Upper limit of detection of separate hydrated aluminate or sulfoaluminate phases. Curve 2: Substantially complete reaction of C_3S. Curve 3: Possible low-temperature field of formation of $C_3SH_{1½}$. Curve 4: Lower limit of formation of C_2S α-hydrate. Curve 5: Lower limit of high-temperature range of formation of $C_3SH_{1½}$ Curve 6: Region of maximum formation of CSH gel. Key to experimental points:

◇, ettringite
⬖, CSH gel } + C_3S, β-C_2S, C_3A, & $Ca(OH)_2$
⬗, —
○, ettringite, C_4AH_{13} [a]
◒, C_4AH_{13} [a]
◓, C_4AH_{13} [a], CSH gel
◐, CSH gel } + β-C_2S, $Ca(OH)_2$, & (?) C_3S
◑, C_2S α-hydrate
●, C_2S α-hydrate, $C_3SH_{1½}$
□, C_4AH_{13} [a], ettringite
⧗, (?) ettringite
⧖, (?) ettringite (?) $C_3SH_{1½}$
◩, (?) $C_3SH_{1½}$
◪, CSH gel, $C_3SH_{1½}$ } + C_3S, β-C_2S, & $Ca(OH)_2$
⬓, CSH gel, (?) $C_3SH_{1½}$
⬒, CSH gel
■, CSH gel, C_2S α-hydrate

[a] C_4AH_{13} or related phases such as low-sulfate calcium sulfoaluminate.

Neat Cement Pastes

The results are shown in figure 1; the main conclusions are as follows:

(1) Separate aluminate or sulfoaluminate phases (ettringite and C_4AH_{13} or low-sulfate calcium sulfoaluminate) are formed with certainty only at 18 °C, though there were doubtful indications of ettringite at 50 °C. The results do not confirm Kalousek's conclusion [2] that hydrated aluminate or sulfoaluminate phases are formed transiently at 50–100 °C, though X-ray methods are possibly less sensitive than differential thermal analysis for detection of these compounds. No evidence of C_3AH_6 was found in any of the neat cement pastes.

(2) Disappearance of unreacted cement compounds is naturally more rapid with rising temperature; no C_3S nor C_3A could be detected after about 3 days at 100 °C (fig. 1, curve 2). The ratio of β-C_2S to C_3S appeared from inspection of the X-ray patterns to increase steadily with time at all temperatures studied, suggesting that the hypothesis of equal fractional hydration rates is not obeyed. There is evidence that C_3A reacts less quickly than is sometimes supposed; lines were found that seemed to be attributable to it for up to 1 day at 100° or 105 °C.

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[1] Figures in brackets indicate the literature references at the end of this paper.

(3) The immediate products of hydration of the C_3S and β-C_2S are probably $Ca(OH)_2$ and a lime-rich tobermorite-like gel. This probably does not differ greatly from that formed at room temperature, and its Ca:Si ratio is probably in the region 1.5–2.0. It will be called CSH gel. Curve 6 defines the conditions under which formation of this gel appeared from the X-ray evidence to be at a maximum.

(4) C_2S α-hydrate forms at 125 °C and above, to at least 200 °C, the highest temperature studied. The probable boundary of its field of formation is given by curve 4.

(5) Tricalcium silicate hydrate forms definitely above about 165 °C (curve 5). There were indications of its formation also at 50 and 75 °C (curve 3); this conclusion is based on the appearance of an X-ray spacing of 8.7 A, which is one of the strongest for this phase.

(6) Calcium hydroxide was always present. It might be supposed that less of this phase would form above 165 °C, because of the formation of tricalcium silicate hydrate. If there was less, it was not apparent from the X-ray photographs; probably not enough tricalcium silicate hydrate was formed.

Comparison with the results of earlier investigators—These results are broadly similar to those obtained by Buckle and Taylor [3] for C_3S pastes. The temperature ranges over which tricalcium silicate hydrate is formed are somewhat different in the two cases; the low-temperature range is more constricted with cement, and even its existence is not quite certain. The high-temperature range extends to slightly lower temperatures with cement. No evidence was obtained of the formation of hillebrandite at 80–120 °C, as reported by Kalousek, nor of inversion of β- to give γ-C_2S, as found by Funk [4, 5] on hydrothermal curing of pastes of β-C_2S containing certain stabilizers. The formation of C_2S α-hydrate at 175–185 °C confirms the results of Kalousek [2] and Sanders and Smothers [6], neither of whom, however, reported the formation of tricalcium silicate hydrate. The non-appearance of C_3AH_6 confirms the findings of earlier workers.

Cement-Quartz Pastes: General Survey of the Reactions

The main results are given in figures 2 to 7 and table 2. As well as the phases there indicated, quartz was always found, though sometimes only in traces. Some general conclusions are as follows:

Minimum temperature of reaction between cement and quartz—Runs made at 18 and 75 °C with cement-quartz mixtures gave no indication that the behavior of the cement was significantly influenced by the presence of the quartz (table 2). At or above 85 °C this is no longer true. The first sign of reaction is that less $Ca(OH)_2$, or none at all, is detected (fig. 2). New phases, formation of which could be attributed directly to the presence of the quartz, were first detected at 115 °C, when tobermorite was found after one day in a paste of high quartz:cement ratio (fig. 3).

Phases formed in autoclaved cement-quartz pastes—The hydrated phases found in pastes cured at 85 to 200 °C were CSH gel, $Ca(OH)_2$, tobermorite, C_2S α-hydrate, xonotlite, CSH(A) or scawtite, and possibly a phase of the hydrogarnet type. Tricalcium silicate hydrate was not found except in one case.

TABLE 2. *Phases detected in cement-quartz pastes for curing times other than 25 hours*

Temp. °C	Time	Ratio quartz: cement [a]	Crystalline phases detected [b]				
			C_3S	β-C_2S	T	CSH(A)	Others
18	36 days	1.00	+	+			CH, E, C_4
75	5 days	1.00	+	+			CH, C_3A, TSH
125	18 hrs	1.00	?	?	+		α, HG(?)
155	5 days	0.45	?	?	+	+	HG(?), α
155	4 hr	1.00	+	+			C_3A, HG(?)
155	5 days	1.00			+	+	Xon(?)
165	4 hr	1.00	?	?	+		
175	4 hr	3.00	?	?			CSH gel
175	12 hr	3.00			+		
185	4 hr	1.00	+	+	+	+	

[a] By weight.

[b] T=tobermorite, CH=$Ca(OH)_2$, E=ettringite or related phase, C_4=C_4AH_{13} or related phase, TSH=tricalcium silicate hydrate, α=C_2S α-hydrate, HG=hydrogarnet, Xon=xonotlite.

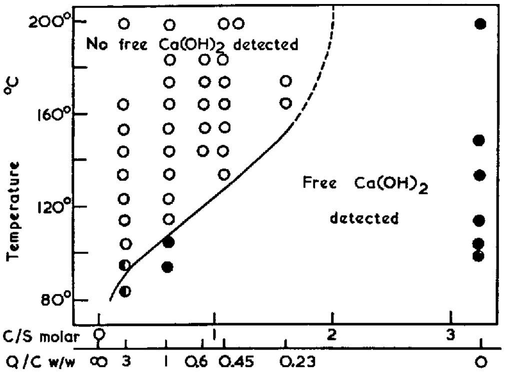

FIGURE 2. *Occurrence of free $Ca(OH)_2$ in cement and cement-quartz pastes cured for 25 hours.*

●, Free $Ca(OH)_2$ detected. ◐, Free $Ca(OH)_2$ doubtful or in traces. ○, No free $Ca(OH)_2$ detected.

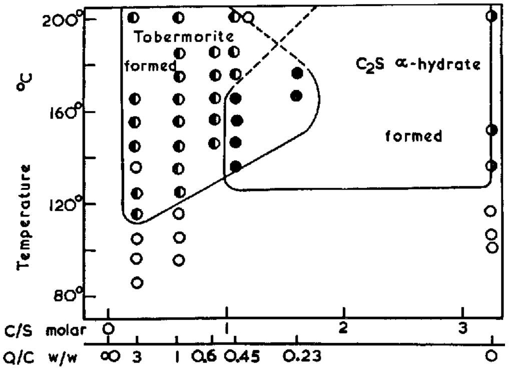

FIGURE 3. *Occurrence of tobermorite and of C_2S α-hydrate in cement and cement-quartz pastes cured for 25 hours.*

○, Neither phase detected. ◐, Tobermorite detected. ◑, C_2S α-hydrate detected. ●, Both phases detected.

The influence of quartz on the rate of reaction of the cement—Figure 4 shows the effect of quartz on the temperature needed to obtain complete reaction of the cement within 25 hours. The results are only approximate, but there appears to be a definite trend towards more rapid reaction as the proportion of quartz is increased. Even at 200 °C, the β-C_2S had not completely reacted in the neat cement pastes, but with quartz : cement ratios of 1 or more, complete reaction of both C_3S and C_2S was always attained at 150 °C or over. As with neat cement pastes, C_3A was remarkably persistent. It seems usually to persist for at least 1 day at temperatures up to about 100 °C, irrespective of cement: quartz ratio. There are indications that in the presence of quartz, C_3A may react less rapidly than in neat cements. It was found after 1 day at 145 °C for a quartz:cement ratio of 0.45, and after 4 hr at 155 °C (table 2).

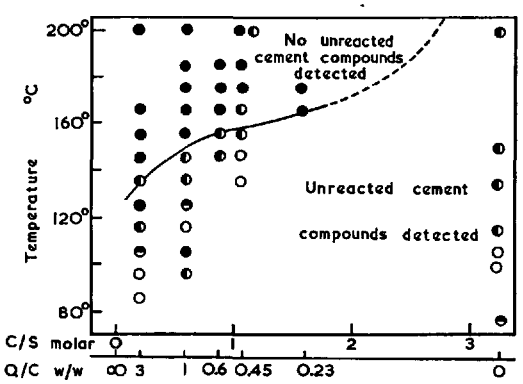

FIGURE 4. *Occurrence of unreacted cement compounds in cement and cement-quartz pastes cured for 25 hours.*

○, C_3S, β-C_2S, and C_3A detected. ◒, C_3S, β-C_2S detected. ◐, β-C_2S, (?) C_3S detected. ●, No anhydrous phases detected.

Conditions of Formation of Individual Phases in Cement-Quartz Pastes

CSH *gel*—Detection of this phase in quartz-cement pastes was not satisfactorily achieved by the methods used. A poorly crystallized phase structurally related to tobermorite was probably present in most or all of the products.

Tobermorite—Figure 3 shows the field of temperature and composition in which this phase was detected after 25 hours' curing. The minimum temperature needed for its formation in detectable quantity in pastes having about the same C/S ratio as to tobermorite is about 125 °C. This temperature probably depends on the cement: quartz ratio. Tobermorite was often a major product. The maximum yield seems likely to be attained at overall C/S ratios of about 0.8 (quartz : cement about 0.65) and temperatures around 180 °C. At higher temperatures, xonotlite tends to form, probably at the expense of tobermorite.

C_2S *α-hydrate*—This compound is formed at overall C/S ratios of 1 or more (quartz:cement ratios below about 0.5), above about 125 °C (fig. 3 and table 2). This minimum temperature of formation seems not to be much influenced by the quartz:cement ratio within this range. C_2S α-hydrate was often a major product.

Xonotlite was a minor product in pastes of high quartz:cement ratio cured at 180 °C or above (fig. 5).

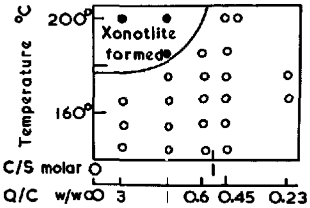

FIGURE 5. *Occurrence of xonotlite in cement-quartz pastes cured for 25 hours.*

●, Xonotlite detected. ○, No xonotlite detected.

$Ca(OH)_2$—As already noted, formation of this compound is largely suppressed in the presence of quartz. The minimum temperature needed to avoid its formation probably decreases with rising quartz:cement ratio. The curve shown in figure 2 is partly conjectural; more data would be needed to establish its position definitely. At quartz:cement ratio 1 and curing time one day, $Ca(OH)_2$ was not detected at autoclave temperatures above about 105 °C.

CSH(A)—This phase appeared irreproducibly in a field centered on overall C/S 1.0, temperature 180 °C (table 2 and fig. 6). It was often formed within 1 day, and in one case within 4 hours. The lack of reproducibility contrasts with the situation regarding the phases so far mentioned. This supports the view (Buckner, Roy, and Roy, [7]) that CSH(A) is a quaternary phase containing CO_3^{2-}, essentially the same as scawtite, and is formed only in the presence of CO_2. McConnell and Murdoch's studies on natural scawtites [8] suggest that the minimum amount of CO_2 needed to permit formation of this phase may be low. The tendency to form scawtite is possibly greater in small laboratory specimens than in the interiors of the much larger ones used in commercial practice.

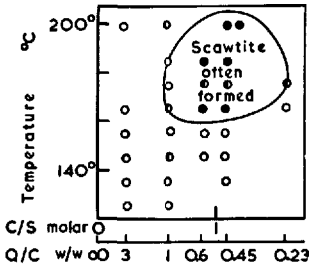

FIGURE 6. *Occurrence of scawtite or CSH(A) in cement-quartz pastes cured for 25 hours.*

●, Scawtite detected. ◐, Scawtite doubtful. ○, No scawtite detected.

Hydrogarnet-type phases—Some evidence was obtained of the formation of a phase related to C_3AH_6 and the hydrogarnet family in a number of specimens. These lay in a field centered on an overall C/S ratio of 0.9, and a temperature of 165 °C (fig. 7 and table 2). As with CSH(A), the phase appeared irreproducibly. The evidence consisted of the presence of a weak powder line of spacing 5.05 ± 0.1 A. This is in the correct range for one of the strongest reflections for phases belonging to this family, although it is probably significantly lower than the value of 5.14 A reported for C_3AH_6.

With a few specimens, other, unidentified weak powder reflections were observed. The most important of these was of spacing 6.0–6.1 A. It was shown by several specimens with quartz: cement ratio 0.4–1.0 and curing temperature 155 to 200 °C.

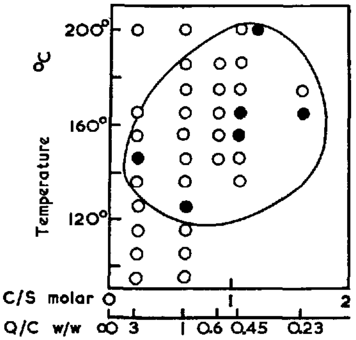

FIGURE 7. *Possible occurrence of hydrogarnet-type phase in cement-quartz pastes cured for 25 hours.*

●, Hydrogarnet-type phase probably occurs. ○, No hydrogarnet-type phase detected. Ring outlines field in which this phase appears to be formed.

The Course of Reaction in Cement-Quartz Pastes at 85 to 200 °C

The primary reaction is probably always the hydration of the cement to give a lime-rich CSH gel and $Ca(OH)_2$. It seems probable that if any hydrated aluminate or sulfoaluminate phases are formed at all they are quickly decomposed, their components becoming incorporated in the CSH gel. There is some evidence that above 120 °C the Al_2O_3 may separate again partly or completely from the gel, giving a phase of hydrogarnet type. In general, the Al_2O_3 seems to have only a minor influence on the subsequent behavior of the CSH gel.

If no quartz is added, the CSH gel tends above 125 °C to recrystallize, giving C_2S α-hydrate; above 165 °C, tricalcium silicate hydrate can also form. This latter phase can form only as a result of reaction between the gel and $Ca(OH)_2$ crystals that have previously separated from it. Its formation probably represents a beginning of equilibrium crystallization.

The first effect of the quartz is to restrict the separation of $Ca(OH)_2$; one or more poorly crystallized tobermoritelike phases is presumably formed. So long as unreacted quartz grains remain, there is probably a zoning of these phases around them, material of low C/S ratio, possibly similar to CSH(I), forming nearest the quartz grains, and more lime-rich material, perhaps CSH(II), farther away. Very little quartz is needed to prevent formation of tricalcium silicate hydrate at 165 °C or above; a quartz : cement ratio of 0.1 is probably enough.

At 120 to 180 °C, the important processes are the recrystallization of lime-rich gel to give C_2S α-hydrate, and of lime-poor gel to give tobermorite. These processes can occur simultaneously over a limited range of overall C/S ratios. Formation of tobermorite is favored by a high quartz:cement ratio, but if this rises above about 0.7 ($C/S \leq 0.8$) the product is likely to contain a substantial amount of unreacted quartz.

At the higher temperatures the process is complicated by the formation of additional phases. CSH(A) and xonotlite (figs. 5 and 6) are probably formed by recrystallization of tobermorite. Other phases, such as hillebrandite or "Phase F" may be similarly formed from C_2S α-hydrate or from CSH(II) at low quartz:cement ratios; not enough suitable runs were made to establish if this formation does in fact occur.

Comparison With Results of Other Investigators

In the main, these results agree well with those of Kalousek [2], Sanders and Smothers [6], and Neese, Spangenberg, and Weisskirchner [9]. This agreement is especially good as regards formation of tobermorite and of C_2S α-hydrate. None of the earlier workers reported the formation of xonotlite or of CSH(A), but this can be attributed to the narrower range of conditions studied. A more important divergence lies in the probable detection of a hydrogarnet-type phase in the present case, though this cannot yet be considered as certain. The present results do not support Neese's view that nekoite is formed under certain conditions.

The results may also be compared with those obtained for lime-quartz pastes (Aitken and Taylor, [1]. On the whole, there is a close similarity, the cement behaving essentially as a source of both lime and silica, but certain differences are apparent:

(1) Tobermorite is formed over a wider range of overall C/S ratios (0.2–1.6) with cement than with lime (0.33–1.08). The minimum temperature at which it was detected was also slightly lower with cement (115 °C) than with lime (125 °C). These differences can possibly be attributed to the presence of Al_2O_3 in the cement; according to Kalousek [10], Al_2O_3 favors the formation of tobermorite.

(2) Gyrolite was not found when cement was used. Its absence is possibly not significant, as its formation in lime-quartz pastes is slow, and

not many runs were made with cement where the combination of time and temperature was such that formation of gyrolite might have been expected.

(3) Xonotlite was formed less readily with cement. The lowest temperature at which it was found was 180 °C, against 165 °C with lime. This can possibly be attributed to the presence of Al_2O_3 in the cement (Kalousek, [10].

(4) In general, reaction seems to be slower with cement. In every run, unreacted quartz was found in the product, though sometimes only in small amounts; with the lime-quartz pastes, the quartz often reacted completely. Because of this slower reaction, there is a tendency with cement for any given hydrated compound to form most readily when the overall C/S ratio is less than that of the compound, as with tobermorite (fig. 3) or xonotlite (fig. 5). This was not observed with lime.

(5) CSH(A) was formed with cement but not with lime; hillebrandite and "Phase F" were formed with lime but not with cement. These differences may not be significant.

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Paper III–S7. Two Different Ways of Hydration in the Reaction of β-Ca_2SiO_4 With Water at 25 to 120 °C[*]

Herbert Funk

Synopsis

β-Ca_2SiO_4 is transformed into tobermorite-like calcium silicate hydrates in two different ways:

(1) By reaction with pure water, β-C_2S is able to hydrate directly to give needle-shaped tobermorite. The needles originated from a single crystal of β-C_2S are oriented to each other. In this course of hydration β-C_2S crystals take up H_2O directly, being altered continuously with increasing water content. This is shown by X-ray diagrams as well as by optical observations of the intermediate products which no longer contain anhydrous β-C_2S and are not yet completely formed tobermorite.

(2) β-C_2S forms foil-like or platy tobermorite through the solution phase. Exclusively this course of reaction is observed, if certain additives are used ($CaCl_2$, supersaturated solution of $Ca(OH)_2$, seed crystals). Unlike the products of the direct hydration (1) the partly hydrated products of the solution-phase reaction consist of mixtures of foil-like tobermorite and residual anhydrous β-C_2S. Addition of seed crystals of tobermorite foils to the mixture of β-C_2S and water stops the slower direct hydration reaction, and foils of tobermorite, rather than needles, are formed through the solution phase.

(3) β-C_2S as well as γ-C_2S is practically quantitatively transformed into dicalcium silicate α-hydrate, $Ca_2OH(HOSiO_3)$, at 100 to 200 °C through the solution phase, if seed crystals of this compound are added. After addition of tobermorite seed crystals at 100 °C β-C_2S as well as γ-C_2S is transformed into tobermorite through the solution phase.

Résumé

β-Ca_2SiO_4 se transforme en hydrates de silicate de calcium comparable à un tobermorite, de deux façons différentes:

(1) Par réaction à l'état solide, β-C_2S est transformé par H_2O en tobermorite aciculaire, dans lequel les aiguilles sont orientées les unes envers les autres. Dans cette réaction solide les cristaux de β-C_2S absorbent H_2O, continuellement modifiés par l'accroissement de la teneur en eau. Les diagrammes de rayons X indiquent ce fait aussi bien que les observations optiques. Il y a formation de produits intermédiaires qui ne contiennent plus de β-C_2S anhydre et ne sont pas encore des tobermorites complètement formés.

(2) β-C_2S forme un tobermorite en feuilles ou en plaques dans la phase de solution. Ce cours de réaction est atteint à l'aide de certains additifs ($CaCl_2$, solution sursaturée de $Ca(OH)_2$, grains de cristaux). A la différence du produit de la réaction solide, les solides en partie hydratés consistent en mélange de tobermorite en feuille et de β-C_2S anhydre résiduel. L'addition de grains de cristaux de feuilles de tobermorite arrête l'hydration plus lente à l'état solide, et ce sont des feuilles de tobermorite, plutôt que des aiguilles, qui sont formées dans la phase de solution.

(3) β-C_2S comme γ-C_2S est presque quantitativement transformé en α-hydrate de silicate dicalcique, $Ca_2OH(HOSiO_3)$, à 100–200 °C dans la phase de solution, si des grains de cristaux de ce composé sont ajoutés. Après addition de grains de cristaux de tobermorite à 100 °C, β-C_2S ainsi que γ-C_2S est transformé en tobermorite dans la phase de solution.

Zusammenfassung

β-Ca_2SiO_4 kann auf zwei verschiedenen Wegen tobermoritähnliche Calciumsilikathydrate bilden:

(1) β-C_2S kann mit reinem Wasser direkt unter Bildung von Tobermoritnadeln reagieren. Die aus einem Einkristall von β-C_2S entstehenden Nadeln sind optisch zueinander orientiert. Bei diesem Hydratationsweg nehmen die β-C_2S-Kristalle direkt H_2O auf, wobei sie mit steigendem Wassergehalt kontinuierlich verändert werden, wie es sowohl die Röntgendiagramme als auch die optischen Beobachtungen zeigen. Es werden Zwischenprodukte gebildet, die kein wasserfreies β-C_2S mehr und noch keinen fertig gebildeten Tobermorit enthalten.

(2) β-C_2S kann über die Lösungsphase folien- oder plattenförmigen Tobermorit bilden. Dieser Reaktionsweg wird ausschließlich beobachtet, wenn bestimmte Zusätze beigefügt werden ($CaCl_2$, übersättigte Lösung von $Ca(OH)_2$, Impfkristalle). Im Unterschied zu den Produkten der direkten Hydratation (1) bestehen die teilweise hydratisierten Produkte der Lösungsphasenreaktion aus Gemischen, die Tobermoritfolien und restliches wasserfreies β-C_2S enthalten. Durch Impfkristalle aus Tobermoritfolien wird die langsamere direkte Hydratation des β-C_2S unterbrochen und es entstehen durch die Lösungsphase Tobermoritfolien anstelle von Nadeln.

(3) β-C_2S wird ebenso wie γ-C_2S praktisch quantitativ bei 100–200 °C durch die Lösungsphase in Dicalciumsilikat-α-Hydrat, $Ca_2OH(HOSiO_3)$, umgewandelt, wenn Impfkristalle dieser Verbindung zugefügt werden. Durch Zugabe von Tobermorit-Impfkristallen wird sowohl β-C_2S als auch γ-C_2S bei 100 °C durch die Lösungsphase in Tobermorit umgewandelt.

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[*] Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Institut für anorganische Chemie, Deutsche Akademie der Wissenschaften zu Berlin, Germany.

Introduction

By hydration of the cement components C_3S and β-C_2S, tobermorite-like calcium silicate hydrates have been observed as foils, needles, plates, or laths, or mixtures of them. The X-ray diagrams of these different forms are either extraordinarily similar or identical; for brevity they are designated as tobermorite, but it would be better to call them tobermorite-like phases.

In a previous work [1] [1], the formation of the needle-shaped tobermorite-like phase with the composition $2CaO{\cdot}SiO_2{\cdot}2H_2O$ at 100 °C from β-C_2S with water has been found to occur by direct hydration of β-C_2S. To differentiate this direct hydration of β-C_2S crystals by H_2O (as liquid or vapor) from the phase formed by reaction through the solution, it was called "direct" or "solid-state" hydration. Formerly, also McConnell [2, 3] had observed that the hydration of β-C_2S (larnite) and of α'-C_2S (bredigite), both occurring in nature, led to the tobermorite-like phase (plombierite) in the oriented form.

Hydration of β-C_2S in the Solid State With the Formation of Needle-Shaped Tobermorite

Sufficiently stabilized β-C_2S [2] was allowed:

(1) to mix with water (1:10 up to 1:50) at 25 °C by rotation in polyethylene bottles, or

(2) to stand with water, or saturated $Ca(OH)_2$ solution in pasty consistency (1:2.5), in silver crucibles at 25 or 100 °C.

These conditions led to the formation of needle-shaped tobermorite-like calcium silicate hydrate as a final product, which had a composition of $1.5CaO{\cdot}SiO_2{\cdot}1.5H_2O$ (at 25 °C) to $2CaO{\cdot}SiO_2{\cdot}2H_2O$ (at 100 °C).

Optical Investigation

From time to time, samples were taken from the reaction mixtures (β-C_2S with H_2O), and changes occurring at the crystals were microscopically observed. On the surface of the crystals, taken from partly hydrated intermediates, there was a zone of decreased refractive index which extended progressively into the crystal. With a water content of $\sim 1H_2O/SiO_2$ (after having been dried in vacuo over P_2O_5) most crystals practically became optically uniform again. The refractive index decreased from $n=1.71$–1.73 (β-C_2S), to $n=1.67$–1.68 (intermediate product with $\sim 1H_2O/SiO_2$). After the hydration up to a content of $\sim 1H_2O/SiO_2$ the crystals remained optically active and still rotated the plane of polarized light uniformly. Amorphous portions which might consist of fine-grained tobermorite, have not been found during this solid state hydration. Portions of amorphous, optically nonoriented tobermorite are to be seen only in case of hydration proceeding through the solution phase.

Electronmicroscopic Investigation

Some photographs, characteristic for changes observed in the crystals, show that the β-C_2S crystals (fig. 1(a)) have a more layer-like structure after the action of water. After three days action of water at 100 °C, e.g., about 1.1 H_2O/SiO_2 has been bound (fig. 1(b)). After four days at 100 °C the substance contains 1.4 H_2O/SiO_2; with this or higher water content, crystals often split off columnar or needle-shaped fragments (fig. 1(c)). Beta-dicalcium silicate crystals treated with water for 20 days at 100 °C have the composition, e.g., $1.9CaO{\cdot}SiO_2{\cdot}2.0H_2O$; their X-ray pattern is similar to that of tobermorite (see following section). Tobermorite needles arising from a β-C_2S crystal often still hold together, and the contour of the starting crystal is still to be seen (fig. 1(d)).[3]

Crystals of an intermediate product with $<1H_2O/SiO_2$, obtained after two days action of water on β-C_2S at 100 °C, seem only little changed in their appearance. But on treating this substance with ultrasonics of low intensity the hydrated crystals disintegrate into needles (fig. 1(e)), showing them also to have been changed in their interior by the water; anhydrous β-C_2S remains completely unchanged when treated in the same way.

Amorphous tobermorite had not been found in the intermediates and therefore the water content was assumed to be found in the crystals; this assumption corresponds to the results of optical observation. The water taken up by the β-C_2S crystals extends also into the interior of the crystals indicated by the decreased refractive index, and also by the easy splitting into needles by ultrasonics. That this alteration occurs in the β-C_2S crystals remaining undissolved becomes once more evident by the changes of the X-ray pattern described below.

X-ray Investigation

Debye photographs of intermediate substances formed of β-C_2S containing 0.5 to 1 H_2O/SiO_2 show only an increase of background. With a counter-tube goniometer we have recognized in these substances:

(1) a general decrease of the intensities of the reflections of β-C_2S,

(2) a change of the relative intensities of reflections of β-C_2S, proceeding to the vanishing of certain reflections.

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[1] Figures in brackets indicate the literature references at the end of this paper.

[2] One percent by weight of Na_2SO_4, or 0.3 percent by weight of $Ca_3(BO_3)_2$ was added to γ-C_2S (diameter of crystals, 10–50 μ). In the case of stabilization with 1 percent of Na_2SO_4, the mixture was heated three times for one hour to 1,100 °C in a platinum dish with a lid, and well mixed afterwards. Insufficiently stabilized β-C_2S may be re-transformed into γ-C_2S by action of water, if the grain size is about 0.01 mm or more [4].

[3] Thin, long laths of tobermorite have been observed to grow from small needles, if these have been allowed to stand—especially at 100 °C—with water (for instance if needles were used as seed crystals).

X-ray photographs according to the Guinier method demonstrate the change of intensity most distinctly. The reflections in the diagram of β-C_2S do not become weaker equally, as the substance is progressively hydrated (see fig. 2c, d). Only certain reflections vanish, which often are not those weakest in intensity (in fig. 2 marked by arrows). On the other hand, the pattern of the hydrated substance has left unchanged other, weaker, reflections (in fig. 2 marked by x). The diagram of the hydrated intermediate substance, therefore, does not contain a symmetrically weakened diagram of β-C_2S, although there are many reflections common to both. The new reflection appearing at 1.82 A, also present in tobermorite, is marked by a double arrow.

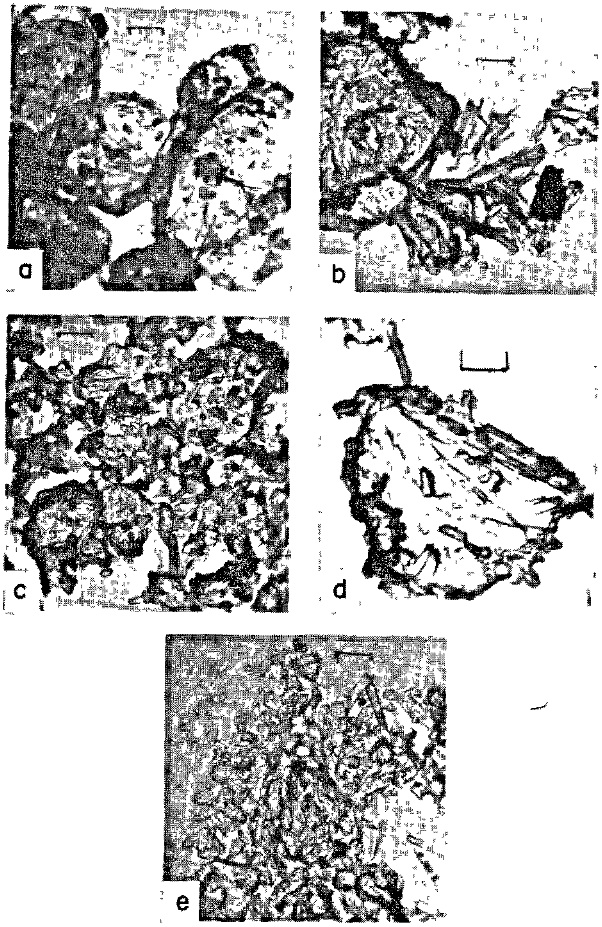

FIGURE 1. *Electron-micrographs of β-C_2S in different stages of hydration.*

a. β-C_2S (stabilized with 1% Na_2SO_4).
b. β-C_2S, 3 days 100 °C (1.1 H_2O/SiO_2).
c. β-C_2S, 4 days 100 °C (1.4 H_2O/SiO_2).
d. β-C_2S, 20 days 100 °C (1.9 $CaO \cdot SiO_2 \cdot 2.0\ H_2O$).
e. β-C_2S, 2 days 100 °C (0.9 H_2O/SiO_2) treated with ultrasonics.

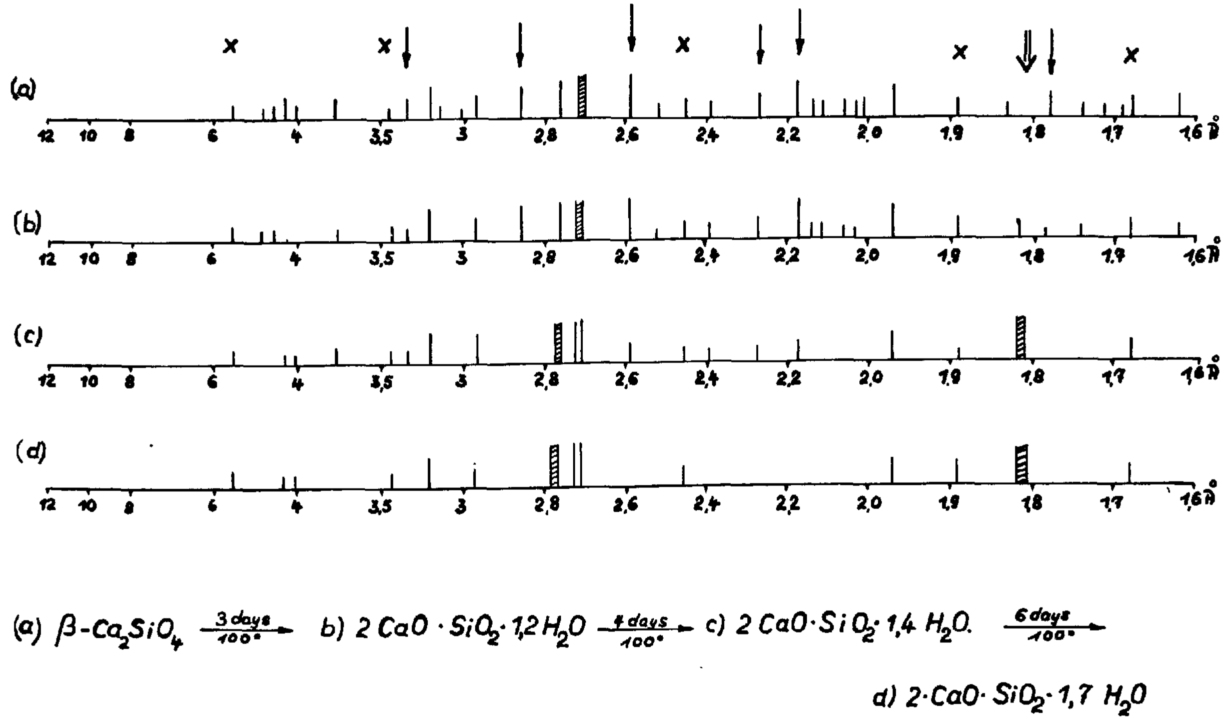

FIGURE 2. *X-ray patterns of β-C_2S in various stages of hydration.*

Conclusion

The changes of the X-ray patterns of the intermediate substances, corresponding to optical and electronmicroscopical observations, must be interpreted in the following way: β-C_2S remaining undissolved hydrates by the action of water that probably reacts as H^+ and OH^- ions. Every β-C_2S crystal is continuously altered according to the increase of its water content. This change may be observed by optical methods and by the continuous alteration of the X-ray patterns of the products on progressive hydration.

β-C_2S Hydrated Through Solution by the Formation of Foil-Like or Platy Tobermorite

Hydration of β-C_2S under special conditions yields tobermorite also in the form of foils or plates. The special conditions are those in which additives are supplied either to the water added ($CaCl_2$, supersaturated solutions of Ca $(OH)_2$) or to the reaction mixture (as seed crystals). There is evidence that foil-like or platy tobermorite, formed by additives in a shorter time of reaction, occurs through the solution phase.

β-C_2S Hydration in Shorter Time by Additives

Mixtures with additives were prepared in the same way as described before, in the form of pastes or by rotating them with the respective solutions. A survey of the times of hydration of β-C_2S by different solutions is given in table 1.

Pure water as well as lime water (saturated with 1.6 g $Ca(OH)_2$/l) leads to tobermorite needles after a hydration time of 140–200 days, as shown in columns 1 and 2, respectively. The fact that that needles are formed by hydration in the solid state is shown, as previously stated, by the variable diagram of intermediate substances which are incompletely hydrated. A supersaturated solution of $Ca(OH)_2$ (2.2 g/l, column 3), such as may occur in contact with C_3S, and therefore usually is present in the cement paste, shortens hydration time to about 100 days, during which the tobermorite phase is formed in foils. Complete hydration takes place in 30 to 40 days if a 15-percent $CaCl_2$ solution is applied.

If samples, still incompletely hydrated, are taken (see columns 3 and 4, reactions in which foil-like tobermorite is formed), microscopic observation shows mixtures of optically amorphous masses with residual anhydrous β-C_2S. X-ray diagrams also show that tobermorite is present with anhydrous β-C_2S. Formation of these nonoriented tobermorite crystals (seen in the electronmicroscope as foils) mostlikely occurs through the solution phase. The characteristic difference from the direct hydration of β-C_2S to give needle-like tobermorite is the fact that the intermediate products of the solution reaction contain foils and give no X-ray photograph with an altered diagram of β-C_2S. If it is true that tobermorite foils are formed through solution, then this reaction may be expected to be induced by addition of seed crystals of foil-like tobermorite to β-C_2S with pure water.

Tobermorite Foils as Seed Crystals: Hydration of C_2S Through the Solution Phase

Undissolved β-C_2S is hydrated by pure water at 25 and 100 °C to yield needle-shaped tobermorite as described before. If, however, 10 percent by weight of tobermorite foils are added, β-C_2S will be completely transformed into foil-like tobermorite after 60 to 70 days at 25 °C. After approximately 30 days the reaction product contains only half of the water content of the final product. Optical, electron-optical, and X-ray examinations of such incompletely hydrated products show that the greatest part of the substance is tobermorite foils, the rest being anhydrous β-C_2S. This means that the addition of seed crystals causes hydration of β-C_2S through the solution phase. Parallel runs, under the same conditions but without addition of tobermorite foils, always yielded needles formed by the solid-state hydration.

If the hydration products consist of tobermorite foils, the mass seems to be less stiff than if needles are formed by solid-state hydration. Tobermorite foils as seed crystals frequently lead not only to more foils but to relatively large, platy crystals (approximately 10–100 μ long). Besides foil-like

TABLE 1. *Hydration of* β-C_2S

β-C_2S (stabilized by 1% of Na_2SO_4; particle size 5—40μ); allowed to stand with aqueous solution (1:3) at 25 °C.

	1	2	3	4	5
	Pure water	$Ca(OH)_2$ solution, saturated (1.60 g/l)	$Ca(OH)_2$ solution supersaturated (2.2 g/l)	$CaCl_2$ solution 15%	Seeded with tobermorite foils
Completely hydrated after	~200 days	~140 days	~100 days	30-40 days	~70 days.
Crystal shape of tobermorite (electron microscope).	Needles	Needles	Foils	Foils and plates (lamellar).	Foils.
X-ray pattern of an incompletely hydrated sample.	Intermediate pattern (variable).	Intermediate pattern (variable).	β-C_2S+tobermorite	β-C_2S+tobermorite	β-C_2S+tobermorite.

and platy tobermorite, with a 10-percent $CaCl_2$ solution, frequently a shrouding zone around the β-C_2S crystals occurs, having a gel-like and shapeless appearance in the electronmicroscope.

Gamma-dicalcium silicate as well as β-C_2S is completely transformed into tobermorite foils in 10 days at 100 °C after addition of a 15-percent $CaCl_2$ solution or seed crystals of tobermorite foils. Seed crystals of dicalcium silicate α-hydrate, $Ca_2OH(HOSiO_3)$, completely yield dicalcium silicate α-hydrate from β-C_2S or γ-C_2S at 100 to 200 °C.

Conclusions

β-C_2S hydrates in two different ways:

(1) In a slow direct hydration, β-C_2S crystals, remaining undissolved, take up H_2O. After 140 to 200 days, an oriented transformation into tobermorite needles is observed.

(2) At a certain minimum concentration of $CaCl_2$ or $Ca(OH)_2$ in aqueous solution, namely,

(a) 1 molar in $CaCl_2$, or

(b) 0.03 molar in $Ca(OH)_2$ (supersaturated), exclusively foil-like or platy tobermorite rather than needles is spontaneously formed from β-C_2S at 25–100 °C through the solution phase.

Tobermorite foils are also formed from β-C_2S with water at 25 and 100 °C by the addition of tobermorite foils under conditions in which, without seed crystals and with pure water, only the formation of needle-shaped tobermorite is observed. Both types of tobermorite are able to form setting masses. The formation of tobermorite needles from β-C_2S with water at 100 °C does not occur in preference to a formation of $Ca_2OH(HOSiO_3)$ (C_2S α-hydrate) if seed crystals of C_2S α-hydrate are added or spontaneously formed.

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Paper III-S8. Infrared Absorption of Some Compounds in the CaO-SiO_2-H_2O System*

Charles M. Hunt

Synopsis

Infrared absorption spectra of γ-C_2S, β-C_2S, C_3S, and the hydration products of C_3S have been obtained in the 300 to 5000 cm^{-1} region, using the KBr pressed-pellet technique. Spectra of okenite, gyrolite, Loch Eynort tobermorite, afwillite, and hillebrandite, in the form of natural minerals, and a synthetic xonotlite have also been measured. The vibrations associated with the SiO_4 groups are of great value for identifying the compounds but because of their complexity are difficult to interpret in terms of structure. The OH bending vibrations near 1650 cm^{-1} are either weak or absent in these compounds. This would be consistent with crystal structures in which water is largely, or in some cases entirely, in the form of OH groups. The position of the OH stretching vibrations suggests some degree of hydrogen bonding and also unbonded OH in some of these hydrates. None of the compounds, however, appears to contain hydrogen bonds of the diversity and strength of those reported in afwillite.

Résumé

Les spectres d'absorption infrarouge de γ-C_2S, β-C_2S, C_3S, et les produits d'hydratation de C_3S ont été obtenus dans la région de 300 à 5000 cm^{-1}, en employant la technique KBr de granules comprimées. Les spectres d'okenite, de gyrolite, de tobermorite de Loch Eynort, d'afwillite, et d'hillebrandite, sous forme de minéraux naturels, et un xonotlite synthétique ont également été mesurés. Les vibrations associées aux groupes de SiO_4 sont de grande valeur pour l'identification des composés, mais à cause de leur complexité il est difficile de les interpréter en termes de structure. Les vibrations OH dues à la flexion dans le voisinage de 1650 cm^{-1} sont faibles ou absentes dans ces composés. Ceci serait compatible avec les structures cristallines dans lesquelles l'eau se présente pour une grande part, ou dans certains cas entièrement, sous forme de groupes OH. La position des vibrations OH dues à la tension suggère qu'il y a dans une certaine mesure un lien d'hydrogène ainsi que OH non-lié dans certains de ces hydrates. Aucun des composés, cependant, ne paraît comporter de liens d'hydrogène ayant la diversité et la résistance de ceux notés dans l'afwillite.

Zusammenfassung

Ultrarotabsorptionsspektra des γ-C_2S, des β-C_2S, des C_3S und der Hydratationsprodukte des C_3S wurden von 300 bis 5000 cm^{-1} unter Benutzung zusammengepreßter KBr Kügelchen aufgenommen. Die Spektra des Okenits, des Gyrolits, des Loch-Eynort-Tobermorits, des Afwillits und des Hillebrandits wurden als natürliche Mineralien, und außerdem auch das Spektrum eines synthetischen Xonotlits gemessen. Die Vibrationen, die zur SiO_4-Gruppe gehören, können zur Identifizierung der Verbindungen gut benutzt werden, aber wegen ihrer großen Kompliziertheit sind sie schwierig für Strukturanalyse zu benutzt werden. Die OH-Biegungsschwingungen in der Nähe von 1650 cm^{-1} sind in diesen Verbindungen nur schwach vorhanden, oder sie fehlen vollständig. Das stimmt mit den Kristallstrukturen, in denen das Wasser zum grossen Teil oder sogar nur als OH-Gruppen vorkommt, gut überein. Die Lage der Spannungsschwingungen des OH läßt vermuten, daß Wasserstoffbindung zum Teil auftritt, und daß einige dieser Hydrate nicht gebundene OH-Gruppen haben. Aber man gewinnt den Eindruck, daß keine dieser Verbindungen Wasserstoffbindungen der Mannigfaltigkeit und Stärke besitzt, wie man sie vom Afwillit kennt.

Introduction

In their review papers for this symposium, Brunauer and Greenberg [1] [1] and Taylor [2] have briefly discussed the infrared absorption of the calcium silicate hydrates. The present paper undertakes to extend this discussion and introduce absorption spectra of a few of the compounds which are referred to in these papers.

Heller and Taylor [3] have compiled optical and X-ray data for a number of the calcium silicates and calcium silicate hydrates. Infrared spectroscopy offers an additional means of characterizing these materials. The spectra in the interval 300 to 5000 cm^{-1} presented here have been obtained partly for this purpose and also to study the SiO_4 and OH vibrations for information related to structure.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the National Bureau of Standards, Washington.

[1] Figures in brackets indicate the literature references at the end of this paper.

Methods and Materials

Measurement of Spectra

The compounds were measured by the KBr pressed-pellet technique [4,5]. The pellets contained a milligram of compound and approximately 250 mg of KBr. In some cases, pellets with only 0.3 to 0.5 mg of compound were also measured. The spectra were obtained without a blank pellet in the reference beam, and transmission values are uncorrected for losses caused by reflection and scattering. A small spurious absorption appears at 2940 cm^{-1} and is marked in the figures by an asterisk. Others have noted similar absorption in KBr pellets [6]. The spectra at 620 to 5000 cm^{-1} were obtained immediately after heating the pellets in vacuum at 100 °C, overnight or usually much longer. Those at 300 to 620 cm^{-1} were measured without this treatment.

The spectra were obtained with a Beckman IR-4 double-beam spectrometer. Cesium bromide prisms were used for the range 300 to 620 cm^{-1}, and NaCl prisms for the range 620 to 5,000 cm^{-1}.

Materials

Gamma dicalcium silicate was prepared from calcium carbonate and silica gel. The mixture was heated to 1,410 °C and then formed into pellets under pressure and reheated twice. The product was finally heated to 660° to complete reversion to the γ-form.

Beta dicalcium silicate was prepared the same way as γC_2S, except that 0.4 percent of boric acid was added to stabilize the compound, and the heating at 660° was omitted.

Tricalcium silicate was prepared by heating a mixture of calcium carbonate and silica at 1,400 °C. The product was reground, made into a paste with water, and carefully reheated to 1,400 °C. This process was repeated two more times.

Microscopic examination of the synthetic calcium silicates indicated that they were predominantly homogeneous materials containing small amounts of impurities. The powder X-ray patterns were in agreement with ASTM patterns.

Paste-cured C_3S was obtained by reacting equal weights of water and C_3S for a period of 14 months at 100 °F. The product contained 20 percent of water after vacuum-drying at 100 °C.

Loch Eynort tobermorite was obtained from Dr. G. F. Claringbull of the British Museum of Natural History. The sample is designated as part of B.M. 1937, 1490 and has been described by Claringbull and Hey [7], and also Gard and Taylor [8].

The other natural minerals were obtained from Dr. G. S. Switzer of the National Museum, Washington, D.C. They are listed with nominal chemical formula [3], source, and identifying museum number as follows:

Okenite, $CaO \cdot 2SiO_2 \cdot 2H_2O$, from Disco Island, Greenland, museum No. 94,524,

Truscottite, $CaO \cdot 2SiO_2 \cdot 1/2H_2O$, from Redjang Lebong mine, Sumatra, museum No. 95,872,

Gyrolite, $2CaO \cdot 3SiO_2 \cdot 2H_2O$, from Disco Island, Greenland, museum No. 112,506,

Afwillite, $Ca_3(SiO_3OH)_2 \cdot 2H_2O$, type specimen from Dutoitspan mine, Kimberley, South Africa, museum No. 95,237,

Hillebrandite, $2CaO \cdot SiO_2 \cdot H_2O$, from type location, Ternates mine, Velardena, Durango, Mexico, museum No. 95,767.

Microscopic examination of afwillite and gyrolite indicated nearly homogeneous materials. Hillebrandite was predominantly homogenous, but contained a few isolated particles of different refractive index. Okenite and truscottite contained noticeable amounts of intimately distributed material of different refractive index.

Powder X-ray patterns of afwillite and hillebrandite were in excellent agreement with those of Heller and Taylor [3]. The other minerals showed all of the principal lines of the compound in question, but gyrolite had a small extraneous line at 4.43 A, okenite had some calcite lines, and truscottite had some quartz lines and a few other unidentified lines.

Xonotlite was prepared by E. S. Newman of the National Bureau of Standards. It has been previously described [9].

Results

The absorption spectra of the compounds investigated are shown in figures 1 and 2. Figure 1 shows the spectra of γ-C_2S, β-C_2S, and C_3S and also paste and ball-mill-hydrated C_3S. Figure 2 presents the spectra of compounds in the CaO-SiO_2-H_2O system, arranged in the order of increasing CaO/SiO_2 ratio. With the exception of xonotlite, all of the specimens in figure 2 are natural minerals.

Discussion

General Spectral Features

Gamma dicalcium silicate, β-C_2S, and C_3S show broad absorption in the 700 to 1200 cm^{-1} region. This feature is common to the spectra of most silicates [10], and is associated with a number of vibrational modes associated with Si—O linkages. D. M. Roy [11] has also measured γ-C_2S and β-C_2S in this region and obtained patterns between 700 and 1200 cm^{-1} somewhat similar to the ones in figure 1. She found γ-C_2S to give an altered spectrum in KBr pellets, which suggests that under some circumstances this compound may be subject to anion exchange or other effects sometimes observed in KBr [12, 13, 14, 15, 16]. However, the 700-to-1200-cm^{-1} part of the spectrum in figure 1 resembles Roy's spectrum in nujol mull rather than her KBr spectrum. Possibly this may be due to the short (15 seconds) mixing time used in preparing the pellets. Launer [17] has also measured the spectrum of β-C_2S at 620 to 5000 cm^{-1}. The comparable parts of Roy's and Launer's patterns are slightly sharper than the one shown in figure 1. The very small band at 1260 cm^{-1} is very possibly due to the boric acid stabilizer in the compound [18]. It is absent from Launer's β-C_2S which was prepared without a stabilizer. The method of preparation is described by King [19].

When C_3S is hydrated as a paste, the spectral detail in the 700-to-1200-cm^{-1} region is lost, and the center of this broad absorption shifts to higher frequency. This particular preparation shows no band at 12.1 μ where Van Bemst [20] reported an absorption band in CSH-II. In the region 3000 to 4000 cm^{-1} there is a sharp band at 3620 cm^{-1}, due to $Ca(OH)_2$ in the product, and a broader band near 3450 cm^{-1} somewhat similar to the one found in Loch Eynort tobermorite. The OH bending vibration near 1650 cm^{-1} is broad in hydrated C_3S but comparatively sharp in Loch Eynort tobermorite. Also noteworthy are the spectral differences between these materials in the range 300 to 600 cm^{-1}.

Kalousek and Roy [21] have prepared a synthetic tobermorite with a CaO/SiO_2 ratio of 0.8 and a spectrum in the interval 620 to 5,000 cm^{-1} similar to that of Loch Eynort tobermorite. On the other hand, their calcium silicate preparations of larger CaO/SiO_2 ratio bear more resemblance to paste-hydrated C_3S. According to Brunauer and Greenberg [1], the tobermorite obtained by hydration of C_3S or β-C_2S resembles a high-lime tobermorite far more than a low-lime tobermorite. This is also true of the infrared spectra.

The similarity between Kalousek and Roy's hydrates having a large CaO/SiO_2 ratio and paste-hydrated C_3S also includes the strong band between 1400 and 1600 cm^{-1} which is due to the 0.5 percent of CO_2 found in the material. A carbonate contamination in $Ca(OH)_2$ or a high-lime calcium silicate hydrate produces stronger absorption in the region 1400 to 1600 cm^{-1} than a comparable amount of carbonate in a low-lime material [22].

Brunauer, Copeland, and Bragg [23] have shown that C_3S hydrated in a ball mill gives afwillite as a hydration product. Figure 1 shows the infrared absorption spectrum of a ball-mill preparation made in their laboratory. The spectrum may be compared with that of natural afwillite shown in figure 2. The patterns show some differences in detail, but there is good correspondence between the positions of the principal absorption bands. The bands are less sharp in ball-mill-hydrated C_3S than in the natural mineral, particularly in the region of longer wavelengths. The ball-mill-hydrated product shows a sharp band at 3620 cm^{-1} due to $Ca(OH)_2$. This band is absent from the natural material.

Examination of the spectra of the calcium silicate hydrates in figure 2 shows that most of the patterns are sufficiently distinctive to be of value in identifying the minerals. The bands at 1500 and 875 cm^{-1} in okenite and gyrolite clearly show the presence of calcite as a contaminant. Hillebrandite, truscottite, and xonotlite also show a small absorption near 1500 cm^{-1}.

Kalousek and Roy [21] have determined the spectrum of a natural xonotlite in the region 620 to 5000 cm^{-1}. Their spectrum resembles the corresponding part of the spectrum in figure 2 quite closely, except that their pattern shows slightly less detail near 680 and 980 cm^{-1}, and the band at 3430 cm^{-1} is weaker. They also have noted that this latter band is weaker in natural than in synthetic xonotlite, particularly in preparations made at lower temperatures.

Berkovich, Keiker, Gracheva, Zevin, and Kupreeva [24] have measured the spectrum of a synthetic tobermorite in the interval 830 to 5000 cm^{-1}. Their product shows less spectral detail than the natural mineral or Kalousek and Roy's preparation, but it does not resemble the hydrated C_3S.

SiO_4 Vibrations

It would be possible to account for considerable complexity in the absorption spectra of the silicates from the fundamental vibrations of the SiO_4 tetrahedra, even neglecting possible absorptions due to harmonics, combination bands, and lattice vibrations. This may perhaps best be shown by briefly reviewing the vibrational behavior of the free tetrahedron and considering the modifications of the vibrations as the tetrahedron is incorporated in a crystal. According to the theory of molecular vibrations [25a, 26, 27], any nonlinear molecule of five atoms should have nine fundamental vibrations. However, in XY_4 molecules of tetrahedral symmetry only four fundamental frequencies appear [10, 25b, 28], because a number of vibrations have the same frequency, that is to say are degenerate. Of the four fundamental vibrations of the tetrahedron, only two are infrared active. This is summarized briefly in table 1.

TABLE 1. *Fundamental vibrations of tetrahedral* XY_4 *molecule*

Vibrational species	Number of vibrations	Frequencies of SiO_4 ion[a]	
		cm^{-1}	
A_1 nondegenerate	1	800	Raman active.
E doubly degenerate	1	500	Raman active.
F_2 triply degenerate	2	625, 1050	Infrared and Raman active.

[a] Data from Landolt Bornstein, vol. I, pt. 2, p. 258, based on Raman spectra of glasses.

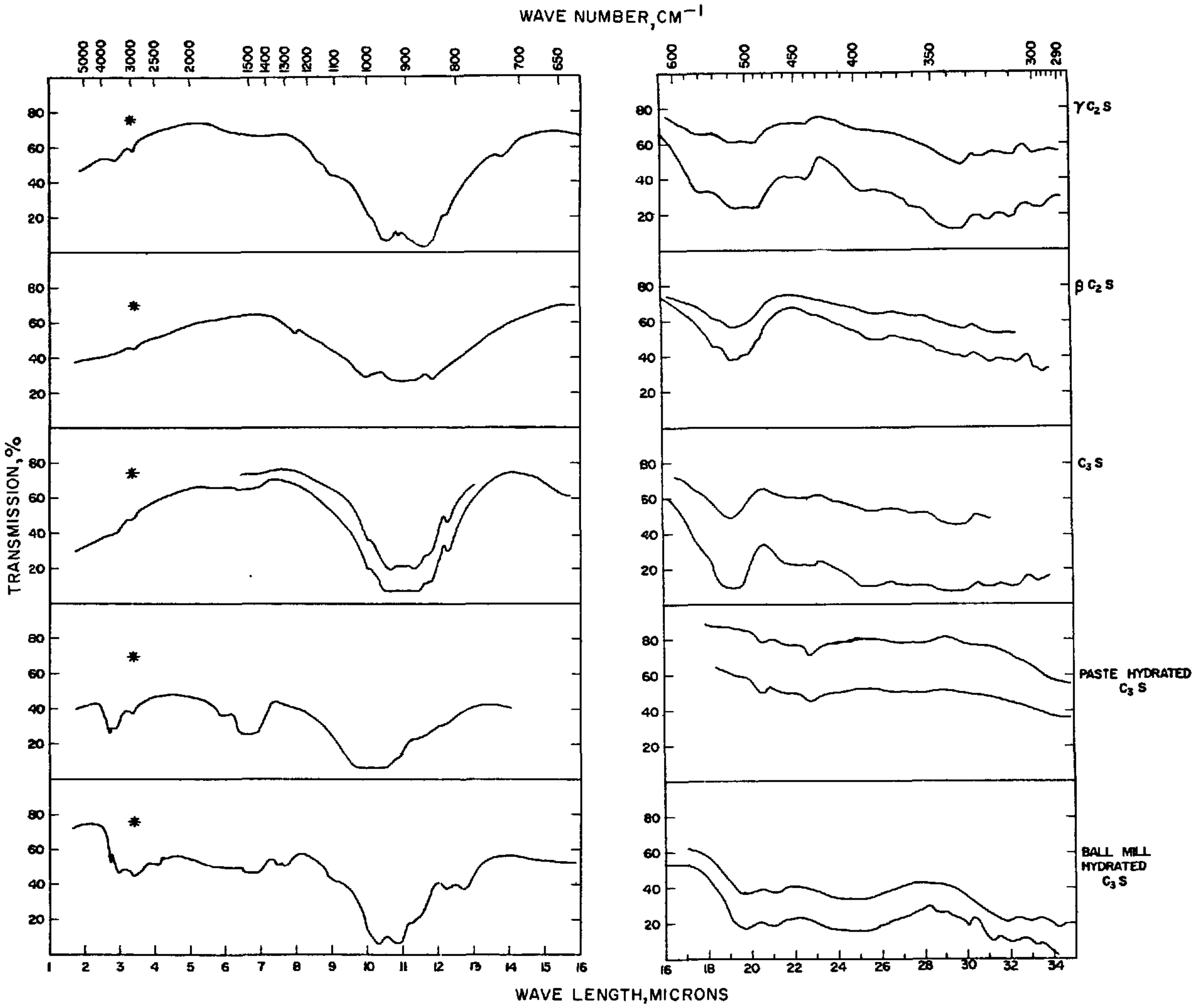

FIGURE 1.—*Infrared absorption spectra of* γ-C_2S, β-C_2S, C_3S *and paste- and ball-mill-hydrated* C_3S.

The pellets corresponding to the lower curves contained 1 mg of compound in 250 mg KBr, and those for the upper curve, where two curves are shown, contained 0.3–0.5 compound in 250 mg KBr. *Denotes there is small absorption in the spectrum of the KBr in this position.

If the SiO_4 group is part of a crystal lattice, the crystal plays a dominant role in determining which vibrations appear in the spectrum. If the oxygens are no longer equivalent, as is usually the case in a crystal, instead of vibrating as a tetrahedron the SiO_4 group vibrates as a body of lower symmetry. This means that degenerate vibrations may be split into separate frequencies, and vibrations which are inactive in the free tetrahedron may be infrared active in the crystal.

Schaeffer, Matossi, and Wirtz [10] have suggested that absorption between 8 and 12 μ in the spectrum of silicates arises from one of the triply degenerate vibrations of the SiO_4 tetrahedron. If this hypothesis is correct, one of the reasons why absorption in this region is broad and complex in so many silicates may be that splitting of these vibrations occurs.

Halford [29] has outlined a method for predicting the number of fundamental vibrations of a crystalline solid when the space group symmetry and number of molecules per unit cell are known It has been quite successful with some simple compounds. In γ-C_2S, which has space-group symmetry Pbnm and cell contents 4(Ca_2SiO_4) [3, 30, 31], the SiO_4 group occupies sites having mirror-plane symmetry. According to Halford's method it should vibrate according to the selection rules for a body having only mirror-plane symmetry. Under these circumstances, the SiO_4 group should have nine fundamental vibrations, all of which are infrared and Raman active. The absorption spectrum of γ-C_2S in figure 1 shows at least this number of vibrations, disregarding absorptions below 400 cm^{-1} which include, or might be entirely due to, translational lattice vibrations From single-crystal measurements [30], as well as analogy with Na_2BeF_4 [31], γ-C_2S has the olivine structure in which the SiO_4 groups are present as isolated tetrahedra, but because of the restrictions of the crystal they do not vibrate as free tetrahedra. However, it would be possible

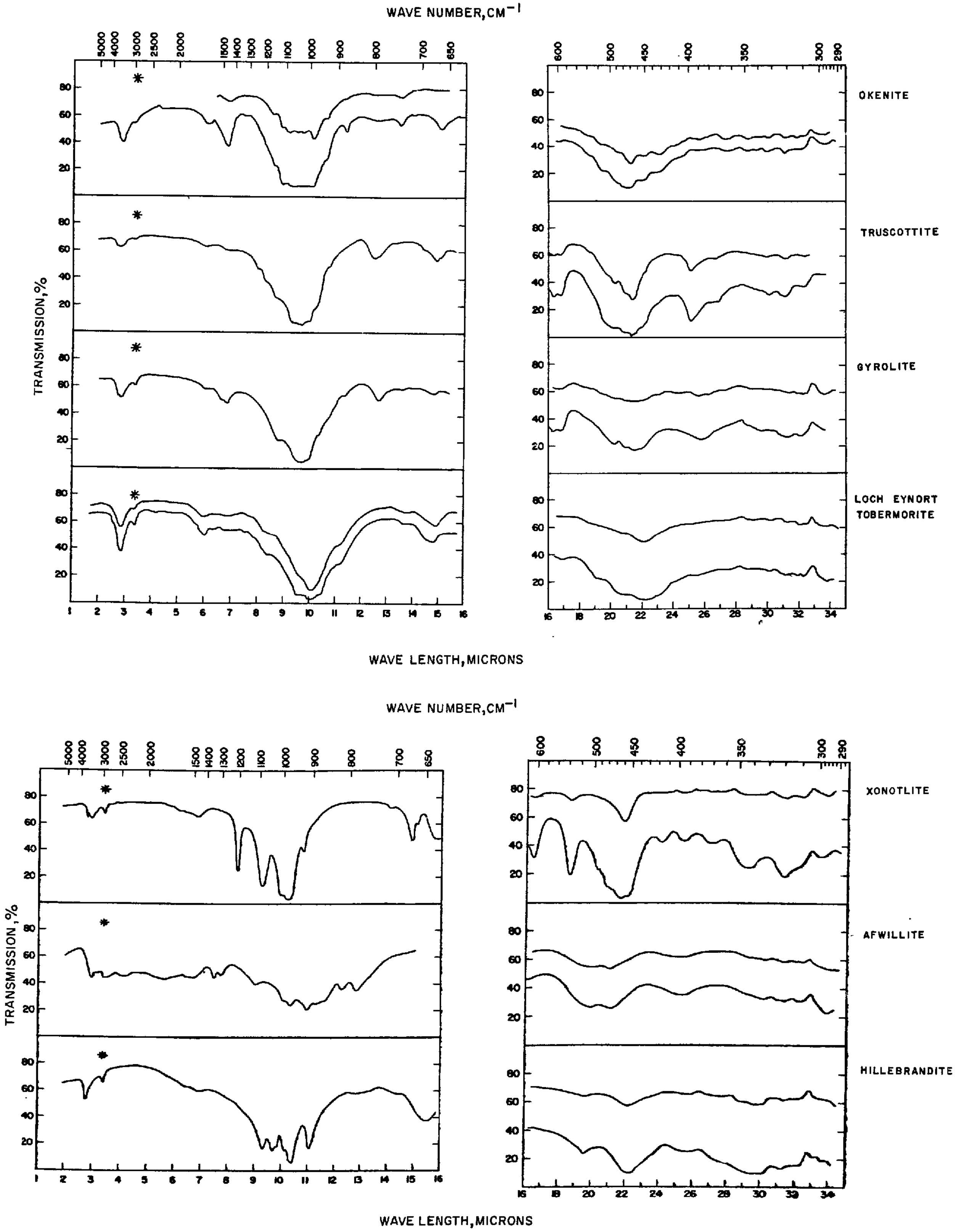

FIGURE 2.—*Infrared absorption spectra of minerals in the* CaO-SiO_2-H_2O *system.*

The pellets corresponding to the lower curves contained 1 mg of compound in 250 mg KBr, and those for the upper curve, where two curves are shown contained 0.3–0.5 mg of compound in 250 mg KBr. *Denotes there is small absorption in the spectrum of the KBr in this position.

to make some plausible correlations between the absorption bands in γ-C_2S and the four frequencies of the free tetrahedron if the three closely grouped bands at 861, 917, and 948 cm^{-1} arise from the splitting of one triply degenerate vibration, the bands at 490, 512, and 560 cm$^{-}{}_{1}$ arise from splitting of the other triply degenerate vibration, the bands at 440 and 454 arise from splitting of the doubly degenerate vibration, and the band at 726 cm^{-1} is due to the nondegenerate vibration. Bands unaccounted for in this assignment would be harmonics, combination bands, and lattice vibrations.

Beta dicalcium silicate has space-group symmetry $P2_1/n$ and four molecules per unit cell [3, 32]. According to the structural analysis of Midgley [32], the SiO_4 tetrahedra are in general positions. Therefore, the site symmetry cannot be used directly to determine the selection rules for the vibrations of SiO_4 in β-C_2S as in γ-C_2S. The spectrum of β-C_2S in figure 1 contains a group of vibrations at 503, 518, and 539 cm^{-1} and another group of vibrations at 844, 909, and 1010 cm^{-1}. These two groups of bands may plausibly be interpreted as derived from splitting of the two triply degenerate vibrations in the free tetrahedron. However, the spectra of Roy [11] and Launer [17] suggest that there may possibly be more spectral detail to account for in well-crystallized material.

For the more complicated silicates, correlation of bands in the 350 to 1250 cm^{-1} region with crystal structure remains empirical. Descriptively speaking, a structure in which the SiO_4 tetrahedra are all equivalent might be expected to have fewer bands than a structure in which SiO_4 is present in more than one kind of environment. However, since a single SiO_4 group could account for as few as two infrared active fundamentals or as many as nine, depending on crystal symmetry, the number of bands in the spectrum affords a rather insensitive test of the complexity of a silicate structure. Furthermore, in ring, chain, and sheet structures, where covalent bonds between SiO_4 groups may be present, the model of SiO_4 tetrahedra subject to the modifying effects of a crystal field is not applicable.

OH Vibrations

Some of the OH absorptions in the calcium silicate hydrates are weak, and KBr is somewhat hygroscopic. This hygroscopicity offers no problem in detecting strong OH absorptions but makes the measurement of weak bands difficult. It is common practice to use a blank pellet in the reference beam to compensate for absorbed water in KBr. Another procedure, suggested by Baker [13], is to heat the pellets in vacuum for several hours. This treatment removes absorbed water from KBr rather effectively, and because rediffusion is slow permits measurement of a spectrum. This procedure provides spectra of unhydrated compounds more nearly free of OH absorption than the reference-pellet technique and has been adopted in the present measurements. It unquestionably removes adsorbed water, and in some cases, loosely held combined water from the compounds themselves. Nevertheless, useful empirical comparisons can be made with this procedure, as has been done in figures 1 and 2.

The OH bending vibration which appears near 1650 cm^{-1} in water is weak or absent from the spectra of truscottite, xonotlite, and hillebrandite. Kalousek and Roy [21] have previously noted the absence of this band in xonotlite. According to Lecomte [33, 34] the absence of absorption at this frequency is characteristic of hydroxides. If the OH is attached to a heavy atom by a covalent bond, as for example in methyl alcohol [25c], the OH vibration is shifted to slightly lower frequency. If the OH is in an ionic crystal and is not attached by a covalent bond, as in $Ca(OH)_2$, the bending vibration, if it exists at all, would be more in the nature of a hindered rotation and would appear in a completely different region of the spectrum.

Okenite, tobermorite, and possibly also gyrolite' retain a small OH bending vibration after evacuating the pellets at 100 °C. Kalousek and Roy [21] have reported absorption at 1650 cm^{-1} after heating a synthetic tobermorite at elevated temperature. They have attributed this absorption to interlayer water. As previously mentioned, the hydration product of C_3S also retains an absorption in this position, but it is broad rather than sharply defined as in the better-crystallized tobermorites of smaller CaO/SiO_2 ratio. According to Brunauer and Greenberg [1] the hydration product of C_3S or β-C_2S has a density consistent with a *c*-spacing of 9.3 A after drying at a water vapor-pressure of 5×10^{-4} mm mercury. This spacing should accommodate no interlayer water. Nevertheless, in the case of hydrated C_3S, a small bending vibration is retained after heating in vacuum.

The structure of afwillite contains H_2O molecules as well as OH groups [35]. There is undoubtedly absorption at 1650 cm^{-1} in the spectrum of afwillite, but there is no sharp band in this position. From this point of view, the water in afwillite is different from the water of crystallization of a typical salt hydrate.

The OH stretching vibrations are of particular interest, because they appear at smaller wave numbers in hydrogen-bonded systems [36]. Unbonded OH has a stretching absorption near 3700 cm^{-1}, while hydrogen-bonded OH absorbs at lower frequencies. In the case of water, for example, this change has been demonstrated by comparing the spectrum of a dilute solution of water in carbon tetrachloride with the spectrum of the pure liquid [37]. In the case of crystalline solids, data collected for a large number of compounds show a correlation between the shift in OH stretching frequency and the distance between oxygen atoms in O—H—O bonds [38–45]. Gorman [46] has reviewed much of this evidence. However, simple application of this principle to unfamiliar compounds is complicated by the fact that a few bands which are probably not OH stretching fundamentals have also been found in this region of the spectrum. A spectrum of powdered $Ca(OH)_2$ in KBr shows a predominant sharp band at about 3620 cm^{-1} [22], which would be a very reasonable frequency for an OH stretching vibration without hydrogen bonding. However, Petch and Megaw [47] and Busing and Morgan [48] have shown that oriented single crystals of portlandite have a number of bands. A similar complexity has been observed with brucite [49]. Roy and Roy [50] have raised the question as to which absorption maximum should be chosen for correlation with O—O distance in such cases. The existence of more than one absorption maximum would be expected if OH groups are not equivalent and more than one O—O distance exists in the crystal. However, such an explanation would not apply to portlandite or brucite. In view of the large number of examples in which interatomic distance has been correlated with frequency shift [38–45] the principle has validity, but a certain amount of ambiguity is introduced by the fact that bands other than OH stretching fundamentals appear in the region of the spectrum where these fundamentals occur.

Under the resolution obtained in the present measurements, okenite, truscottite, and tobermorite show single broad stretching absorptions. The frequency displacement of approximately 200 cm^{-1} suggests hydrogen bonding of strength comparable with that found in liquid water.

The spectrum of paste and ball-mill-hydrated C_3S both show a sharp absorption near 3620 cm^{-1} due to $Ca(OH)_2$ which contains no hydrogen bonds. They also show broad absorption at longer wave lengths due to the presence of hydrogen bonds of moderate strength in the calcium silicate hydrates. The spectra of gyrolite and xonotlite show somewhat analogous double absorption, suggesting the presence of OH groups both with and without hydrogen bonding in the compounds themselves.

Hillebrandite shows a double peak near 3600 cm^{-1}. This position does not suggest very strong hydrogen bonding. However, broadening of the band near the top suggests some perturbation of the OH stretching frequency.

The spectrum of afwillite between 2000 and 3600 cm^{-1} has been carefully studied by Petch, Sheppard, and Megaw [51], with a CaF_2 prism. They have measured both powdered material and oriented single crystals. They have also used polarized radiation to determine the direction of vibrations where possible. From crystal-structure considerations [35], they postulate six positions where hydrogen bonds occur. Three of these have interatomic distances close to 2.7 A, which would correspond to absorptions at wave numbers of the order of 3000 cm^{-1}, and three have interatomic distances close to 2.5 A, which would correspond to much smaller wave numbers. In powdered afwillite they found bands at approximately 2400, 2800, 3130, and 3340 cm^{-1} as well as absorption at smaller wave numbers which was difficult to resolve. The spectrum in figure 2 shows the bands at 2400, 2800, and 3340 cm^{-1}, but the 3130 cm^{-1} band is not resolved. This spectrum also shows that unresolved absorption extends well below 2000 cm^{-1}. If the absorption between 1500 and 3400 cm^{-1}, both resolved and unresolved, results from the six hydrogen bonds suggested by Petch, Sheppard, and Megaw [51], comparison with the other calcium silicate hydrates in figure 2, suggests that none of these compounds have as many or as strong hydrogen bonds as those found in afwillite.

The author is indebted to Professor Ellis R. Lippincott of the University of Maryland for helpful discussions of the theory and interpretation of infrared spectra, and to Dr. Deane K. Smith of the Portland Cement Association Fellowship at the National Bureau of Standards for discussion of X-ray crystallography of β-C_2S and γ-C_2S. The author is also indebted to those mentioned in the text who provided specimens for this study.

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Discussion

Rustum Roy

In recent studies of the infrared spectra of the hydrated magnesium and aluminum silicates Stubican and Roy[1, 2] have adopted an empirical approach which takes advantage of the ability to control precisely by synthesis the cations (including H^+, D^+) involved in the structure. In connection with the present paper it is only relevant to point out that many of the assumptions regarding the selection rules in solids do not prove to be of any real value. Furthermore, it has been shown that only with Si^{4+} (or other tetravalent metal ions) is there any meaning to the assignment of a particular frequency to a metal-oxygen stretching or bending mode. Even with Al^{3+}, and especially with divalent ions, the rest of the structure and the contrapolarizing effect of the cations in the second sphere of coordination have such large effects on the frequency at which a particular vibration mode appears, that assignment at fixed frequencies is not very meaningful in most cases. The present state of the most definite assignments in layer silicates showing the range of their variation with substitution is shown in summary form in figure 1. It may be of some help in suggesting interpretations of some of the spectra presented by Dr. Hunt. One of the most interesting results, part of which appears in figure 1, is the verification of the previous tentative assignment of the 11μ band in kaolinite as the bending mode of O-H. It will be noted that this vibration is labelled H-O-Al to indicate the importance of the cation to which the $(OH)^-$ is attached: for example it will be seen that the same vibration appears at about 12μ in

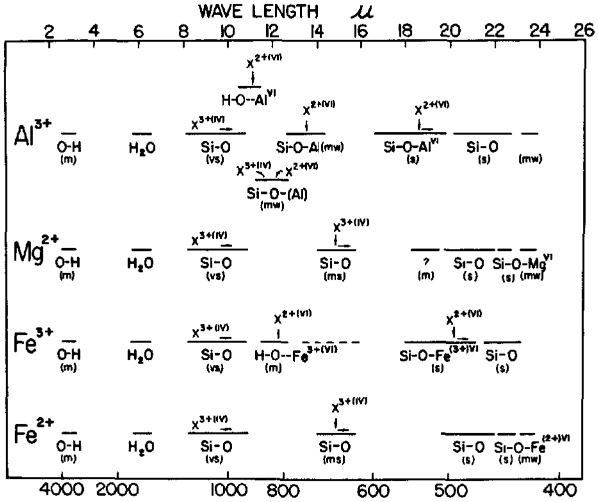

FIGURE 1. *Infrared absorption in layer silicates.*

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H-O-Fe^{3+}. These bands are all shifted by about a 1.37 ratio when D is substituted for H. They also respond to Ga^{3+} substitution and presumably appear only at much longer wave lengths with divalent cations such as Mg^{2+}. Therefore, H-O-Ca bending moments may not appear at low enough frequencies to be detected here.

Exceptions to this scheme may occur in the case of strongly polarizing ions such as Zn^{2+} or Cd^{2+} in which case the absorptions may well appear below 15μ.

(Note—This discussion is Contribution Number 60-58 of the College of Mineral Industries, The Pennsylvania State University.)

Closure

C. M. Hunt

The problem of identifying the vibrational modes and assigning frequencies is difficult when dealing with polymeric materials. The concept of symmetry and its role in determing the number and kind of vibrations, which is applicable to simple molecules, is mainly of descriptive value when applied to more complex structures. However, even on a descriptive basis it serves as a reminder that a change in crystal symmetry could lead to a change in the number, kind, and position of bands in the infrared absorption spectrum. More empirical study of compounds of known structure is needed, and the work with synthetic layer minerals referred to by Dr. Roy is an important step in this direction.

Aside from considerations of symmetry, the "ionic" or "covalent" character of the M—O bonds themselves is also important in determining the vibrational characteristics of the crystal. Miller and Wilkins[1] concluded from the examination of spectra of a number of sulfates, nitrates, carbonates and other polyatomic anions that their absorption frequencies were sufficiently characteristic to have analytical value, even though the cation also exerted some effect on the spectrum. The N—O, S—O, and C—O bonds in these anions have considerable directional or "covalent" character. Al—O, Fe—O, and Mg—O bonds undoubtedly have more "ionic" or nondirectional character than bonds in these typical polyatomic anions or Si—O bonds in silicates. The "ionic" or "covalent" character of the bonds would be more important than valence per se in determining the presence or absence of characteristic frequencies.

Returning to figures 1 and 2 in the original paper, Roy's comments also point up the desirability of examining deuterium analogs of the calcium silicate hydrates in the figures to identify Si—O—H bending modes which at present have not been distinguished from Si—O frequencies.

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Paper III–S9. Crystalline Solubility and Zeolitic Behavior in Garnet Phases in the System $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}H_2O$*

Della M. Roy and Rustum Roy

Synopsis

The earlier confusion on the formation of hydrogrossularites from the grossularite composition is shown to be due to failure to attain equilibrium. Anhydrous grossularite can be synthesized with water catalysis at least as low as 600 °C. Stable solid solutions have been prepared only from C_3AH_6 to $C_3AS_2H_2$, the latter being the most stable (360 °C at 2000 atm). Phases with lattice constants only slightly larger than grossularite (up to 11.90 A) can be prepared from silica-rich members of the series, but these are thought to be metastable.

Solid solution along the join $C_{12}A_7$-C_3AS_3 was very limited in extent, although some change in the lattice constant and refractive index of $C_{12}A_7$ was observed in mixtures on the join.

Data obtained by means of a recording balance demonstrate clearly a zeolitic behavior of "$C_{12}A_7$", as the phase adsorbs varying amounts of H_2O with varying temperature. This phase is more accurately described as a hydrous phase under atmospheric condition with the composition of about $C_{12}A_7H$. Metastable "hydrogrossularite" formed through very short runs at intermediate temperatures showed a similar behavior, but rehydration was no longer complete after dehydration above 800 °C.

Résumé

Il est indiqué que la confusion antérieure sur la formation d'hydrogrossularites à partir de la composition du grossularite a pour cause l'insuccès à atteindre l'équilibre. La synthèse du grossularite anhydre peut être réalisé avec catalyse de l'eau à une température au moins aussi basse que 600 °C. Les solutions solides stables n'ont été préparées que de C_3AH_6 à $C_3AS_2H_2$, ce dernier étant le plus stable, (360° à 2000 atm.). Les phases avec constantes de réseau seulement légèrement plus grandes que celle du grossularite (jusqu'à 11.90A) peuvent être préparées à partir de membres de la série riches en silice, mais on a des raisons de penser que ceux-ci sont métastables.

La solution solide était très limitée le long de la ligne $C_{12}A_7$-C_3AS_3, cependant on observa des changements concernant la constante de réseau et l'indice de réfraction de $C_{12}A_7$ dans les mélanges sur la ligne.

Les résultats obtenus au moyen d'une balance enregistreuse démontrent clairement un comportement zéolitique de "$C_{12}A_7$", puisque la phase absorbe des quantités variables de H_2O avec la température variable. Cette phase est décrite plus précisément comme phase aqueuse sous condition atmosphérique avec la composition approximative de $C_{12}A_7H$. "L'hydrogrossularite" métastable formé pendant de très courts intervalles à des températures intermédiaires se comportait de la même façon, mais la réhydratation n'était plus complète après une déshydratation au-dessus de 800°.

Zusammenfassung

Die widersprechenden Angaben in der älteren Literatur über die Bildung der Hydrogrossularite aus Grossularitzusammensetzungen müssen darauf zurückgeführt werden, daß in den älteren Arbeiten die Gleichgewichte nie erreicht worden sind. Wasserfreier Grossularit kann mit Wasserkatalyse bei 600 °C synthetisiert werden, und vielleicht auch bei tieferen Temperaturen. Stabile feste Lösungen sind nur von C_3AH_6 bis $C_3AS_2H_2$ synthetisiert worden, und die letztgenannte Verbindung ist die stabilste (360 °C bei 2000 Atmosphären). Phasen mit Gitterkonstanten, die nur ein wenig größer als die des Grossularits sind (bis 11.90 Å), können von den silikatreichen Gliedern der Reihe hergestellt werden, aber es sieht so aus, als ob diese metastabil sind.

Feste Lösungen an der Verbindungslinie $C_{12}A_7$-C_3AS_3 kommen nur in einem kleinen Bereiche vor, aber einige Veränderungen der Gitterkonstante und des Brechungsindex des $C_{12}A_7$ wurde in den Mischungen an dieser Linie gefunden.

Messungen, die mit Hilfe einer Registrierwaage erhalten wurden, zeigen deutlich, daß $C_{12}A_7$ sich wie ein Zeolith benimmt, da diese Phase schwankende Mengen Wassers als Funktion der Temperatur aufnimmt. Diese Phase sollte doch unter atmosphärischen Bedingungen besser als ein Hydrat beschrieben werden, daß ungefähr die Zusammensetzung $C_{12}A_7H$ hat. Der metastabile, sogenannte Hydrogrossularit, welcher in kurzzeitigen Experimenten bei nicht zu hohen Temperaturen dargestellt wird, zeigte dasselbe Verhalten, aber er hat nicht mehr den alten Betrag Wassers gebunden, nachdem er einmal bei 800° C dehydratisiert worden ist.

Introduction

The knowledge of phase equilibrium relationships between the hydrogarnet C_3AH_6 and its silica-bearing counterpart grossularite, C_3AS_3, is important in understanding processes of hydration in aluminous cements. In addition to these two cubic garnets, a third closely related cubic compound $C_{12}A_7$, stable at relatively high temperatures is involved in the equilibria. The system $CaO\text{–}Al_2O_3\text{–}H_2O$, extensively investigated at low temperatures, has been studied by Majumdar

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the College of Mineral Industries, Pennsylvania State University, University Park, Pennsylvania.

and Roy [1][1] at elevated temperatures, and a review of literature up to 1956 included. They showed that at elevated pressures (~1000 atm) C_3AH_6 is the only stable calcium aluminate hydrate within the temperature range 100–200 °C, and that above this temperature $C_4A_3H_3 + Ca(OH)_2$ are in equilibrium with H_2O at elevated pressures (in contrast to the ready formation of $C_{12}A_7$ through dehydration of C_3AH_6 at atmospheric pressure). $C_4A_3H_3$ in turn decomposes to $C_{12}A_7 + Ca(OH)_2 + H_2O$ above 710 °C. A review of more recent literature on the system $CaO-Al_2O_3-H_2O$ *is given in the present symposium* [2].

The data available on the equilibria involved with the addition of silica are less complete. Yoder [3] attempted to synthesize grossularite from the C_3AS_3 composition at various temperatures and pressures, presumably forming "hydrogarnets" from the single composition. Flint, McMurdie, and Wells [4] produced garnets along the join C_3AH_6–C_3AS_3 and discussed the relationship of such hydrogarnets and those containing iron to sulfate resistance in cements, showing that both Fe_2O_3 and SiO_2 were important in increasing the resistance to sulfate attack [5]. Carlson [6] contemporaneously with work by the authors [7] formed crystalline garnets ranging from pure C_3AH_6 to C_3AS_3, but found that the cell constant of the garnet formed was a function of both temperature and compostition, as well as time, and the results were complicated by the presence of nonequilibrium phases.

The present investigation was begun with the hope of reconciling certain inconsistencies and obtaining new data as follows:

(1) From a single composition, C_3AS_3, Yoder claimed to have obtained a variety of products. How can this represent equilibrium?

(2) No data supported the existence of a complete solid-solution series between C_3AS_3 and C_3AH_6 at a single temperature. Does such a series exist, and if so, what are the temperature limits?

(3) The effects of time, temperature, and pressure as separate parameters in the crystallization of these phases were not well defined.

(4) The equilibrium relationships of $C_{12}A_7$ in the C–A–S–H system are not well established.

Experimental Procedure

Essentially amorphous mixtures of compositions along the C_3A–C_3AS_3 and $C_{12}A_7$–C_3AS_3 joins as shown in figure 1 were made by decomposition of alcohol-water solutions of calcium and aluminum

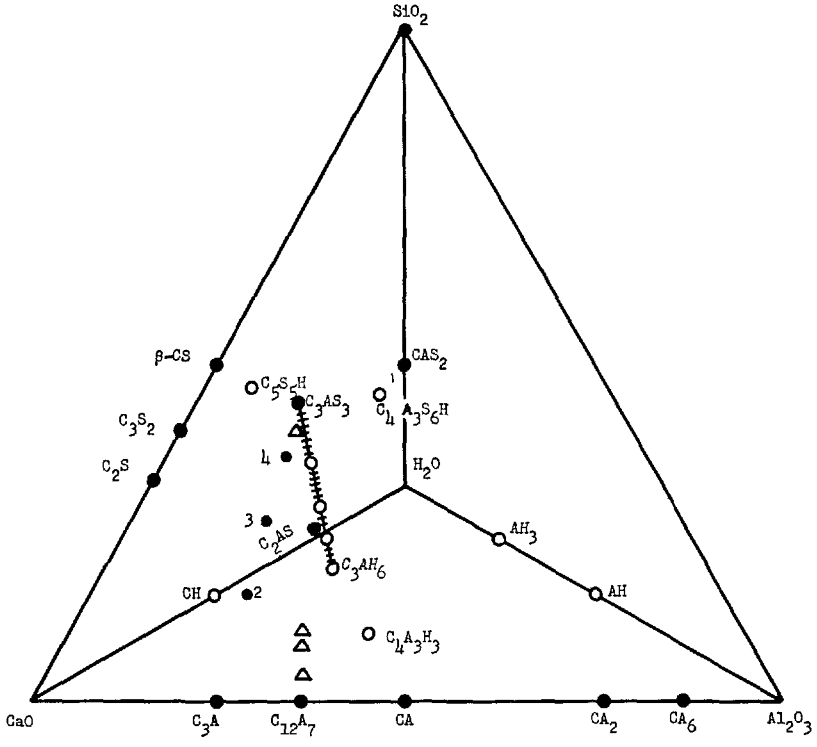

FIGURE 1. *Tetrahedron of the* C–A–S–H *system.*

Solid dots represent anhydrous compositions on the C_3A-C_3AS_3 join studied, open circles the correponding hydrated phases. Triangles represent $C_{12}A_7$-C_3AS_3 join compositions.

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[1] Figures in brackets indicate the literature references at the end of this paper.

nitrates with ethyl orthosilicate or Ludox (colloidal silica) (see Roy [8], Koizumi and Roy [9]). Some glasses were also used for the grossularite composition. Mixtures were treated hydrothermally (Roy and Tuttle, [10]) for periods of time varying from 1 hour to 3½ months. In many runs samples were held in gold-foil envelopes, but since it was desired to prevent transfer of material, many samples were contained in sealed gold or palladium tubes.

Grossularite Composition Crystallized at Different Temperatures

While several studies of the crystallization of presumed hydrogrossularites have been made starting with the grossularite composition C_3AS_3, it is clear that such a process is beset with unnecessary problems. When a hydrogrossularite appears from a total composition of C_3AS_3 it is usually assumed that silica has been leached out. Our results using hermetically sealed systems, however, gave the same result and directly disproved this suggestion. Furthermore a series of longer and longer runs made with the grossularite composition showed conclusively that one is dealing for the most part merely with failure to obtain equilibrium in short runs. In figure 2 the effect of length of run on the unit cell of the garnet formed demonstrates this point. Moreover, in runs under equivalent conditions, gels yield a more nearly anhydrous garnet than do glasses, indicating the danger of metastability when using glassy starting materials. Next, the cell dimension and index of refraction of the garnet formed from the grossularite composition at different temperatures was studied, and the results are shown in figure 3. Duration of the runs in most cases was at least one week, and the pressure was 2000 atm. Essentially pure grossularite with negligible water content, having $n=1.736$ and $a_0=11.86$ A is formed between 550 °C and 860 °C. Above 860 °C at 1000 atm. grossularite decomposes to wollastonite + anorthite + gehlenite. In the range 550 °C to 400 °C the garnet lattice is slightly expanded ($a_0=\sim 11.92$A max.) with a corresponding decrease in index of refraction, although the latter is higher than the range of hibschite, plazolite, and most of the naturally-occurring "hydrogrossular" minerals which are indicated on the left scale. The significance of the slightly expanded structures obtained below 550 °C is discussed in more detail in a later section. Anhydrous grossularite is therefore a stable phase at least as low as 600 °C and does not appear to require any pressure for its formation at equilibrium, the water pressure merely catalyzing the reaction. Anhydrous grossularite crystallized at 750 °C could not be rehydrated at 525 °C or 325 °C.

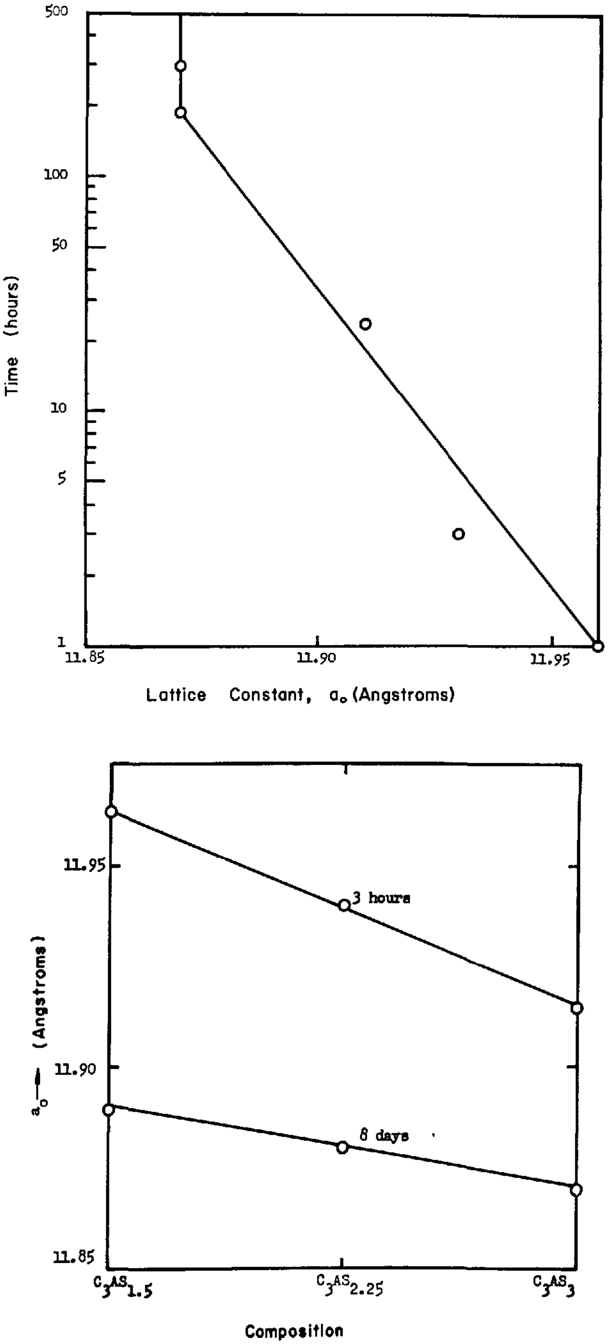

Figure 2. (a) *Lattice constant* a_0 *of grossularite formed from* C_3AS_3 *at 550 °C and 10,000 psi as a function of time.* (b) *Lattice constant obtained from various compositions in short and long runs.*

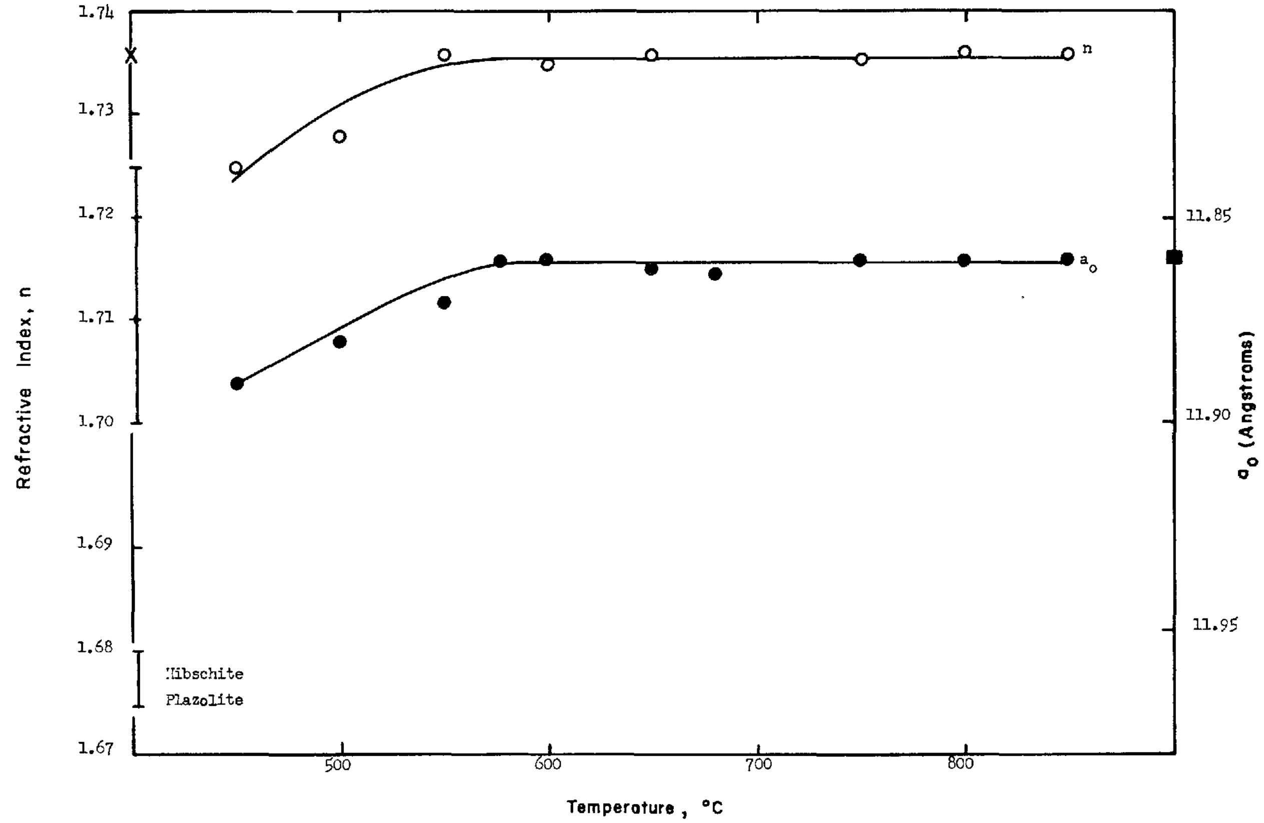

FIGURE 3. *Lattice constant a_0 and refractive index n of grossularite formed at different temperatures.*

Hydrogarnet Solid Solutions

The formation of a complete series of solid solutions from C_3AH_6 to C_3AS_3 was never achieved at a single temperature, and the evidence strongly suggests that the complete series is not stable. Two possible types of "hydrogarnets" are formed—one apparently a stable series extending from C_3AH_6 to about $C_3AS_2H_2$ at relatively low temperatures, and the other at intermediate temperatures (300–600 °C) probably metastable and limited in extent from grossularite to about $C_3AS_{2.75}H_{0.5}$. These assumptions are based on the data obtained as follows:

Runs up to the maximum stability temperature of C_3AH_6 (about 300 °C at 2000 atm.) yielded single-phase solid solutions extending beyond about $C_3AS_{1.5}H_3$, probably as far as $C_3AS_2H_2$, but other phases in addition to hydrogarnet were formed from mixtures richer in silica. The stability of such phases was tested by increasing the duration of the runs in a series, which did not affect the product materially. Typical results are given in figure 4, which shows the lattice constant a_0 of garnet or hydrogarnet formed as a function of composition at certain significant temperatures. The cell constant of the hydrogarnet solid solution formed at 300 °C between C_3AH_6 and $C_3AS_2H_2$ can be expressed by an almost straight line interpolation between the values for C_3AH_6 and C_3AS_3, although, as mentioned above, the solid-solution series was not complete. Instead of crystallizing grossularite, high-silica mixtures yielded hexagonal anorthite plus the appropriate calcium silicate hydrate in addition to a hydrogarnet.

Runs at the next higher temperature 350 °C yielded from the 1.5 SiO_2 composition a nearly single-phase hydrogarnet having, however, a much smaller a_0 than that formed at 300 °C. Compositions on either side yield a hydrogarnet which has very nearly the same cell dimension as that from the $C_3AS_{1.5}$ composition, mixed with other phases. These data suggest a maximum thermal stability of a hydrogarnet near the 1.5 mole SiO_2 composition (perhaps as high as 2.0 SiO_2 and stable only below about 360 °C). At 450 °C grossularite containing very little H_2O and having a_0=11.89 A was obtained from C_3AS_3, as well as in other compositions up to $C_3AS_{1.5}$, in which it was mixed with other phases. At 500 to 600 °C the garnet formed was essentially anhydrous, with a_0=11.86–11.88 A.

In addition to changes in lattice constant, changes in the intensity pattern of the X-ray reflections from hydrogarnet solid solutions obtained at 300 °C are observed, and typical patterns of different compositions are given in table 1. Increase in silica content diminishes the intensities of the low-angle reflections.

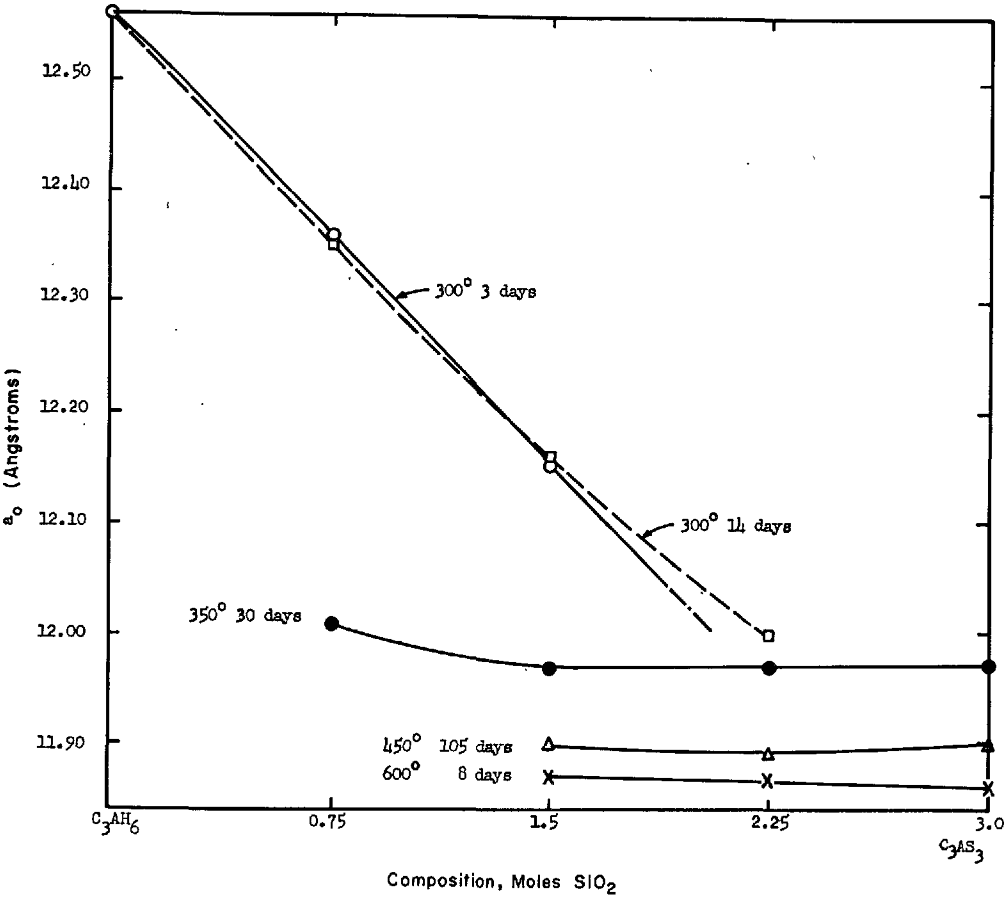

FIGURE 4. *Lattice constant of garnet formed on* C_3AH_6-C_3AS_3 *join at different temperatures.*

TABLE 1. *Intensities of reflections in hydrogarnets formed at 300 °C*

Composition	Mol. ratio				*hkl*											
	CaO	Al_2O_3	SiO_2	H_2O	211	220	310	321	400	420	332	422	431, 510	521	440	611, 532
1141	3	1	0.75	(4.5)	4	2	--------	2.5	5	10	(vw) 2	2.5	2.5	5	--------	6
1142	3	1	1.5	(3)	2	1.5	--------	--------	5	10	--------	2	2	3	--------	3
1157	3	1	2	(2)	1	--------	--------	--------	4.5	10	--------	1.5	1	2.5	--------	2.5

Temperature-Composition Diagram for C_3A–C_3AS_3 Mixtures

The results of studies along the C_3AH_6-C_3AS_3 join are summarized in a temperature-composition diagram in figure 5, illustrating the phases formed under water pressures of 1000 to 2000 atm from the anhydrous compositions indicated on the abscissa. A single-phase area is shown as existing stably only from $C_3A(H_6)$ to about $C_3AS_2(H_2)$; the hydrogarnet of maximum thermal stability is near the latter composition, stable to about 360 °C while higher-silica compositions yield this hydrogarnet+hexagonal anorthite+(probably) xonotlite. Grossularite or a slightly expanded hydro-grossularite (metastable?) mixed with $C_4A_3H_3$ and $Ca(OH)_2$ are formed at intermediate temperatures, while $C_{12}A_7$ is formed above the decomposition temperature of $C_4A_3H_3$. Above 860 °C grossularite decomposes to wollastonite+gehlenite+anorthite. The join CS-$C_{12}A_7$ furthermore appears to be stable at high temperatures. Dashed lines indicate probable relations. The alternative explanation of our data would entail moving the horizontal line at 360° to about 550 °C which would mean that a complete series of stable solid solutions could form and that the low-temperature silica-rich assemblages were metastable.

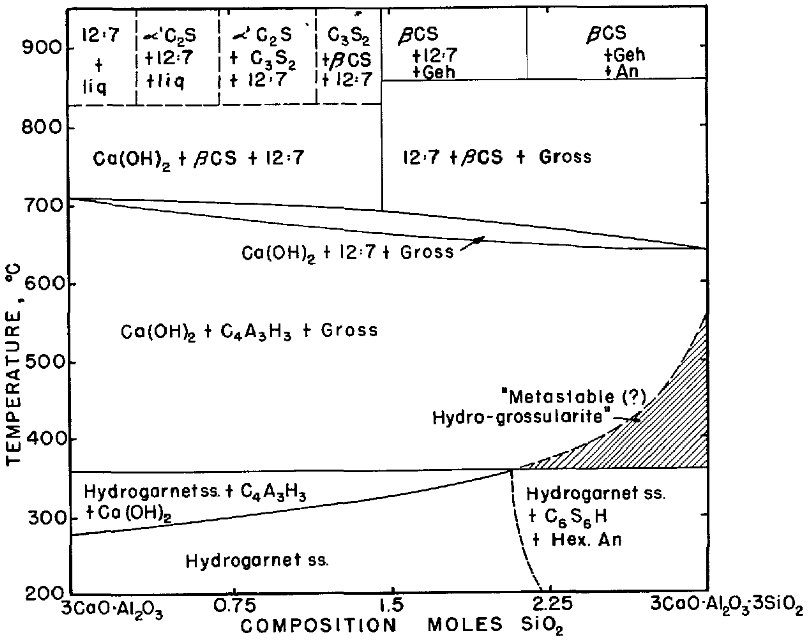

FIGURE 5. *Temperature-composition diagram for the* C_3A-C_3AS_3 *join at 2,000 atm* H_2O *pressure.*

An alternative interpretation would be to move the phase boundary at 360° to 550°, making the silica-rich hydro-grossularite stable, and the silica-rich low temperature assemblages metastable.

The Join $C_{12}A_7$–C_3AS_3

Early results obtained on the join C_3AS_3–C_3AH_6 indicated that the $C_{12}A_7$ formed at higher temperatures from decomposition of members near C_3AH_6 was variable with respect to index of refraction, lattice constant, and the intensity pattern of the X-ray reflections. Solid solubility of C_3AS_3 in $C_{12}A_7$ might be postulated to explain the differences. The compound $C_{12}A_7$ has a unit cell size only slightly larger than that of grossularite, and it was thought probable that the open structure of $C_{12}A_7$ [11] would enable it to incorporate silica into its lattice without any very drastic effects.

In order to test this theory, mixtures along the join $C_{12}A_7$–C_3AS_3 were made at molar ratios of 90:10, 80:20, 75:25 and 10:90, using $C_{36}A_{21}$ and $C_{24}A_8S_{24}$ as equivalent formulas for $C_{12}A_7$ and C_3AS_3, respectively.

The results unfortunately were not unequivocal. While in a single run a very slight decrease in cell constant with increasing C_3AS_3 was observed, from one run to another the values overlapped. Furthermore, even in the 10 percent C_3AS_3 mixture a second phase was usually detected (gehlenite), and no clear determination of refractive index changes in the $C_{12}A_7$ could be made because of the very small crystal size obtained in sealed tubes. The indices are, however, higher than those usually reported, being 1.610±0.002 for a sample prepared hydrothermally at 750° and 1,000 atm and in mixtures where SiO_2 was present were as high as 1.624±0.003, which would suggest some incorporation of SiO_2 into the structure. Certain differences in the intensity pattern of the X-ray reflections were observed, but were not entirely consistent. The overall results can merely be taken to suggest a small extent of crystalline solubility of C_3AS_3 in $C_{12}A_7$.

Zeolitic Behavior of H_2O in "$C_{12}A_7$"

One of the most unexpected findings of this study was the remarkable dehydration behavior of "$C_{12}A_7$" and the hydrogarnet series (e.g., $C_3AS_{1.5}H_3$). In contradistinction to normal discrete hydrates in which above a certain temperature for a certain partial pressure of H_2O the composition of the phase(s) remains constant, zeolites absorb and desorb water as a function of temperature (with p_{H_2O} fixed) without structural change. It was found that $C_{12}A_7$ can absorb water even at 1000 °C at a p_{H_2O} of 16 mm. Figure 6 shows the recording balance records of adsorption and desorption of water at a pressure of 16 mm as the temperature is varied. The solid curve was run at a heating rate of 3 °C per minute, while the circles show the relative weight of the sample after holding at the indicated temperature for several hours (in all cases except the

1200 °C point). All the steps indicated are reversible on heating and cooling.

Furthermore, there appears to be a correlation of the index of refraction and lattice constant of $C_{12}A_7$ with water content: Anhydrous $C_{12}A_7$ prepared at 1330 °C and examined immediately had $n=1.616 \pm 0.002$, while that prepared hydrothermally at 750 °C and 2,000 atm had $n=1.610 \pm 0.002$. A slight increase in cell dimension with increasing H_2O content was observed as follows: for the d_{642} spacing: 1330 °C=1.6006; 300 °C (at $p_{H_2O}=16$ mm)=1.6012; and 750 °C, 2,000 atm=1.6019 (all ±0.0002 A). The effect of water on the $C_{12}A_7$ properties therefore appears to be more consistent than the effect of solid solution with C_3AS_3. Indeed it is clear that $C_{12}A_7$ under ordinary atmospheric condition is not an anhydrous phase at all but rather a hydrate fairly close to the composition $C_{12}A_7H$.

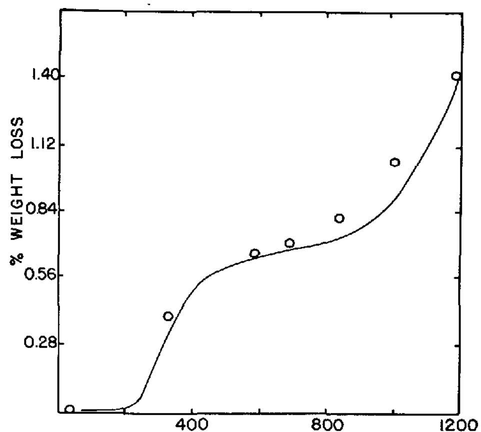

FIGURE 6. *Recording balance data for* $C_{12}A_7$.
Heating curve at 3 deg per minute.

"Hydro-Grossularite"

In line with the conclusion that hydrogarnet solid solution was limited to the C_3AH_6–$C_3AS_2H_2$ region, and that such solid solutions were stable to only about 360 °C, an attempt was made to determine the nature of the slightly hydrated product obtained near the C_3AS_3 composition at intermediate temperatures. First, the time study made at 550 °C and 10,000 psi (see fig. 2) revealed that expanded hydrated structures were obtained at first in very short runs, but that increased time resulted in a product approaching grossularite, both for C_3AS_3 and intermediate compositions (in the latter case mixed with other phases).

The hydration-dehydration behavior of some of these apparently metastable products was studied by means of the recording balance. Figure 7 shows some of the results from a phase formed at 520 °C, 10,000 psi for 2½ hours, a garnet with $a_0=11.91$ A. The curve was obtained by heating at 6 °C per minute at $p_{H_2O}=16$ mm, while the circles represent values after heating for several hours. The arrows from the 600° and 625 °C points indicate reversibility, but the 850° product rehydrated only partly on cooling to 300°, as shown by the dashed line. In this respect the "hydro-grossularite" differs from $C_{12}A_7$, although the "zeolitic behavior" persists at least as high as 625 °C, and involves approximately 3 percent reversible loss or gain.

Additional runs were made in attempt to rehydrate crystalline grossularite which had been synthesized at 750 °C and 30,000 psi. The results were negative at 325 °C and 30,000 psi and 525 °C and 55,000 psi. Results of other runs to determine whether or not a little H_2O could be stably incorporated into the structure of an intermediate composition, $C_3AS_{2.6}$, were not too conclusive. An expanded lattice with $a_0=11.92$ A was formed after 24 hours at 525 °C and 55,000, but decreased with increasing time.

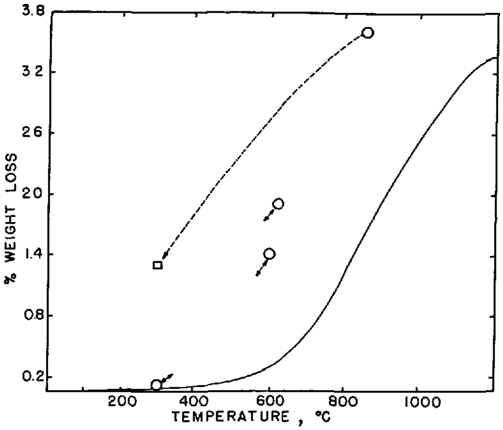

FIGURE 7. *Recording balance data for "Hydro-grossularite."*
Heating curve at 6 deg per minute.

From all our data it is clear that in glasses and gels of composition near grossularite, the calcium-aluminum-rich phases always crystallize first metastably, leaving some silica which then reacts very slowly to give the equilibrium phase. In addition the possibility of quite a different type than the tetrahedral hydroxyls may also enter the structures.

This study is part of a research program on polymorphism and subsolidus phase equilibria sponsored by National Science Foundation grants G–1000 and G–4648.

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Paper III–S10. Calcium Exchange in Systems of $x\mathrm{CaO{\cdot}SiO_2{\cdot}}y\mathrm{H_2O\text{-}Ca(OH)_2\text{-}H_2O}$*

T. Thorvaldson, F. W. Birss, and K. G. McCurdy

Synopsis

The exchange of calcium between hydrated C_3S and solutions of $Ca(OH)_2$ in equilibrium with it was studied. Two types of exchange seem to occur, one a rapid and the second a slow process. Comparisons are made between the exchange behavior of hydration products formed in the unsaturated range, a hydration product formed in supersaturated calcium hydroxide, and afwillite.

Résumé

Etude est faite de l'échange de calcium entre le C_3S et les solutions de $Ca(OH)_2$ en équilibre. Deux types d'échange semblent se produire, l'un est un procédé rapide et l'autre un procédé lent. Des comparaisons sont établies entre le comportement d'échange des produits d'hydratation formés dans le domaine non saturé, d'un produit d'hydration formé dans la solution de l'hydroxide de calcium sursaturé, et de l'afwillite.

Zusammenfassung

Der Kalziumaustausch zwischen hydratisiertem C_3S und $Ca(OH)_2$-Lösungen, die im Gleichgewicht stehen, ist untersucht worden. Augenscheinlich ereignen sich zwei Arten des Austausches: eine vollzieht sich schnell, die andere aber langsam. Die Austauschverhalten der hydratisierten Produkte, welche von der ungesättigten Lösung gebildet werden, des Hydrates, welches in übersättigten Kalziumhydroxyd geformt wird, und des Afwillits, werden verglichen.

Introduction

The very interesting paper of Brunauer and Greenberg on the hydration of C_3S and β-C_2S presents a clear account of the problems and the difficulties met with in the study of the hydration of the silicates of portland cement and gives an excellent report of the progress to date in that field.

The experiments which we wish to describe have been in progress somewhat intermittently during the last eight years. They grew out of attempts to determine the molar ratio of CaO/SiO_2 (referred to as r in what follows) in the hydration products of C_3S and β-C_2S without carrying the hydration to completion [1].[1] C_3S and β-C_2S labeled with the radioactive isotope Ca-45 were hydrated, with agitation, in a solution of calcium hydroxide near saturation or in the metastable region of supersaturation, and the fraction of the isotope appearing in the solution was plotted against moles of lime liberated per mole of the silicate. The curve obtained was then compared with theoretical curves for various r values, derived on the assumption that the silicate passes through the solution in the process of hydration. A general equation connecting the fraction of the isotope liberated to the solution and the r-value of the hydrated silicate was developed. This equation was developed on the assumption that exchange of calcium between the solution and the hydration product, after its precipitation from the solution, was negligible during the time of the experiment. A similar method was used for determining the value of r by using unlabeled C_3S, hydrated in a solution of lime labeled with Ca-45.

Considering the poor crystalline condition of the solid hydration product and the variation of its CaO/SiO_2 ratio with the concentration of calcium hydroxide in solution, one would expect at least a moderately rapid exchange of calcium ions between the solution and the hydrated solid. This exchange would affect the radioactive count of the solution and therefore also the curve for the radioactivity of the solution against lime liberated per mole of silicate. The amount of change in the curve would vary with the time of the experiment. The two extreme cases, no exchange and complete equilibrium exchange of the isotope, are readily subject to mathematical treatment. The object of the original work was to develop an experimental method by which r could be determined without completing the hydration of the silicate and to obtain evidence as to whether its probable value in a saturated or slightly supersaturated solution of lime at 21 °C. approximated 1.5 or 2.0. It so turned out that even with the extreme condition of complete exchange the theoretical curves were not altered sufficiently to affect the conclusion that the value of r in a saturated solution of calcium hydroxide, at 21 °C., under the conditions of the experiments approached 1.5. However, if one is to use the

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the University of Saskatchewan, Saskatoon, Canada. (Co-author Birss is now at the University of Alberta).

[1] Figures in brackets indicate the literature references at the end of this paper.

theoretical expressions for calculating exact values of r from data obtained by the tracer method under given conditions, exchange becomes of major importance. This led to a further study of exchange in such systems.

A theoretical paper has been prepared and submitted for publication by Fraser W. Birss in which mathematical expressions, by which r may be calculated, are developed on the basis of tracer methods for various mechanisms of hydration of the "through-solution" type, as well as for "direct" hydration, and for "hybrid" mechanisms combining some of the features of through-solution and direct hydration.

The tracer method has been tested by its application to the better understood mechanism of the hydration of plaster of paris, where the product is known, at least when excess of water is used, to separate from supersaturated solution as well-formed crystals of gypsum. The experimental results for the hemihydrate labeled with Ca-45 agreed well with the assumption of a through-solution mechanism for the hydration, and indicated no appreciable exchange between calcium ions in solution and the calcium in the crystals of gypsum after formation, in the time required for the hydration experiments. [2]

Experimental

In 1953 one of us decided to make a study of the exchange of calcium between a solution of calcium hydroxide, labeled with Ca–45, and completely hydrated C_3S. The hydrations were carried out by placing C_3S and carbon-dioxide-free water in sealed steel tubes lined with pure silver or fine gold and revolving the tubes, end over end, at 30 revolutions per minute for long periods of time in a room thermostated at 21 °C (and in later experiments at 25° and 8 °C).

The tubes were then centrifuged and two 25-ml portions of the clear supernatant liquid titrated with 0.06 M HCl using modified methyl red as indicator. The liquid removed was replaced by a solution of exactly the same concentration of calcium hydroxide containing the labeling agent Ca–45, and the tubes replaced on the shaker. From time to time they were centrifuged and 3 replicate samples of 0.5 ml were removed for counting. The counting times for each sample were such as to give 1 percent standard deviation (about 10,000 counts). Each replicate was counted three times and the 9 results averaged. Corrections were made for background, radioactive decay, and for coincidence if necessary. The above applies to all the experiments unless otherwise stated.

The HCl was standardized against individual samples of CaO, freshly prepared from purified low-alkali $CaCO_3$ (less than 0.002 percent of Na_2O). The value obtained by titration was checked by gravimetric determination of calcium with excellent agreement. The two samples of C_3S used were prepared, in platinum, from highly purified silica and the $CaCO_3$ described above, in an induction furnace. The analysis follows:

Sample	*CaO (Total)* %	*SiO_2* %	*R_2O_3* %	*CaO (free)* %
1–37	73.75	26.21	0.07	0.04
1–53	73.71	26.22	nil	0.03

The first three tubes were on the shaker for $10\frac{1}{2}$ to 11 months. They gave final concentrations of 3.15, 10.20, and 20.45 millimoles CaO per liter and calculated r-values of 1.00, 1.272, and 1.392, respectively. Dissolved SiO_2 was determined, and correction was made in calculating the lowest r-value. No silica was found in the liquid in the other tubes. Later control experiments, the tubes containing solutions of calcium hydroxide but no C_3S, showed no change in titer after being shaken for several months.

The exchange experiments gave a rapid loss in the activity [2] of the solution during the first 12 hours, indicating rapid exchange of calcium, the percentage loss during this period increasing with the r-value of the hydrate. After 12 hours the rate of loss of activity decreased greatly. Calculations of the ratio of the moles of lime not exchanged per mole of SiO_2 indicated that this ratio, in the case of $r=1.27$ and 1.39, reached a gently sloping plateau at a value slightly above 1 in two to five days. For $r=1.00$ the plateau was not so evident, and the exchange continued at a more rapid pace.

The calculations were made by means of the expression x (the moles of lime in the solid hydrate which at a given time have reached exchange equilibrium with the solution)$=a\left(\frac{\mathrm{T}}{\mathrm{A}}-1\right)$ where a=moles of lime in the solution; T=total activity in the system; A=total activity in the solution.

The moles of lime not exchanged per mole of silica$=\frac{m-x}{s}$, where m=moles of lime and s=moles of silica in the solid hydrate. T and a were corrected for the removal of activity and lime from the solution due to a previous sampling. The results are given in figure 1 [3].

Other hydrations were carried out on the shaker, at 25 °C, for periods of from 10 to 31 months. After adding the isotope the change in activity with time was treated graphically. (Four 0.5 ml replicates were taken at each sampling and counted as above, and the 12 values for activity were averaged.)

The specific activity of the lime in solution was calculated at each sampling. The log of the specific activity was then plotted against time. This plot gave a straight line, after a short initial period, and by extrapolation to zero time (i.e., the time of the introduction of the isotope) one

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[2] The term "activity" will be used to denote radioactive count.

can separate the effect on activity of the slow and the initial fast exchange, the latter usually being complete in 2 to 3 days. Figure 2 for a hydrate of $r=1.404$, and figure 3 for one with $r=1.05$, are examples of the curves obtained.

From the initial activity of the solution and the extrapolated value for the slow process, one may calculate the exchange of activity with the solid during the fast process and the amount of calcium in the solid which reached exchange equilibrium with the calcium in the solution (i.e., equal specific activity). As the weights of calcium and silica in the hydrated silicate are known from the hydration data, one may then calculate the molar ratio of the lime *not exchanged* to the silica in the solid.

This calculation may be accomplished in a single step by substituting the experimental values in the equation

$$r_0=\frac{(a_0+m)A_1-a_0A_0}{sA_1}$$

where

r_0=molar ratio of the calcium *not exchanged* by the fast process to the total silica in the hydration product

A_0=initial activity of the solution (reg/0.5 ml/min)[3]

A_1=the extrapolated activity of the solution-time curve at zero time (reg/0.5 ml/min)

a_0=total CaO in the solution at the beginning of the exchange reaction (millimoles)

m=total CaO in the hydration product (millimoles)

s=total SiO_2 in the hydration product (millimoles).

As an alternative to the above one obtains the same result by plotting the logarithm of the specific activity of the CaO in the solid hydrate against time, extrapolating the curve for the slow reaction to zero time and calculating r_0.

Table 1 gives a summary of the results of the hydration and exchange experiments.

TABLE 1. *Summary of results*

Experiment	Weight C_3S	Time of hydration	Final conc. $Ca(OH)_2$ in solution [a]	Overall molar CaO/SiO_2 ratio	Calc. r_0	Temperature
	g	*mo*	*mM*			°*C*
121 [b]	0. 0257	11	3. 15	1. 00	0. 76	21
122	. 1007	10. 5	10. 20	1. 272	1. 09	21
123	. 2168	11	20. 45	1. 392	1. 14	21
502	. 1007	14	10. 30	1. 261	--------	21
503	. 2168	14	20. 40	1. 391	--------	21
56 [c]	. 1000	11	12. 39	1. 323	1. 05	25
58	. 1000	24	12. 54	1. 296	0. 95	25
57	. 1000	31	12. 39	1. 328	1. 06	25
62	. 1850	11	19. 88	1. 405	0. 98	25
59	. 1850	10. 3	19. 89	1. 404	. 94	25

[a] Saturated solution of $Ca(OH)_2$ at 21 °C—20.95 millimoles/liter
at 25 °C—20.15 millimoles/liter [7].

[b] Experiments 121–123, 502 and 503: C_3S 1–53 was hydrated in 75 ml H_2O.

[c] Experiments 56–59 and 62: C_3S 1–37 was hydrated in 75 ml of solution containing 2.55 millimoles CaO/liter.

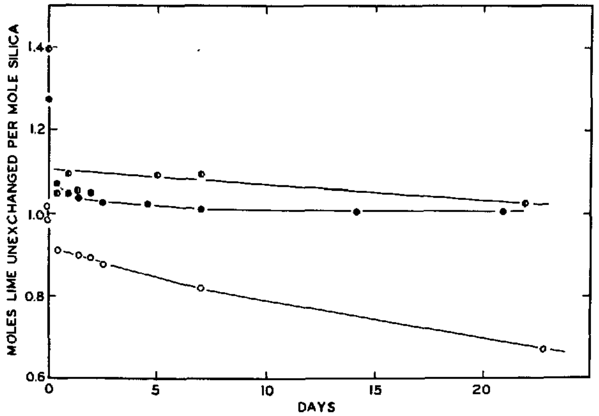

FIGURE 1. *Calcium exchange in an equilibrium system: Labeled* $Ca(OH)_2$ *solution-solid hydrated* C_3S *at 21 °C.*
◑, $CaO/SiO_2=1.39$; ●, $CaO/SiO_2=1.27$; ○, $CaO/SiO_2=1.00$.

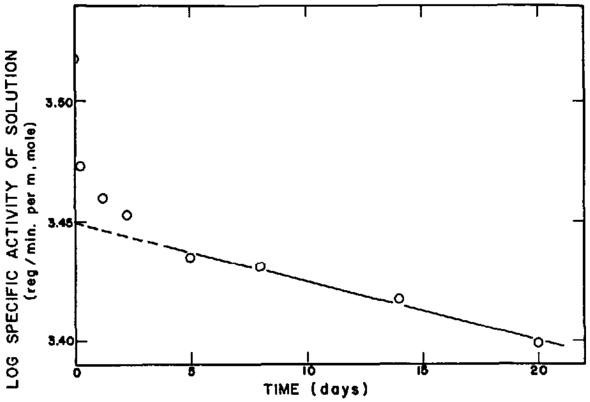

FIGURE 2. *Calcium exchange in an equilibrium system: Labeled* $Ca(OH)_2$ *solution-solid hydrated* C_3S *at 25 °C.*
CaO/SiO_2 ratio=1.40.

Accelerated Hydration of C_3S

The long time, and the uncertainty as to the time required, for complete hydration represent difficulties in studying the hydration products of C_3S. Ball-mill hydration and quantitative X-ray analysis used by Brunauer and Greenberg (paper III–1, this Symposium) are partial remedies for these difficulties. The authors have accelerated hydration greatly by introducing a mass of crumpled thin pure silver foil into the silver lined reaction tubes. Such baffling of the flow of liquid with movable foil caused formation of colloidal silver in the liquid, but blanks indicated that this did not materially affect the titer of the lime solutions. The hydration of C_3S in some instances appeared to be complete in less than 3 weeks, but most of the hydrations by this method were continued up to 2 months. Consistency was not quite as good as in the experiments of table 1, and the titers tended to be higher, giving lower r-values, possibly due to variation in the size of the particles of the

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[3] One register (reg.) = 64 counts.

hydration product. The presence of the colloidal silver and the fine subdivision of the hydrate made the accurate determination of refractive index more difficult, but no material of refractive index higher than 1.60 was discovered, indicating the absence of afwillite. The results obtained by this method are given in table 2.

Parallel exchange experiments were made with afwillite.[4] Its behavior is entirely different from that of the hydration products of C_3S. In solutions of high concentration there is at first a very slight and equivalent drop both in concentration and activity of the solution with no further significant changes. This is further evidence that the products in table 2 were similar to those of table 1 and that appreciable amounts of afwillite were not present.

TABLE 2. *Accelerated hydrations of C_3S, using baffles*

Experiment at 25 °C	Weight of C_3S No. 1-37	Time of hydration	Final conc. $Ca(OH)_2$	r	r_0
	g	*mo*	*mM/liter*		
5-59 [a]	0.1850	0.75	20.4	1.36	0.96
6-59	.1850	.75	20.5	1.35	0.90
8-59	.1850	1.5	20.2	1.38	1.06
9-59	.1850	2.0	19.9	1.41	0.89
10-59	.1850	2.0	20.3	1.37	1.03
11-60	.1600	3.5	18.1	1.35	1.04
5-60 [b]	.0265	2.0	3.1	1.05	0.85
6-60	.0458	2.0	5.1	1.10	.82
at 8 °C [c]					
1-60	.2350	5.0	22.43	1.37	1.08
2-60	.2350	5.0	22.67	1.36	0.97
3-60	.1175	5.0	12.13	1.24	1.05

[a] Experiments 5-, 6-, 8-, 9-, 10-59 and 11-60 were hydrated in 75 ml of a solution containing 2.66 millimoles CaO/liter.

[b] Experiments 1-, 2-, 3-, 5- and 6-60 were hydrated in 75 ml of water.

[c] Saturated solution of $Ca(OH)_2$ at 8 °C—22.5 millimoles/liter [7].

Discussion

When interpreting the experimental results one should bear in mind that the system remains in chemical equilibrium during the exchange of calcium between the liquid and solid phases. The hydroxyl concentration of the liquid phase as determined by titration and that of calcium as determined by semi-micro quantitative analysis, remain unchanged and chemically equivalent. The isotope effect of Ca-45 may be considered negligible. The change in the distribution of the radioisotope between the solution and the hydrate is thus a measure of the exchange of calcium between the two phases.

At first it was the intention to eliminate the calculation of the decay of the radioisotope by counting a control solution stored in a pyrex glass container. It was found that the loss in activity of the control solution was greater than that calculated from the half-life of Ca-45. Solutions stored in the gold and silver lined tubes did not show this discrepancy. Apparently there was appreciable exchange of calcium between the solution and the glass of the container. The decay was therefore calculated on the basis of a half-life of Ca-45 of 165 days, the value determined experimentally. This is in good agreement with the latest figures found in the literature.

From the experimental results it is obvious that a large part of the calcium present in the solid hydration product of C_3S is subject to comparatively rapid exchange with calcium present in the equilibrium solution and that the amount of this labile calcium increases with the ratio of lime to silica in the hydration product. The remainder of the calcium exchanges at a very slow rate.

The similarity of the exchange curves to those for the adsorption of a solute from an aqueous solution by a solid powder may suggest that one is simply dealing with the attainment of equilibrium by an exchange of the calcium-45 ions in the solution with the ordinary calcium ions already present in a typical adsorbed layer on the surface of the hydrated silicate. However, for a number of reasons it is difficult to accept this view:

(1) The reader is referred to the evidence for the preferential adsorption of water and low adsorption of lime by tobermorite in paper III–1 by Brunauer and Greenberg.

(2) Our experiments on hydration of C_3S under greatly varying conditions support this finding. By microscopic measurements it was found that the average diameter of the crystalline aggregates of the hydrate in experiment 57 (at 31 months) was about twice that of the particles of experiment 56 (at 11 months, table 1). There was, however, no significant difference between the equilibrium concentrations of lime (or the r-values) of the two experiments. Our baffled hydrations, which gave very finely divided hydration products, tended to give r-values somewhat lower than the corresponding long-term hydrations. Thus, there is no indication of an increase in the adsorption of lime with decrease in particle size, which might be expected to give rise to an increase in surface area.

(3) Hydrations at 8 °C gave markedly lower r-values for the solid hydrate than those at 25 °C. This would mean *less* adsorption at the lower temperature.

(4) Exchange of radioactive ions in solution with ions in the surface layers of ionic crystals usually reaches equilibrium in a few minutes. Paneth and Vorwerk [5] found that when a finely divided precipitate of lead sulfate was shaken with a saturated solution containing some Pb-112, a steady state was attained in about one minute.

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[4] The sample of afwillite was kindly supplied to the senior author in 1929 by John Parry [4] and was composed of pure crystalline material from the original discovery at Kimberley. Our analysis gave CaO, 49.30%; SiO_2, 34.12%; and H_2O, 16.44% after drying at 100 °C.

Singleton and Spinks [6] added a small amount of Sr-90 to precipitated strontium sulfate in equilibrium with its solution and found that, with shaking, the primary exchange reaction was complete in less than one minute, while a slower secondary process or processes continued for one to two hours. This compares to days required in the case of the hydration product of C_3S.

(5) In several of our exchange experiments the initial activity of the solution (i.e., at zero time), calculated on the basis of the law of mixtures, was compared with the experimental value obtained after violent shaking by hand for one minute with subsequent centrifuging (10 min). For C_3S hydration products of medium r-values the two agreed within the expected 1 percent statistical variation while for products with high r-values the drop in activity was slightly in excess of this. Had there been a large amount of adsorbed lime on easily accessible solid surfaces one would expect a rapid drop in the activity of the solution during the first minute. The above applies only to aged precipitates. It is well known that fresh precipitates behave differently, probably because of recrystallization on aging.

One is thus tempted to suggest that the exchange experiments distinguish between two categories of calcium with a marked difference of chemical bonding in the crystal lattice and that the exchange takes place throughout the whole mass of the hydration product, therefore being much slower than ordinary adsorption, but still quite fast compared to exchange with the lime of the basic crystal lattice.

Some experimental difficulties were encountered. On centrifuging, the hydrated silicate tends to form a solid cake which may be difficult to disperse by mechanical shaking. The slowing up of the fast exchange (e.g., fig. 2) may result. A possible remedy would be ultrasonic dispersion. After the preliminary experiments the number of samplings were reduced to the minimum required to define the curve for the slow exchange (e.g., fig. 3). Test samples were also removed by filter sticks without centrifuging.

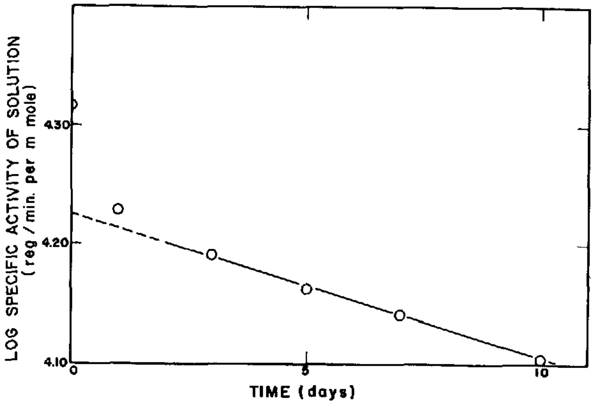

FIGURE 3. *Calcium exchange in an equilibrium system. Labeled* $Ca(OH)_2$ *solution-solid hydrated* C_3S *at 25 °C.* CaO/SiO_2 ratio = 1.05.

Exchange in Hydration Products Formed in the Supersaturated Region

Two hydrations at 21 °C. (without baffling) were begun with the object of maintaining the concentration, by periodic dilution, in the metastable region just above saturation. Actually, during the 12-month hydration, the supersaturation varied from 2 to 22 percent. The CaO/SiO_2 ratios in the solids were 1.99 and 1.98. The rapid exchange indicated ratios of CaO (not exchanged) $/SiO_2$ of between 0.5 and 0.6 in 12 hours, and of less than 0.5 in 3 days, followed by slow exchange. Thus, instead of a hydration product giving the typical exchange curves of figures 1 to 3, the initial rapid exchange accounted for three-fourths of the total lime in the solid phases. White's test for calcium hydroxide was strongly positive and microscopic examination of the hydration products disclosed many large crystals of calcium hydroxide. Exchange experiments with finely divided calcium hydroxide crystals indicated that the slow secondary exchange may have been due to the calcium hydroxide in the hydration product.

These experiments indicate that hydration of C_3S under conditions of supersaturation, and in the presence of the calcium hydroxide phase, may produce a hydration product which exchanges all its lime very rapidly. The experimental result should, however, be considered subject to confirmation.

It should be noted that in these two experiments there was appreciable absorption of carbon dioxide due to the many openings of the reaction vessels for titration in order to follow the degree of supersaturation. The other hydration products (tables 1 and 2) were free from contamination of carbon dioxide at the start of the exchange experiments, and only in those used for the determination of an excessive number of points on the exchange curves could any material of high birefringence be detected in the hydration products.

The authors are greatly indebted to William A. G. Graham, Roger Kelly, and Betty-Gene Lepine for assisting from time to time with the preparation of the hydration products used in the exchange experiments. They also wish to express their appreciation to Dr. K. J. McCallum for valuable advice, and to Dr. A. R. Byers, Professor of Geology, University of Saskatchewan, who on many occasions made microscopic examinations of both the original silicates and the reaction products.

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Paper III-S11. Kinetics of Reaction in the System $CaO-SiO_2-H_2O$*

P. E. Halstead and C. D. Lawrence

Synopsis

The kinetics of the reaction between colloidal silica powder and lime solution, in the temperature range 10 to 50 °C, indicate a through-solution mechanism with the dissolution of silica as the slow step. The activation energy obtained for the process is 16.7 kcal/mole.

It has been found possible to express the concentration of silica and lime in solution during the reaction, and in the equilibrium system CSH—solution finally produced, in terms of a solubility product relationship.

Résumé

La cinétique de la réaction entre la poudre de silice colloidale et la solution de chaux, dans la gamme des températures 10 à 50 °C, indique un mécanisme qui s'opère par la voie de la solution, la dissolution de la silice constituant le stade lent. L'énergie d'activation obtenue pour ce processus est de 16,7 kilocalories/molécule-gramme.

On a constaté que la concentration de la silice et de la chaux en solution pendant la réaction, et dans le systéme d'équilibre CSH—solution finalement produite, peut être exprimée en fonction du produit de solubilité.

Zusammenfassung

Die Kinetik der Reaktion zwischen kolloidalem Siliciumoxyd-Pulver und Kalklösung, im Temperaturbereich 10 to 50 °C, deutet auf einen Mechanismus hin, der sich durch Vermittlung der Lösung vollzieht, wobei die Auflösung des Siliciumoxydes die langsame Stufe darstellt. Die bei diesem Vorgang erhaltene Aktivierungsenergie beträgt 16,7 Kilocal/Mol.

Dabei war es möglich, die Konzentration des Silicium-oxydes und des Kalkes in der Lösung während der Reaktion, sowie im Gleichgewichtssystem CSH—endgültig gebildete Lösung, in eine das Löslichkeitsprodukt enthaltende Beziehung auszudrücken.

In recent years considerable attention has been paid to the composition of the solid phase in the system $CaO-SiO_2-H_2O$ and in particular to the lime:silica ratio of the solid in equilibrium with calcium hydroxide solution of various concentrations. Comparatively little work has been reported on the composition of the liquid phase in equilibrium with calcium silicate hydrates. This paper reports the results of some measurements of reaction kinetics in the system and of the composition of the liquid phase.

In 1934 Cummins and Miller [1] [1] followed the reaction between saturated calcium hydroxide and siliceous powders by conductivity measurements, and at equilibrium, by analysis. In these experiments the reaction velocities were affected considerably by the nature of the siliceous particles, and in general equilibria were only established after a period of several days.

Also in 1934, Flint and Wells [2] made an extensive study of the solubility of silica in calcium hydroxide solutions and obtained curves relating the concentrations of $Ca(OH)_2$ and SiO_2 in equilibrium in aqueous solution. Families of curves were obtained, of the same general form but differing according to the source of the solutions, i.e., whether obtained by reaction of $Ca(OH)_2$ and SiO_2, or by decomposition by hydrolysis of various calcium silicate hydrates. A month was allowed for the systems to reach equilibrium.

In 1950 Taylor [3] reported a few measurements of the silica concentration in solution in equilibrium with solid calcium silicate hydrates of various lime:silica ratios. In these experiments also, the time taken to attain equilibrium was days or months.

In the work reported here, experiments similar to those mentioned above have given similar results but in a much shorter time and with fewer apparent anomalies. An interpretation of the results is offered on the basis of classical solution theory.

Experimental

The mechanism of the reaction between silica powder and calcium hydroxide solution is relatively complicated on account of the presence of divalent calcium ions and the fact that the reaction product is comparatively insoluble in water. As an exploratory step, therefore, the simpler reaction between silica and sodium hydroxide solution was studied. In other experiments calcium hydroxide solution was substituted for the sodium hydroxide solution.

The apparatus used for the reactions consisted of a Pyrex three-necked flask of either 30-ml or

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Research and Development Division of the Cement and Concrete Association, London, England.

[1] Figures in brackets indicate the literature references at the end of this paper.

1-liter capacity immersed in a constant-temperature water bath.

The larger vessel was used for both the sodium hydroxide and calcium hydroxide experiments, and samples of solution were withdrawn from it for silica determination through a porous polyvinyl chloride filter equivalent in porosity to a No. 4 sintered glass filter. Since, for the measurement of calcium hydroxide concentration it was not necessary to withdraw samples of solution, the smaller vessel was used for calcium hydroxide reactions when only calcium hydroxide concentrations were to be measured.

A known volume of calcium hydroxide or sodium hydroxide solution was introduced into the vessel, precautions being taken to prevent contact with atmospheric carbon dioxide.

After the solution had reached the temperature of the water bath, a weighed amount of silica powder (B.D.H. "Colloidal Silica Powder" of specific surface ca. 220 m^2/g.) was introduced as quickly as possible. A magnetic stirrer in the vessel kept the silica powder in suspension and the concentration of the solution uniform.

Measurement of Concentration of Calcium Hydroxide in Solution

The method of measuring the concentration of the calcium hydroxide in solution consisted of measuring its electrical conductivity using a dip cell (Mullard type E. 7591) and a Wheatstone bridge fed from an alternating current supply of frequency 1 kc. Earphones were used to balance the bridge. From the conductivity and a previously constructed calibration curve, the concentration of the solution could be determined.

The electrical conductivity of calcium hydroxide solution is essentially due to the hydroxyl ions present and in the range of concentrations encountered in this work provides an easier and more accurate method of measuring small changes in $Ca(OH)_2$ concentration than titration with versenate or acid solutions. Conductivity measurements are particularly convenient in that they permit analysis to be made without removal or loss of material and without exposure to atmospheric CO_2. It is important, however, to keep the temperature of the solution closely controlled.

Measurements of the conductivity of calcium hydroxide solutions and of the lime-silica reaction were made over the range 10–50 °C and a range of concentration of 0.0025–0.025 mole/liter. The corresponding range of conductivity was such that the measured resistance of the solution lay between 200 and 2,000 ohms. The results of these measurements were in close agreement with the empirical relationship

$$\Lambda_t = \Lambda_{25}[1 + x(t-25)]$$

where Λ_{25} = equivalent conductivity at 25 °C
and x = empirical constant = 0.017.

A figure of $x=0.018$ has been quoted by Glasstone [4].

The Debye-Hückel-Onsager equation applied to $Ca(OH)_2$ solutions at 25 °C gives:

$$\Lambda_c = 252 - 210\sqrt{c}$$

At $c=0.0034$ g equivalents/liter, $\Lambda_c=239.5$. The experimental value obtained was 240.

Measurements of Concentrations of Sodium Hydroxide in Solution

The conductivity measurements which provided a convenient method of measuring the concentration of calcium hydroxide solution were used in a similar fashion to measure the concentration of sodium hydroxide in the reaction solutions in the range 0–40 mm/liter.

Measurement of the Concentration of Silica in Solution

Samples of solution withdrawn through the filter from the reaction vessel were analyzed colorimetrically for silica content.

The standard procedure [5] was followed. Citric acid was added to prevent interference by calcium ions and 1:2:4 aminonaphthol-sulfonic acid was used as reducing agent. The optical density of the molybdenum blue coloration was measured in a Spekker absorptiometer using 4-cm cells and Ilford No. 608 red filters (transmitting only light of wavelength 6400 A or longer) with a mercury vapor lamp.

Five minutes were allowed for the yellow molybdate complex to develop before adding the citric acid and reducing agent. Development of the molybdenum blue complex took a further twenty minutes, and thereafter the optical density remained constant for several hours. Using a standard silica solution a straight-line calibration graph of concentration against optical density was obtained over the range 0–0.03 mM silica/liter. The concentration range obtained in this work was 0–12 mM/liter, and samples were diluted to bring them within the calibrated range.

It was found that a suspension of the silica powder in water gave no blue coloration when subjected to the above procedure; therefore, traces of silica powder which might have passed through the filter were unlikely to have caused any errors in the determination.

Results and Discussion

In the experiments involving reaction between sodium hydroxide and silica powder, the results obtained fit the expression

$$1-(x)^{1/3}=Kt$$

where x=fraction of silica remaining in solid form after time t, by assuming that the rate-determining step was dissolution of silica from the surface of spherical particles. The rate of solution was independent of hydroxyl-ion concentration in the range 15–40 milliequivalents/liter. The average activation energy for the reaction was found to be 18±1 kcal/mole over the range 25 to 45 °C. In the particular conditions of the experiment, approximately 55 percent of the silica enters solution in the first hour at 35 °C. The progress of the reaction as silica enters solution is accompanied by a corresponding decrease in sodium hydroxide, or more precisely, hydroxyl-ion concentration. The relationship between dissolved silica and decrease in hydroxyl ion could not be explained by the formation of any simple silicate ion in solution. The number of moles of silica entering into solution was at all times greater than the number of gram-equivalents of hydroxyl ion removed.

On examining the results from similar experiments in which the sodium hydroxide was replaced by calcium hydroxide, a very different pattern of reaction was observed (figs. 1 and 2). The characteristic features are:

(1) A sharp initial fall in calcium hydroxide concentration, occurring in the first minute of reaction, followed by a steady fall in the next few hours at approximately one tenth of the rate of reaction found for the sodium hydroxide reaction and independent of the calcium hydroxide concentration, with an average activation energy of 16.7 kcal/mole over the temperature range 10–50 °C.

The rate of reaction fell as the reaction progressed in a similar way to the sodium hydroxide reaction.

(2) An initial very rapid rise in silica concentration in solution, followed by a less rapid fall to a concentration which remained stable for a short period and then rose slowly as the reaction proceeded.

We interpret these phenomena in the following way:

(1) The initial sharp fall in the calcium hydroxide concentration represents adsorption of $Ca(OH)_2$ by the silica particles. The amount of $Ca(OH)_2$ adsorbed is roughly equivalent to a layer of Ca^{2+} ions on the surface of the silica particles one ion thick.

A similar initial reaction was observed by Cummins and Miller [1] and ascribed to the formation of a superficial layer of highly hydrated calcium silicate on the surface of the silica particles.

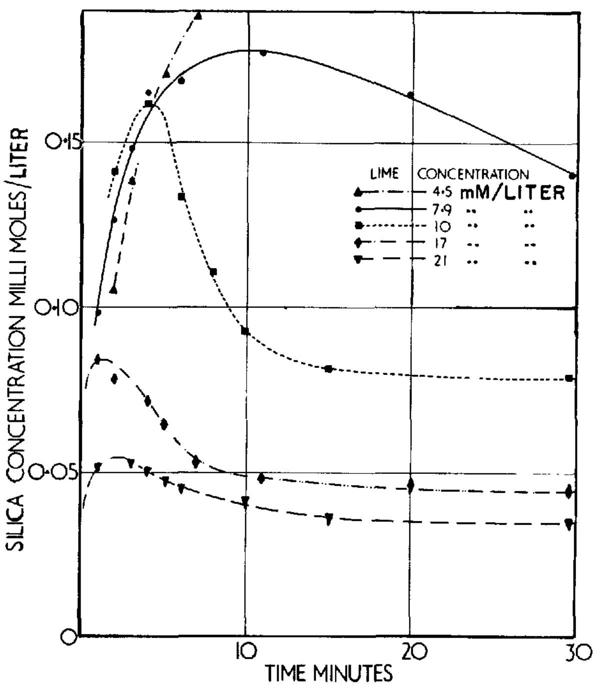

FIGURE 1. *Initial stage of the reaction of colloidal silica and lime solution at 45 °C.*

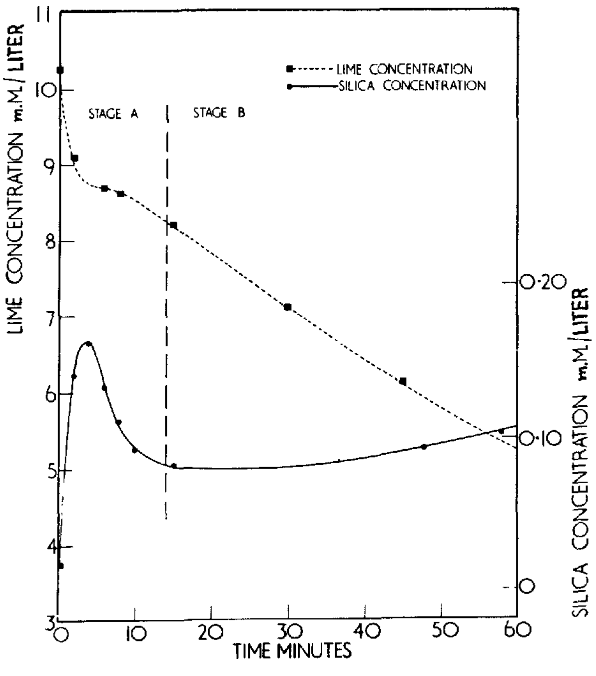

FIGURE 2. *Reaction of colloidal silica and lime solution at 45 °C.*

The continuing fall in calcium hydroxide concentration takes place as the main chemical reaction precipitates calcium silicate hydrate from solution.

(2) The initial rapid rise in silica concentration represents simple solution of the silica and occurs at a rate comparable with that obtained in the sodium hydroxide experiments. The fall in silica concentration occurs at a point of critical supersaturation with respect to calcium silicate hydrate in solution. The silica concentration thereafter is controlled at the saturation point of calcium silicate hydrate, i.e., silica is entering and leaving solution at the same rate. The saturation concentration of silica in solution rises as the calcium hydroxide concentration of the solution is reduced by the progress of the reaction.

On this interpretation, the rate-determining step is the same in both reactions studied. In support of this theory, the activation energies of the two processes are nearly identical, and the rate of reaction is independent of hydroxyl-ion concentration in both reactions. The very much lower rate obtained using calcium hydroxide may be explained by the more ready adsorption of calcium ions onto the surface silicate groups. If, as seems likely, only silicate groups can undergo depolymerization, the adsorption of a calcium ion, removing the negative charge on the surface silicate group, removes the possibility of that group entering solution. In effect, the surface area of the particles available for dissolution is reduced in the presence of calcium ions.

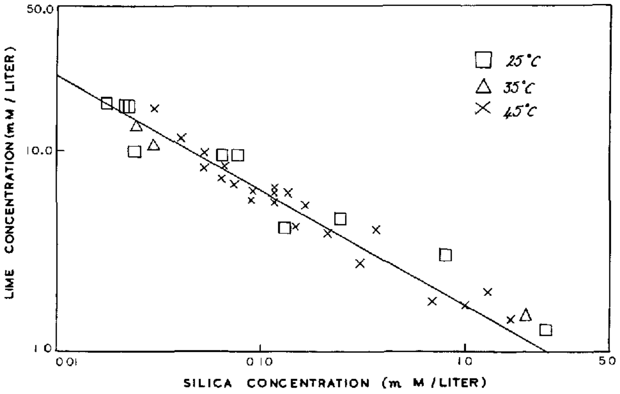

FIGURE 3. *Solution concentrations during lime-silica reaction.*

The form of the graph of lime and silica contents of the reaction solution, after the initial stage, led us to examine the relationship between lime and silica content of solutions in equilibrium more generally and we have found that the experimental values taken over a wide range of conditions fit the relationship:

$$[\mathrm{Ca(OH)_2}]^x\ [\mathrm{SiO_2}]=K$$

remarkably closely. (See fig. 3.)

The regression of $[\mathrm{Ca(OH)_2}]$ on $[\mathrm{SiO_2}]$ gives a "best fit" at $x=1.9$ and $K=3.4$ with correlation coefficient $r=-0.95$. It is particularly interesting to find that lime-silica concentrations measured after 15 min fit the above curve as well as measurements on the equilibrium system. We have found no suggestion of an inflection of the curve at low lime concentrations, indicative of a reduced silica concentration below a peak occurring at about 0.075 g CaO/liter as reported by Flint and Wells [2].

The similarity of this result to a solubility product suggests that in solution something resembling a salt such as C_2SH may exist, i.e., Ca_2SiO_4·aq. This accords with the suggestion of Flint and Wells [2] that in the system $CaO–SiO_2–H_2O$ at 30 °C, the calcium silicates present are salts of orthosilicic acid H_4SiO_4 which would by progressive replacement of hydrogen by calcium ions form hypothetical calcium silicates hydrates of C:S ratio of 1:2, 1:1, 3:2, and 2:1.

The significance of the "solubility product" in cement hydration seems to be that in a cement and water paste any increase in $Ca(OH)_2$ concentration must force elimination of silica from solution in the liquid phase.

Thus whilst there exists a discrete liquid phase the formation of hydrated calcium silicates can reasonably be explained by a through-solution mechanism.

At $Ca(OH)_2$ concentrations above about 2 mM/liter the equilibrium concentration of silica in solution is exceedingly small and the $CaO:SiO_2$ ratio in solution at a $Ca(OH)_2$ concentration of 20 mM/liter must be about 90:1. It is possible that the peculiarities of crystal growth of calium silicate hydrates may be a consequence of the great difference in $CaO:SiO_2$ ratio in the solids and in the "mother liquor" from which they separate.

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Discussion

Sidney A. Greenberg

The work reported in the paper is very interesting. It is clear to all that the kinetics and mechanisms of solution of colloidal silicas in basic solutions are important to an understanding of the processes proceeding in concrete mixtures. However, the authors do not refer to some recent work which has been published on this subject. The conclusions of the authors, nevertheless, are in complete agreement with the previously published work.

In a paper by O'Connor and Greenberg [1] it was shown that silica dissolves in sodium hydroxide solutions according to the equation

$$C_p^{1/3}=C_{p0}^{1/3}-k_3t \qquad (1)$$

where C_p and C_{p0} are the amounts of silica at time t and at zero time, respectively, and k_3 is a constant. This equation was derived on the assumptions that the rate of solution is proportional to the surface area and that the particles are spheres. It was later reported [2] that silica reacts with calcium hydroxide solutions with concentrations greater than 0.0036 molar according to eq (1). The mechanism proposed for the reaction is the same as that given by Halstead and Lawrence.

A detailed study of the initial chemisorption reaction of calcium hydroxide by silica has been discussed in detail [3]. It was shown that the surface of silica is covered by acidic silanol groups, SiOH, which react immediately with calcium hydroxide in an acid-base reaction.

The nature and amount of silicic acid dissolved in sodium hydroxide and calcium hydroxide solutions have been discussed [4–6] and the subject is reviewed by Brunauer and Greenberg [7]. It was shown that several equations explain the composition of the silicate solutions. One is for electroneutrality.

$$2[\mathrm{Ca^{++}}] \text{ or } [\mathrm{Na^+}]=[\mathrm{OH^-}]+[\mathrm{H_3SiO_4^-}]+2[\mathrm{H_2SiO_4^{--}}] \qquad (2)$$

and another is for material balance

$$[\mathrm{SiO_2}]_t=[\mathrm{H_4SiO_4}]+[\mathrm{H_3SiO_4^-}]+[\mathrm{H_2SiO_4^{--}}] \qquad (3)$$

where the quantities in brackets are concentrations in moles/l. The relative quantities of the three species of silicic acid are controlled by the dissociation constants of the acid [4, 5]. The relationship between the calcium and silicic acid concentrations for solutions in contact with hydrates of C/S mole ratio 1/1 and above is controlled by the activity product,

$$K=a_{\mathrm{Ca^{++}}}a_{\mathrm{H_2SiO_4^{--}}} \qquad (4)$$

which is equal to 10^{-7} at 25 °C [6, 7].

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Paper III–S12. The Influence of High-Pressure Steam on the Process of Hardening of Calcium and Magnesium Silicates and Cements of Different Compositions*

P. I. Bozhenov, V. I. Kavalerova, V. S. Salnikova, and G. F. Suvorova

Synopsis

Autoclave curing of building units made of cellular concrete, dense concrete, and silicate concrete is one of the progressive technologic methods which makes possible the production of precast building elements in a comparatively short time (12 to 14 hours). In the practical production of building units, autoclaving is widely used at a pressure of 8 to 12 atm, and corresponding temperature of 174 to 191 °C.

The authors give details of investigations carried out in the USSR, which show the influence of high pressure steam (up to 200 atm) on the processes of hydration and hardening of cementing materials containing calcium and magnesium silicates.

The investigations show that under the conditions of increasing steam pressure and temperature, the hydration of the cementing material, the processes of concrete hardening, and the interaction of cementing material with aggregates occur more intensively. There is an optimum limit of pressure and an optimum regime of autoclave curing for each kind of cementing material, depending on its mineralogical composition. For example, cementing materials of the type of belite cements (with high C_2S contents), which includes some industrial wastes, such as nepheline slurry, blast furnace slags and Martin slags, and slate ashes, require intensive curing within the range of 16 to 25 atm and reduced regimes of autoclaving.

Autoclaving the materials with high contents of MgO or magnesium silicates at steam pressure of 25 to 50 atm gives new high-quality materials.

The use of high pressure steam (16 to 25 atm) in autoclave technology permits a reduction of the general technological cycle of autoclave treatment by as much as 5 to 7 hours.

The examples given show that autoclaving with high pressure steam provides solutions of such important problems in the building industry as reducing the time required for hardening precast concrete products and widening the raw material base by use of industrial wastes and natural rock minerals containing magnesium.

Résumé

L'autoclavisation des éléments constructifs en béton cellulaire, béton plein et béton de silicates se présente comme un des procédés les plus avancés qui permet d'obtenir les éléments préfabriqués en un laps de temps relativement court.

La production des éléments constructifs comprend une large utilisation de l'autoclave (vapeur à haute pression et température 8–12 atm et 174–191 °C).

Le rapport fait part des recherches effectuées en URSS qui montrent l'influence de la vapeur à haute pression sur les procédés d'hydratation et de durcissement des liants contenant les silicates calciques et magnésiques.

Les recherches affirment que, lorsque la pression et la température de la vapeur s'augmentent, on arrive à une intensification de l'hydratation des liants, des procédés de durcissement des bétons, et des réactions entre les liants et les agrégats.

Chaque sorte de liant, selon sa propre composition minéralogique, présente une limite optimum de pression et son propre régime d'autoclavisation.

Ainsi, les liants du type des ciments bélites (avec une forte teneur en C_2S), y compris certains déchets industriels—par exemple, le laitier de haut fourneau et la scorie Martin, le schlamm de néphéline, les cendres volantes des schistes, exigent un traitement intensif, compris entre les limites de 16–25 atm et des régimes réduits d'autoclavisation.

On obtient des nouveaux matériaux de construction de haute qualité à l'aide de l'autoclavisation à vapeur sous pression de 25 à 50 atm des matières contenant une forte teneur en MgO ou en silicates magnésiques.

L'utilisation de la vapeur à haute pression (16–25 atm) durant l'autoclavisation permet de réduire le cycle technologique général jusqu'à 5–7 h.

L'exposé du rapport démontre que l'autoclavisation à vapeur de haute pression donne la possibilité de résoudre des problèmes d'importance magistrale pour l'industrie du bâtiment, tels que la réduction du délai de durcissement des éléments préfabriqués et l'extension de la base des matières premières, grâce à l'utilisation des déchets industriels et des minéraux de roches naturels contenant le magnésium.

Zusammenfassung

Die Dampfhärtung von Bauteilen aus Leichtbeton, Schwerbeton und Silikatbeton ist ein sehr modernes Verfahren, welches die Möglichkeit gibt in relativ kurzer Zeit fertige Bauteile zu erhalten.

Die Herstellung von vorgeformten Bauteilen mit Dampferhärtung unter Druck von 8–12 Atm (bei 174–191°) ist weit verbreitet.

Der Vortrag gibt eine Übersicht von den Untersuchungen in USSR, die den Einfluss von Dampfdrücken bis zu 200 Atm auf die Vorgänge der Hydratation und Härtung von solchen Bindemitteln zeigen, die Silikate von Calcium und Magnesium enthalten.

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*Fourth International Symposium on the Chemistry of Cement, Washington, 1960. Contribution from the Academy of Construction and Architecture, Leningrad, U.S.S.R.

Die Untersuchungen zeigen, dass mit steigendem Dampfdruck und Temperatur die Hydratation von Bindemittel, der Verlauf der Härtung des Betones, und das Aufeinanderwirken der Zuschlagstoffen mehr intensiv stattfindet.

Jedes Bindemittel zeigt abhängig von seiner mineralogischer Zusammensetzung ein optimales Dampfhärtungsverfahren.

Zum Beispiel, Bindemittel wie Belitzemente (mit hohem C_2S Gehalt) sowie eine Reihe von industriellen Abfällen, Hochofen und Martin-Schlacke, Nephelin-Schlämme, Schiefer, Flugasche, erfordern eine intensive Dampferhärtung innerhalb der Grenze von 16–25 Atm.

Bindemittel mit einem hohen Gehalt von MgO oder Magnesiumsilikaten bei einer Dampferhärtung von 25–50 Atm, liefern neue hochwertige Baustoffe.

Die Hochdruck Härtetechnik, 16 bis 25 Atm, macht es möglich die Zeitdauer des Dampfhärte-Verfahrens um 5 bis 7 Stunden zu verkürzen.

Die vorgeführten Beispiele zeigen, dass das Dampfhärte-Verfahren mit hohen Dampfdrücken die Lösung von solchen Aufgaben, die in der Bauindustrie auftreten, wie die Verkürzung der Härtezeit von vorgeformten Betonteilen und die Erhöhung der Auswahl von Rohmaterialien, ermöglichen, sodass industrielle Abfälle und unverarbeitetes Gestein, das Magnesium enthält, verwendet werden können.

The production of precast building units, based on the technical properties of calcium silicate hydrate, is a rather young but rapidly developing building-materials industry.

There are certain scientific and practical achievements in the production of concrete and reinforced-concrete products, but a number of important problems of technology must be investigated, that is, the choice of cementing material, which takes an active part in the development of the structural properties of hardened concrete.

The quality of concrete, hardened at normal temperature, from 1 to 45 °C, greatly depends on cement "activity."

The development of technical properties of concrete by hydrothermal curing depends upon some other conditions and is defined by the physicochemical properties of cementing material and aggregates, and particularly the autoclave regime (duration of curing, temperature, and steam or water pressure, in which milieu hardening takes place).

The investigations, carried out by the Leningrad Building Institute and the Academy of Architecture and Building (Leningrad filial), showed that under certain circumstances of hydrothermal curing it is possible to produce high-quality precast members from various cementing materials, that is, from sand and lime, from a number of industrial waste products which contain calcium and magnesium silicates, and lastly by suitable technological curing of some rocks.

In the concise reports of Bernal, "The Structures of Cement Hydration Compounds," of Steinour, "The Reactions and Thermochemistry of Cement Hydration at Ordinary Temperature," and of Kalousek, "The Reactions of Cement Hydration at Elevated Temperatures," delivered at the Third International Symposium on the Chemistry of Cement, there are data that furnish a basis for judgment on the conditions of formation of hydrosilicates. In the period since the third Symposium took place, the formation of hydrosilicates has become of great interest and there are many new facts characterizing the dynamics of calcium silicate hydrate formation.

N. A. Toropov considers that as of 1959 the conditions of formation of the following calcium silicate hydrates have already been studied to some degree.

1. low-temperature:
    $CSH(I)\ 0.8CaO{\cdot}SiO_2{\cdot}aq$
    $C_2SH(II)\ 1.5\text{–}2.0CaO{\cdot}SiO_2{\cdot}aq$
2. tobermorite group of minerals:[1]
    $5CaO{\cdot}6SiO_2{\cdot}nH_2O$
3. gyrolite—$2CaO{\cdot}3SiO_2{\cdot}2H_2O$
4. afwillite—$3CaO{\cdot}2SiO_2{\cdot}2H_2O$
5. foshagite—$4CaO{\cdot}3SiO_2{\cdot}H_2O$
6. xonotlite—$6CaO{\cdot}6SiO_2{\cdot}H_2O$
7. hillebrandite (β-hydrated dicalcium silicate)
8. α-hydrated dicalcium silicate—$2CaO{\cdot}SiO_2{\cdot}H_2O$
9. c-hydrated dicalcium silicate—$2CaO{\cdot}SiO_2{\cdot}0.3\text{–}1.0H_2O$
10. tricalcium hydrosilicate—$3CaO{\cdot}SiO_2{\cdot}2H_2O$

Besides these, the following calcium silicate hydrates are also known:

11. okenite—$CaO{\cdot}2SiO_2{\cdot}2H_2O$
12. truscottite—$CaO{\cdot}2SiO_2{\cdot}0.5H_2O$
13. nekoite—$CaO{\cdot}2SiO_2{\cdot}2H_2O$

Furthermore, calcium chondrodite was recently found having a structure like that of magnesium chondrodite. And, moreover, there are some references in the literature to hydrated tricalcium silicate, foshalassite—$5CaO{\cdot}3SiO_2{\cdot}3H_2O$, di- or tetrahydrated dicalcium silicate—$2CaO{\cdot}SiO_2{\cdot}2\text{–}4H_2O$, and the hydrosilicate $6CaO{\cdot}3SiO_2{\cdot}H_2O$.

At present, 17 hydrated calcium silicates are known and somewhat studied, and it is obvious that their number will increase.

From numerous publications it is clear that the chemical composition and structure of hydrated calcium silicates can vary within broad limits. It is necessary to pay attention to the capacity of hydrated calcium silicates for change of bound water and, what is particularly important, for change in the ratio $CaO{:}SiO_2$ depending on the initial material and the conditions of hydrothermal curing.

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[1] Among the tobermorite group of minerals there are some hydrates differing from one another by the number of H_2O molecules in the elementary cell. These hydrates are the following:
a. 14A-hydrate, plombierite
b. 11A-hydrate, tobermorite proper
c. 10A-hydrate
d. 9A-hydrate, riversideite
(The number of angstroms standing before the word "hydrate" gives the characteristic d_{002} which distinguishes the tobermorites.)

Scientists dealing with the problems of experimental mineralogy and petrography have carried out numerous investigations, discovering the role of water during mineralogical processes, which made it possible for W. I. Vernadsky to write in 1923: "In the chemistry of the earth's crust water plays a unique role which cannot be compared with that of any other substance, and by different means it penetrates into nearly all mineral solids of the upper and partly deeper thermodynamic shells of the earth's crust, and gives with them varied types of chemical compositions of different strengths."

In fact, nature gives us numerous examples of different hydrated compositions, including hydrated silicates, having sometimes important technical properties (asbestos, hydromicas) owing to which they are assigned to the category of mineral resources.

It is necessary to mention a certain gap between theoretical investigations in which experiments are often carried out at high pressure, 100 to 3,000 atm, at temperatures from 300 to 1,000 °C, on the one hand, and the practice of hydrothermal steam curing limited to 70 to 90 °C or autoclaving at 175 to 200 °C, on the other hand.

Such a situation was created as the result of the underestimating, by practicing engineers, of the value of theoretical investigations of the physical chemistry of silicates and the thermodynamic properties of water and steam at high pressures and temperatures.

Concrete strength depends not only on cement "activity," but also on the methods of mixing and molding, and particularly on the hardening conditions.

Modern science and technology allow us to state that it is possible to develop a technology by which cement of low activity provides in a short time products with the necessary structural properties.

The results of the investigations carried out in the USSR on the problem of the influence of high-pressure-steam treatment on developing technical qualities of cement paste, depending on raw materials and regime of curing, are given in our report.

As already mentioned, there is in the technical literature enough information about hydrosilicate synthesis.

In this connection, the following names are known: Le Chatelier—1904; Michaelis—1909; Schlapfer and Niggli—1914; Thorvaldson and Shelton—1923; Lerch and Bogue—1927; Flint and Wells—1934; Keevil and Thorvaldson—1936; Lapin—1938; Michalchenko—1947; Butt—1949; Bozhenov—1952; Wolfson—1949; Toropov—1952; Taylor—1950; Bessey—1951; Kalousek—1951; Bernal—1952; Hansen—1953; Sanders and Smothers—1957; Berkovich—1958, and many others.

In these investigations, with the exception of Butt, Wolfson, Bozhenov, Sanders and Smothers and some others, the technical characteristics of the products obtained have not been studied, and there are still few data characterizing the technological conditions necessary for obtaining products with specified properties.

In many cases, industrial waste products contain large quantities of low-basic calcium and magnesium silicates. Such materials are often slow hardening under normal conditions but acquire enough strength after autoclave treatment. It is known that mixtures containing free lime and silica, after treatment with high-pressure steam, give high-strength building stone, owing to the hydrosilicates formed.

The method of hydrothermal curing in steam-curing chambers at temperatures lower than 100 °C, widespread at the present time, requires a long-run steam-curing cycle and cement of high activity.

Lately, technologists often speak of increasing the temperature and steam pressure during hydrothermal curing. The USSR, the USA, Sweden, and some other countries are moving in this direction now.

Pressure increase, and consequently temperature increase, contribute to more rapid progress of hydration and greater use of cementing-material energy, leading to reduction of the time of technological curing, and allowing one to turn out products of higher quality using less time, energy, and labor.

The results of our investigations, given below, show that autoclave curing is a powerful means of obtaining hydrosilicates from various materials that are chemically passive under normal conditions.

Calcium Silicates

Calcium-silicate-hydrate synthesis is rather difficult under normal temperature conditions. Therefore, the results of investigations are often contradictory. The majority of researchers consider that under normal conditions only two hydrosilicates, CSH(I) and $C_2SH(II)$, are formed.

At higher temperatures, calcium silicate formation occurs more rapidly and in a more complicated way than under normal conditions of temperature and humidity. Consequently, we know of many more hydrosilicates obtained by means of hydrothermal curing.

Some researchers have obtained hydrosilicates by hydrothermal synthesis, bringing together limewater or lime with silica gel or crystalline highly dispersed silica; others have studied the structure and composition of compounds appearing under various conditions as the result of calcium-silicate or portland-cement hydration.

In our laboratory, the behavior of synthetically obtained β-$2CaO{\cdot}SiO_2$, with addition to it of CaO and SiO_2, was studied during hydrothermal curing. (Bozhenov, Kavalerova, 1958.)

Mixtures in the proportions $CaO:SiO_2=1:1$, 3:2, 3:1, and 7:2 were prepared.

The specimens were exposed to autoclave treatment at pressures of 8, 25, and 100 atm, with curing at maximum pressure for 8 hr. Steam increase and decrease, depending on the pressure value, took about 1.5 to 2.5 hr. For autoclaved and dried specimens the compressive strength was determined; then their free lime and silica contents also were determined. The amounts of lime and silica reacting with β-$2CaO \cdot SiO_2$ were determined from the difference between the amounts of added CaO or SiO_2 and the amounts found free after autoclave treatment.

It was found that during hydrothermal curing of synthetically obtained β-$2CaO \cdot SiO_2$ free calcium hydroxide was liberated in the following quantities: at 8 atm—0.12 percent, 25 atm—5.64 percent, 100 atm—2.49 percent.

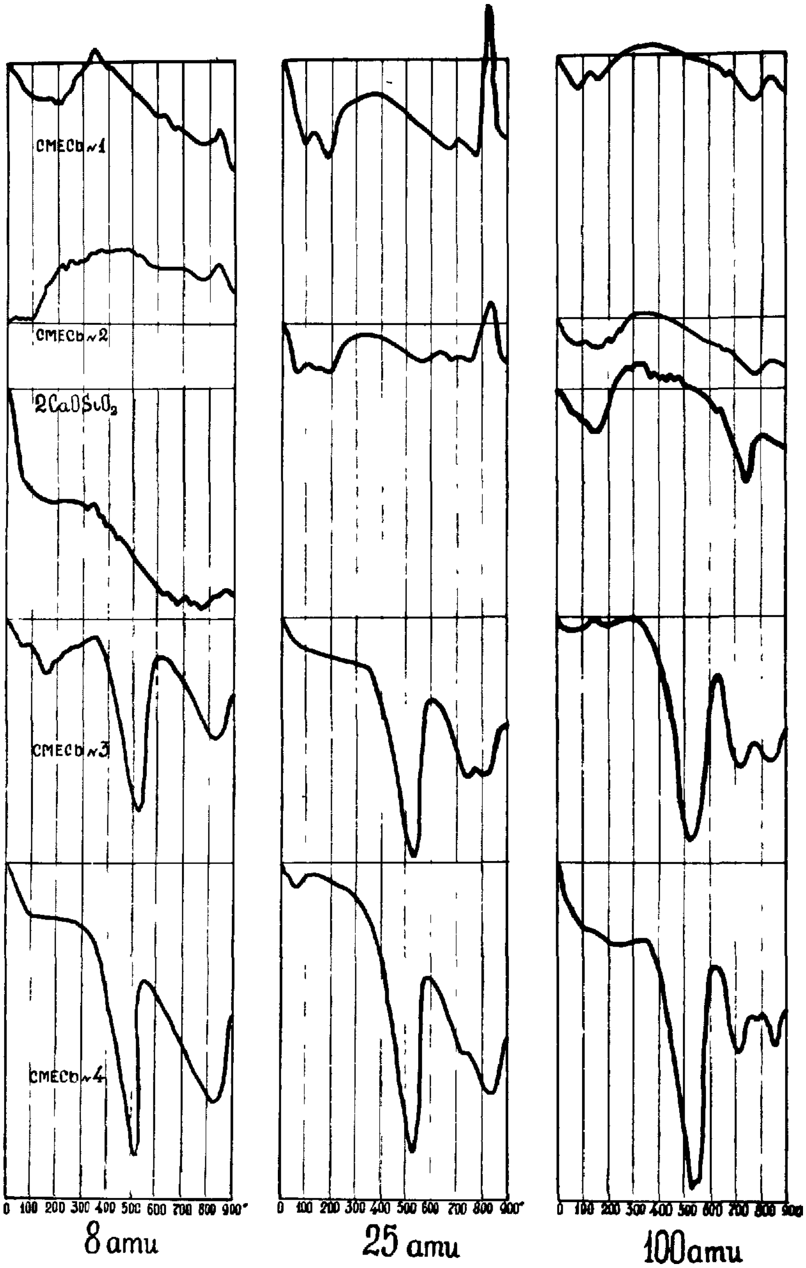

Figure 1. *Thermograms of* $2CaO \cdot SiO_2$ *and mixtures with lime or silica (autoclaved at 8, 25, or 100 atm).*

No. 1—$C_2S+34.94\ SiO_2=CS$
No. 2—$C_2S+17.44\ SiO_2=C_3S_2$
No. 3—$C_2S+32.56\ CaO=C_3S$
No. 4—$C_2S+48.82\ CaO=C_7S_2$

TABLE 1. *Autoclave reaction of dicalcium silicate with lime* [a]

CaO added, relative to C_2S	Lime bound in autoclave, relative to C_2S		
	Autoclave pressure		
	8 atm	25 atm	100 atm
Percent	*Percent*	*Percent*	*Percent*
32.56	19.17	17.99	17.06
48.82	32.42	30.02	30.45

[a] Maximum pressure maintained for 8 hr; pressure increase and decrease times, 1.5 to 2.5 hr.

As seen from tables 1 and 2, in the process of autoclave treatment β-$2CaO{\cdot}SiO_2$ interacts both with CaO and SiO_2.

From the data of table 1 it is seen that:

a. For the same composition the quantity of bound CaO decreases somewhat with increase in pressure.

b. The quantity of CaO bound during autoclave treatment of C_2S-CaO mixtures depends on the mixture composition. Consequently, during autoclaving, chemical equilibrium is established between the hydrosilicate that is formed, and the free calcium oxide content.

Table 2 data show that β-$2CaO{\cdot}SiO_2$ is able to interact with silica, forming less basic calcium hydrosilicates:

a. The higher the steam pressure in the autoclave, the more the SiO_2 interacts with β-$2CaO{\cdot}SiO_2$;

b. At the same steam pressure the amount of bound silica is practically stable, not depending on the initial mixture composition.

TABLE 2. *Autoclave reaction of dicalcium silicate with silica* [a]

SiO_2 added, relative to C_2S	Silica bound in autoclave, relative to C_2S		
	Autoclave pressure		
	8 atm	25 atm	100 atm
Percent	*Percent*	*Percent*	*Percent*
34.94	11.40	11.24	15.07
17.44	9.50	11.00	16.34

[a] Maximum pressure maintained for 8 hr; pressure increase and decrease times, 1.5 to 2.5 hr.

The differential-thermal-analysis (DTA) curves of the products obtained show a more complicated picture than Kalousek and other investigators have observed. From figure 1, considerable change of the hydration products obtained can be noticed depending on mixture composition and autoclaving conditions. Consequently, during hydrothermal curing, activity of the C_2S increases, and as a result it energetically interacts intensively both with lime and with silica, forming calcium hydrosilicates of different compositions depending on the autoclaving conditions and the initial mixture composition.

It can be assumed that during autoclaving β-$2CaO{\cdot}SiO_2$ undergoes considerable structural change, and that this change is reflected in the compositions and qualities of the products obtained.

The strength characteristics of the specimens tested, given in figure 2, show that the strength of neat β-$2CaO{\cdot}SiO_2$ continuously increases as the pressure is increased. Less basic calcium hydrosilicates formed (with the addition of SiO_2) have

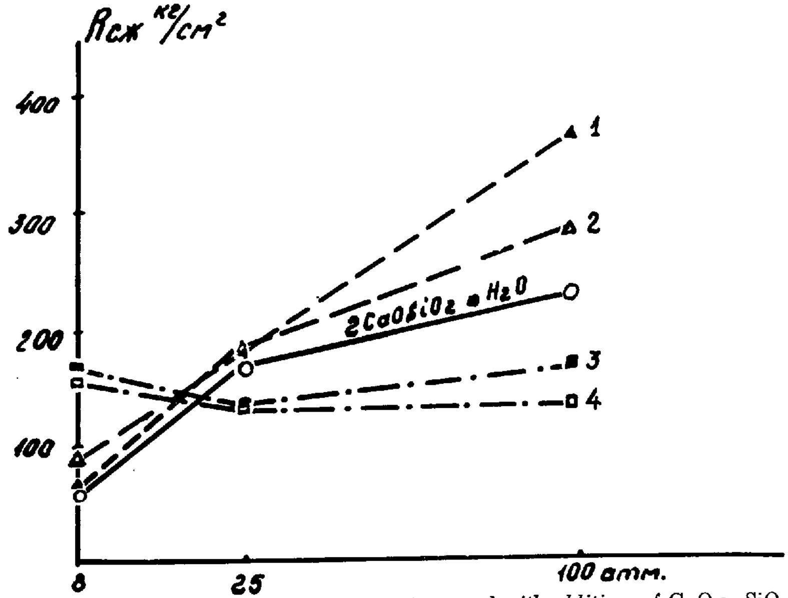

FIGURE 2. *Strength of* β-$2CaO{\cdot}SiO_2$, *alone and with additions of* CaO *or* SiO_2.

No. 1—C_2S+17.44 SiO_2=C_3S_2
No. 2—C_2S+34.94 SiO_2=CS
No. 3—C_2S+48.82 CaO=C_7S_2
No. 4—C_2S+32.56 CaO=C_3S

(Ordinate: compressive strength, kg/cm². Abscissa: steam pressure, atm.)

TABLE 3. *Compressive strength of nepheline slurry with added lime or ground silica sand, after autoclaving* [a]

Composition of the cementing material			Compressive strength of paste specimens, tested at once after autoclaving
Slurry	Lime	Sand	
Percent	*Percent*	*Percent*	*kg/cm²*
100	0	0	217
87	13	0	277
85	15	0	255
83	17	0	197
80	20	0	191
100	0	0	262
95	0	5	272
90	0	10	331
85	0	15	315
80	0	20	220
65	0	35	250
25	0	75	148

[a] Maximum pressure 8 atm, maintained for 8 hr; pressure increase and decrease times, 2 hr.

TABLE 4. *Compressive strength of plant-autoclaved units made with nepheline cement and cured for various times*

Period of curing before steam treatment	Compressive strength	
	1:6 plastic mortar units, 40 x 40 x 50 cm	Concrete cubes,[a] 20 x 20 x 20 cm
Hours	*kg/cm²*	*kg/cm²*
3	65	--------
9	94	184
12	140	204
24	56	166

[a] Slurry, 80 percent; lime, 15 percent, gypsum, 5 percent.

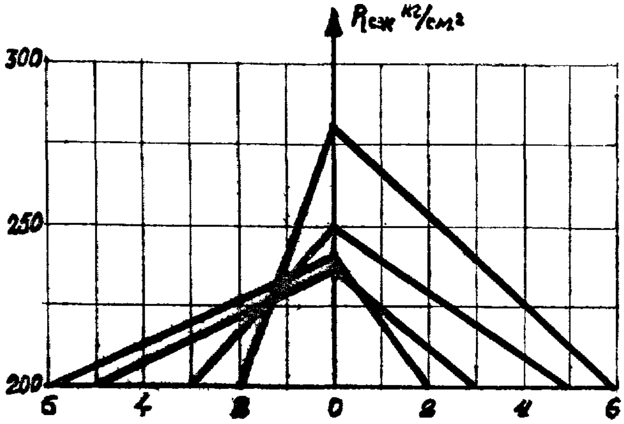

FIGURE 3. *Dependence of the compressive strength on the autoclaving regime.*

(Ordinate: compressive strength, kg/cm². Abscissa: left, period of pressure increase; right, period of pressure decrease, in hours.)

greater strength than neat belite (C_2S). This difference increases with pressure increase in the autoclave. Pressure increase from 8 to 100 atm caused a gain in strength of 4 to 5 times.

The strength of the highly-basic hydrosilicates (mixtures prepared with the addition of CaO) practically does not change as the pressure increases.

Consequently, by regulating the gross compositions of the initial mixtures and the conditions of hydrothermal curing, the structural qualities of autoclaved materials can be varied over rather a broad range.

For increasing the strength, it is expedient to prepare the mixtures that give the less basic hydrosilicates, and to increase the temperature of autoclave treatment.

In some publications there are references to the transition of β-$2CaO{\cdot}SiO_2$ to γ-$2CaO{\cdot}SiO_2$ during autoclave treatment. We have, therefore, investigated the behavior of γ-$2CaO{\cdot}SiO_2$ during hydrothermal curing. These investigations have shown that during autoclave curing γ-$2CaO{\cdot}SiO_2$ is able to react with both lime and silica, forming calcium hydrosilicates.

The results obtained were proved with precast nepheline slurry containing about 80 percent of dicalcium silicate (Bozhenov, Kavalerova—1956–1958). Nepheline slurry is a waste material from production of aluminum oxide and is a cementing material of low activity at normal hardening. The chemical analysis of the slurry showed that it contained in percent: SiO_2, 28.63; Al_2O_3, 3.13; Fe_2O_3, 4.80; TiO_2, 0.30; P_2O_5, 0.48; CaO, 52.97; R_2O, 2.18; MgO, 2.12; and ignition loss, 3.89. The existence of great amounts of β-$2CaO{\cdot}SiO_2$ in the nepheline slurry was confirmed by means of X-ray analysis.

In table 3 are shown the strength characteristics of nepheline slurry with addition of 13 to 20 percent of lime or dispersed ground silica sand in the amount of 5 to 75 percent, after autoclaving at 8 atm in accordance with the regime 2–8–2 (hours during which steam pressure was increased, maintained constant, and then decreased).

From the table it is clear that during autoclaving some quantities of lime and particularly dispersed ground silica sand increase nepheline slurry activity.

In table 4 are shown the results of plant testing of 40- x 40- x 50-cm units made with 1:6 mortar, and 20-cm cubes of nepheline-cement concrete (slurry 80%, lime 15%, and gypsum 5%).

From the table it is clear that increase of the time of curing of specimens before steam treatment to 12 hr leads to strength increase up to 20 to 25 percent.

The influence of the rate of increase and decrease of steam pressure on the compressive strength developed in the autoclave is shown in figure 3. It is seen that for the same duration of autoclave curing, rapid increase and slow decrease of pressure insure the greatest strength of the specimens.

Units of the size 40 x 40 x 50 cm prepared of 1:4 nepheline-cement mortar were cured in the autoclave with different rates of pressure increase and decrease but with equal total durations of autoclaving of 9 hr.

The data of table 5 show that the greatest strength is obtained under the conditions of rapid pressure increase and the slowest steam decrease in accordance with the regime 1–3–5.

The data obtained are in contradiction with the established views on the influence of different stages of autoclave curing. Usually operators avoid speeding up the pressure increase, apprehending the appearance of temperature stress in the products.

The influence of temperature stresses during pressure increase is overestimated, and the factors decreasing this stress are not taken into consideration. These factors are steam condensation which takes place as the result of the fact that during pressure increase the temperature of specimens is lower than the steam temperature in the autoclave, and the exothermal reaction of hydration which leads to more rapid heating of the inner layers of the specimens than would occur if only heat conduction were operative. In the stage of steam-pressure decrease, temperature stresses occur, mainly owing to the fact that during decompression a temperature difference is created between the autoclave and specimens. As the result of heat inertia the specimens appear to be overheated, leading to intensive steam generation which creates additional stresses, particularly on the specimen surface.

It appears from the above that rate of pressure increase does not play a great role in the development of strength in products during autoclave curing, but instead, the duration of decrease of steam pressure does play an important part.

The influence of the intensity of steam pressure on concrete strength of nepheline cement was studied by Stakheyev in 1955–1957. The test results given in figure 4 show that during autoclave treatment of nepheline-cement concrete, the optimum pressure is 24 atm.

Variation of the time of curing at maximum pressure from 8 to 0 hr and increase of the steam pressure from 8 to 100 atm influenced the strength of specimens in different ways. On autoclaving at 8 to 15 atm and curing for 0 hr at maximum pressure, the minimum strength of the specimens was obtained. Increase of the curing time to 8 hr at these pressures increased the strength of the specimens.

TABLE 5. *Compressive strength of 1:4 nepheline-cement mortar 40 x 40 x 50 cm specimens autoclaved under different regimes. Maximum pressure 8 atm, mixing water 13 percent*

Autoclave regime	Compressive strength at 28 Days
Hours [a]	*kg/cm* [2]
3-5-1	67
1-5-3	83
1-3-5	112

[a] These numbers represent the time in hours during which the steam pressure was respectively increased, maintained at the maximum, and decreased.

Quite different results were obtained with specimens autoclaved at 50 and 100 atm. In this case, the specimens exposed to autoclaving for 0 hr at maximum pressure (peak autoclaving) had the highest strength.

These experiments have shown once more that the higher the pressure the shorter the process of autoclaving must be. The reason for the strength gain and its decrease with pressure increase from 8 to 100 atm ought to be found in change of composition and structure of the hydrated products.

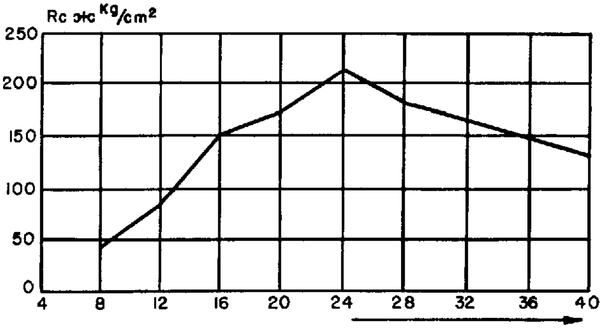

FIGURE 4. *Influence of steam pressure on the strength of nepheline-cement concrete.*
(Ordinate: compressive strength, kg/cm². Abscissa: steam pressure, atm.)

Magnesium Silicates

Magnesium hydrosilicate synthesis is described in the literature to a considerable degree. A number of Soviet and foreign scientists have synthesized talc, antigorite, chrysotile, and some other magnesium hydrosilicates at high temperature and pressure. Magnesium hydrosilicate synthesis was accomplished by use of the individual oxides. But in all these large and generally interesting publications, attention was not given to the study of the technical characteristics of the products obtained. The majority of these works were carried out from the point of view of experimental mineralogy and petrography.

Our investigations on the preparation of artificial hydrosilicates are of applied character, and magnesium hydrosilicates capable of reacting with water under certain conditions have been used as initial raw material, instead of the individual oxides. This procedure has practical significance, since magnesium silicates are rather widely spread in nature (serpentine, olivine).

Magnesite, $MgCO_3$, is a valuable raw material for obtaining technical products of high quality (metallic Mg, fire-proof materials and others). In nature it is found more rarely than magnesium silicates.

The main task of our work is investigation of the conditions for obtaining magnesium hydrosilicates from natural minerals and study of the technical characteristics of the products obtained.

With this aim, at the chair of building materials of the Leningrad Building Institute, systematic work has been carried out since 1954 dealing with the study of binding and some other properties of different natural magnesium silicates (Bozhenov, Salnikova—1956).

Cementing properties of magnesium silicates have been studied in the USSR by: Medvedev—1933, Syromyatnikov—1934, Jung—1946, Budnikov and Berezhnoi—1949, Budnikov and Mchedlov-Petrosyan, Mchedlov-Petrosyan—1951, 1953.

Our work showed the possibility of widening the number of usable natural silicates containing magnesium. Minerals of different chemical composition and varied crystalline structure were investigated. Taking into consideration the fact that the genesis of magnesium-containing hydrosilicates is connected in the majority of cases with the action of water vapor and high temperatures, the method of autoclaving has been used.

Minerals were investigated at different degrees of water removal because of the fact that the loss of water at the time of heating sometimes caused alteration of the crystal lattice and the appearance of active phases.

The experiments showed that the majority of minerals set in rather a short time. (See table 6.) It should be noted that the setting time varied depending on the temperature of dehydration.

Serpentine olivine, chrysotile asbestos, clinochlore, garnierite, and hydroboracite were studied thoroughly. For determination of the temperatures of dehydration in minerals, the curves of loss in weight on heating up to 1,000 °C were obtained, based on the method of dynamic weighing using a torsion balance.

Instead of the widely used method of reading the heating curves, the method of stepped increase of temperature was worked out, namely: temperature increase (5 °C per minute) was stopped as soon as a decrease in weight was noted, and the

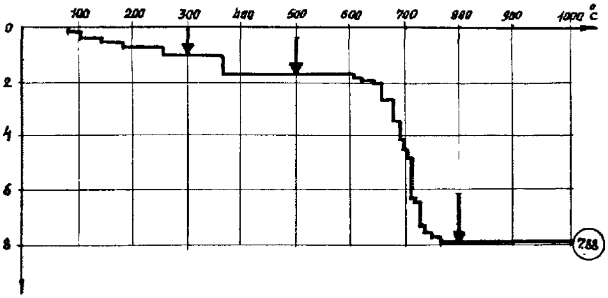

FIGURE 5. *Curve of dynamic weighing of serpentine olivine.* (Ordinate: weight loss, percent. Abscissa: temperature.)

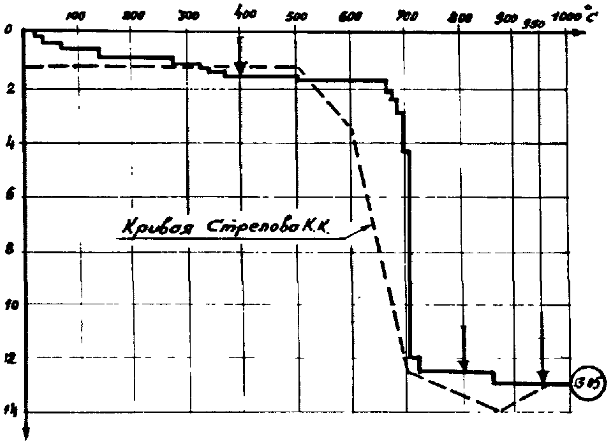

FIGURE 6. *Curves of dynamic weighing of chrysotile asbestos.* (Ordinate: weight loss, percent. Abscissa: temperature. Dotted curve, data of Strelov.)

TABLE 6. *Effect of temperature of dehydration on the subsequent setting times of water-mineral pastes*

No.	Mineral	Chemical formula	Temp. of dehydration	Setting time	
				Initial	Final
			°C	hr:min	hr:min
1	Vesuvianite	$3CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$	110	4:00	4:30
2	Vesuvianite	$3CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$	800	5:13	7:33
3	Tremolite	$2CaO \cdot 5MgO \cdot 8SiO_2 \cdot H_2O$	110	6:10	7:30
4	Tremolite	$2CaO \cdot 5MgO \cdot 8SiO_2 \cdot H_2O$	800	9:40	24:30
5	Actinolite	$2CaO \cdot 5(Mg,Fe)O \cdot 8SiO_2 \cdot H_2O$	110	4:53	6:30
6	Actinolite	$2CaO \cdot 5(Mg,Fe)O \cdot 8SiO_2 \cdot H_2O$	800	4:50	6:07
7	Chrysotile asbestos	$3MgO \cdot 2SiO_2 \cdot 2H_2O$	800	8:10	21:00
8	Chrysotile asbestos	$3MgO \cdot 2SiO_2 \cdot 2H_2O$	950	5:00	7:12
9	Serpentine olivine		110	7:50	20:40
10	Serpentine olivine		800	2:04	3:53
11	Talc	$3MgO \cdot 4SiO_2 \cdot H_2O$	110	(1)	(1)
12	Talc	$3MgO \cdot 4SiO_2 \cdot H_2O$	800	48:00	48:00
13	Clinochlore No. 1	$12MgO \cdot 2Al_2O_3 \cdot 7SiO_2 \cdot 10H_2O$	110	(3)	(3)
14	Clinochlore No. 1	$12MgO \cdot 2Al_2O_3 \cdot 7SiO_2 \cdot 10H_2O$	800	0:55	(1)
15	Clinochlore No. 2	$12MgO \cdot 2Al_2O_3 \cdot 7SiO_2 \cdot 10H_2O$	110	27:00	47:00
16	Clinochlore No. 2	$12MgO \cdot 2Al_2O_3 \cdot 7SiO_2 \cdot 10H_2O$	800	6:48	7:48
17	Garnierite [2]		110	(3)	(3)
18	Garnierite [2]		180	48:00	72:00
19	Phlogopite	$K_2O \cdot 6MgO \cdot Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$	800	(3)	(3)
20	Muscovite	$K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$	800	10:00	23:00

[1] No setting during 72 hours.

[2] "Garnierite" is not a pure mineral.

[3] No setting during 48 hours.

TABLE 7. *Strengths of pressed specimens of water-mineral pastes after normal hardening*

No.	Mineral	Temp. of dehydration	Mixing water	Compressive strength				Bending strength		
				9 days	1 month	3 months	1 year	1 month	3 months	1 year
		°*C*	*Percent*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*
1	Chrysotile asbestos	800	9	6	7	14	17	3.3	3.7	4.6
2	Chrysotile asbestos	950	9	23	7	6.7	0	2.7	2.3	1.2
3	Serpentine olivine	800	7	6	18	18	20	4.8	5.1	6
4	Clinochlore	800	7	0	1.7	2.5	0	1.2	2.1	2.3
5	Garnierite	180	14	10.9	48	34	26	11.4	5.5	4.3
6	Hydroboracite	670	11	10	19	60	89	6.7	16.8	23.3
7	Hydroboracite	700	11	2	6.2	12	----------	2.3	3.7	----------

TABLE 8. *Strengths of pressed specimens of water-mineral pastes after autoclaving at 8 atm*

No.	Mineral	Temp. of dehydration	Compressive strength				Bending strength		
			Age of the specimens before autoclaving						
			7 days	28 days	3 months	1 year	28 days	3 months	1 year
		°*C*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*
1	Chrysotile asbestos	800	108	126	102	90	55	38	38
2	Chrysotile asbestos	950	90	90	96	90	22	41	12
3	Serpentine olivine	800	154	138	132	126	49	45	42
4	Clinochlore	800	29	53	49	36	15.6	15.2	18.1
5	Garnierite	180	48.2	42	39	0	5.7	9.6	0
6	Hydroboracite	670	296	350	200	211	54	41	25
7	Hydroboracite	700	----------	192	87	----------	38	38	----------

specimen was cured under thermostatic conditioning until the weight was constant for 3 to 4 min. The temperature of the specimen was then again increased at the rate of 5 °C per minute until decrease of the weight of the specimen was again noted, and so on.

In figures 5 and 6 the curves obtained by this method of dynamic weighing are given. These curves have been used for establishing the temperatures for firing the specimens (in the figures they are marked with arrows).

It is clear from tables 7 and 8 that the strengths of the specimens cured in high-pressure steam exceed by many times the strengths of the specimens that were conventionally cured.

The investigations showed that the process of hardening of chrysotile asbestos and serpentine olivine occurred more intensely at higher temperatures.

These data show the possibility of the wider use of autoclaving for experimental mineralogy too, because by changing the steam-curing conditions one can judge the stability of investigated material.

The data obtained by thermal analysis (figs. 7, 8, 9, 10, 11) make it possible to form judgments about new formations. The higher the pressure of the steam in hydrothermal treatment the greater is the similarity between the hardened chrysotile-asbestos and serpentine-olivine pastes and the natural minerals. The data of petrographic analysis of hydrated samples of chrysotile asbestos and serpentine olivine provide evidence relative to the hydrated compounds formed in the process of hydrothermal curing.

Tests showed that the effectiveness of autoclaving of magnesium silicates increased with pressure increase.

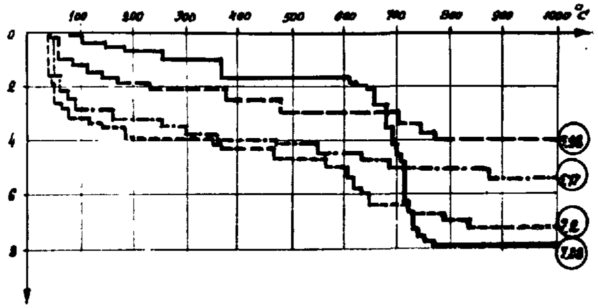

FIGURE 7. *Curves of dynamic weighing of serpentine olivine (temperature of dehydration, 950 °C).*
(Ordinate: weight loss, percent. Abscissa: temperature.)

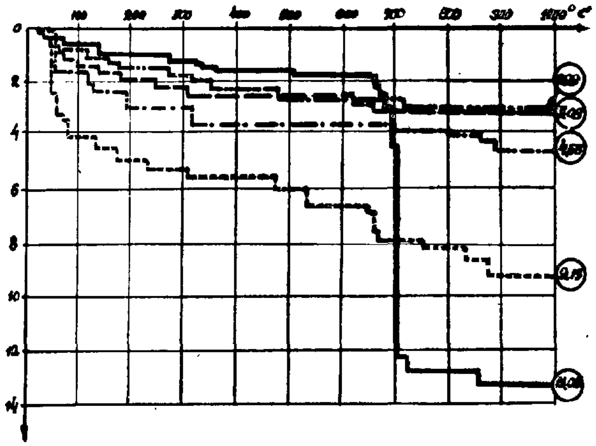

FIGURE 8. *Curves of dynamic weighing of chrysotile asbestos (temperature of dehydration, 950 °C).*
(Ordinate: weight loss, percent. Abscissa: temperature.)

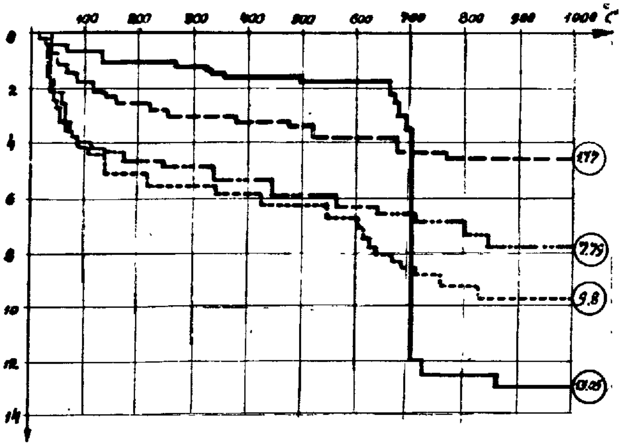

FIGURE 9. *Curves of dynamic weighing of chrysotile asbestos (temperature of dehydration, 800 °C).*
(Ordinate: weight loss, percent. Abscissa: temperature.)

The high mechanical strengths of dehydrated magnesium silicates, obtained on autoclaving, table 9, made it feasible to investigate their applicability as building materials.

Under laboratory conditions a new autoclaved material somewhat like asbestos cement was obtained wherein portland cement was entirely replaced by thermally cured (at 700 to 900 °C) nonclassified wastes of asbestos factories (Bozhenov and Salnikova—1958). Technical properties of the slabs obtained are given in table 10. A valuable property of the new material is its stability in aggressive environments and at high temperatures, which is of practical interest for special constructions.

TABLE 9. *Compressive strength of water-mineral pastes*

No.	Cementing material	Temp. of dehydration	Compressive strength at 9 days			
			Normal hardening	Autoclaved at		
				8 atm	15 atm	100 atm
		°C	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*
1	Serpentine olivine	800	0	154	147	239
2	Chrysotile asbestos.	800	29	108	86	154
3	Chrysotile asbestos.	950	23	208	238	287

TABLE 10. *Technical qualities of pressed slabs after autoclaving at 8 atm*

Material	Composition of mixture	Binding strength		Density	Water absorption
		1 day	1 year		
		kg/cm²	*kg/cm²*		*Percent*
1. Asbestos-magnesium slabs.ᵃ	85% of cementing material of fired wastes+15% of asbestos 1V c	234	310	1.69	16-24
2. Asbestos-cement slabs.ᵇ	85% of portland cement +15% of asbestos 1V c	305	310	1.96	16-24

[a] The slabs obtained on the basis of fired wastes with aggregate of asbestos are called "asbestos-magnesium."

[b] Asbestos-cement slabs were produced simultaneously with asbestos-magnesium slabs and under the same conditions

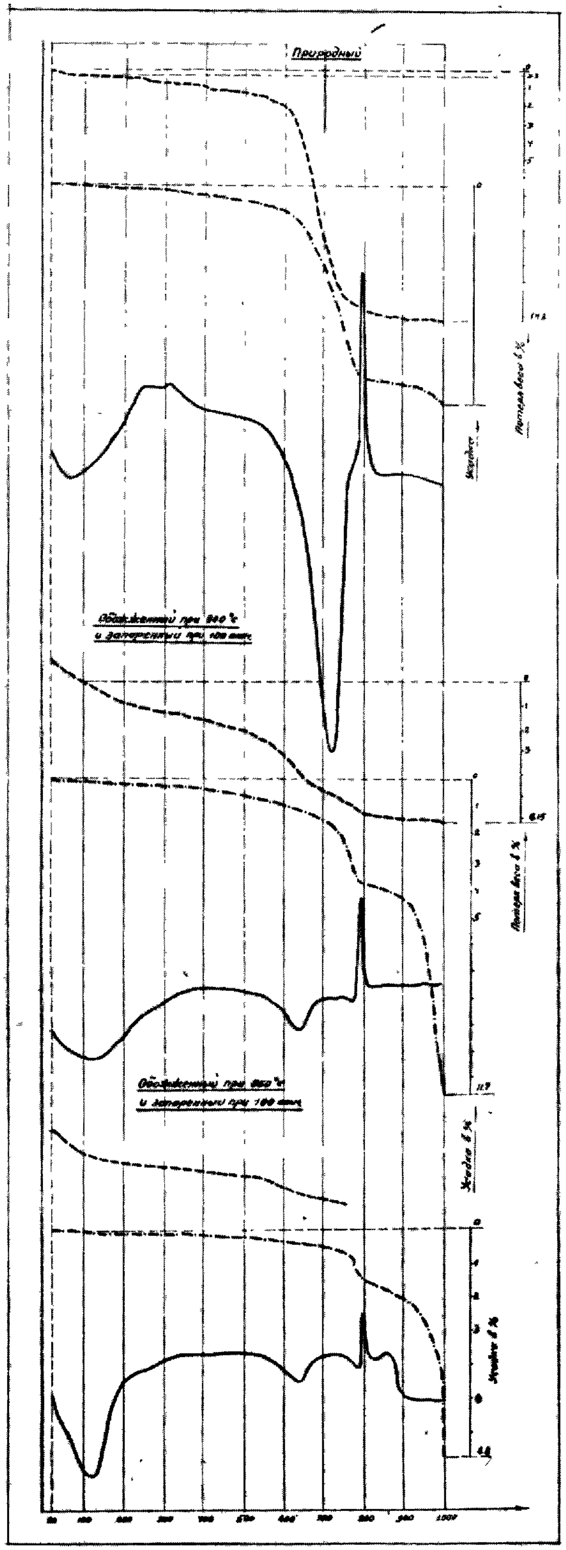

FIGURE 10. *Curves of complex thermal analysis of chrysotile asbestos.*

Abscissa: temperature, °C. Upper set of curves: untreated sample. Middle set: dehydrated at 800 °C and steam cured at 100 atm. Lower set: dehydrated at 960 °C and steam cured at 100 atm. Dashed curves, weight loss, percent; dot-and-dash curves, shrinkage, percent; solid curves, thermal effects.

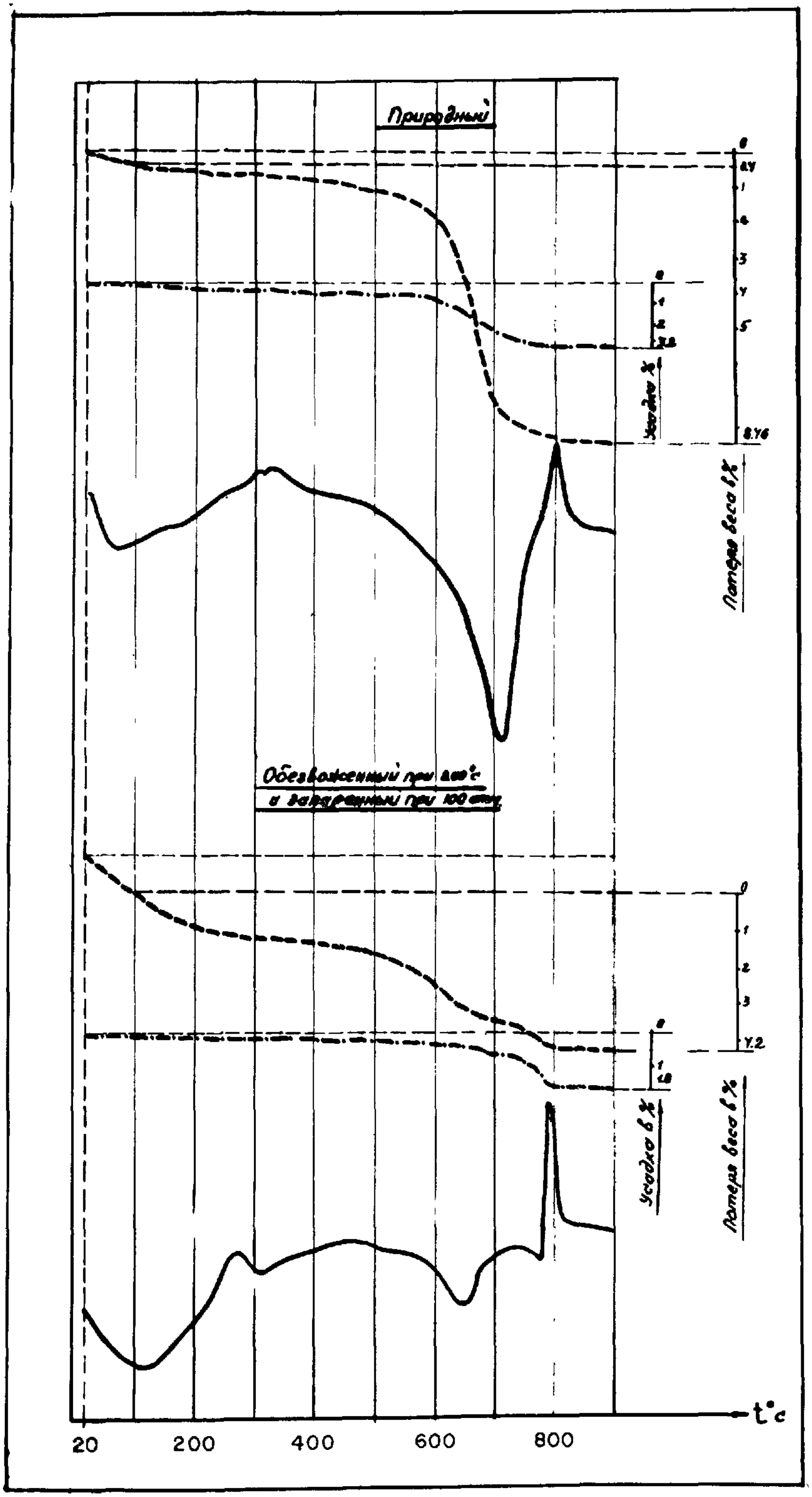

FIGURE 11. *Curves of complex thermal analysis of serpentine olivine.*
Abscissa: temperature, °C. Upper set of curves: untreated sample. Lower set: dehydrated at 800 °C and steam cured at 100 atm. Dashed curves, weight loss, percent; dot-and-dash curves, shrinkage, percent; solid curves, thermal effects.

Tests of specimens autoclaved at steam pressure of 200 atm (Rakitskaya—1959) showed compressive strengths increasing nearly 4 times as compared with the strengths of the specimens autoclaved at 10 atm.

In specimens produced from portland cement with 15 percent asbestos aggregate we observe strength decrease under conditions of pressure increase.

From the results of laboratory and pilot-plant investigations we can say that autoclaved materials of varied utility can be obtained, based on magnesium silicates.

Martin slags contain about 20 minerals: calcium silicates, magnesium silicates, periclase, and some other compounds. It was established that Martin slags can be used as cementing material in the production of autoclaved building products of dense and cellular structure.

The study of a great number of Martin slags showed that all of them were able to hydrate. Hydrothermal curing has great influence on slag hardening. Under normal conditions, hardening of slags proceeds slowly; upon autoclave treatment the strength of specimens increases 50 to 60 times.

For example, specimens tested after autoclaving at 8 atm attained strengths as follows:

in paste —270 kg/cm^2
in 1:1 mortar—575 kg/cm^2
in 1:3 mortar—340 kg/cm^2 in compression and 75 kg/cm^2 in bending.

The strength of some slags reached 700 kg/cm^2 in one year.

Side by side with high cementing properties of slags, some slags were found to have the capability of bloating and cracking in the process of autoclave treatment. This behavior is probably connected with the presence of periclase, MgO.

The results of work carried out over several years allows us to state that the use of high-pressure steam makes it possible to obtain building materials with interesting qualities, on the basis of new raw materials. Great prospects are open for the efficient use of natural resources and the complete use of raw minerals.

Autoclave Curing of Cementing Materials with High-Pressure Steam (8 to 200 atm)

The study of the chemical processes of hardening of portland cement clinker under normal and hydrothermal conditions enabled us to conclude that at high temperature and pressure the reactions of minerals and water occur more intensively than under mormal conditions of temperature and humidity, and that the products of autoclave hardening have their own specific character.

Experimental work and theoretical considerations in the field of hydrothermal curing of cement, concrete, and lime-sand mixtures led to the suggestion that since autoclave treatment of the cited materials accelerates the hardening processes by as much as 30 times even at 8 atm (174 °C), more intensive curing at high steam pressure might be even more effective. Unfortunately, before 1950 this question had undergone neither experimental nor plant-scale study, and there were no pertinent data in the literature.

The theoretical foundations for physicochemical processes taking place under hydrothermal conditions were only partly studied, and dealt with natural calcium hydro-compounds and the products of hydrosilicate synthesis in the system CaO-SiO_2-H_2O.

It is impossible not to mark the fact that with the use of the method of artificial hydrothermal synthesis of hydrated minerals the development of experimental mineralogy and petrography, and the science of crystallochemistry of silicates as well, have considerably outstripped the practical application of hydrothermal curing.

For the first time, in 1950, we began an investigation (P. I. Bozhenov and G. F. Suvorova, 1955) of the influence of high-pressure steam (from 8 to 200 atm, in the temperature range from 174 to 364 °C) on cements of different mineralogical compositions.

The aim of the investigation was the study of the dynamics of reaction of cement and its physicochemical properties, and investigation of new formations of hydrated cements under a wide range of pressures which would make it possible to learn more profoundly the technology of building products fabricated by autoclaving.

Before describing the results of the work, it is necessary to remark that during 1950 to 1960 great improvements were achieved in theoretical work and in the practical perfection of the technological production of autoclaved building materials.

All said above leads to the conclusion that autoclave curing of building materials is one of the most effective and progressive technological methods in the building materials industry, as is generally recognized.

The first experiments had for their object the establishment of the general requirements for autoclave hardening of cements at high pressures and temperatures. It was also desired to investigate the composition and structure of the new formations in the products of cement hardening, after autoclave curing.

Cement specimens of different mineralogical composition were exposed to autoclaving. Their compositions are given in table 11.

For providing the necessary pressure, a laboratory autoclave-bomb was made, with capacity of 500 cm^3 and for a working pressure of 300 atm. Specimens 3 × 3 × 3 cm were prepared of neat cement paste of plastic consistency and of 1:3 plastic mortars.

TABLE 11. *The influence of autoclaving on the strength of cement paste and mortars of different mineralogical composition*

	Cement No.	A C		5 C		4 C		3 C		2 C		B C		C	
Minerological composition of cement in %.	C_3S	59		57		47.6		47.2		33.3		28		20.5	
	C_2S	18		18		26.0		29.4		37.7		46		54.7	
	C_3A	4		7.6		10.7		6.9		12.7		5		15.1	
	C_4AF	15		14.2		10.9		15.2		14		17		1.2	
Regime of hardening		*kg/cm²*	%	*kg/cm²*	%	*kg/cm²*	%	*kg/cm²*	%	*kg/cm²*	%	*kg/cm²*	%	*kg/cm²*	%
		Cement paste (1:0)													
Normal hardening during 28 days		965	100	1450	100	1165	100	1175	100	1260	100	845	100	835	100
Autoclaving at	8 atm	520	54	1060	73	760	65	530	45	620	49	520	73	440	53
	15 atm	510	53	680	47	560	48	570	49	580	46	770	91	232	28
	25 atm	190	19	210	14	205	18	126	11	190	15	480	57	156	19
	50 atm	180	18	140	9	87	7.5	75	6	106	8	300	35	80	9
	100 atm	105	11	143	10	77	7	53	5	120	10	105	12	83	10
	200 atm	70	7	80	6	41	3	43	4	45	4	65	8	67	8
		Cement mortar (1:3)													
Normal hardening during 28 days		348	100	192	100	140	100	111	100	370	100	230	100	166	100
Autoclaving at	8 atm	313	90	236	123	175	125	225	203	380	103	425	185	235	142
	15 atm	430	124	315	164	185	132	240	216	396	107	460	200	290	175
	25 atm	600	172	312	162	226	162	220	198	430	116	365	159	227	137
	50 atm	330	95	175	91	120	86	132	119	242	66	220	96	205	123
	100 atm	165	48	135	70	113	81	134	121	214	58	193	84	179	118
	200 atm	175	22	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	145	88

Autoclave curing of the specimens was carried out at the following pressures and temperatures:

8 atm—174 °C
15 atm—200 °C
25 atm—225 °C
50 atm—365 °C
100 atm—310 °C
200 atm—364 °C.

The rate of temperature increase and decrease in the autoclave corresponded to 1.2 degrees per minute. Upon reaching the chosen value, the pressure was kept constant for 6 hr. The compressive strength of the specimens was determined just after autoclaving, and after rather long times of normal storage (up to 1 year) as well.

The results of tests of the compressive strength of specimens autoclaved at pressures of 8 to 200 atm are given in table 11.

In the investigated range of pressures, the strength of the specimens achieved its maximum for cement paste at pressures of 8 to 15 atm and for cement mortars at pressures of 15 to 25 atm. On intensification of hydrothermal curing (to 200 atm) a tendency toward reduction of strength was observed.

Hydration of cements with high contents of active minerals (C_3S and C_3A) occurs rather rapidly even when autoclaving at the lower pressures (8 to 10 atm), but cementing materials with high contents of slowly hardening components such as C_2S require more intensive autoclaving (up to 15 atm).[2]

High-pressure steam has greater influence on cement mortar (1:3).

The use of steam at the pressure of 15 to 20 atm for all the cements increased the compressive strength of specimens by 2 to 3 times as compared with the strength of the specimens at the age of 28 days under conditions of normal hardening, and by 30 to 50 percent in comparison with autoclaving at 8 atm. Belite cement, particularly, was greatly affected by autoclaving.

On autoclave treatment, silica sand as an aggregate plays an active part in the development of physicochemical properties, depending on autoclaving conditions.

The latest investigations showed that the long regime adopted for the first experiments was apparently inexpedient, particularly when using high-pressure steam.

Numerous experiments with different initial materials showed that when using high-pressure steam it is necessary to reduce the general technological cycle of hydrothermal curing from the 12 to 14 hr regime at 8 atm to a 4 to 8 hr regime at 16 to 25 atm (fig. 12).

On the basis of a great number of experiments, it appeared possible to use a new technological method of treatment—autoclaving of materials at high pressure without curing. This was called "peak regime" (increasing+decreasing).

Figure 13 presents the results of one of the experimental series on the determination of peak regime influence on the hardening of cement mortar of the composition 1:3, of plastic consistency.

The analysis of the given material confirms the great advantage of using high-pressure steam (16 to 20 atm) in comparison with autoclaving at 8 atm, because of the possibility of reducing the duration of the general technological cycle of curing of building materials by one-half while simultaneously increasing the qualitative indices.

The experiments show that the relative effect of autoclaving is higher for belite cements than

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[2] The autoclaving of neat cement paste (1:0) is considered here.

for cements with high contents of C_3S and C_3A (see table 11). This conclusion was proved with nepheline cement, as its mineralogical composition consists mainly of $2CaO\cdot SiO_2$ (80 to 85 percent) (see fig. 14).

Proved possibilities (on the basis of tests with portland cement) of sharp reduction of the autoclaving regime by increase of pressure to 15 to 25 atm became a basis for conducting investigations on the behavior of lime-sand mortar, using high-pressure steam.

In figure 15 are presented the results of tests obtained by Petrenko (1952 to 1956) during his study of the influence of steam pressure on the strength of lime-sand mortars prepared with sands of different grain fineness. From figure 15 it is clear that the maximum strength corresponds to a pressure of 15 to 25 atm. Increase of the total surface of the quartz sand grains increases the strength. In order to learn the influence of lime, special tests were carried out. Their results are given in table 12.

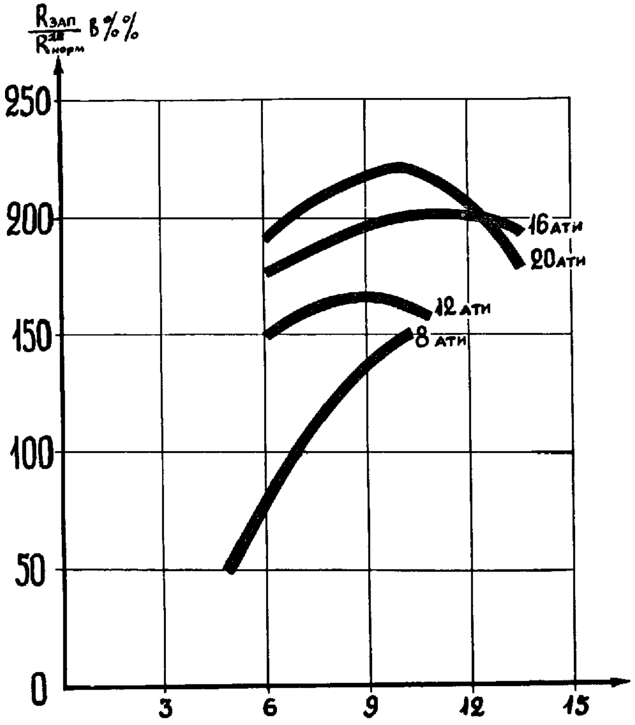

FIGURE 12. *Strength dependence of cement mortars and concrete on time of autoclaving.*

(Ordinate: ratio of compressive strength of steam-cured to normally hardened specimens, percent.

(Abscissa: autoclaving period, hours. Pressures indicated in atm.)

P	Pressure Regime			Compressive Strength		
	Increase	Hold	Decrease	Total		
	hr	*hr*	*hr*	*hr*	*kg/cm²*	%[a]
8	2.5 5	2.5 0	2 5	10	286 274	159 152
12	2.5 5	5 0	2.5 5	10	296 284	165 158
16	3 5	4 0	3 5	10	360 358	200 200
20	5	0	5	10	403	216

[a] Relative to 28-day strength of 180 kg/cm².

P	Pressure Regime			Compressive Strength		
	Increase	Hold	Decrease	Total		
8	*hr* 2.5	*hr* 0	*hr* 3	*hr* 5.5	*kg/cm²* 110	%[a] 60
12	2	0	4	6	274	152
16	3	0	3.5	6.5	319	178
20	2	0	4	6	337	187
	4	0	2	6	359	200

[a] Relative to 28-day strength of 180 kg/cm².

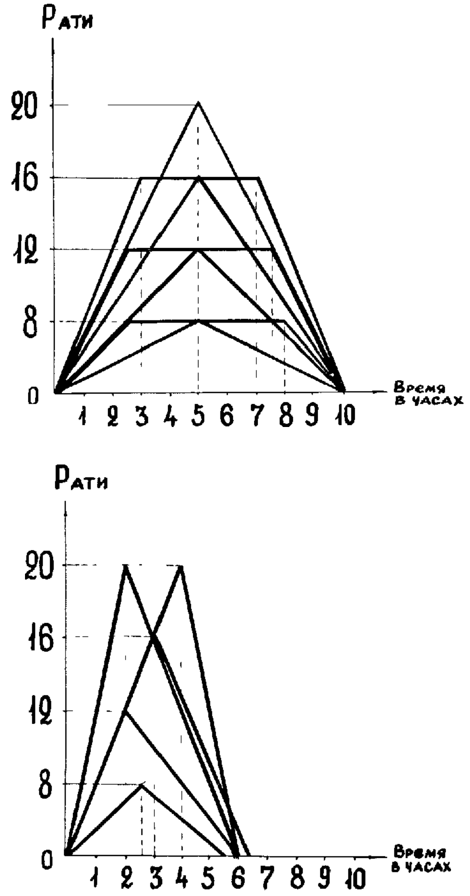

FIGURE 13. *"Peak-regime" influence on hardening of cement mortar of the composition 1:3 of plastic consistency.*

(Ordinate: steam pressure, atm. Abscissa: autoclaving period, hr.)

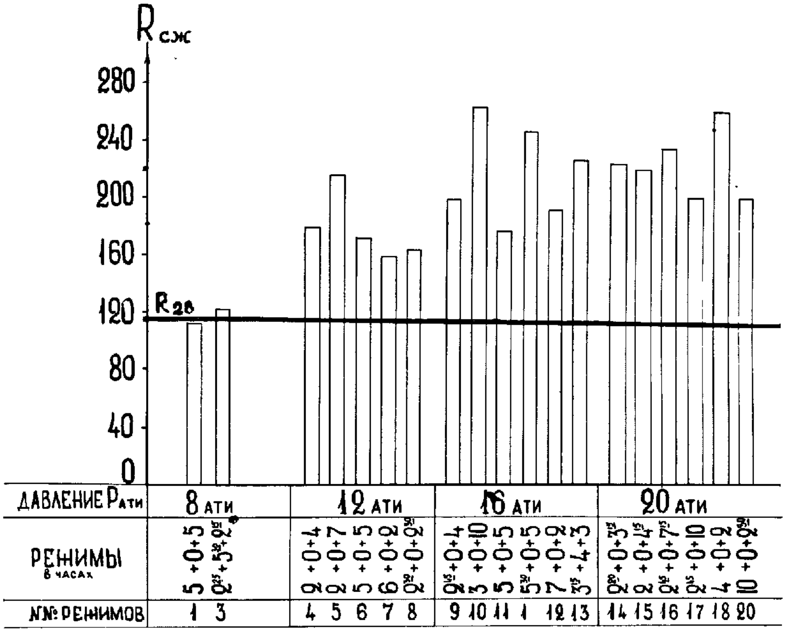

FIGURE 14. *Influence of different regimes of autoclaving on strength of nepheline-cement mortars.*

(Ordinate: compressive strength, kg/cm². Data below graph indicate pressure in atm, regime in hr, and number of regime, respectively.)

TABLE 12. *The influence of high-pressure steam curing on the strength of lime-sand mixes*

Composition of mixture lime-sand, %	Compressive strength in kg/cm², pressure at (atm)									
	8	10	12	14	16	19	22	25	40	100
10:90	350	355	**368**	364	360	363	331	268	214	175
15:85	321	339	323	**366**	327	321	298	305	286	154
25:75	459	656	580	691	750	**828**	730	750	698	493
30:70	320	491	519	780	713	807	850	**934**	885	531

From table 12 it is clear that the optimum pressure value changes, depending on the mixture composition.

With increase of the lime content in mixtures, the maximum value of strength moves in the direction of higher pressures, up to 25 atm inclusive. Tests carried out confirmed that for lime-sand mixtures, too, it is necessary to reduce the duration of autoclaving with increase of the steam pressure in the autoclave.

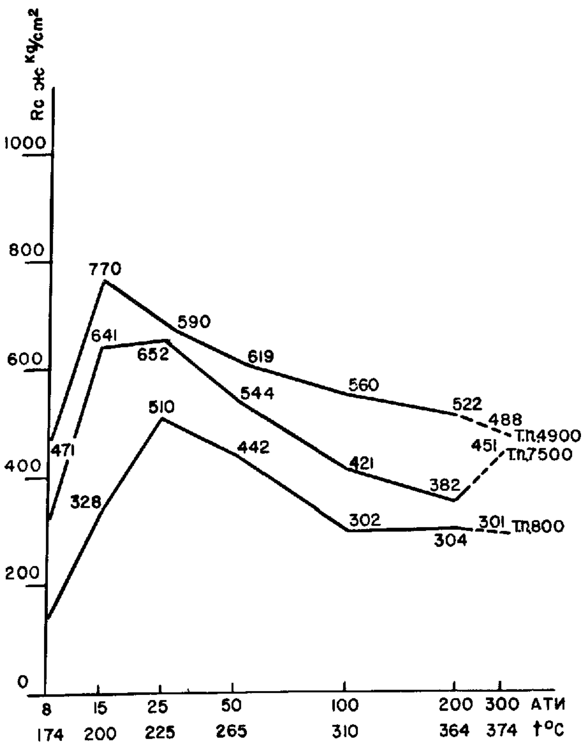

FIGURE 15. *Influence of steam pressure on the strength of lime-sand mortars.*

(Ordinate: compressive strength, kg/cm². Abscissa: steam pressure, atm, and temperature. Specific surface of sand, cm²/g, is indicated at right of curves.)

Regularities, proved during the investigations, in the change of the compressive strength of cement and lime-sand materials depending on the autoclaving regime, led the authors to study the dynamics of new formations in dependence on the mineralogical composition of the initial materials and the autoclaving regime by means of differential thermal analysis, the method of dynamic weighing, petrography, X-ray analysis, and some other methods of investigation.

The thermographs of cements hydrated at different pressures are given in figures 16 and 17.

Comparative analysis of thermal effects indicated by the heating curves showed that during autoclave curing new products of hydration are developed, quite different from the products of normal hardening in composition and structure.

Endothermic effects observed in the intervals of 100 to 140 °C, 200 to 250 °C, 400 to 450 °C are characteristic of the loss of free water and the

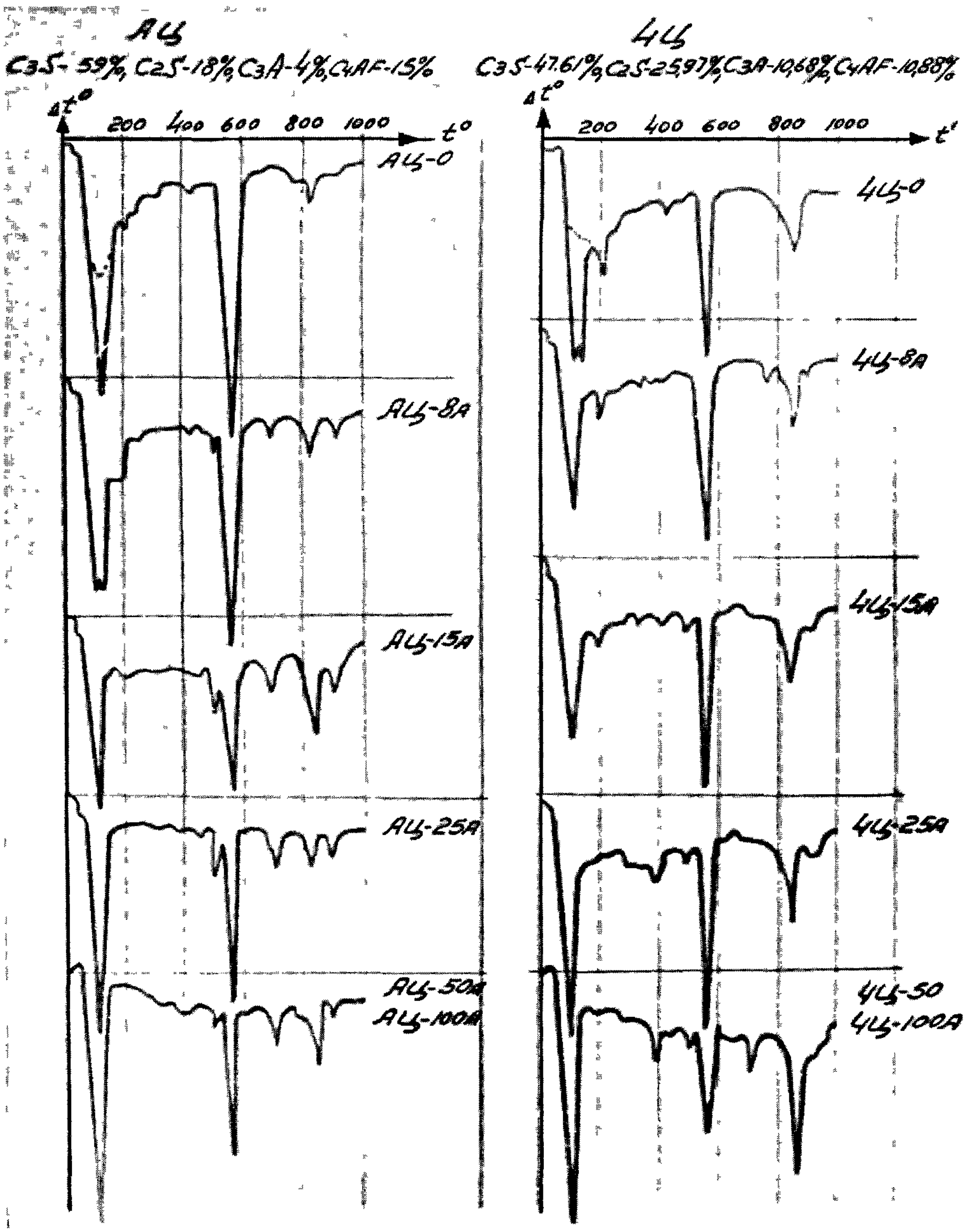

FIGURE 16. *DTA curves of cement paste (1:0) after autoclaving at 8 to 100 atm.*

Left column: cement AC; right column: cement 4C. Top curves: cement hardened under normal conditions; other curves: after autoclaving at pressures indicated.

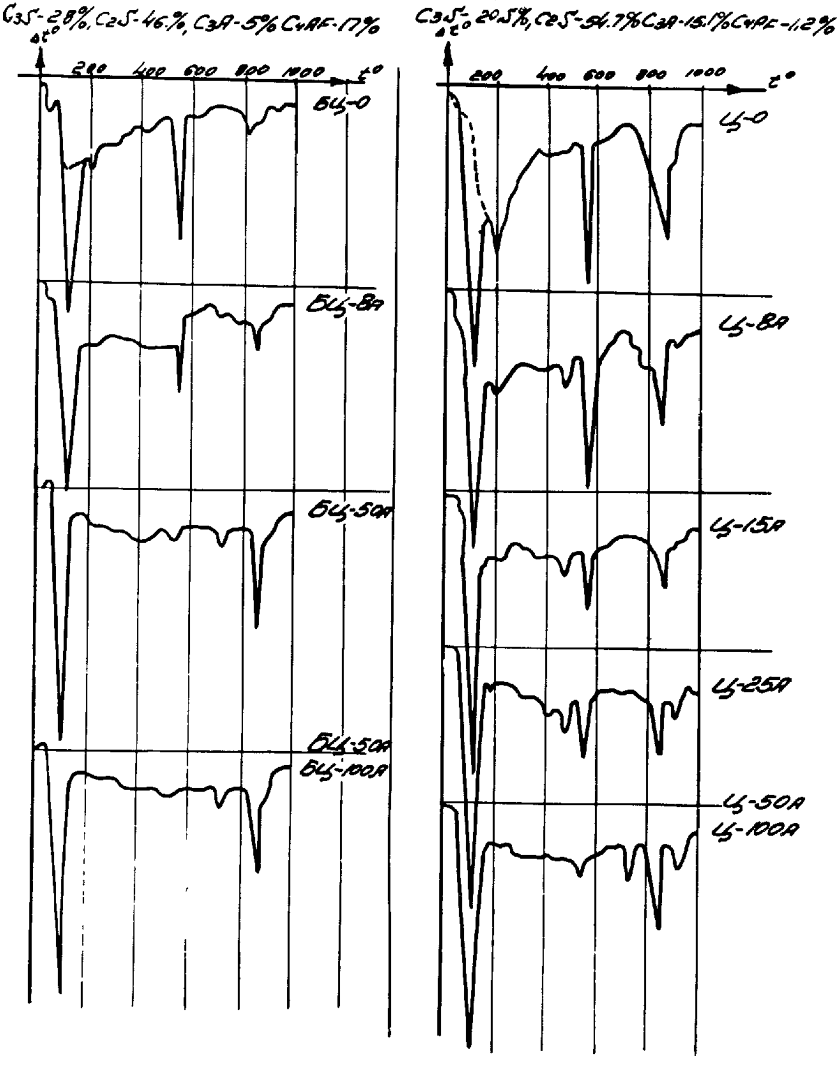

FIGURE 17. *DTA curves of cement paste (1:0) after autoclaving at 8 to 100 atm.*

Left column: cement BC; right column: cement C. Top curves. cement hardened under normal conditions; other curves: after autoclaving at pressures indicated.

evaporation of capillary moisture which exists in gel products of cement hardening.

In all the cases of pressure increase, gradual decrease and even disappearance of the endothermic effect at 550 to 580 °C, characteristic of the decomposition of $Ca(OH)_2$, was observed, showing the combination of lime in new products of hydration.

Clearly expressed endothermic drops in the intervals of 620 to 740 °C and 800 to 900 °C characterize crystalline structures of calcium hydrosilicates of varied composition appearing under conditions of high pressure and temperature on one hand and decarbonation of $CaCO_3$ (second effect) on the other hand.

The investigation of the products of cement hydration by the method of dynamic weighing in the process of heating up to 1,000 °C confirmed that with pressure increase in autoclave treatment new products of hydration are formed (fig. 18).

With pressure increase, gradual decrease of free and weakly-bound water was observed, as characterized by the loss of moisture in the interval 100 to 400 ° C. Gradual diminishing of the content of $Ca(OH)_2$ was confirmed also, as by the DTA curves.

Increase of the hydrated products which lose water in the narrow temperature interval 640 to 720 °C was observed.

Comparing the dehydration curves of the investigated cements with those for nepheline slurry, hydrated for a year, and for a sand-lime mixture autoclaved at 15 atm, one can see that in these cases new formations have similar composition not depending on the initial materials.

Petrographic investigation of specimens of normal and autoclave hardening confirmed the increase of the degree of hydration and cement crystallization with increase of pressure. So we can confirm that densification of the gel products

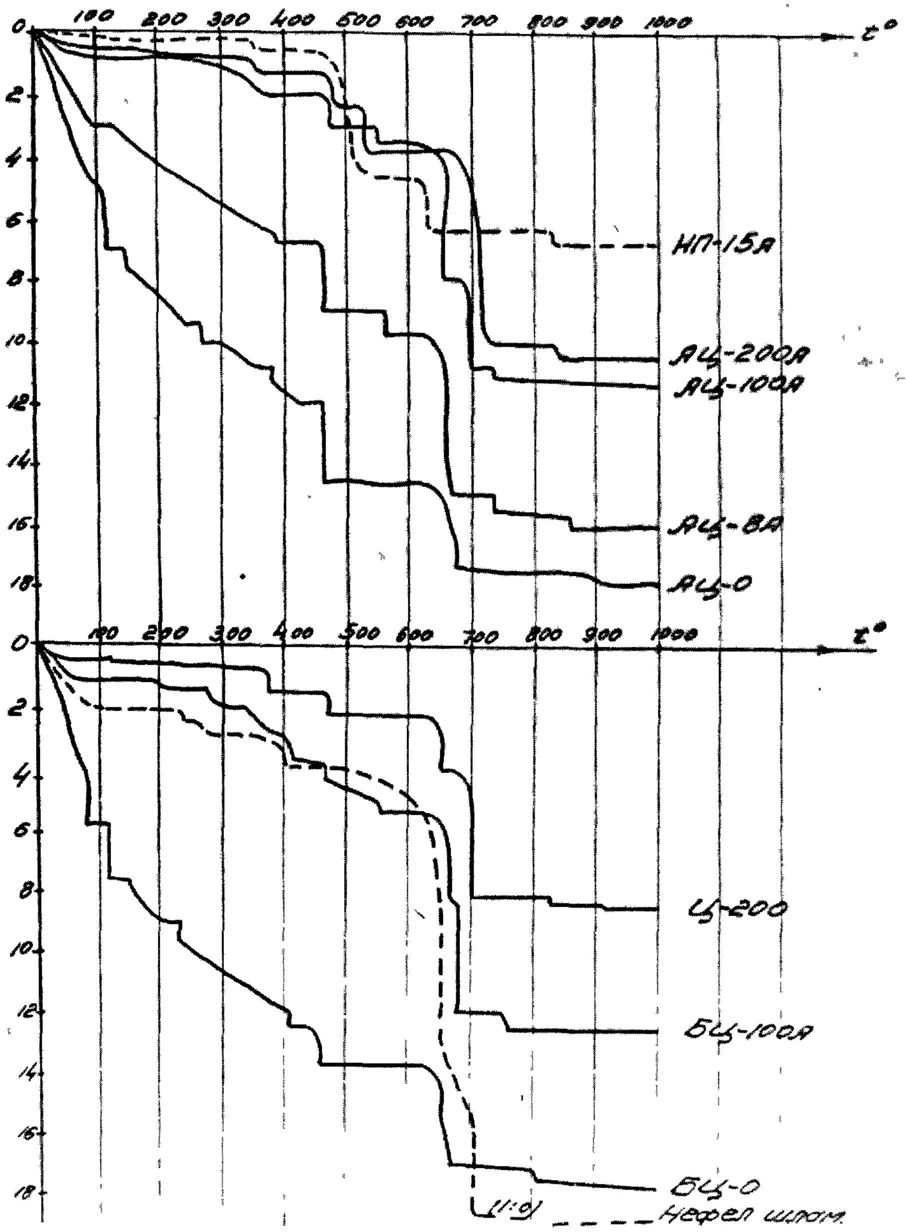

FIGURE 18. *Curves of dynamic weighing of cement-paste (AC, BC, C).*
(Ordinate: weight loss, percent. Abscissa, temperature, °C.) Curves, top to bottom:
lime-sand mixture, 15 atm.
AC, 200 atm.
AC, 100 atm.
AC, 8 atm.
AC, hardened under normal conditions
C, 200 atm.
BC, 100 atm.
BC, hardened under normal conditions
nepheline slurry

of hardening provides firmer binding, that, on the contrary, increased crystallization at high pressure promotes a decrease of the compressive strength of hardened cement paste owing to the formation of a coarsely crystalline modification, of fragile structure.

The results obtained permit the assumption (according to Sheykin—1944) that in hardening cement, the most rational proportions of gel and crystalline components are those that give the optimum value of mechanical strength. Predominance of one phase over the other reduces the physicochemical properties of the hardened cement paste. Therefore, the optimum regime and intensity of hydrothermal curing depend on the mineralogical composition of the cement, which in its turn is connected with the different rates of hydration of different clinker minerals.

Thermographic investigations carried out provide some material for explaining the process of interaction of CaO and SiO_2 in commercial lime-sand mortars. In figure 19 is given the thermogram (curve I) ($CaO:SiO_2=1:1$) of the mortar. Before the test, quick lime was hydrated to lime hydrate. The thermogram shows the existence of three main substances in the composition of the initial mortar: $Ca(OH)_2$, by the endothermal effect of dehydration at 500 to 550 °C; SiO_2, by the polymorphous conversion of α-quartz at 573 °C; and $CaCO_3$, for which dissociation begins at 780 °C and ends at 920 °C.

On treatment of mortars having the ratios $CaO:SiO_2=1:10$, 1:3, and 1:1 (curves II, III, IV) in the autoclave at a pressure of 16 atm for 8 hr, one observes the following changes of thermal effects (fig. 19):

1. Increase of the products of hardening within the temperature interval of dehydration at 120 to 400 °C. The gel structural component, formed by submicroscopical new formation, loses so-called "zeolitic water," over this range of temperature.
2. Increased endothermic effect at 450 C°, which in this case refers to the dehydration of $Mg(OH)_2$.
3. The endothermic effect representing the polymorphous conversion of α-quartz (573 °C) decreases with increase of basicity of the composition because of the fact that in lime-rich mortar a great amount of SiO_2 interacts with lime (in fig. 19, compare curves I and IV).
4. In the temperature interval 680 to 750 °C, the endothermic effect is interpreted as dehydration of calcium hydrosilicate, possibly of crystalline structure. Recrystallization of these dewatered hydrates is followed by sharp exothermic reaction in the range of 800 to 850 °C, which is so pronounced that it covers completely the endothermic effect of $CaCO_3$ dissociation, occurring at the same temperature interval, and possibly accelerates the latter process.

On the thermograms one notices the increase of the area representing recrystallization with the increase of new formations.

The following series of curves (fig. 20) reflects the influence of the intensity of hydrothermal curing on lime-sand mortars. Up to 25 atm (225 °C) one notes a considerable gel phase which on the curves is characterized by a wide area of endothermic effect at 100 to 400 °C.

If the autoclave treatment is carried out at temperatures higher than 225 °C, this effect on the heating curves is absent, implying the absence of a gel phase.

As in the preceding series of tests, the endothermic effect at 573 °C shows the phase conversion of α-quartz.

At the temperature of 620 °C, the removal of bound water from calcium hydrosilicates begins.

The dehydration reaction is completed at 680 to 740 °C. As shown, not only the quantity but also the composition of new formations depend on the autoclave curing regime.

The endothermic effect of calcium hydrosilicate dehydration is, in all cases, followed by an intense exothermic reaction beginning at 800 °C and ending at 840 to 850 °C. This effect may be explained by phase conversion of the dehydrated part of the calcium hydrosilicate.

One can judge the irreversibility of this reaction by the repeated thermogram (fig. 21), which showed no effects except the polymorphous conversion of quartz.

The results of thermal analysis of lime-sand mortars, prepared with sands of different specific surfaces showed no essential qualitative differences in new formations.

On hydrothermal curing, the processes of hydrosilicate formation are of complicated character,

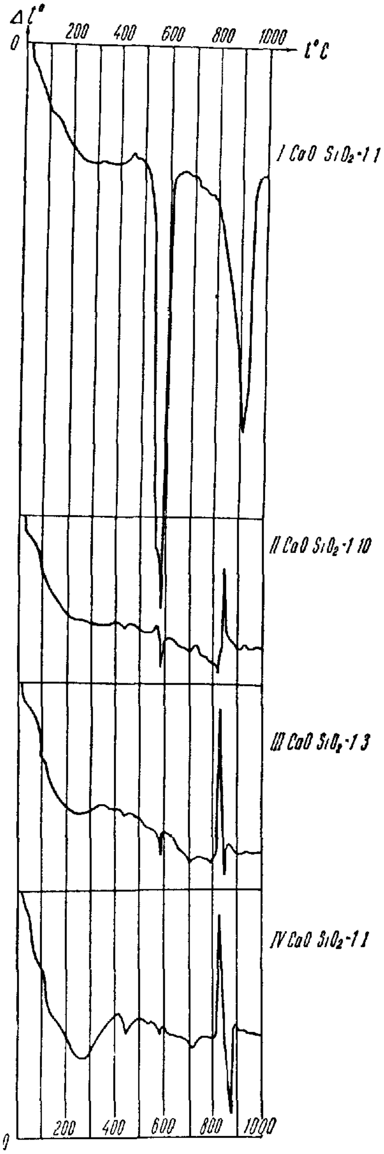

FIGURE 19. *DTA curves of lime-sand mortars autoclaved at 16 atm. for 8 hours. (Curve I, before autoclaving)*

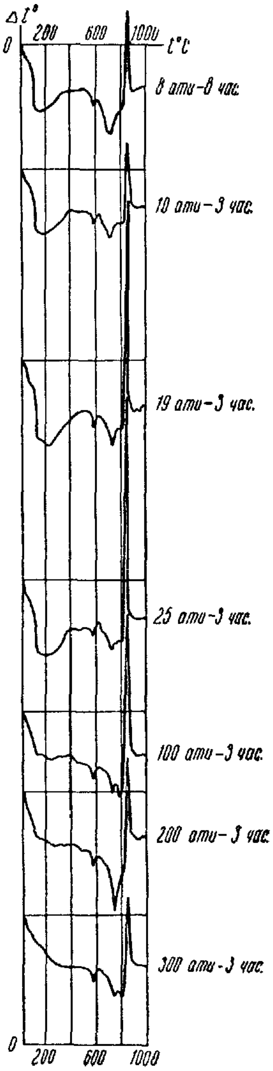

Figure 20. *DTA curves of lime-sand mortars autoclaved at 8 to 300 atm.*

(Figures at right give pressure in atm. and time in hr.)

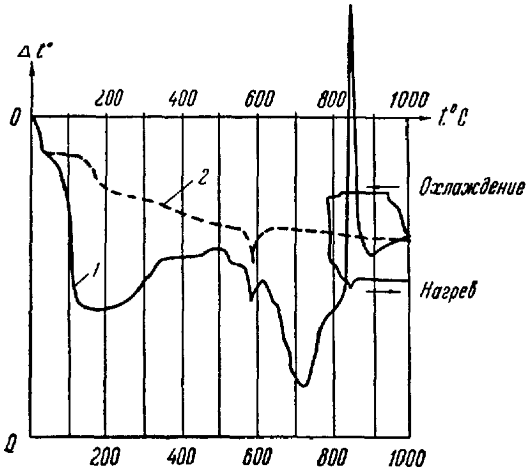

Figure 21. *No. 1—The first thermogram.*
No. 2—The second thermogram.

and combinations formed with increase of curing time or temperature are able to change the basicity and the quantity of structurally-bound water.

The results of chemical analysis given in table 13, show that with increase of steam pressure the quantity of bound CaO is nearly constant, and the content of soluble SiO_2 increases considerably, i.e., the quantity of less-basic hydrosilicates increases owing to interaction of previously formed new formations with silica.

Summarizing the investigations carried out we can draw the following conclusions:

1. In the investigated range of autoclaved lime-sand mortars (8 to 300 atm), complete binding of lime with the silica of the sand occurs. The absence of the endothermic effect of $Ca(OH)_2$ dehydration at 550 °C points to this conclusion.
2. New formations—hydrosilicates of different composition—interact with quartz, forming less-basic hydrosilicates when the pressure increases or the autoclave curing lengthens.
3. The strength of lime-sand brick depends on the structure and quantity of new formations and the interrelation of the gel and crystalline phases. Low-temperature curing (10 atm) leads to predominantly gel-like hydrosilicates, while curing at

Table 13. *Data of chemical analysis of autoclave-cured samples*

Composition of mortar, lime: sand	Fineness of mortar grinding, cm²/g	Pressure-time atm-hr	Free CaO	CaO found	Insoluble SiO_2	Soluble SiO_2	Soluble silica relative to dried mortar	Hygroscopic moisture	Bound H_2O+CO_2
				%	%	%	%	%	%
1:3	7500	8-8	None	16.46	50.97	15.90	20.80	1.68	6.62
		10-3	None	17.52	56.01	14.16	17.65	2.62	7.05
		19-3	None	17.52	51.48	19.06	23.60	1.48	6.75
		25-3	None	17.38	51.05	18.93	23.60	2.52	5.90
		100-0	None	17.86	49.74	23.61	28.15	1.12	3.79
		200-0	None	18.30	51.16	19.90	24.80	0.21	6.02
		300-0	None	18.24	50.29	22.86	27.40	none	4.13
1:3	5200	8-8	None	18.13	51.32	15.95	20.45	1.65	8.25
		12-3	None	17.93	50.34	17.16	21.86	1.83	7.08
		12-6	None	17.66	48.82	17.70	22.20	2.54	7.10
		12-24	None	17.04	49.16	20.45	25.35	2.58	6.04

50 to 200 atm leads predominantly to hydrosilicates with crystalline structure. The maximum strength requires rational proportions of both phases.

4. The data obtained confirm the assumption that by choosing the optimum regime of autoclaving it is possible to obtain products with high strength, i.e., there is a possibility of controlling the process of mineral formation.

5. On the basis of the investigations carried out it may be proved that use of high-pressure steam in the manufacture of silicate products allows one to shorten the autoclaving cycle considerably. Consequently, the autoclave turnover will increase, and the production of plants making building products and units will increase, together with simultaneous improvement of the quality of the product.

General Conclusions

1. Autoclave treatment, by means of high-pressure steam, of products based on various cementing materials is one of the most effective technological methods for considerably accelerating the hardening.

2. The optimum steam pressure in the autoclave depends on the mineralogical composition of the cementing materials. Cements with high contents of active components (C_3S, C_3A) autoclaved at the pressure of 16 atm require a sharp reduction of the curing regime, because at this pressure the process of hardening of such cementing materials achieves the stable state more rapidly.

Cementing materials with high contents of C_2S and C_4AF, and lime-sand mortar, need more intensive autoclaving in the range of 16 to 25 atm, with reduced regime of curing.

3. In all cases of production of building products at high pressure (15 to 25 atm), it is necessary to reduce the duration of the general cycle of autoclave curing at 8 atm from the 12 to 14 hr employed to 4 to 8 hr.

4. The analysis of products of autoclave hardening of cementing materials shows that for low-temperature curing (8 to 12 atm) the gel structure prevails in the end-product; for high-temperature curing (25 to 200 atm), hydrocompounds of crystalline structure prevail.

5. For obtaining materials with optimum qualities it is necessary to achieve the most rational proportion between the gel and crystalline phases in the end product.

6. By changing the regime of autoclaving it is possible to control the process of the formation of minerals, and thus to obtain products with the necessary structural properties.

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Paper III–S13. Concerning the Hydration Products of C_3S and β–C_2S*

H. G. Kurczyk and H. E. Schwiete

Synopsis

The calcium silicates $3CaO{\cdot}SiO_2$ and β-$2CaO{\cdot}SiO_2$ undergo set, when mixed with small quantities of water (w/c—0.1 to 0.5), in a manner similar to portland cement. This stiffening process is accompanied by the formation of a hydrous calcium silicate. This product of hydrolysis and hydration has a variable chemical composition, and was earlier designated in cement literature as "gel" or as "the gel phase." Electron microscope studies have shown conclusively that this calcium hydrosilicate is crystalline. It crystallizes in the form of needles. The crystallites have an average length of 5000 A. Dynamic differential calorimetry and quantitative X-ray analysis have permitted the determination of the composition or $CaO{:}SiO_2$ ratio of this phase as 1.8 to 1.9.

Electron diffraction diagrams show that the hydration product of $3CaO{\cdot}SiO_2$ and β-$2CaO{\cdot}SiO_2$ is morphologically and structurally similar to the mineral tobermorite, $Ca_5Si_6O_{18}H_2{\cdot}4H_2O$. It is therefore designated as the "tobermorite-like phase." Further fine structure studies by means of electron beams and X-rays have yielded the elementary cell of the tobermorite-like phase.

The lattice constants are: $a_0=11.2\pm0.3$ A
$b_0=7.32\pm0.07$ A
$c_0=27$–28 A
$\alpha=\beta=\gamma=90°$

The crystalline lattice is strongly distorted. The tobermorite-like phase has the same structural elements as tobermorite. It differs from the latter only in that between the layer packets of tobermorite additional Ca^{++}- and OH^--ions are deposited. The exact positions of these ions could not be determined. However, with the results of the investigation as a basis, a hypothetical structure formula could be set up for the tobermorite-like phase:

$$Ca^x[Ca_4Si_6O_{16}(OH)_2][Ca^x(OH)_2]_n$$

$n=5$–7. The calcium atoms with unknown lattice coordination are designated by x.

Résumé

Les silicates de calcium, $3CaO{\cdot}SiO_2$ et β-$2CaO{\cdot}SiO_2$, subissent le phénomène de prise quand on les mélange à de petites quantités d'eau (e/c–0.1 à 0.5), d'une façon comparable au ciment portland. Cette réaction de durcissement s'accompagne de la formation d'un silicate de calcium hydraté. Ce produit d'hydrolyse et d'hydratation a une composition chimique variable, et on le trouve désigné précédemment dans la littérature du ciment sous le nom de "gel" ou "phase de gel". Des études au microscope électronique ont révélé d'une manière concluante que cet hydro-silicate de calcium est cristallin. Il se cristallise sous forme d'aiguilles. Les cristaux sont de 5000 A de long en moyenne. La calorimétrie dynamique différentielle et l'analyse quantitative des rayons X ont permis de déterminer que la composition ou le rapport $CaO{:}SiO_2$ de cette phase est de 1.8 à 1.9.

Les diagrammes de diffraction électronique indiquent que le produit d'hydratation de $3CaO{\cdot}SiO_2$ et β-$2CaO{\cdot}SiO_2$ est par sa morphologie et sa structure semblable au tobermorite minéral $Ca_5Si_6O_{18}H_2{\cdot}4H_2O$. On le désigne par conséquent sous le nom de "phase semblable au tobermorite". Des études supplémentaires de fine structure au moyen de rayons électroniques et de rayons X ont donné la cellule élémentaire de la phase semblable au tobermorite.

Les constantes du réseau sont: $a_0=11.2\ \pm0.3$ A
$b_0=7.32\ \pm0.07$ A
$c_0=27$–28 A
$\alpha=\beta=\gamma=90°$

Le réseau cristallin est fortement déformé. La phase semblable au tobermorite a les mêmes éléments de structure que le tobermorite. La seule différence d'avec ce dernier réside dans le fait que des ions supplémentaires de Ca^{++} et OH^- sont déposés entre les paquets de couche de tobermorite. Les positions exactes de ces ions n'ont pas pu être déterminées. Cependant, sur la base des résultats de la recherche, on a pu établir une formule hypothétique de structure pour la phase semblable au tobermorite:

$$Ca^x[Ca_4Si_6O_{16}(OH)_2]\ [Ca^x(OH)_2]_n$$

$n=5$–7. Les atomes de calcium avec coordination de réseau inconnue sont désignés par x.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from Institut für Gesteinshüttenkunde, Rhein. Westf. Technische Hochschule Aachen, Germany.

Zusammenfassung

Die Calciumsilikate 3 $CaO \cdot SiO_2$ und β-$2CaO \cdot SiO_2$ erstarren nach dem Ansetzen mit kleinen Wassermengen (W/Z=0,1 bis 0,5) ähnlich wie der Portlandzement. Dieser Erstarrungsvorgang ist mit der Bildung eines wasserhaltigen Calciumsilikates verbunden. Dieses Hydrolysen- und Hydratationsprodukt hat eine wechselnde chemische Zusammensetzung und wurde früher in der Zement-Literatur als "Gel" oder als "Gelphase" bezeichnet. Elektronenmikroskopische Untersuchungen ergaben eindeutig, daß dieses Calciumhydrosilikat kristallin ist. Es kristallisiert nadelförmig. Die Kristallite haben eine mittlere Länge von 5000 Å. Mit Hilfe der dynamischen Differenzkalorimetrie und der quantitativen Röntgenanalyse konnte die Zusammensetzung bzw. das CaOS:iO_2-Verhältnis dieser Phase mit 1,8–1,9 ermittelt werden.

Elektronenbeugungsdiagramme zeigen, daß das Hydratationsprodukt von $3CaO \cdot SiO_2$ und β-2 $CaO \cdot SiO_2$ dem Mineral Tobermorit $Ca_5Si_6O_{18}H_2 \cdot 4H_2O$ morphologisch und strukturell sehr ähnlich ist. Es wird daher mit dem Namen "tobermoritähnliche Phase" bezeichnet. Weitere Feinstrukturuntersuchungen mit Elektronenstrahlen und Röntgenstrahlen ergaben die Elementarzelle der tobermoritähnlichen Phase:

Die Gitterkonstanten betragen:

$$a_0 = 11{,}2 \pm 0{,}30 \text{ Å}$$
$$b_0 = 7{,}32 \pm 0{,}07 \text{ Å}$$
$$c = 27 - 28 \text{ Å}$$
$$\alpha = \beta = \gamma = 90^\circ$$

Das Kristallgitter ist stark fehlgeordnet. Die tobermoritähnliche Phase enthält die gleichen Strukturelemente wie der Tobermorit. Sie unterscheidet sich vom letzteren dadurch, daß zwischen den Schichtpaketen des Tobermorits zusätzlich Ca^{++} und OH^--Ionen eingelagert sind. Die genaue Lage dieser Ionen konnte nicht ermittelt werden. Basierend auf den Untersuchungsergebnisse konnte eine hypothetische Strukturformel der tobermoritähnlichen Phase aufgestellt werden:

$$Ca^x[Ca_4Si_6O_{16}(OH)_2]\ [Ca^x(OH)_2]_n$$

$n = 5$–7. Die Calciumatome mit unbekannten Gitterkoordinaten sind mit x bezeichnet.

Introduction

The calcium silicates β-Ca_2SiO_4 and $Ca_3(SiO_4)O$ are the principal components of portland cement clinker.

The hydration products of these components play a decisive role in the hardening process of portland cement. A final explanation of the course of hydrolysis and hydration of calcium silicates would constitute an important contribution to the theory of hardening of hydraulic cementing materials.

It has been known for a long time that the calcium silicates C_3S and β-C_2S, like cement itself, take a set when mixed with a "small" quantity of water and yield a product which is relatively strong in compression. This setting process is associated with the formation of a hydrous calcium silicate. This product of hydrolysis and hydration has a varying chemical composition and was formerly designated in cement literature as "gel" or as the "gel phase".

H. F. W. Taylor [1][1] established that this gel phase is identical with a synthetically obtained calcium silicate hydrate, which he designated as CSH(I). It is characteristic of this phase that its composition can vary over a wide range (CaO: SiO_2=0.8–1.5) without loss of its fundamental structure. Furthermore, it is characteristic that no stoichiometric relation of lime to silica and water could be established for this compound.

C. F. Claringbull and M. H. Hey [2] found that Taylor's CSH(I) was structurally very similar to the natural mineral "tobermorite"—$5CaO \cdot 6SiO_2 \cdot 5H_2O$. X-ray diagrams of tobermorite and CSH(I) show good agreement in d-values and intensities. Because of this agreement, all phases having a tobermorite-like X-ray diagram have been denoted in German literature as "tobermorite-like" phases.

Experimental Analysis of the Hydration Products in the Systems: C_3S-H_2O and β-C_2S-H_2O

Favorable conditions for analytical investigation of the calcium silicate hydrates that are formed exist only if the reaction involved in their formation has been completed, i.e., if the hydration products are no longer interspersed with remnants of unreacted initial substances. This condition is satisfied in tests in which the initial substances are shaken with water or lime water. This test method, however, does not reproduce conditions

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[1] Figures in brackets indicate the literature references at the end of this paper.

existing in a mortar layer, since the decisive concentration conditions are quite different here. For this reason, we hydrated the calcium silicates C_3S and β-C_2S with small quantities of water (w/c—0.5), and believe that our test conditions successfully reproduced conditions of practice. This test method is naturally beset with some difficulties, as the pastes never reach the stage of completed reaction. X-ray determination of the nonhydrated initial substances permitted us to overcome this difficulty.

The initial substances, C_3S and β-C_2S, were synthesized through solid-state reactions. The β-C_2S lattice was successfully stabilized by an admixture of 0.5 percent of B_2O_3.

The alkali content of the synthetic calcium silicates was as follows:

	C_3S	β-C_2S
Na_2O+K_2O	0.019%	0.019%

The ground samples of C_3S and β-C_2S (4000 Blaine) were mixed with water (w/c=0.5) and hydrated in plastic tubes in a thermostat at 30 °C. The hydrated samples were investigated by means of dynamic differential calorimetry (DDC), roentgenographically, and with the electron microscope after 1, 2, and 3 months.

Test Methods

An important aid in determining the course of the reaction is the determination of free lime hydrate in the hydration products. In this determination we used B. Franke's [3] acetic acid ester-isobutyl alcohol method. We found, however, that the solvents used attacked the finely crystalline calcium silicate hydrates, especially after several hours of boiling. A suitable method of determining free $Ca(OH)_2$ was found in dynamic differential calorimetry.

Dynamic Differential Calorimetry (DDC)

In comparison with differential thermal analysis (DTA) DDC permits a quantitative determination of the thermal effects. Like DTA, the DDC method is based on the familiar differential method. The significant innovation in DDC lies in the fact that the temperature measurements are not taken at the center of the specimens (fig. 1b), but on metal accessories (platinum cups) (fig. 1a), from which the total heat requirement of the samples is established. The advantage of this method over DTA consists also in that the sample under study can be weighed following every peak.

A detailed report on "Fundamental Principles and Scope of Application of the Dynamic Differential Calorimeter" was published by H. E. Schwiete and G. Ziegler in *Reports of the German Ceramic Society* (*Ber. der DKG*), V. 35, 1958, pp. 193–204.

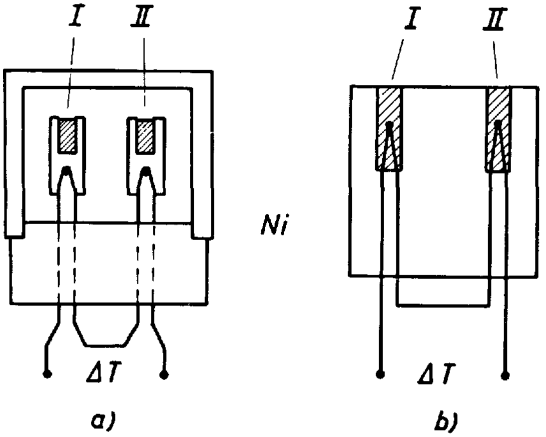

FIGURE 1. *Arrangement for (a) dynamic differential calorimetry and (b) DTA.*

Determination of the Quantity of Liberated $Ca(OH)_2$ by Means of DDC

The reaction:

$$Ca(OH)_2 \rightarrow CaO + H_2O$$

is associated with an endothermic effect which is proportional to a corresponding peak area on the DDC diagram (fig. 2). This area (F) was determined by means of a planimeter. With the aid of the final weight of the sample (E_2) and a calibration value (K), the quantity of liberated CaO can be determined from the following equations:

$$\frac{\text{moles CaO}}{\text{moles } \beta\text{-}C_2S} = \frac{0.757(F/K)}{E_2} \cdot 3.08 \cdot \frac{100}{H}$$

$$\frac{\text{moles CaO}}{\text{moles } C_3S} = \frac{0.757(F/K)}{E_2} \cdot 4.04 \cdot \frac{100}{H}$$

where:

E_2(g)=final weight of the sample after heating to 1000 °C (in a DDC determination)

F(cm^2)=area of the $Ca(OH)_2$ decomposition peak

K(cm^2/g)=calibration value for the determination of $Ca(OH)_2$

0.757; 3.08; 4.04=conversion factors

H=percent of hydrated C_3S or β-C_2S (resp.) obtained by X-ray diffraction (counter tube).

The values obtained for the quantities of CaO liberated during hydration served for the computation of the CaO: SiO_2 ratio in the calcium silicate hydrate phase formed in the systems C_3S-H_2O and $\beta-C_2S-H_2O$.

$CaO:SiO_2$-ratio of the calcium silicate hydrate phase in the C_3S-H_2O system; w/c=0 5; hydration temperature 30°C:

After 1 month	*After 2 months*	*After 3 months*
1.88	1.87	1.92

$CaO:SiO_2$-ratio of the calcium silicate hydrate phase in the $\beta-C_2S-H_2O$ system; w/c=0.5; hydration temperature 30 °C:

After 1 month	*After 2 months*	*After 3 months*
1.86	1.80	1.85

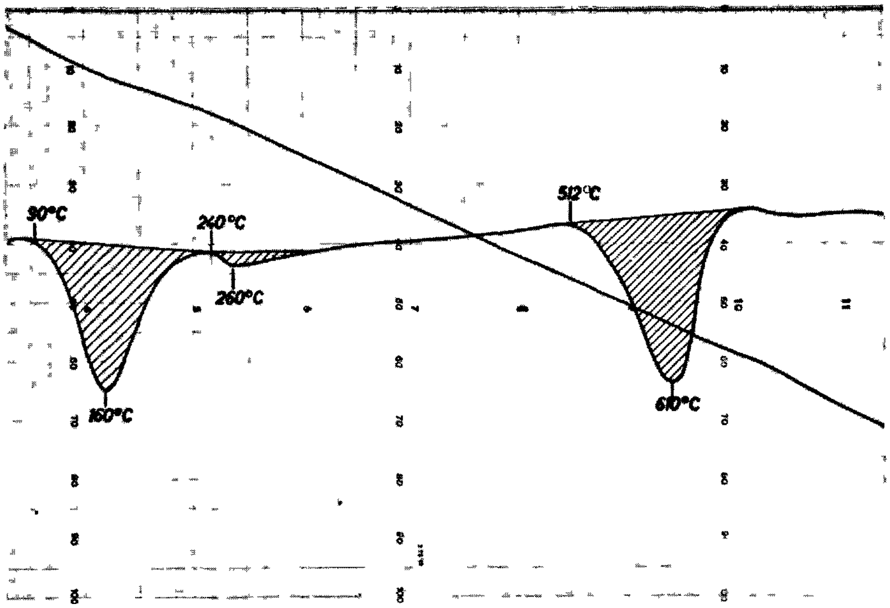

FIGURE 2. *DDC-plot of hydrated* C_3S *(30 °C; w/c=0.5; duration of hydration—1 month).*
512 °C—dehydration of $Ca(OH)_2$

Electron Microscope Studies

First we followed the hydration process of tricalcium silicate in its initial stage. Figure 3 shows two electron micrographs of single C_3S particles hydrated on the object holder with a drop of water. After every examination the samples were stored in a moist atmosphere. After

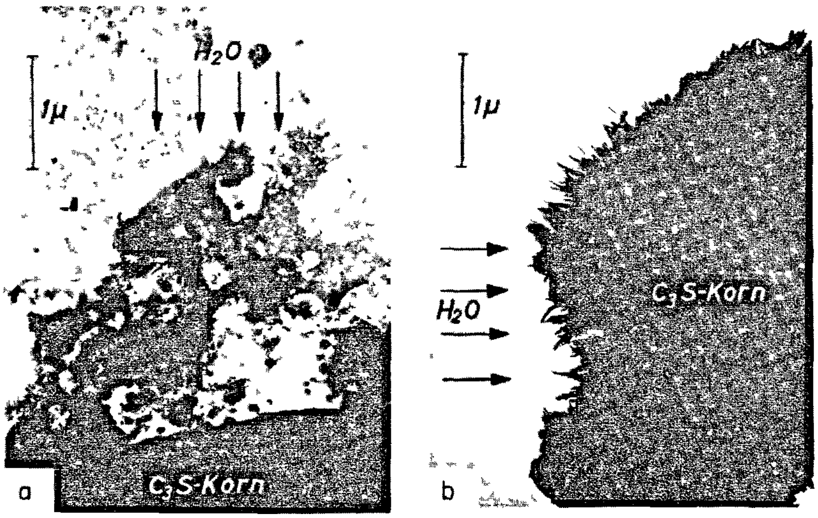

FIGURE 3. *Electron micrograph of hydrated* C_3S.
(a) hydrated 1 hour, (b) hydrated 5 days

5 days the crystallization nuclei of the calcium silicate hydrate phase can already be detected. This study was followed by studies of C_3S and β-C_2S pastes. The micrographs (figs. 4 and 5) reveal needle-shaped hydration products. Electron diffraction is needed to identify these crystallites. Figure 6 shows a small area diffraction micrograph taken from the first series of the investigation. Table 1 presents the computed d_{hkl}-values of the entire investigated series.

The d_{hkl}-values obtained above are not sufficient to compute the lattice constants of the hydration products. For this reason we tried to obtain the hydrosilicate phase in a pure state so as to permit a larger area to be diffracted. We hoped that such multiple crystal diffraction would yield a diagram with more rings. We produced the hydrosilicate phase in anhydrous insobutyl alcohol in which C_3S with particle size less than 1 μ was reacted with water (w/c=1). The hydrosilicate phase thus obtained appears in figures 7 and 8.

The electron micrographs (figs. 9 and 10) were irradiated at a low electron beam intensity. The dotted rings are produced by the β-C_2S hydration

TABLE 1

No.	I	d_{hkl}	Selected area
		A	
1	s	3 1–2 8	CSH—needle-shaped from C_3S pastes.
	w	1 79–2 8	
2	s	3 0–2 8	Do.
	w	1 80	
3	s	3.0–2 8	Do.
	w	1.80	
4	s	3 1–2 8	CSH—needle-shaped from β-C_2S pastes.
	w	----------	
5	s	3.0–2 8	Do.
	w	1.82	

FIGURE 4. *Electron micrograph of hydrated* C_3S, *w/c=0.5; duration of hydration, 1 month; hydration temperature, 30 °C; average length of calcium silicate hydrate crystals, 5,000A.*

product (w/c=0.5), the sharp bright rings by the gold calibration preparation.

A comparison of the *d*-values of C_3S and β-C_2S hydration products shows that C_3S and β-C_2S at low w/c ratio yield identical hydration products. A comparison of these values with *d*-values of Taylor's CSH(I) phase also shows good agreement. Deviations occur only in intensities, a fact evidently attributable to the difference in the effects of electron beams and X-ray beams on the crystalline lattice.

We mentioned in the introduction that Taylor's CSH(I) phase is structurally similar to the naturally occurring mineral tobermorite. As our hydration products conformed to the CSH(I) phase (differences were recorded only in the basa

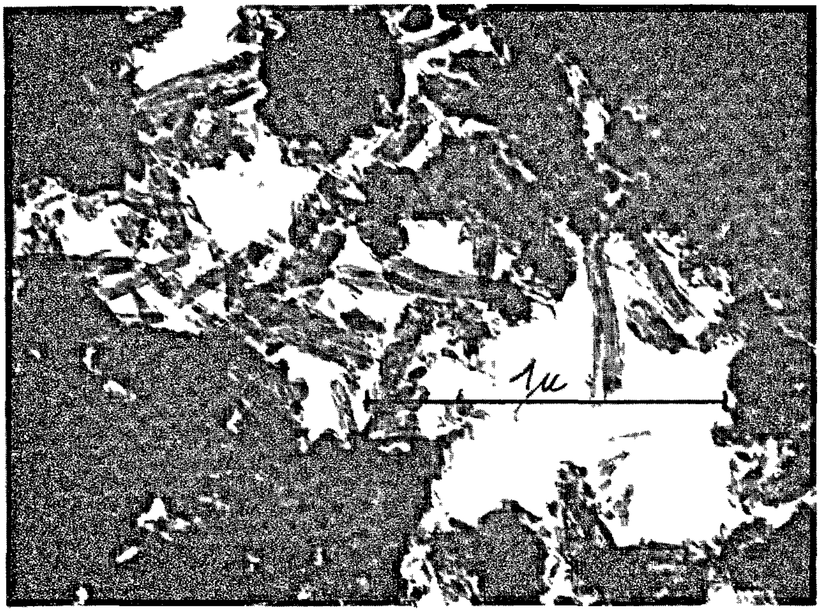

FIGURE 5. *Electron micrograph of hydrated* β-C_2S; *w/c=0.5; duration of hydration, 1 month; hydration temperature, 30 °C.*

Prepared in isobutyl alcohol with ultrasonic pulse (10 min). Average length of the calcium silicate hydrate crystals: 5,000A.

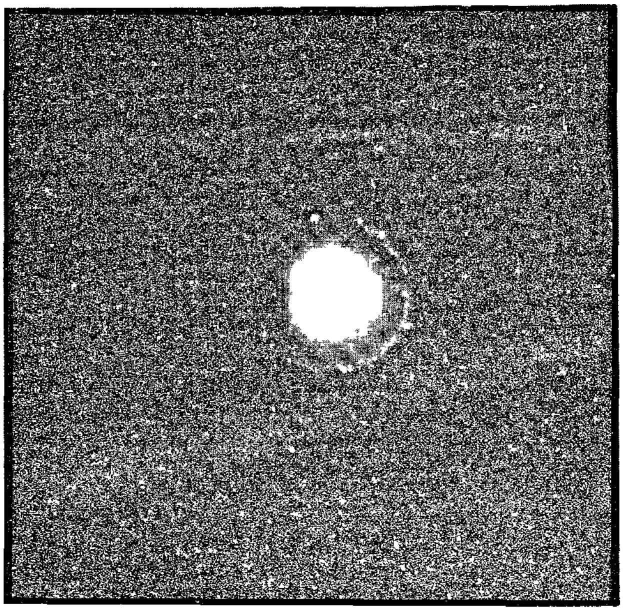

FIGURE 6. *Diffraction diagram of the* C_3S *hydration product (crystal bundles).*

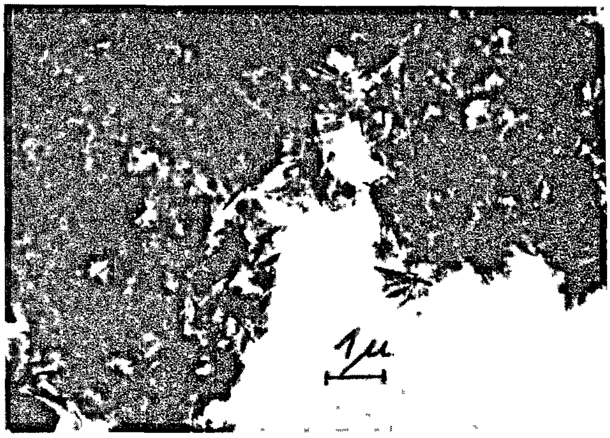

FIGURE 7. *Electron micrograph of CSH, the hydration product of* C_3S; *w/c=1.0; hydration temperature, 30 °C.*

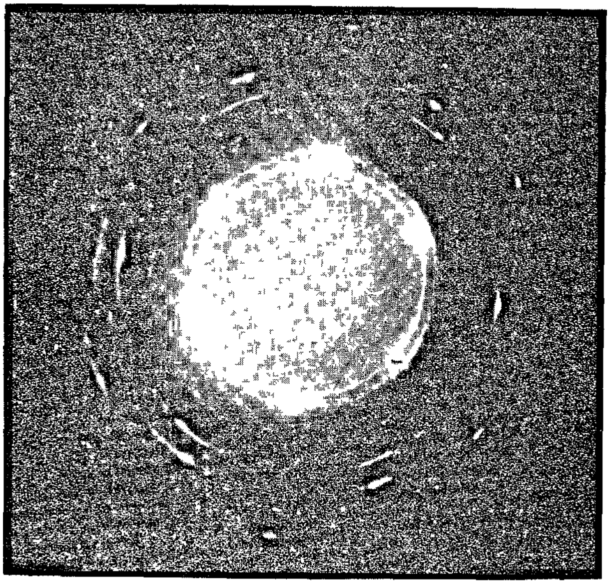

Figure 8. *Diffraction diagram for figure 7.*

Calibration value: $\lambda \cdot L = 52.2$ Amm.

d_{hkl}-values computed from diffraction diagram

Ring radius, r	I	d_{hkl}
mm		*A*
17.1	vs	3.06
18.7	vs	2.80
24.1	w	2.17
28.6	s	1.83
30.3	w	1.73
32.3	s	1.62
35.0	s	1.495
38.1	w	1.371
41.2	w	1.270
44.7	w	1.169

diffraction) they must also bear a structural likeness to tobermorite. Surprisingly, this similarity does not apply when the chemical composition of tobermorite is compared to that of our hydration products. Natural tobermorite, $Ca_5Si_6O_{18}H_2 \cdot 4H_2O$, has a $CaO:SiO_2$ ratio of 0.83, while our DDC studies yielded for C_3S and β-C_2S hydration products a $CaO:SiO_2$ ratio from 1.8 to 1.9. This remarkable feature of the tobermorite-like phase must be related to the character of the tobermorite lattice. Some data on the structure of tobermorite are already available in the literature [4]. Its final structure has not yet been defined.

Figure 9. *Electron micrograph of hydrated β-C_2S.*
Duration of hydration: 3 months; Hydration temperature: 30 °C.

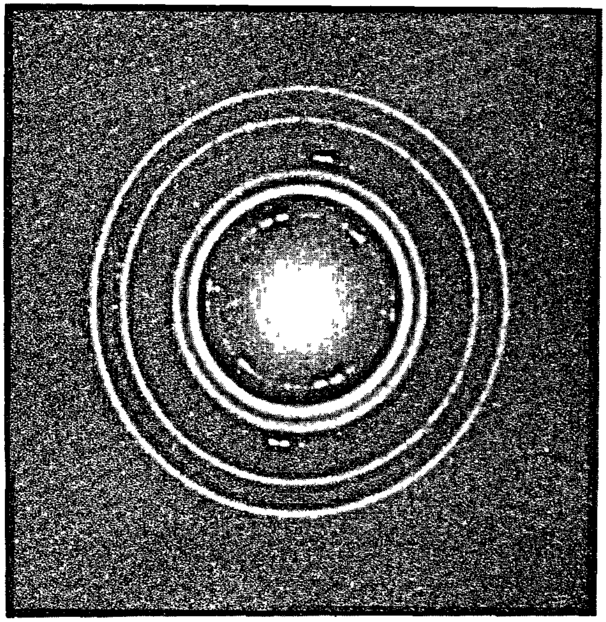

Figure 10. *Small-area diffraction diagram for zone A (fig. 9)*

Calibration value: $\lambda \cdot L = 52.7$ Amm.

d_{hkl}-values computed from diffraction diagram

Ring radius, r	I	d_{hkl}
mm		*A*
17.30	s	3.05
19.00	s	2.78
28.75	s	1.83
32.40	w	1.77
38.50	w	1.37

Electron Microscope Studies of Single Tobermorite Crystals

Single tobermorite crystals (figs. 11 and 12) were isolated by means of selective screening and their diffraction patterns examined. Figures 13, 14, 15, and 16 show electron diffraction pictures of such single crystals. We present two diagrams side by side, figure 17, in which the left diffraction diagram represents the b^*-c^* zone of the reciprocal lattice, while the right diagram is that of the a^*-b^* zone. The position of the point interferences shows that the crystals lie at (100) and (001). No (010) points could be established.

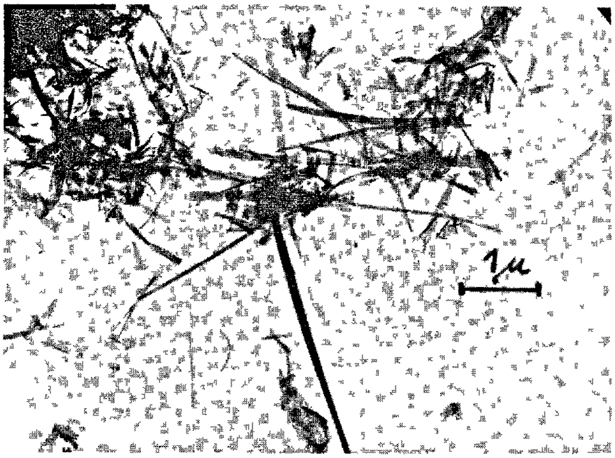

FIGURE 11. *Electron micrograph of synthetic tobermorite*—$5CaO \cdot 6SiO_2 \cdot 5H_2O$.

FIGURE 12. *Electron micrograph of synthetic tobermorite*—$5CaO \cdot 6SiO_2 \cdot 5H_2O$.

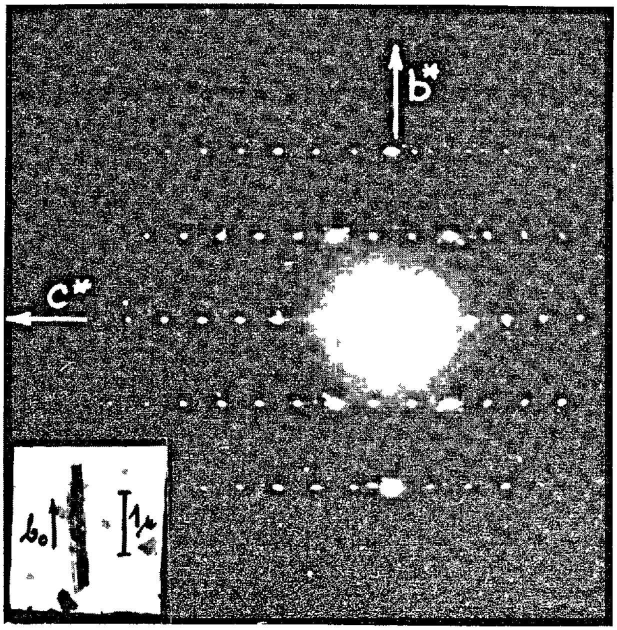

FIGURE 13. *Tobermorite single-crystal diffraction diagram; (100) normal to electron beam; irradiated in the a_0 direction.*

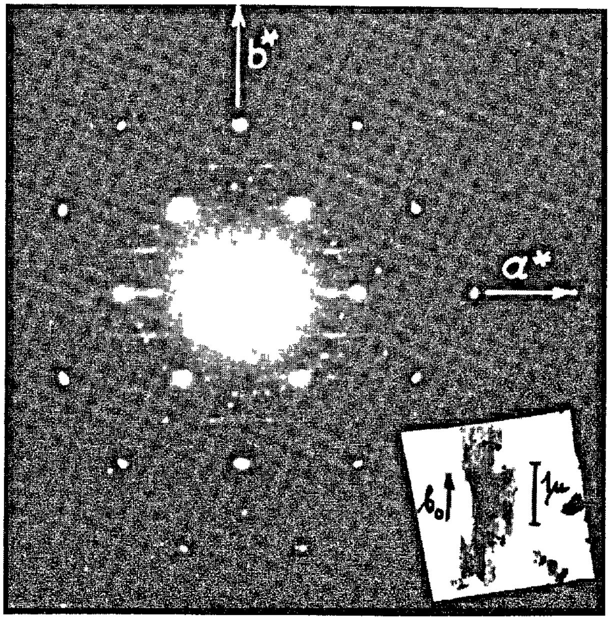

FIGURE 14. *Tobermorite single-crystal diffraction diagram; (001) normal to electron beam; irradiated in the c_0 direction.*

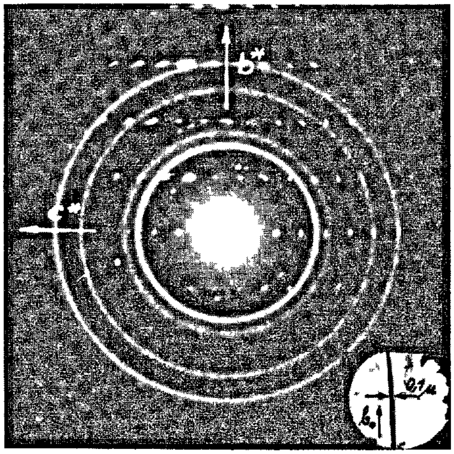

FIGURE 15. *Tobermorite single-crystal diffraction diagram; (100) normal to electron beam; irradiated in the a_0 direction.*
Ring pattern gold calibration substance

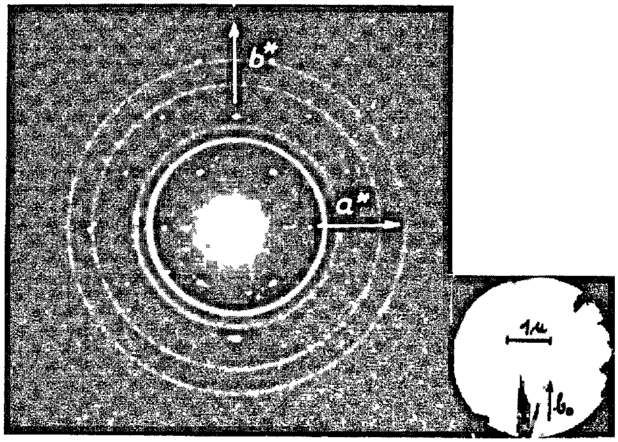

FIGURE 16. *Tobermorite single-crystal diffraction diagram; (001) normal to electron beam; irradiated in the c_0 direction.*
Ring pattern gold calibration substance

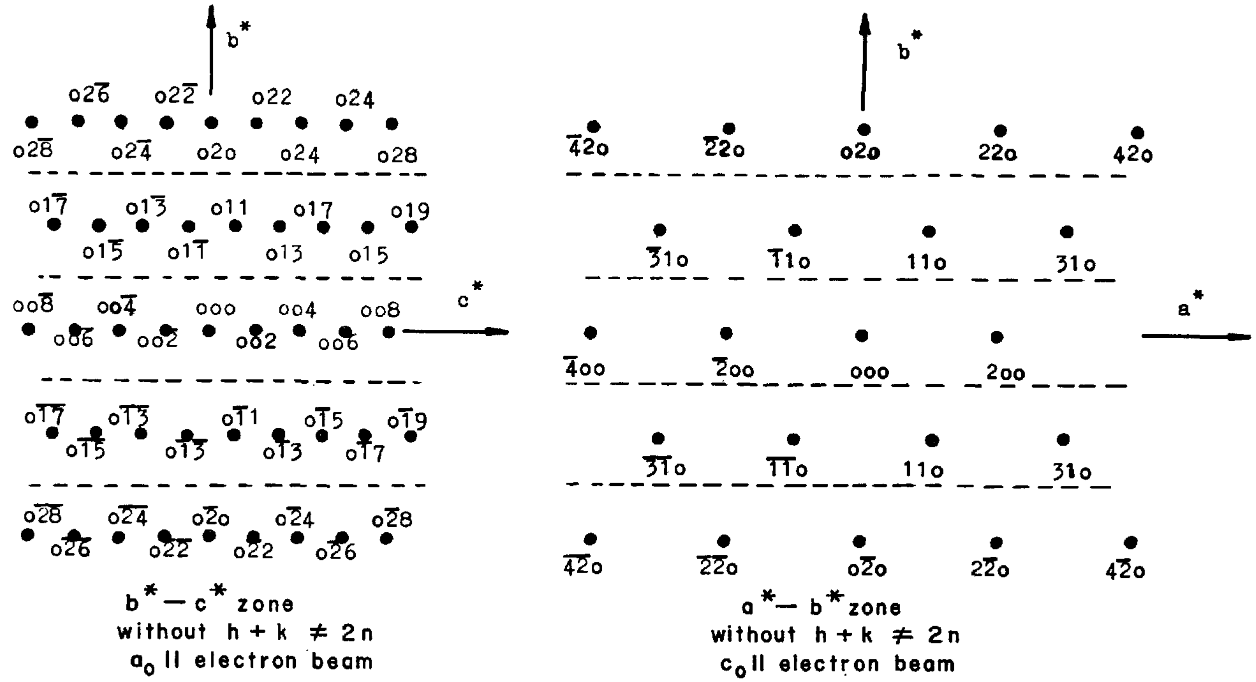

FIGURE 17. *Indexing of electron diffraction diagrams of tobermorite single crystals.*

Results

The following lattice constants were determined on the basis of electron diffraction diagrams:

Tobermorite	*Tobermorite-like phase*
$a_0=10.9\pm0.30$ A	$a_0=11.2\pm0.30$ A
$b_0=7.32\pm0.07$ A	$b_0=7.32\pm0.07$ A
$c_0=17.15\pm0.09$ A	$\gamma=90°$.
$\alpha=\beta=\gamma=90°$	

From X-ray diffraction, we have:

Tobermorite	*Tobermorite-like phase*
$a_0=10.9\pm0.30$ A	$a_0=11.2\pm0.30$ A
$b_0=7.32\pm0.07$ A	$b_0=7.32\pm0.07$ A
c_0(EI.)$=17.15\pm0.09$ A	----------------
c_0(X-ray)$=22.4\pm0.05$ A	c_0(X-ray)$=27.0$–28.0 ± 0.05 A

We can see that there is a difference of 5.2 A between c_0 values of tobermorite obtained with the electron microscope and with X-ray diffraction. This difference is related to the interlayer water in tobermorite. Tobermorite contains 4 moles of H_2O per formula unit. This water is lodged between the stable elements of the structure as in montmorillonite. It is driven off by the strong electron bombardment and the individual structural packets become superimposed. The electron beams thus produce a one-dimensional contraction of the elementary cell in the direction of the *c*-axis from 22.4 to 17.15 A. The superimposed stable structural elements of tobermorite are probably not oriented ideally, as parallel to c^* there appear streak-shaped reflections which point to a disturbance in the lattice with respect to the *c*-axis.

Structure of the Tobermorite-Like Phase

Electron-microscope studies have shown that the hydration products of tricalcium silicate and β-dicalcium silicate are morphologically and structurally very similar to the mineral tobermorite, $Ca_5Si_6O_{18}H_2 \cdot 4H_2O$. The lattice constants a_0 and b_0 of tobermorite and of the tobermorite-like phase are identical (figs. 18 and 19). This justifies the assumption that these two phases consist of identical structural elements. According to Megaw and Kelsey [4] tobermorite is a layered mineral, a view confirmed by our diffraction patterns. The tobermorite packets consist of two layers of a combination of 4CaO with SiO_4 three-link chains ("dreierketten") on (001) surfaces which run parallel to *b*. These layered packets are so packed one on the other that the SiO_4 chains are superimposed. The tubular voids between the SiO_4 chains accommodate the remaining Ca and O atoms, whose exact positions are not fixed. The water lodged in the packet (1 H_2O per formula unit) is present in all probability in the form of OH groups connected with the Si ions. Interlayer water is present between the packets. The packet contains four formula units, $Ca_5[Si_6O_{16}(OH)_2]$.

In the tobermorite-like phase we have a $CaO:SiO_2$ ratio of 1.8 to 1.9. It must therefore be assumed that the excess CaO is built in between the packets. This arrangement is indicated by the magnitude of the c_0 spacing of the tobermorite-like phase, $c_0=27$–28 A. In between the individual packets we thus have a space of 10 to 11 A.

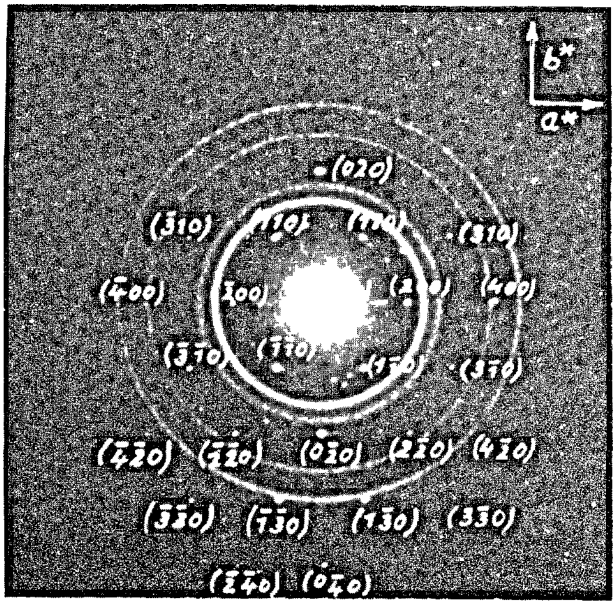

Figure 18. *Tobermorite single-crystal diffraction diagram* a^*-b^* *zone;* $a_0=10\ 9\pm0\ 3$ *A;* $b_0=7\ 32\pm0\ 07$ *A.*

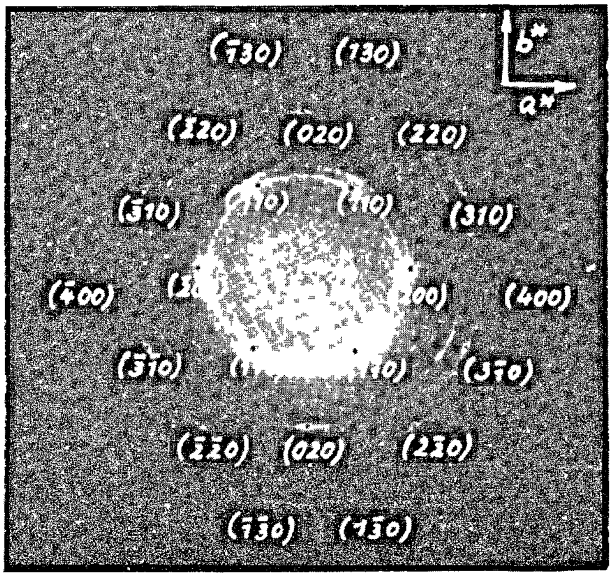

Figure 19. *Multiple-crystal diffraction diagram of the tobermorite-like phase*

1 8–1 9CaO SiO_2 $n H_2O$ $a_0=11\ 2\pm0\ 3$ A, $b_0=7\ 32\pm0\ 07$ A.

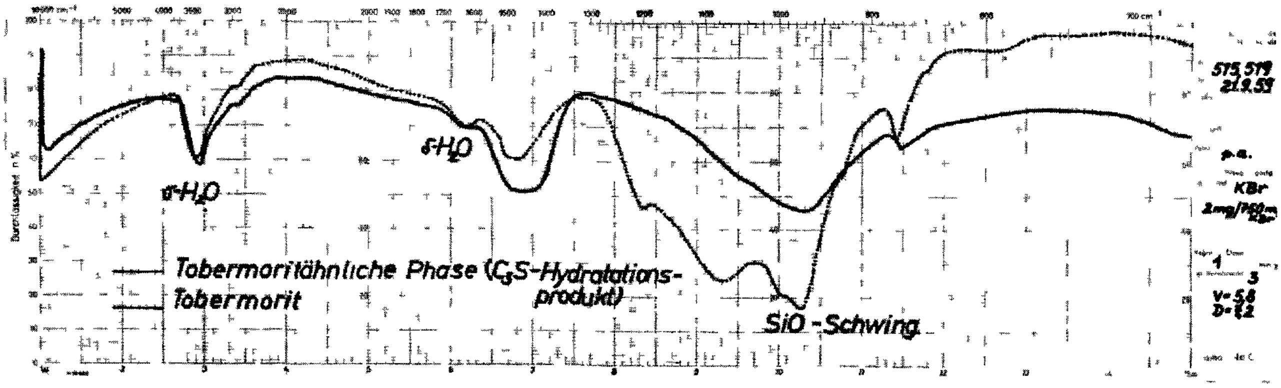

Figure 20. *Infrared absorption spectra.*

Solid line, tobermorite-like phase (C_3S hydration product), dotted line, tobermorite

One can imagine that this space is filled with hydrated or solvated Ca ions. However, the Ca-OH groups must be present without orientation as no additional *hkl* diffraction lines could be observed for the tobermorite-like phase. Such phenomena are also encountered with certain expansive clays.

On the basis of the above we have evolved a hypothetical structural formula for the tobermorite-like phase. The formula includes the composition of the stable packets, according to Megaw and Kelsey, and the $Ca(OH)_2$ groups packed between the layers. The Ca atoms with unknown lattice constants are denoted by *x:*

$$Ca^x[Ca_4Si_6O_{16}(OH)_2]\ [Ca^x(OH)_2]_n$$

$n=5–7$.

Infrared (IR) absorption studies confirm the similarity between the hydration products and tobermorite (fig. 20).

In conclusion we must state that our views on the structure of the tobermorite-like phase are based on an idealized picture. A final answer to the question of how the additional Ca and OH ions are inserted or entrapped can be given only when it is possible to take pictures of single crystals of tobermorite-like crystals, which is very difficult in view of the small dimensions of the crystals.

However, it can be accepted with certainty that the hydration products of C_3S and β-C_2S are crystalline. The continuous change of the concentration relations in a mortar layer permits the formation of only highly disoriented crystallites which is clearly revealed by the electron-diffraction patterns.

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SESSION IV. CHEMISTRY OF HYDRATION OF PORTLAND CEMENT

Paper IV-1. Early Hydration Reactions of Portland Cement*

Kenneth T. Greene

Synopsis

The literature dealing with the early hydration reactions of portland cement at ordinary temperature, published since the Third International Symposium in London in 1952, is reviewed. Considerable research has been reported on various aspects of the hydration of the individual compounds of cement. Our knowledge of the hydration of portland cement itself is less extensive.

The general course of the early chemical reactions of hydration is traced, and the nature and composition of the products of hydration of the alumina-bearing phases are discussed. The reactions of the aluminates and ferrites predominate at very early ages, those of the silicates from about the time of initial set onward.

The solution-precipitation and solid-phase reaction theories, two possible mechanisms of cement hydration, are considered in the light of published data. It is concluded that both types of process may be involved, with solution and precipitation probably prevailing immediately after water contact, while the solid-phase type of reaction may typify the later hydration. The later hydration rate is probably controlled, in most cements, by diffusion of water through the layers of gelatinous hydration products.

The chemical and physical nature of the cement gel is discussed in relation to the development of structure in the paste. The evidence indicates that setting and hardening are intimately connected with the development of a very high surface area in the gel, and that both physical and chemical forces are involved.

Résumé

L'exposé passe en revue la littérature qui traite des réactions du début d'hydratation du ciment portland à température ordinaire, littérature publiée depuis le Troisième Symposium International de Londres en 1952. Les résultats d'études considérables sur les différents aspects de l'hydratation des composés individuels du ciment ont été rapportés. Notre connaissance de l'hydratation du ciment portland proprement dit est moins extensive.

Le cours général des premières réactions chimiques de l'hydratation est retracé et la nature et la composition des produits d'hydratation des phases contenant de l'alumine sont discutées. Les réactions des aluminates et des ferrites prédominent au tout début, celles des silicates environ dès le moment de la prise initiale, et de là continuent.

Les théories sur la réaction de la solution-précipitation et la réaction de la phase solide, deux mécanismes possibles de l'hydratation du ciment, sont examinées à la lumière des résultats publiés. On en conclut que les deux types de réaction peuvent se présenter l'un et l'autre, la solution et précipitation l'emportant probablement sitôt après le contact avec l'eau, tandis que le type de réaction de la phase solide est caractéristique de l'hydratation ultérieure. La vitesse d'hydration ultérieure est probablement contrôlée, dans la plupart des ciments, par la diffusion de l'eau à travers les couches de produits d'hydratation gélatineaux.

La nature chimique et physique du gel de ciment est discutée en fonction du développement de la structure dans la pâte. Il est démontré que la prise et le durcissement sont intimement liés au développement dans le gel d'une large surface spécifique et que des forces physiques aussi bien que chimiques interviennent.

Zusammenfassung

Die Literatur des ersten Hydratationsreaktionen des Portlandzements bei Zimmertemperatur, die nach dem Dritten Internationalen Symposium des Jahres 1952 in London veröffentlicht wurde, wird besprochen. Viele Arbeiten über die verschiedenen Hydratationsstufen einzelner Verbindungen des Zementes sind erschienen, aber unsere Kenntnisse der Hydratation des Portlandzements selber sind nicht so vollständig.

Die allgemeine Tendenz der ersten chemischen Hydratationsreaktionen wird besprochen, und die Natur und Zusammensetzung der Hydratationsprodukte der tonerdehaltigen Phasen werden beschrieben. Die Reaktionen der Aluminate und der Ferrite sind bei frischen Zementpasten die maßgebenden; mit der ersten Verfestigung ungefähr machen sich die Silikatreaktionen stärker bemerkbar.

Zwei Mechanismen der Zementhydratation sind möglich, nämlich die Niederschlagbildung aus Lösungen, und Reaktionen in fester Phase; beide Möglichkeiten werden an Hand der Veröffentlichungen besprochen. Es wird der Schluß gezogen, daß beide Arten Prozesse vorkommen können, wahrscheinlich in der Weise, daß Auflösung und Niederschlagbildung sofort nach Berührung mit Wasser einsetzt, und daß Reaktionen in fester Phase sich während der späteren Hydratation ereignen. Diese spätere Hydratation wird vermutlich bei den meisten Zementen durch die Wasserdiffusion durch die gelatinierten Hydratationsproduktslagen hindurch kontrolliert.

Die chemische and physikalische Natur des Zementgels wird in ihrer Beziehung zur Ausbildung der Pastenstruktur besprochen. Es sieht so aus, als ob die Erstarrung und das Erhärten mit der Ausbildung einer sehr großen Oberfläche des Gels in engster Beziehung stehen, und daß sowohl physikalische als auch chemische Kräfte ins Spiel kommen.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Research and Exploration Departments, Ideal Cement Company, Fort Collins, Colorado.

Introduction

The chemical reactions involved in the hydration of portland cement have been studied with increasing intensity in recent years. It can be truthfully said that much progress has been made in the understanding of these reactions, although it will be admitted by all that there is still much more to learn.

At the Third International Symposium on the Chemistry of Cement held in London in 1952, the current state of knowledge of the chemical reactions of portland cement at ordinary temperature was ably reviewed by Steinour [1].[1] The present paper is an attempt to survey the more significant advances made in this same field since the Third Symposium, giving particular regard to the early reactions, by which the author means those which take place from the time the cement and water first come into contact, through the stage generally described as final set, up to the age of perhaps 2 or 3 days.

As pointed out by Steinour, early research dealt largely with phase equilibria in the simpler systems, $CaO-SiO_2-H_2O$, $CaO-Al_2O_3-H_2O$ and $CaO-Al_2O_3-CaSO_4-H_2O$, and with the hydration of the so-called pure cement compounds. For the most part only limited studies were made on mixtures of cement compounds or on commercial portland cement because of the difficulties of interpretation. Even when hydration studies were made on cement, a large excess of water was frequently used. The results of such experiments, although yielding valuable data, could not be related directly to pastes of ordinary consistency.

It must still be said that the direct study of the chemistry of hydrating cement paste, having water-cement ratios in the practical range, is very difficult, although new and improved methods are gradually increasing our knowledge. The more promising of these include new developments in the study of the liquid phase of hydrating paste and refined techniques for the analysis of the solid hydration products at early ages using X-ray diffraction, differential thermal analysis (DTA), thermogravimetric analysis, and infrared absorption and nuclear magnetic resonance methods.

The present discussion will be limited as much as possible to the hydration of portland cement, since the hydration of the calcium silicates and aluminates is being covered by other contributors to this symposium. However, it will be necessary to refer frequently to the literature on the pure calcium silicates and aluminates because of their intimate relationship with the hydration of cement. It will be necessary to deal in considerable detail with the normal hydration reactions involving gypsum. It is not the purpose of this paper, however, to discuss the problem of abnormal reactions, such as false set, except as it has a bearing upon the hydration of a normally retarded cement.

A survey of the published work on cement hydration since the Third Symposium reveals an extensive literature with regard to the hydration products formed when C_3S, C_2S, C_3A, C_4AF, etc. react with water. On the contrary, there appears to be relatively little new information available on the very early reactions in actual portland cement paste, particularly the reactions taking place within the first few minutes of water contact. While it is realized that research on the pure compounds is essential, and to a considerable extent must precede that upon cement paste, nevertheless the present writer believes that the time has come for more concerted attempts to correlate the results of the two lines of investigation.

There are undoubtedly numerous unpublished data bearing upon the problem of the very early hydration reactions of cement which, if made available, could contribute significantly to an understanding of this complex question. Some information of this nature has been obtained in the laboratories of the Ideal Cement Company and will be reported later in the present paper.

General Course of Early Chemical Reactions

Composition of Liquid Phase

Ordinary portland cement containing gypsum for control of setting time, usually about 4 or 5 percent, begins to react extremely rapidly when mixed with water. In fact the reaction is so rapid as to be properly termed immediate and is, consequently, very difficult to measure. It is known that lime, sulfate, and alkalies enter the solution swiftly in a paste having a water-cement ratio in the range of 0.4 or 0.5. The $Ca(OH)_2$ concentration soon reaches saturation, and lime continues to dissolve to give a supersaturated solution.

If the calcium sulfate is essentially in the form of the dihydrate, the solution will generally rapidly become saturated, but not supersaturated to any great degree, with $CaSO_4$. If calcium sulfate hemihydrate or other dehydrated forms of gypsum are present in the cement, it is well known that the solution may become supersaturated with $CaSO_4$ also. However, since we are here assuming that the gypsum is in its fully hydrated form, this situation will not be considered.

Various investigators have studied the chemical composition of extracts from cement pastes taken at various times after mixing. One of the most extensive of such studies was that of Kalousek, Jumper, and Tregoning [2]. Their results showed appreciable amounts of alkalies, lime, sulfate, and

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[1] Figures in brackets indicate the literature references at the end of this paper.

hydroxide at periods of time as short as 7 min, while the concentrations of alumina, iron, and silica were very low. Recent work by Strelkov [3] also indicated low values for silica in solution and also for alumina at periods of time as short as 2 min after mixing. Steinherz and Welcman [4] obtained similar results with solutions separated 1 min after mixing cements with 60 percent of water. Hansen [5, 6, 7] obtained information which led him to believe that the concentrations of silica and alumina are very low, even as early as 1 min after mixing. However, data for times less than 1 min are generally lacking, and Steinour [8] in his discussion of Hansen's most recent paper [7] points out that it is not proven that the concentrations of alumina and silica do not reach high values immediately upon mixing, followed by a decline to the values which have been determined at 1 min and longer. In fact, it seems very likely that this is the case. At any rate, it can be said that after a relatively short period of time the solution becomes essentially one of Na^+, K^+, Ca^{++}, SO_4^{--}, and OH^- ions.

If equilibrium prevailed during the first few moments after water contact, it would be a relatively simple matter to infer the concentration of lime and sulfate, if the concentrations of the alkalies were known, because the solubilities of calcium hydroxide and calcium sulfate are determined by the concentration of alkalies in this system. These relationships were shown by the work of Hansen and Pressler [9]. However, the solution is in a state of very rapid change for some time after mixing, and thus equilibrium criteria cannot be applied during this period.

Identity of Calcium Sulfoaluminate

Although there is considerable uncertainty concerning the exact state of affairs in these first moments, a few things are known with a reasonable amount of assurance. First, it is obvious that the lime-bearing constituents of the clinker begin to hydrolyze immediately with release of calcium hydroxide into the solution. The principal source of this calcium hydroxide is probably the C_3S, although the C_3A and calcium aluminoferrite phase may also contribute a part.

At the same time Al_2O_3 from the alumina-bearing phases is reacting rapidly with the sulfate made available by the solution of the gypsum, and the ample amount of calcium hydroxide now present in the liquid phase. The product of this reaction is fundamentally a calcium aluminate sulfate, commonly called calcium sulfoaluminate, the identity of which has been the subject of some controversy.

The question has been whether the calcium sulfoaluminate produced initially is the high-sulfate form represented by the formula $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31H_2O$, known also by the mineral name ettringite, or the so-called monosulfate or low-sulfate form, $3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$. The work of Jones [10], of D'Ans and Eick [11], and Eitel [12] showed that the compound stable under equilibrium conditions is the high-sulfate form. However, due to the fact that we do not have equilibrium conditions or anything approaching them in the first few moments, some investigators have been of the opinion that the low-sulfate form might be produced first as a metastable phase, later converting to the high-sulfate form.

Steinour [13] suggested that the product formed might be different, depending on whether or not the solution is already saturated with $Ca(OH)_2$ and $CaSO_4$ when the aluminates begin to react. He believed that saturation with $Ca(OH)_2$ and $CaSO_4$ should favor the low-sulfate form.

Previous to the Third Symposium, Kalousek, Davis, and Schmertz [14] had applied the method of differential thermal analysis (DTA) to hydrating cement paste and interpreted their results to mean that the high-sulfate sulfoaluminate is the initial product formed. More recently Taylor [15], using X-ray diffraction, detected the high-sulfate form at the age of 1 day.

Manabe and Kawada [16], using solutions containing radioactive sulfur-35, reported that in fresh cements the formation of calcium sulfoaluminate occurs immediately after mixing with water. These authors do not specify which calcium sulfoaluminate is meant, but presumably it is the high-sulfate form.

Indications of Differential Thermal Analysis

It may be appropriate at this point to introduce data obtained by the writer in the laboratory of the Ideal Cement Company which pertain directly to this problem. The method of differential thermal analysis has been used in our laboratories for nearly 5 years in the study of cement hydration. The equipment which we use is available commercially and is illustrated in figure 1. Four samples can be analyzed simultaneously, with the curves being recorded automatically. Various heating rates are available, but the rate most commonly used in our studies has been 10 °C per minute. The temperature limit of this apparatus is about 1,100 °C.

With regard to the DTA method it should be emphasized that variables, such as heating rate, particle size and weight of the sample, and configuration of the furnace, affect the shape and features of the curves produced. This variability must be borne in mind when comparing results obtained in different laboratories or on equipment of different design. The results are generally only qualitative, or at best, semiquantitative, but are quite useful when properly interpreted.

It should be stated also that the method of drying is very critical in the differential thermal analysis of hydrated cements. Too severe drying must be avoided because some of the less stable hydration products will be destroyed or dehydrated to the extent that some of the thermal effects will be diminished. We have found that vacuum drying at room temperature is generally satisfactory. The evacuation is carried out

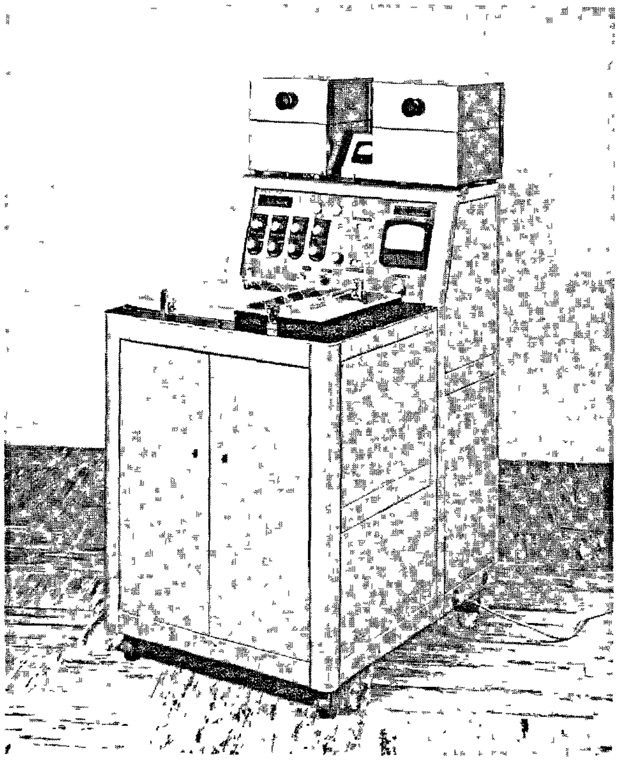

FIGURE 1. *Apparatus for differential thermal analysis.*

at a pressure of perhaps 1 or 2 mm of mercury and usually is not prolonged beyond the point at which the free water is removed (about 2 or 3 hr for young pastes). Special techniques to stop hydration are used when the period of hydration is very short.

In connection with the data about to be presented, mention should be made of other reports on cement hydration using the DTA method, recently published by Lommatzsch [17], Rey [18], and Mchedlov-Petrosyan, Bunakow, Goworow, Latischew, Lewtschuk, and Sstrelkowa [19]. Rey, in particular, points out some of the difficulties inherent in this method, and precautions which must be taken. He emphasizes the importance of the manner of drying as it affects the shape of the DTA curves.

Figure 2 illustrates the DTA curves obtained in our laboratory on a typical cement hydrated for various periods of time up to 7 days, along with a curve for the unhydrated cement. The curve for the latter shows a typical double endothermic reaction for gypsum between about 140 and 170 °C. Slightly below 500° there is a broad endotherm which is believed to be related to calcium hydroxide formed during exposure to the air. Between 700 and 800° is a long, broad endotherm caused by calcium carbonate, also produced through exposure.

After 5 min hydration, a new, rather sharp, endothermic peak is seen at about 130°. This peak is attributed to the high-sulfate calcium sulfoaluminate ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$). The gypsum double peak is still present, but it is reduced in size. At 1 hr the calcium sulfoaluminate has increased considerably in amount, and the gypsum has decreased somewhat further. At 4 hr there has been a continuation of the reaction producing sulfoaluminate and, in addition, a small new peak has appeared just above 500°, indicating the start of formation of crystalline calcium hydroxide.

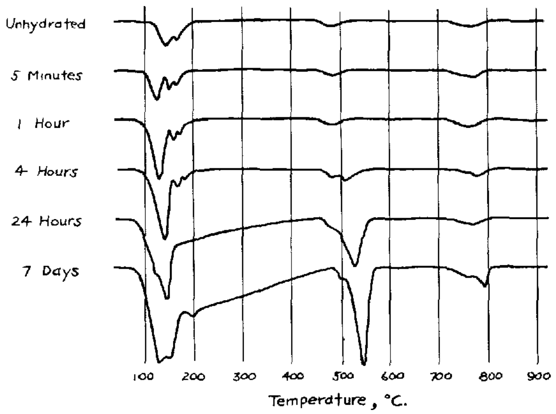

FIGURE 2. *DTA curves of a portland cement hydrated for various lengths of time.*

The reason for the double character of the peaks in the vicinity of 500° is not entirely clear. A possibility is that the small endotherm represents chemisorbed water held on the surface of free lime particles, while the second, larger peak is due to the more coarsely crystalline calcium hydroxide formed by crystallization from solution. In another set of experiments it was found that the presence and size of the small peak correlated fairly well with the free-lime content of the cements studied.

At 24 hr a marked increase in calcium hydroxide is recorded, but the chief interest now focuses on the low-temperature dehydrations. The double peak of gypsum is now seen to be absent, and a distinct shoulder is visible on the low-temperature flank of the sulfoaluminate peak. At 7 days this shoulder has grown so as to become a peak exceeding that of the sulfoaluminate. Experiments run on clinker without added gypsum, to be described later, indicate that this peak is due to calcium silicate hydrate. The peak is particularly sensitive to the manner of drying and can be almost eliminated from the thermograms by prolonged vacuum drying at a low pressure.

A new endotherm at about 200° is seen in the curve for the 7-day sample. This peak is attributed to the low-sulfate calcium sulfoaluminate ($3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$) or possibly to a solid solution of this compound with tetracalcium aluminate hydrate ($4CaO \cdot Al_2O_3 \cdot 13H_2O$). The question of the composition of this phase will be discussed in more detail further on. Other experiments not illustrated indicate that this phase ordinarily makes its first appearance at some time between 24 and 48 hr.

One additional feature should be mentioned in connection with the 7-day curve. The rather definite upward slope of the line between 200 and 500° suggests that some water is being lost gradually from the paste in this temperature range. This effect is noticeable but less pronounced at 24 hr. It undoubtedly correlates with the work of other investigators [20, 21, 22, 23], using thermogravimetric methods, which shows that water is lost over quite an extended temperature range from hydrated calcium silicates and hydrated cement paste. Of interest also are the growth of the calcium hydroxide peak between 24 hr and 7 days, and the increase in the size of the calcium carbonate endotherm between 700 and 800°.

Returning to the question of the identity of the calcium sulfoaluminate first formed during hydration of a cement, these curves and many others similar to them, which have been obtained in our laboratory, have convinced the writer that under ordinary circumstances the high-sulfate form is always the first to form. Experiments in which the hydration is topped after 2 min give similar results, although the quantity of this phase is less than at later periods.

When the quantity of gypsum is sufficient, which is the case with most cements, the high-sulfate sulfoaluminate always forms initially, followed by the appearance of the low-sulfate form, or a closely related phase, after the gypsum has been used up. We have attempted to confirm these indications by means of X-ray diffraction, but the results have not been too successful thus far. It is believed that a heavy-liquid concentration technique, similar to that employed by Taylor [15], would indicate the presence of the high-sulfate form even at very early ages.

An indirect confirmation of the above conclusions was found in experiments made with clinker without gypsum added, or with insufficient gypsum for normal retardation. DTA curves illustrating these results are given in figures 3 and 4. The curve for clinker hydrated for 5 min (fig. 3) shows no sign of the typical endothermic peak associated with the high-sulfate sulfoaluminate, but instead shows an endotherm in the neighborhood of 200 °C.

A peak in this location has been correlated by other investigators, as well as ourselves, with the hexagonal tetracalcium aluminate hydrate ($4CaO{\cdot}Al_2O_3{\cdot}13H_2O$) or a related solid solution [14, 18]. It will be noted that this endotherm persists up to the age of 7 days. Figure 4 shows the results at 4 hours' hydration with the same clinker, to which was added 1 percent, 2 percent, and 4 percent of gypsum.

It appears that 1 percent of gypsum was not sufficient to prevent the formation of the $4CaO{\cdot}Al_2O_3{\cdot}13H_2O$ for this period of hydration, since this form, as well as the high-sulfate sulfoaluminate, is present in small amount in this sample. Two percent of gypsum has resulted in a fairly large amount of high-sulfate sulfoaluminate and has effectively prevented the formation of $4CaO{\cdot}Al_2O_3{\cdot}13H_2O$. The sample with 4 percent of gypsum shows the high-sulfate sulfoaluminate and an excess of unreacted gypsum.

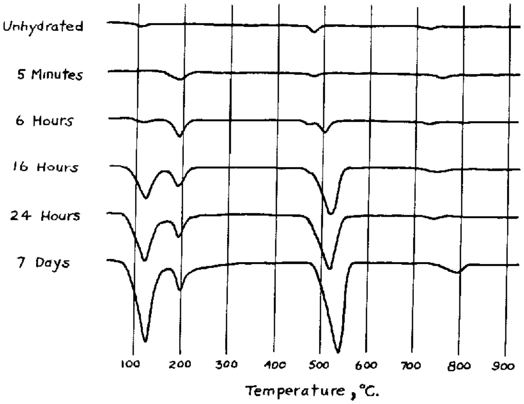

FIGURE 3. *DTA curves of a portland cement clinker hydrated without gypsum for various lengths of time.*

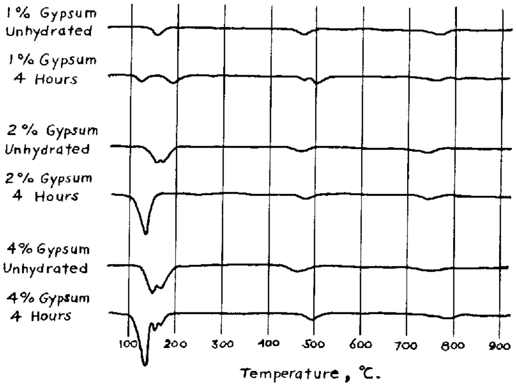

FIGURE 4. *DTA curves of a portland cement clinker hydrated with various amounts of added gypsum.*

The suggestion of Steinour, previously mentioned, that formation of the low-sulfate sulfoaluminate may be favored initially when hydration takes place in a solution already saturated with $Ca(OH)_2$ and $CaSO_4$, was investigated using the same cement as in the experiments of figure 2. The cement was hydrated for 2 min at a water-cement ratio of 0.4, both with distilled water and saturated $Ca(OH)_2$-$CaSO_4$ solution. Hydration was stopped by stirring the paste into an excess of acetone, filtering, and drying in vacuum for 1 hr.

The DTA curves obtained are shown in figure 5. It will be noted that the endotherm for the high-sulfate sulfoaluminate is present in the upper curve (at about 120 °C) but is almost completely suppressed in the lower curve. However, it is significant that there is no indication (at about 200 °C) of the presence of the low-sulfate or solid-solution phase in either curve.

Perhaps a word should be said here in explanation of the prominent endotherms between 100

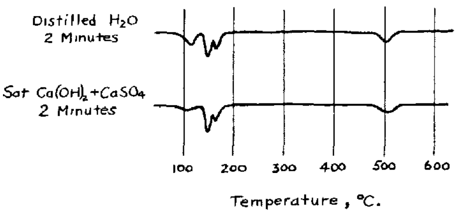

FIGURE 5. *DTA curves of a portland cement hydrated for two minutes with distilled water and with a solution saturated with* $Ca(OH)_2$ *and* $CaSO_4$.

and 150° in several of the curves of figure 3. These endotherms could be attributed mistakenly to the high-sulfate sulfoaluminate were it not for the fact that they were obtained on samples of clinker to which no gypsum had been added. The percentage of SO_3 in the clinker itself is too small to produce any such quantity of sulfoaluminate.

There is considerable reason for believing that these endotherms are due to calcium silicate hydrate, as mentioned previously. It will be noted that the size of the endotherms associated with this phase, when dried similarly, increases with time at a rate roughly proportional to the quantity of calcium hydroxide, strongly suggesting that they are related to the hydration of the calcium silicates.

Simplified Summary of Reactions

Based on the foregoing considerations, the writer would like to suggest the following as a simplified statement of the course of the early hydration reactions at ordinary temperature: An ordinary portland cement, when mixed with water to form a paste of a water-cement ratio in the range of 0.4 or 0.5, and cured in a moist atmosphere, begins to react immediately. The gypsum and alumina-containing phases of the clinker immediately start to react to form the high-sulfate calcium sulfoaluminate. Tricalcium silicate also starts to hydrolyze at a very early stage, and the solution soon becomes supersaturated with calcium hydroxide.

The calcium sulfoaluminate gradually increases in amount, and the gypsum is gradually used up by reaction with the aluminates. The gypsum has generally disappeared after about 24-hr hydration. Sometime later, depending upon the amount of gypsum present and the characteristics of the particular cement, the low-sulfate calcium sulfoaluminate, or a solid solution of this compound with hexagonal tetracalcium aluminate hydrate, begins to make its appearance as a solid phase.

Concurrently with the sulfate-aluminate reactions. the C_3S is hydrating, and as evidence of this, crystalline calcium hydroxide begins to form. This compound can sometimes be detected by DTA after 2 or 3 hr. It continues to increase in amount with time, and is a rough indicator of the development of the calcium silicate hydrate phase. Dicalcium silicate hydrates also, but at a much slower rate than the C_3S, and contributes its share to the total calcium silicate hydrate.

The minor clinker constitutents, such as the alkalies, may alter the rate of hydration of a cement, but the present evidence seems to indicate that the chemical nature of the hydration products is not radically altered by the percentages of these minor constituents normally present. The role of the iron-containing phases in the early hydration reactions is uncertain at the present time. Some investigators believe that compounds analogous to the calcium sulfoaluminates are formed, or perhaps solid-solution compounds containing both iron oxide and alumina. More will be said of this subject later.

Nature and Composition of Alumina-Bearing Phases

Absence of $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$

It is perhaps appropriate at this point to explain the absence of the cubic tricalcium aluminate hexahydrate ($3CaO{\cdot}Al_2O_3{\cdot}6H_2O$) from the above picture of the early hydration reactions. Previously cited phase equilibria studies [10, 11, 12] have shown that this compound is the stable phase in equilibrium with calcium hydroxide and high-sulfate sulfoaluminate in the system $CaO–Al_2O_3–CaSO_4–H_2O$. These studies also showed that the hexahydrate, although stable, is greatly retarded in its crystallization, and the low-sulfate double salt forms instead.

Kalousek, Davis, and Schmertz [14] found no evidence of the hexahydrate in hydrating cement, although they did find evidence of its presence in clinkers hydrated for 28 days and longer. Their conclusion was that only very small amounts of SO_4^{--} are required to inhibit the formation of the hexahydrate and that this SO_4^{--} stabilizes the hexagonal structure of the low-sulfate double salt or solid solution. Later work appears to confirm this explanation.

Experiments conducted in our laboratories have suggested another factor which does not seem to have been mentioned by other investigators. This is the effect of the calcium silicates on the hydration of the tricalcium aluminate. It is well known that tricalcium aluminate when mixed alone with water hydrates very rapidly, producing mainly hexahydrate along with some tetracalcium aluminate hydrate and dicalcium aluminate hydrate ($2CaO{\cdot}Al_2O_3{\cdot}8H_2O$). It hydrates somewhat less rapidly when mixed with saturated calcium hydroxide solution, but still produces considerable $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$.

In our experiments we found that when C_3A was mixed with C_3S, or a mixture of C_3S and C_2S, and hydrated, the hexahydrate was prevented from forming, and only the hexagonal calcium aluminate hydrate was produced. We have not found evidence of the hexahydrate by DTA in either clinkers or cements at ages up to 7 days. However, this is not to say that this compound may not form after longer periods of hydration.

The retarding action of calcium hydroxide is also frequently mentioned in the literature, particularly as it applies to the hydration of the calcium aluminates. Thus, it would seem that the hydration of the C_3A in a cement, particularly at early ages, is controlled by the combined effect of the calcium sulfate, the calcium hydroxide, and the calcium silicates present.

New Data on Hydrated Calcium Aluminates and Sulfoaluminates

The actual composition of the hexagonal solid-solution phase at various stages of hydration is a problem which requires further elucidation. It appears to have been generally accepted by most investigators that the low-sulfate calcium sulfoaluminate and the tetracalcium aluminate hydrate form a solid-solution series. However, it has not been possible up to this time, so far as the writer is aware, to determine the position in this series of the hexagonal phase present in a hydrating cement at any particular time. Unfortunately, the DTA curves of the two end members of the series are very similar, particularly the curves arising from the small amounts present in hydrating cement. The published X-ray diffraction patterns [24] also are similar, but possibly differ enough so that with refined techniques the X-ray method might be used to indicate the composition of the solid solution.

Considerable material is found in the recent literature on the calcium aluminate hydrates and the calcium sulfoaluminate compounds. Nicol [20] studied the reactions of the pure calcium aluminates with a limited amount of water, using the methods of thermogravimetric analysis and X-ray diffraction.

Roberts [25] studied the calcium aluminate hydrates and reported several hexagonal forms which had not been described previously. At 25 °C a hydrate with the formula, $4CaO \cdot Al_2O_3 \cdot 19H_2O$, was found which Roberts believed to be the stable form in contact with solution. It appears from this work that $4CaO \cdot Al_2O_3 \cdot 13H_2O$ is actually a dehydrated form of this more highly hydrated compound. Roberts found two forms of the $13H_2O$ hydrate and also two other tetracalcium aluminate hydrates having water contents of $11H_2O$ and $7H_2O$. Thus, the situation appears to be quite complex, and much additional work will be required to correlate these compounds with those which may be present in actual hydrating cements.

Astreeva and Lopatnikova [26] have recently studied the composition and properties of the hydrated calcium sulfoaluminates. They state that the composition and structure of the sulfoaluminates arising from the various alumina-bearing cement clinker compounds differ, basing their conclusion on microscopic, chemical, electron-diffraction, and electron-microscope determinations. Two of the conclusions of these authors are of particular interest. They state that during the hydration of the aluminates and aluminoferrites in the presence of gypsum, the high-sulfate sulfoaluminate always forms independently of the quantity of gypsum, and that if insufficient gypsum is present to react with all of the calcium aluminate to form the high-sulfate sulfoaluminate, the remainder forms the hexagonal hydrated calcium aluminate ($4CaO \cdot Al_2O_3 \cdot 13H_2O$). They further state that the calcium monosulfoaluminate or low-sulfate form is not produced.

These conclusions are presumably based on differences in the measured properties of the phases. Astreeva and Lopatnikova also observed that part of the water of crystallization can be driven off from crystals of the hydrated calcium sulfoaluminates without breaking down the original crystal form, but that further removal of water leads to destruction of the crystals.

Turriziani and Schippa [27] have made a detailed study of the system $CaO–Al_2O_3–CaSO_4–H_2O$ by X-ray and DTA methods. They concluded that the DTA method is capable of semiquantitative results in the identification of the various sulfoaluminate phases occurring in this system. According to them, it is possible under favorable conditions to determine with good approximation the range of molar ratios, $CaSO_4:Al_2O_3$, of the solids. These investigators believed that they had observed a new hexagonal phase similar to the low-sulfate sulfoaluminate but possessing a different X-ray diffraction pattern. Further work indicated that the differences in X-ray spacings were related to the humidity conditions under which the samples were dried.

One highly important observation of Turriziani and Schippa relates to the X-ray diffraction patterns and optical properties of solids with a molar ratio, $CaSO_4:Al_2O_3$, of less than unity. The optical properties were found to vary with this ratio, as would be expected in the case of a true solid-solution series. However, the X-ray diffraction patterns of all materials with a molar ratio less than unity showed the lines of tetracalcium aluminate hydrate, as well as those of the low-sulfate sulfoaluminate, irrespective of the $CaSO_4$ content. The intensity of the $4CaO \cdot Al_2O_3 \cdot 13H_2O$ lines increased with decreasing calcium sulfate content, while that of the $3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$ lines decreased. These authors conclude that it is possible that the two compounds may intercrystallize into a solid composed of alternating layers of both compounds. Further work is needed to clarify this situation. If Turriziani and Schippa's observations are confirmed, then the earlier work of Kalousek [28] and Jones [10] must be revised.

Other Complex Hydration Products

Calcium sulfoferrites. It was mentioned previously that compounds analogous to the sulfoaluminates but containing iron oxide in addition to alumina are possibly formed in hydrating cement paste. There is good evidence for the formation of these compounds in the pure oxide systems, but in the cement-water system the evidence is largely circumstantial. In their discussion of Steinour's paper at the Third Symposium [1], Malquori and Cirilli [29] presented data confirming the existence of calcium sulfoferrites analogous to the high-sulfate and low-sulfate sulfoaluminates.

Relatively little can be found in the literature of the intervening years relative to these interesting compounds. Budnikov and Gorshkov [30] have investigated the reactions of calcium aluminates and calcium aluminoferrites with gypsum. Their X-ray diffraction patterns showed the presence of the high-sulfate calcium sulfoaluminate, in mixtures of gypsum with synthetic $6CaO{\cdot}2Al_2O_3{\cdot}Fe_2O_3$, $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$, and $6CaO{\cdot}Al_2O_3{\cdot}2Fe_2O_3$. Reactions of dicalcium ferrite ($2CaO{\cdot}Fe_2O_3$) with gypsum gave lines corresponding to the high-sulfate calcium sulfoferrite. Their original paper was not available to the writer, but the abstract makes no mention of solid solution between the alumina and iron compounds. Malquori and Cirilli [29] believed that such solid solutions were possible.

Contrary to the results cited above, Watanabe and Iwai [31], using electron microscopy, X-ray diffraction, and DTA, observed no compound corresponding to the composition $3CaO{\cdot}Fe_2O_3{\cdot}3CaSO_4{\cdot}31H_2O$ in the hydration products of dicalcium ferrite and calcium sulfate. Schippa [32] recently studied the system $CaO\text{-}Fe_2O_3\text{-}CaSO_4\text{-}H_2O$ and reported the existence of both high-sulfate and low-sulfate analogs. The low-sulfate compound was found to exist in two different hydrated forms, depending on the relative humidity of the medium.

The above investigations were made on systems of pure compounds and, thus, are not directly applicable to cement hydration. The following statement of Steinour in his Third Symposium paper [1] still appears to stand today: "The role of iron oxide in the reactions of cement hydration is still an obscure matter on which much more work must be done."

Calcium silicoaluminates. The possibility of complex phases containing other constituents should not be overlooked. References to various calcium silicoaluminates have appeared frequently in the literature. Thus, we have the phase known as Strätling's compound (also called "gehlenite hydrate") with the formula $2CaO{\cdot}Al_2O_3{\cdot}SiO_2{\cdot}XH_2O$ [33, 34].

Turriziani and coworkers [35, 36, 37] have confirmed the existence of this compound and have identified it in the reaction products of dehydrated kaolin and calcium hydroxide at ordinary temperature. Benton [38] also identified Strätling's compound in the reaction products of calcined kaolin and calcium hydroxide, and of calcined kaolin and portland cement, at 38 °C (100 °F).

Another calcium silicoaluminate is a compound analogous to the high-sulfate calcium sulfoaluminate. This compound was prepared by Flint and Wells [39], who also were able to obtain a phase corresponding to the low-sulfate sulfoaluminate, with the formula $3CaO{\cdot}Al_2O_3{\cdot}CaSiO_3{\cdot}12H_2O$. Mohri [40] has recently reported the formation of one of these phases in the hydration products of preparations in the system $CaO\text{–}Al_2O_3\text{–}SiO_2$ and gives an X-ray diffraction pattern and an electron micrograph.

The hydrogarnet solid solutions should also be mentioned, although their relation to the hydration of cement at ordinary temperature is not at all clear. These compounds can be readily prepared under hydrothermal conditions, but although tricalcium aluminate hexahydrate ($3CaO{\cdot}Al_2O_3{\cdot}6H_2O$) is considered to be one end member of this series, the mixed hydrogarnets have not, to the writer's knowledge, been reported as having been formed at room temperature. However, zur Strassen [41] apparently believes that both hydrogarnets and Strätling's compound (gehlenite hydrate) may be produced during hydration at ordinary temperature. He states that there may be formed, besides calcium silicate, aluminate, and ferrite hydrates, complex hydrates which simultaneously contain lime, alumina, and silica or alternatively lime, alumina, iron oxide, and silica. In experiments described by him there were found only "gehlenite hydrate" and members of the hydrogarnet solid-solution series.

Calcium carboaluminates. Other complex compounds of possible significance are the calcium carboaluminates. At least two forms have been reported, corresponding respectively to the high- and low-sulfate forms of calcium sulfoaluminate. These compounds are important in the present discussion, not only because they may be formed by reaction of a moist hydrating cement paste with carbon dioxide in the air, but also because most cements contain small quantities of alkali carbonates, which may possibly react to produce carboaluminates when the cement is mixed with water.

Bessey [42] prepared both high- and low-carbonate forms with the formulas, $3CaO{\cdot}Al_2O_3{\cdot}3CaCO_3{\cdot}XH_2O$ and $3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}XH_2O$. Although there has been some speculation concerning the possible occurrence of such compounds in hydrating portland cement, evidence for such occurrence has been lacking, and it has been assumed quite generally that calcium carbonate is the only product of the reaction of portland cement with carbon dioxide, as well as with alkali carbonates in cement.

Recently, however, Turriziani and Schippa [43] have identified the low-carbonate form in a film formed on the surface of the water contained in a vessel in which cubes of alumina cement paste had been curing for a period of about 2 years. These authors also prepared this compound in the laboratory, and their identification is based upon the agreement of the X-ray patterns. Carlson [44] in a study of the system $CaO–Al_2O_3–H_2O$ at 1 °C believed that he had obtained a carboaluminate, probably having the formula, $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$, as the result of CO_2 picked up during storage of his reaction mixtures. Budnikov and Azelitskaya [45], in a very recent article on the effect of added electrolytes on the hardening process of C_3A, state that in the presence of 0.5 percent of calcium carbonate, large amounts of gel-like $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 18H_2O$ are formed. Until recently, however, there has been no suggestion that a calcium carboaluminate might be formed in a hydrating portland cement paste.

Some experiments in our laboratories, using the DTA method, may be of interest in this connection. A cement was hydrated for 24 hr at room temperature at a water-cement ratio of 0.35, both with and without 2 percent of sodium carbonate by weight of the cement. The DTA curves are shown in figure 6. Curve No. 2, which represents the cement to which the sodium carbonate had been added, bears a marked resemblance to the curve for the monocarboaluminate given by Turriziani and Schippa [43] in their paper. These data are only suggestive, and it is hoped that it may be possible to confirm the presence of carboaluminate by X-ray diffraction methods.

In spite of considerable evidence indicating the possibility of the formation of various complex alumina-bearing compounds during the early stages of portland cement hydration, it is obvious that our knowledge of the precise state of affairs is very limited. We believe there is good evidence of a compound closely akin to the high-sulfate calcium sulfoaluminate or ettringite which forms at very early ages, and likewise, there is rather convincing evidence of a hexagonal phase related to the low-sulfate sulfoaluminate, which makes its first appearance at a somewhat later time. We do not know, however, to what extent these phases are solid solutions containing appreciable amounts of iron, silica, and carbonates. The solution of this problem is one of great difficulty, and we must expect that progress will be slow.

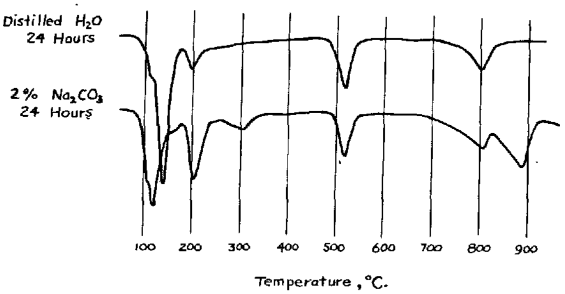

FIGURE 6. *DTA curves of a portland cement hydrated for 24 hr with distilled water and with a solution containing 2 percent of* Na_2CO_3 *by weight of cement.*

An example of the type of question which comes to mind is as follows: Is the hexagonal phase, which appears after the gypsum is depleted, similar to the one which forms almost instantaneously when a clinker without gypsum is mixed with water, or are there significant differences in composition? The phase represented in early hydration of clinker, for example, may be essentially pure tetracalcium aluminate hydrate, whereas the phase appearing later in hydrating cement may possibly represent a more complex solid solution or interlayered compound, containing any or all of the substances mentioned above. It will be necessary first to resolve some of the contradictions in the literature and then, as new methods and techniques make it possible, to correlate the well-established facts on the chemical systems involved with results obtained with the cement-water system.

Reactions of Calcium Silicate Phases

Except for the very rapid hydrolysis reaction of C_3S, whereby the solution quickly becomes supersaturated with calcium hydroxide, the observable reactions of the calcium silicates of cement are much slower than those of the calcium aluminates and aluminoferrites. Thus, definite crystalline compounds cannot usually be identified until calcium hydroxide begins to crystallize after several hours of hydration.

Until recent years it was not possible to distinguish or to conclusively prove the existence of crystalline calcium silicate hydrates in cement paste, and consequently, the calcium silicate hydrates were considered to be essentially amorphous. It is now well-established that the so-called "cement gel" is composed essentially of calcium silicate hydrate crystals but of such a small particle size as to be colloidal in behavior. The "crystallization" theory of Le Chatelier and the "colloidal" theory of Michaelis, long considered to be in opposition to each other, are, thus, now recognized as both being partially correct.

Since the calcium silicate hydrate occurring in portland cement paste is poorly crystallized, even after rather long periods of hydration, it is studied with great difficulty at very early ages. Thus, while we know that the calcium silicates of clinker are entering into hydration reactions from the very moment of water contact, we find that the conventional methods of study do not provide much information concerning the nature of the hydration product initially formed. Nevertheless, it is frequently possible to gain considerable insight into the early chemical reactions by indirect methods.

The literature records a great deal of research on the hydration products of the calcium silicates. However, these studies have of necessity been made on products obtained only after days or weeks of hydration, since the materials obtained at early ages do not give recognizable X-ray patterns (other than that of $Ca(OH)_2$). Consequently, these studies indicate the character of the ultimate hydration products but do not tell us much concerning the nature of these materials during their early stages of formation.

This work, like that relating to the calcium aluminates and ferrites, is properly the subject of another paper being given at this symposium and will not be considered in detail in the present discussion. Suffice it to say here that the hydration product of both C_3S and C_2S at ordinary temperature is generally considered to be a poorly crystallized, extremely fine-grained material resembling the mineral tobermorite. It is essentially the material designated as CSH(I) by Taylor [46] and as CSH(B) by Bogue [47], perhaps mixed also with CSH(II) (Taylor) or C_2SH_2 (Bogue). There is evidence that this tobermorite-like calcium silicate hydrate is also produced in hydrating portland cement paste [15].

It has been mentioned previously in connection with the hydration of the calcium aluminates and aluminoferrites that portland cement reacts very rapidly with water when mixed to form a paste. The same is true for C_3S, but the reaction of C_2S is much slower. The concentration of lime quickly reaches saturation and continues to increase to give a metastable supersaturated solution. This calcium hydroxide probably comes mainly from the C_3S, since pure C_3S behaves similarly. However, the silica in solution is very low at 1 min, which is about the earliest time after mixing at which it has been possible to make measurements. Since the rapid release of calcium hydroxide into the solution is evidence of a considerable early reaction, the question naturally arises as to the form of the silica or calcium silicate which is formed.

It was mentioned previously in connection with the hydration of the alumina-bearing compounds, that although the concentrations of alumina and silica are always found to be very low at 1 min and longer after mixing, there is some reason to believe that they may reach much higher values within the first minute. Whether the silica concentration is initially high would seem to be of great importance, not only with respect to the nature of the very early hydration products of the calcium silicates but also as it relates to the mechanism of hydration. By the latter is meant the more or less traditional dissolution and precipitation theory, versus the topochemical or solid-state reaction theory of hydration. I should like to discuss these questions in some further detail.

Nature of Early Calcium Silicate Hydrate

The similarity between the hydration of pure C_3S and of fully retarded portland cements strongly suggests that the setting phenomenon in cement is produced mainly by the products of the hydration of the C_3S. This has been well stated by Steinour [13]. However, while there is evidence of almost instantaneous reaction of C_3S with water with formation of a supersaturated solution of calcium hydroxide, yet no structure begins to develop until the time of initial set.

These facts strengthen the view that the calcium silicate hydrate is in a colloidal form during this period. This concept would seem to be confirmed by the results of Smirnova, Zaitseva, and Rehbinder [48], indicating that the surface area increases on the order of tenfold during the first 30 to 45 min of hydration. Without here going into the relative merits of the solution-precipitation theory as against the solid-state reaction theory, it would be expected, in any case, that the formation of hydration products on or near the cement grains would rapidly choke or quench the initial rapid reaction. This behavior appears to be the case, although the data on heat liberation obtained by Forbrich [49] and Lerch [50] show that this period of reduced rate of reaction is followed by a period of accelerated reaction prior to initial set. The reason for this delayed acceleration is not clear but must be related in some way to the fundamental mechanism of hydration.

Solid-State Reactions

Cement chemists have proposed from time to time that hydration is fundamentally a group of solid-phase reactions. This mechanism was suggested by Hansen [5] in his discussion of Steinour's paper at the Third Symposium. Hansen has recently developed his hypothesis in greater detail [7]. Jeffery [51] also discusses the question of possible hydration by solid-state reaction. Hansen's argument is based largely on the fact that although C_3A and C_3S appear to react very rapidly with water and with soluble constituents such as chlorides and sulfates in solution, only very small amounts of alumina and silica are found in the extracts as early as 1 min after mixing.

Steinour [8] shows that there is reason to believe that the alumina and silica concentrations may have been much higher during the critical first minute. If this condition were to be demonstrated conclusively, then it seems that the solid-state reaction theory would be rather effectively refuted for this very early age. This statement is particularly true of Hansen's hypothesis, since he assumes diffusion into the solid crystals of the clinker phases but very ittle outward diffusion of dissolved constituents into the solution.

In connection with the question of solid-state or, strictly, in this case, solid-liquid reactions, it should be noted that Strelkov [3] favors this type of mechanism. Strelkov, however, visualizes the formation of reaction products on the surfaces of the grains that are highly soluble because of their poorly ordered structure. These highly soluble products then dissolve and form supersaturated solutions from which the stable hydration products of lower solubility precipitate.

Of interest, also, is Strelkov's observation that when the liquid was extracted under constant pressure, the concentration of dissolved constituents increased with time, and also that the concentration increased with pressure for a given time of extraction. This behavior led him to conclude that the liquid phase is more concentrated in the vicinity of the surface of the hydrating grains than in the interstices between them. Steinherz and Welcman [4] also believe that the hydration processes are topochemical or solid-state reactions or else take place in the very close proximity of the clinker grains. They noted that the chemical composition of the liquid extracted at one minute was not influenced significantly by the fineness of the cement.

Van Bemst [22] concluded, from studies of the hydration of the pure calcium silicates at ordinary temperatures, that the hydration of C_3S first results in CSH(I) by a process of solution and precipitation, before the solution becomes saturated with $Ca(OH)_2$. As the concentration of $Ca(OH)_2$ increases so as to reach saturation or supersaturation, the higher-lime hydrate CSH(II) forms directly on the surfaces of the hydrous silicate grains by an unknown mechanism. This latter behavior certainly resembles a solid-state reaction. Van Bemst believes that the hydration of β-C_2S results in CSH(I), and that the mechanism is qualitatively the same as that for the formation of CSH(I) from C_3S.

Funk [52] found that water vapor alone at 100 °C can act on β-C_2S to produce a high-lime tobermorite phase as loose acicular crystals, but without strength development. An aqueous solution phase was necessary for hardening to take place. From this observation he concluded that some mechanism other than solution and precipitation may be at work during the reaction of water and β-C_2S.

A satisfactory decision on the relative importance of solid-phase reactions in the hydration of cement must await further research. It may well turn out that both solution-precipitation, and topochemical reactions are involved, with the solution-precipitation phenomena predominating at the very early ages, while the later reaction is governed primarily by the solid-state type of mechanism, as suggested by Lea [21, p. 223]. It appears that the evidence is pointing in this direction.

Protective Coatings

One thing is certain; namely, that adsorption and surface effects play a major role in the early reaction process. It seems nearly as certain that part, at least, of the early formed hydration product is deposited on or very near the surfaces of the clinker grains. In the case of grains of C_3A and aluminoferrite, this coating is undoubtedly a phase similar in composition to the high-sulfate calcium sulfoaluminate, based on evidence previously cited. In the case of C_3S grains, the coating is probably a very poorly crystallized calcium silicate hydrate of colloidal particle size. It seems likely that these phases are fairly distinct and "pure" when they originally form, but that as hydration progresses they become more and more intermingled.

It is possible that the coating of calcium sulfoaluminate which forms on the surfaces of the alumina phases, as well as the calcium silicate hydrate which forms on the anhydrous silicate particles, is initially of a colloidal nature and acts as a protective film, slowing down the original very rapid reaction. The concept of protective coatings is, of course, not at all new, but is found in the early cement literature. In the case of C_3A and the calcium aluminoferrite, the coating does not prevent reaction but simply controls it, preventing a rapid hydration of these compounds as long as gypsum is available to maintain it.

The action of the coating on the C_3S grains needs further study. As previously mentioned, it appears that the hydration of C_3S is initially rapid, declining subsequently to a relatively low rate, after which it accelerates again at about the time of initial set. This behavior suggests that for some unknown reason the retarding ability of the coating loses its effectiveness at about this time.

Fractional Rate Hypothesis

Several years ago research workers at the Portland Cement Association reported data which appeared to indicate rather conclusively that the compounds or phases of cement do not hydrate independently or at the same rate as they do when hydrated individually [53, 54, 55]. From the results of three different lines of investigation, these researchers concluded that the cement compounds hydrated at equal fractional rates—that is, when one compound was one-half hydrated, each of the other compounds was also one-half hydrated. Thus, the quantity of any particular compound which had hydrated at a given time was believed to be dependent upon the percentage of that compound present in the cement. This conclusion was rather surprising, since C_3A and C_2S, for example, have greatly differing hydration rates when hydrated individually.

The experimental results which led the P.C.A. investigators to formulate the hypothesis of equal fractional rates were those indicating a constant ratio between the heat of hydration and the non-evaporable or combined water, a constant ratio between surface area and combined water, and equal fractional rates of disappearance of the unhydrated clinker phases as determined by X-ray diffraction.

Before proceeding further, it should be stated that the hypothesis was never suggested as applying to all types of cement, but only to the United States of America Types I and III and not to these in the very early stages of hydration. The hypothesis thus is perhaps not directly pertinent to the subject of this paper, since we are interested here mainly in the early reactions. Yet it is of interest as it illustrates how various approaches can be used to bear upon a particular problem of cement chemistry.

The determination of the rates of hydration of the cement compounds by X-ray diffraction is a direct method and, granting that sufficient accuracy is possible, it should give valid results. The constancy of the ratios between the heat of hydration or specific surface on the one hand, and the nonevaporable water on the other hand, constitutes less direct evidence. Although equal fractional rates of hydration should give constant ratios of heat of hydration and surface area to combined water, it appears that the fractional rates need not be equal to lead to this result.

Thus, we may have fractional rates of hydration for the different phases which differ markedly from one another, yet if these fractional rates bear a constant ratio to one another during hydration, the gel produced will tend to have a constant composition, and constant ratios of heat of hydration and surface area to combined water will be observed. This relationship would hold until one of the phases had completely reacted.

While more precise results may prove the fractional rate hypothesis to apply only imperfectly to the hydration of cement, still the data indicate that once a fairly steady state is developed, the average composition of the reaction products being formed does not change greatly with time. In other words, hydration seems to produce, in general, more and more of the same kind of gel. This average composition would not be expected to hold in the very early stages of hydration, and indeed the data indicate that it does not. The reactions involving the alumina phases and gypsum, which are initially very rapid and later much retarded, appear to be relatively independent of the others.

Diffusion as a Controlling Process

The tendency toward equal or constant fractional rates of hydration of the cement minerals suggests that some mechanism is operating which is able to overcome, to a considerable extent, the characteristic individual hydration rates. This hypothesis is compatible with the idea that, following the initial very rapid reactions, the hydration of cement is controlled by diffusion through the film or coating of hydration products on the cement grains. A very interesting discussion of this matter by zur Strassen has recently been published [56]. He concludes that as an approximation, the hydration of tricalcium silicate is diffusion-controlled, following a square-root law, while that of dicalcium silicate is linear. In C_3S the reaction takes place so rapidly that the supply of water is limited. The reaction therefore follows the law of diffusion, according to which the rate of reaction is inversely proportional to the thickness of the reacting layer. According to zur Strassen, the retarding effect of the gel film applies to C_3A and C_4AF also, but the hydration of C_2S is already so slow that it remains linear for a considerable length of time, and the controlling effect of diffusion comes into play only with a greater thickness of the gel layer.

Taking the experimental data, together with theoretical considerations, we arrive at a picture somewhat as follows: The initial reactions are dominated by the hydration of the aluminate and ferrite phases and their reactions with gypsum. The hydration reactions of the clinker minerals are never truly independent but approach closer to this situation at the beginning of hydration. As coatings of reaction products form, there is a slowing down of the most rapid reactions and a tendency toward equalization of rates or at least the establishment of fairly constant fractional rate ratios between the hydration reactions of the different clinker phases. The overall average hydration rate is controlled largely by diffusion of water through the gelatinous hydration products already formed. With cements unusually high in C_2S, the later hydration is controlled by the very slow intrinsic hydration rate of this compound rather than by the diffusion mechanism.

Chemical Nature of Cement Gel

Related to the problem of relative hydration rates and whether the cement compounds hydrate, to an appreciable degree, sequentially rather than simultaneously, is the question of the chemical constitution of the resulting gelatinous hydration product. As pointed out by Brunauer [54], the gel comes from all the constituents of the cement. Is the gel a very fine-grained physical mixture of chemically different hydration products, or is it fairly homogeneous, even down to molecular dimensions, so that the ultimate gel particles may be thought of as being copolymers of the hydrates?

Hydration studies at early ages favor the concept of chemically distinct hydrates, with DTA curves illustrated earlier in this paper being examples of such evidence. On the other hand, the DTA data of Kalousek, Davis, and Schmertz [14], obtained on older pastes, indicate a merging of the thermal effects of the different hydrates into one large composite peak suggestive of a single homogeneous substance.

The fact that properties such as heat of hydration, surface area, and combined-water content can be calculated as though they were additive with respect to the different cement compounds has been used as an argument in favor of a mixture of distinct hydration products. Brunauer [54] points out, however, that even if the gel is a copolymer of compounds, some additivity would not be surprising. Thus, we may say that the gel probably becomes progressively more homogeneous with time of hydration but that the scale of dimension of this homogeneity is uncertain. Electron microscopy and electron diffraction can be expected to throw additional light on the physical and chemical nature of the ultimate gel particles.

Development of Structure

The physical mechanism of the development of structure in a cement paste, corresponding to setting, has been the subject of much debate. The transition from a mobile or plastic paste to a semirigid mass without plasticity is gradual, but is obvious to any observer. The physical cause of this stiffening or setting is not so obvious.

A paste of normally retarded cement immediately after mixing is a suspension of discrete cement particles in water. Powers [57] and Steinour [58] showed that normally this suspension soon begins to act as one continuous flocculated mass. Their bleeding studies showed that in spite of the rapid chemical reactions which take place on mixing, the bleeding rate is remarkably constant for a considerable time, indicating no radical change in the physical state of the cement suspension.

They interpreted this constancy to mean that the degree of subdivision of the cement was not altering significantly during this period. However, this conclusion is at variance with the results of Smirnova, Zaitseva, and Rehbinder [48], who reported that the surface area may increase tenfold, reaching a maximum value during the first 30 to 45 min. It is difficult to reconcile such a large increase in surface area with a constant bleeding rate.

Most writers seem to view the stiffening of a cement paste as being caused by the increasing volume of hydration products, with a corresponding decrease in distance between particles, until finally plastic flow is greatly restricted, and cohesive forces begin to operate as more and more of the particles are drawn into contact with one another. This mechanism is essentially the picture outlined by Lea [21, p. 223] and, in somewhat more detail, by Jeffery [51]. Hardening then would be due to an increase in the number of "welds" between gel particles as hydration proceeds.

A rather different mechanism of cement setting has been proposed by the Russian school of investigators. This theory, which is based on an earlier one of A. A. Baikov, is developed, with some variations, in papers by a number of authors, including Okorokov [59], Segalova, Rehbinder, and Luk'yanova [60], Rehbinder [61], Sivertsev [62], and Strelkov [3]. The process is thought of as consisting of three distinct phases, which, however, may overlap in time.

The first is a self-induced dispersion or "colloidization" of the cement particles, particularly of the C_3A. This dispersion is followed by the formation of a coagulated thixotropic structure from the dispersion of cement particles and hydration products, and finally by the development of a crystalline structure of new hydrated compounds through crystallization out of a supersaturated solution. The formation of the coagulated structure corresponds to setting, and the strengthening of the structure through formation of crystalline hydrates brings about the later hardening.

Adsorption plays a prominent part in this theory, and the effect of hydrophilic retarders such as calcium lignosulfonate is explained on this basis. These retarders promote the self-dispersion of the cement grains, by which is meant a breaking down into particles of colloidal dimensions and the stabilization of the resultant suspension, thus delaying the coagulation phase. The process is considered to affect the C_3A to the greatest degree, with C_3S affected less strongly. It is believed to operate also in ordinary gypsum-retarded cements without admixtures. The Russian theory combines features of both the earlier crystallization and colloidal theories of cement setting and hardening, placing the colloidal phase at an earlier point in the hydration process than the crystallization phase. Certain aspects of the theory harmonize well with the results of other recent investigations. In particular should be mentioned the prominent place given to adsorption and colloidal phenomena. On the other hand, it contains features which are difficult to reconcile with other data.

One of these apparent conflicts is the evidence for a large increase in surface area of the cement particles during the early stages of hydration, as determined by the rate of adsorption of radioactive calcium-45 [48], and the results of the bleeding studies of Powers [57] and Steinour [58], which indicated that the particle size of the cement did not change significantly.

Also, the Russian theory pictures the setting as being caused primarily by coagulation of the dispersed aluminate phases, whereas there is much other evidence indicating that in the absence of the abnormal "flash" set or "false" set, the C_3S is mainly responsible for the setting. As mentioned previously, pure C_3S sets in a manner very similar to a cement retarded by a sufficient amount of gypsum. According to Rehbinder [61], the hydration processes of the silicate components contribute to the later hardening and strength development, but relatively little to the setting. Additional work is clearly indicated to help resolve these difficulties.

There is no question that the surface area of a cement paste increases tremendously by the time it has set and hardened. The anomaly pertains only to the initial period prior to the attainment of set. To state the question in other words, "Does the surface area of the hydration products increase rapidly soon after mixing, as the work of the Russian investigators indicates, or does it remain relatively unchanged for a considerable length of time, as the bleeding data of Powers and Steinour imply?" In this connection it should be noted that there may be some loss of plasticity in a normal cement paste in the period preceding what is ordinarily called initial set.

Published information on the viscosity or consistency of cement pastes during the early period of hydration is scanty, however, and somewhat lacking in agreement, doubtless due to differences in cements and conditions of test. Dorsch [63] performed experiments which indicated a rapid increase in viscosity of cement pastes for the first hour after mixing, followed by a shorter period during which it remained unchanged. The viscosity then increased again as setting occurred until no flow could be obtained.

Kozlowski [64], in a recent discussion, shows a consistency-time curve for portland cements which indicates a constant low consistency up to 2 hr, followed by a rather sudden and rapid stiffening, with a leveling off at about 4 hr. The original low value was restored by vigorous stirring, after which the paste again stiffened, attaining initial set at about the seventh hour. In these tests the consistency was measured with a penetration rod.

Tests made in our laboratories, using an adaptation of the Halliburton Thickening-Time Tester for oil-well cements, showed no significant thickening up to 2 hr after mixing for pastes of gypsum-retarded cements at a water-cement ratio of about 0.40 and a temperature of 80 °F (27 °C). These results are in agreement with Kozlowski's insofar as they indicate no appreciable structure formation in the first 2 hr. However, it must be emphasized that the test methods were quite different. Our pastes were continuously agitated during this period, while Kozlowski's were not. It is probable, too, that more sensitive methods of measurement would detect changes in consistency at this early age. Further research on this aspect of early hydration should prove fruitful.

A widely held view concerning the development of strength and rigidity in a hydrating portland cement paste is that these properties are probably due to a combination of physical forces often known as van der Waal's forces and chemical-bond forces [54, 55]. Another view emphasizes the idea that the rigidity is derived from the interlocking and intertwining of very minute fibrous crystals [65].

These two concepts are not necessarily in opposition. It is very likely that all of these factors enter into the hardening process. An experiment recently described by Czernin [66] demonstrates in an almost spectacular way the magnitude of the physical or van der Waal's forces when the surface area of a material becomes very great. Czernin ground 100 g of quartz sand to a Blaine surface area of 20,000 cm^2/g and molded this powder with 20 g of water. A specimen formed from this paste was able to support a weight of 10 kg. A nearly completely hydrated cement paste has been shown to contain about 20 percent of combined water and to have a surface area of the order of 2,000,000 cm^2/g. Consequently the high strength obtained by cement in time is not at all surprising.

Hayden [67] presents data which indicate that no more than 0.5 percent of water of hydration may be required to bring about final set. Czernin points out that even 0.5 percent of fixed water may be equivalent to 50,000 cm^2/g of surface area when one considers that 20 percent of combined water produces 2,000,000 cm^2/g of surface area. From this it appears that physical forces related to surface area may contribute significantly to the setting phenomenon.

Conclusion

In summary, we conclude that our knowledge of the hydrated calcium aluminates and ferrites and of the calcium silicates has been materially increased in the last 8 years but that there are still many unanswered questions regarding the details of the hydration of actual portland cement at ordinary temperature. We find the evidence indicating that the initial reactions of hydration are extremely rapid and are dominated by the hydration of the aluminate and ferrite phases and their reactions with gypsum. The C_3S reacts rapidly with water also, and although there is a strong suggestion that the initial setting or development of structure is due primarily to the C_3S, this phenomenon normally does not begin for several hours.

We find considerable evidence that the clinker minerals exert a significant influence on one another during their hydration. They never hydrate in a truly independent manner but approach closely to this situation at the very beginning of hydration. Early reaction products probably form coatings on the cement grains, thereby slowing down the most rapid reactions and tending to produce an equalization of rates or the establishment of relatively constant fractional rate ratios between the hydration reactions of the different clinker phases. It appears that the overall average hydration rate is controlled largely by diffusion of water through the gelatinous hydration products already formed.

The evidence is conflicting as to whether the early hydration reactions are basically the result of solution and precipitation or whether they are more properly described as topochemical or solid-state reactions. It appears likely that the very earliest reactions take place by solution and precipitation, while the later hydration is diffusion-controlled and approaches the solid-phase type of process.

Most researchers agree that the setting or development of structure in a hydrating cement paste is intimately connected with adsorption and the operation of surface forces. The relative importance of physical and chemical forces is not yet clear. There is also some difference of opinion regarding the details of the chemical and physical changes involved in the process of setting. In the author's opinion the setting process is a field where we may expect to see some of the most significant developments in the future.

Research on cement hydration in the next few years will undoubtedly give us the answers to many of the questions now facing us, and some of the differences of opinion will be resolved. As our knowledge progresses we may expect new questions to arise and new differences to develop, but after all is said and done, is not this inevitable and even to be desired if our progress is to be real?

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Discussion

W. C. Hansen

The author refers to the work of Czernin with quartz powder with a surface area of 20,000 cm^2/g as demonstrating the manner in which physical forces might contribute to the strengths of hardened cement pastes. In light of recent work on freshly formed surfaces of silica, there may be some question as to whether or not the strength obtained from a specimen of powdered quartz and water is primarily the result of physical forces.

Benson and Castle,[1] in a review of the literature and from their own work, show that freshly formed surfaces of silica undergo chemical reactions with various materials. Van Lier, de

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Bruyn, and Overbeek[2] studied the solubility in water and solutions of NaOH of powdered quartz before and after treatment with a solution of HF. The untreated powder had an erratic and much higher rate of solution than did the treated powder. They concluded that the surfaces of the particles of the former probably had a combination of cracks, dislocations, and protruding edges that gave this powder an abnormally high rate of solution. The depth of this disturbed layer on the surfaces of the particles was estimated to be approximately 300 A. The acid-treated quartz had a solubility at 25 °C of 1.8×10^{-4} moles/kg.

This work with silica and other powders suggests that disturbed surfaces on particles of portland cement might have pronounced effects during the early reactions of cement with water. It seems that this might be a profitable area for research by those working on cement.

Discussion

Elmer T. Carlson

Dr. Greene made mention of certain complex hydrated compounds generally referred to as silicoaluminates. In the following, I shall not comment on the compound C_2ASH_8, often called Strätling's compound or hydrated gehlenite, the existence of which is now well established. My remarks will be confined to the two silicoaluminates, C_4ASH_{12} and $C_6AS_3H_{30-32}$, reported by Flint and Wells [1],[3] which were considered to be analogous to the well-known sulfoaluminates. These have already been briefly commented on by zur Strassen and Schmitt [2] in their discussion of an earlier paper in this symposium. It was pointed out in the latter discussion that Dörr [3] at one time believed that he had successfully prepared C_4ASH_{12}, but that his later experiments failed to confirm this conclusion. The other compound, $C_6AS_3H_{30-32}$, recently has been reported by Mohri [4] but from his petrographic and X-ray data it appears unlikely that he actually had the same compound as that described by Flint and Wells.

Over a period of several years, numerous attempts have been made in our laboratories to repeat the preparation of C_4ASH_{12}, both by closely following the procedures of Flint and Wells and by systematically varying the proportions of the reactants over a wide range. In all cases, confirmation has been lacking. Data relative to a few typical experiments are given in table 1.

It may be seen that in each case, after storage of the reaction mixtures at room temperature for 2 months, the predominant phase was C_2ASH_8 ("gehlenite hydrate") with lesser amounts of C_4AH_{13} and other phases. Identification was based on X-ray diffraction patterns. The experiments listed in the table are comparable to three of the experiments tabulated by Flint and Wells [1] in their report of the preparation of C_4ASH_{12}.

A large number of similar reaction mixtures have been prepared and studied. It is significant that in most of the experiments, the precipitate was seen, by microscopic examination, to consist of two types of material; one apparently a gel (similar to CSH), the other consisting of platy crystals. Occasionally, after some weeks, C_3AH_6 was also observed. Products that appeared to be homogeneous were obtained only if the initial concentration of Al_2O_3 was less than a rather low, not precisely determined value. In such cases, the precipitate was of the gel type.

In view of this failure to duplicate the preparation of C_4ASH_{12}, it was decided to reexamine the data of Flint and Wells, to see whether they might permit a different interpretation from that given by the authors. The proposed formula for the silicoaluminate was based on chemical analysis, which was undoubtedly accurate, but necessarily based on the assumption of a homogeneous precipitate. The assumption of homogeneity was based on microscopic evidence, which is subject to some uncertainty because of the extreme minuteness of the crystals and their tendency to agglomerate. The refractive indices reported for the proposed silicoaluminate, 1.538 and 1.523, are well within the range of values reported for C_4AH_{13} by various

TABLE 1. *Precipitation from aqueous* CaO-Al_2O_3-SiO_2 *mixtures during two months storage at room temperature*

Experiment number		1	2	3
Initial volume, ml		460	350	300
Weight of oxides present	CaO, g	0.813	0.460	0.661
	Al_2O_3, g	.165	.082	.070
	SiO_2, g	.080	.080	.068
Final concentration of solution	CaO, g/l	1.082	.740	1.126
	Al_2O_3, g/	0.004	.007	0.004
	SiO_2, g/	.001	.001	.002
Molar ratio in ppt, C:A:S		3.0:1:1.0	3 9:1:2.0	6.9:1:1.8
Solid phases present (from X-ray patterns)		C_2ASH_8 C_4AH_{13} C_3AH_6 (little)	C_2ASH_8 C_4AH_{13} CSH (probable)	C_2ASH_8 C_4AH_{13} CH CSH (probable)

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[2] J. A. van Lier, P. L. de Bruyn and J. Th. G. Overbeek, The solubility of quartz, unpublished paper from the Department of Metallurgy, Massachusetts Institute of Technology, submitted to the Journal of Physical Chemistry.

[3] Figures in brackets indicate the literature references at the end of this paper.

investigators. Flint and Wells stated that the X-ray diffraction pattern of the silicoaluminate was very similar to that of C_4AH_{13}. In this connection it should be borne in mind that the X-ray equipment and techniques in use at that time were less advanced than those of the present day. In particular, the patterns failed to register the low-angle reflections which later have been found most useful in distinguishing between various calcium aluminate hydrates. Unfortunately, the X-ray films for the specific preparations for which data were published by Flint and Wells apparently have been lost. Others made during the same period by the same authors, and believed to be essentially duplicates, are, however, still on file. On reexamination, it is found that all the lines may reasonably be ascribed either to C_2ASH_8, to C_4AH_{13}, or to calcium hydroxide. Thus, the evidence for the presence of C_4ASH_{12} appears rather doubtful, and its existence remains unconfirmed. This is in full agreement with the recent conclusions of Dörr, as reported here by zur Strassen and Schmitt [2].

The other silicoaluminate reported by Flint and Wells, $C_6AS_3H_{30-32}$, is a different matter. A few of the original reaction mixtures are still in existence, and the needle-shaped crystals of the supposed silicoaluminate, closely resembling ettringite, are conspicuously present. Unfortunately, they have not yet been successfully separated from the mass of gel-like material with which they are entangled. Inasmuch as this compound was discussed in a recent paper by Carlson and Berman [5], it is unnecessary to go into the details at this time. It may be noted, however, that large amounts of combined carbon dioxide were shown to be present in the precipitates, leading to the conclusion that the supposed $C_6AS_3H_{30-32}$ probably contains CO_2 in partial substitution for SiO_2.

References

[1] E. P. Flint and L. S. Wells, Analogy of hydrated calcium silicoaluminates and hexacalcium aluminate to hydrated calcium sulfoaluminates, J. Research NBS **33**, 471 (1944) RP1623.

[2] H. zur Strassen and C. H. Schmitt, Discussion of the paper, Hydration of calcium aluminates and ferrites, this Symposium, Session III.

[3] F. H. Dörr, Dissertation, Mainz, 1955.

[4] J. Mohri, Calcium silicoaluminate, Semento Gijutsu Nenpo **12**, 43–45 (1958).

[5] E. T. Carlson and H. A. Berman, Some observations on the calcium aluminate carbonate hydrates, J. Research NBS **64A**, 333–341 (1960).

Discussion

T. C. Powers

Referring to Dr. Greene's excellent review, I should like to comment on the apparent conflict between conclusions drawn from some of our studies and the conclusions of Professor Rehbinder and his collaborators, mentioned in Dr. Greene's paper. Reference was made to the fact that our studies of the rate of bleeding (rate of sedimentation in a thick suspension) indicated that the size, shape, and number of cement particles are not altered appreciably by the reactions occurring within the first hour or so after contact with water. In connection with this conclusion, Dr. Greene pointed out that Professor Rehbinder and his collaborators reported that the surface area may increase tenfold before and during the period while bleeding is going on, and that this observation formed a part of the basis of the theory of cement hydration put forward by scientists in the Soviet Union.

In my opinion, there is no conflict between the large increase in specific surface area reported by the Soviet scientists and the deduction from our bleeding tests that the size, shape, and number of cement particles during the first hour or so is about the same as before the initial reactions occurred. Two different methods of observation are involved, from each of which a value for surface area can be calculated, but the results pertain to different aspects of the system.

Direct observation shows that after the initial reaction with water, the cement grains have become coated with a very thin layer of gel.[1, 2] It is obvious that during the period of bleeding the water flows over the surface of the coating and not through it. Since the coating is thin, relative to the diameter of the grain, it is not surprising that the specific surface area calculated from rate of bleeding is practically the same as that calculated from the rate of sedimentation in a nonreactive fluid. Since the presence of the coating has practically no effect, the structure of the coating is likewise of no importance with respect to the results of this method of observation. The calculation of surface area is based on the magnitude of the viscous drag of the particles, and viscous drag depends on the over-all dimensions of the individual particles, including their coatings, and on the concentration of the particles.

On the other hand, the Soviet Union scientists estimated surface area from the interaction between the solid phases in the system and certain ions in the aqueous solution in contact with the solids. Such a method, or a method based on the interaction of the dry solid with individual atoms of water vapor, depends almost entirely on the composition of the coating on the cement grains. Various methods of observation, including the electron microscope, reveal that the coating is composed of particles of the same order of size as those composing the cement gel produced by later stages of the cement reaction, which means that the specific surface area of these particles is ca. 200 m²/g. Therefore, the presence of a small amount of gel coating on the grains is revealed by a large area available to water vapor when the specimen is dry, or to ions when the specimen is in contact with an aqueous solution.

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[1] W. Czernin, A few unsolved problems of cement hydration, this Symposium, paper V-S3.

[2] L. E. Copeland and Edith G. Schulz, Discussion of The microstructure of hardened paste, this Symposium, paper V-2.

Let us consider, for example, a cement having a specific surface area of 3,000 cm^2/g as indicated by viscous drag in water. If 1 percent of the cement has become reacted in forming the coating on the grains, and if the specific surface area of the particles composing the coating is 200 m^2/g by dry weight, the specific surface area as measured by water vapor adsorption would be 24,600 cm^2/g. Thus, the measurement based on adsorption would indicate about eight times as much surface area per gram of cement as would the measurement based on viscous drag. A calculation based on ion exchange should indicate about the same ratio.

From such considerations as those above, it is not clear why our friends in the Soviet Union choose to explain the increase in surface area occurring during the initial stages of reaction by supposing that the cement grains become shattered and dispersed by the physical action of water, and that the new surface area is due to such a breakup of cement grains.

Discussion

A. J. Gaskin

The fact that early reactions in cement pastes may be strongly influenced by adsorption and surface effects is well substantiated. Selective adsorption of ions from the solution phase, and the formation of solid coatings of precipitated reaction products are typical factors determining consistency and setting time.

It may be of interest to mention the influence of another type of surface effect in this connection, i.e., the adsorption of gases by cements in the dry state.

Some of the results of CO_2 and water-vapor adsorption have been discussed in the literature on false set, but there seems to be no record of the effects of adsorption of acid gases such as sulfur dioxide.

It has been noted in the course of our work on false set that adsorption of SO_2 by cements can be very rapid and extensive, some cements taking up as much as 0.1 percent by weight of this gas in a period of a few minutes.

The results of SO_2 adsorption have been somewhat unexpected, in that the very small amounts present in relation to the total sulfate content of the cements have been very effective in retarding certain early reactions.

The least surprising effect found has been the elimination of air-setting tendencies for short periods of storage in a humid atmosphere. This was shown by compacting treated and control cements into blocks and storing these in a damp enclosure on concrete slabs at ground level. The control blocks gained considerable strength over a period of 2 weeks, but the SO_2-treated test pieces remained friable and weak.

The extension of the times for initial and final set which can be brought about by SO_2 treatment of some cements has been less understandable. With some cements, no great changes could be induced by exposure to SO_2, but with others, not greatly different in composition, the adsorption of 0.1 percent of SO_2 by weight caused great delays in setting and hardening. Final set was less affected than initial set, but even so could be extended to twice the normal time. Initial set times could be trebled when sensitive cements were treated with SO_2 especially in the presence of water vapor, when more of the gas is taken up.

Strengths at 3 days were reduced by as much as 10 percent by SO_2 treatments, but 7-day strengths were normal, and one treated cement showed an appreciable gain in strength at 28 days.

The effects of SO_2 on cements are of theoretical rather than practical interest, as it is unlikely that sufficient exposure to the gas will occur under normal manufacturing conditions to become significant. Perhaps the only source of SO_2 generally encountered would be the sulfides present in some clinkers. A little sulfide is common in rotary kiln products, and greater quantities appear in some shaft kiln clinkers. Oxidation of sulfide to SO_2 and immediate transfer of this gas to cement particle surfaces could conceivably occur during cement milling. The intergrinding of portland cement and slag products could similarly result in SO_2 production from sulfide impurities in the slags, and subsequent adsorption of the gas on the cement.

It is of interest to note that SO_2 in the adsorbed state does not persist long in a form which can be leached off the cement and estimated as sulfite. The surface components of cement particles appear to catalyze the oxidation of the gas, or any calcium sulfite produced, and only soluble sulfate can be determined after aeration of the cement. The specific effects of the SO_2 treatment still persist after aeration. Certain other acid gases have essentially similar effects, particularly SO_3 and acetic anhydride.

Acetic acid vapor has been reported to be a useful agent in promoting free flow of cement powder, and in reducing "air-setting" effects. Acetic anhydride is a particularly potent and convenient material which may be used to gain the same results. It is easy to introduce, as spray or vapor, into a cement mill, and is more evenly taken up by cement particles. Apparently it is first adsorbed in a physico-chemical sense, then fixed by cement particle surfaces capable of catalyzing the hydration of the compound and supplying the water required to give the acid, then calcium acetate.

A side-effect of acetic anhydride additions to ball mills is the intense ball-cleaning action produced. A "coated" mill may be cleaned within a very short period by introduction of about 0.05 percent–0.1 percent of the anhydride in vapor form. Continued introduction of this amount of the agent results in the production of cement with depressed 3-day strength.

Discussion

S. A. Greenberg and V. S. Mehra

Dr. Greene makes reference to the compositions of the aqueous phases in contact with portland cements. Recent work in this laboratory makes it possible to explain quantitatively the factors that control the compositions.

Le Chatelier [1] in the last century proposed that portland cement hydrated by solution reactions and precipitation of the products from solutions. A discussion of the mechanism of hydration of C_3S is given in a symposium paper by Brunauer and Greenberg [2]. Recently Budnikov and Kravchenko [3] reported an experimental investigation of the mechanism of hydration of C_3A. Similarly $CaSO_4 \cdot \frac{1}{2}H_2O$ has been shown by Ketelaar and Heijmann [4] to hydrate in two steps: (1) solution of sulfate and (2) crystallization of gypsum from solution. Steinour [5] has proposed that after portland cement comes in contact with water the silicate and aluminate products immediately precipitate so that very little silicon or aluminum remain in solution. In this discussion the solution properties of C_3S, C_3A, and calcium sulfates will be emphasized because these are the most important solution processes in the initial stages of hydration.

It is important to our knowledge of the mechanism by which portland cement hydrates to know whether the aqueous solutions in contact with portland cements are saturated, supersaturated, or unsaturated with respect to products of hydration. This information may be obtained by evaluating the activity solubility products from a knowledge of the compositions of the solutions and the Debye-Hückel [6] equations for calculating activity coefficients. The compositions of some solutions were determined experimentally in this laboratory, but most of the data were taken from the literature. It cannot be assumed that the ion products one obtains for the different species in cement solutions represent equilibrium states. The ion products in the hydrating systems, therefore, were compared with the solubility products for pure systems under equilibrium conditions. In this manner it was possible to determine the degree of saturation of each species. An overall picture of the reactions is given in table 1.

The principal active components of the clinker in the initial stages are C_3S and C_3A. Gypsum plus the hemihydrate, and the alkali sulfates, dissolve immediately. (Dehydrated forms of calcium sulfate are formed during the grinding operations.) The sulfate species react rapidly with C_3A to form sulfoaluminate. Most alkali in cement is present as alkali sulfates; however, alkali is found also to be present in solid solution in some of the phases.

In the solutions there may be found immediately after mixing cement and water the following species: Ca^{++}, OH^-, monosilicic acid H_4SiO_4 and its ions, aluminic acid H_3AlO_3 and its ions, SO_4^{--}, K^+, and Na^+.

According to recent work, the hydrated calcium silicates exhibit variable compositions [2]. Greene reports that in the early stages of hydration the high sulfate sulfoaluminate is found. According to Greene, $4CaO \cdot Al_2O_3 \cdot 13H_2O$ forms from C_3A in the absence of gypsum. Crystalline calcium hydroxide is usually present in the early stages.

Equilibrium Solubility Products

Calcium Hydroxide

The activity solubility product for calcium hydroxide, evaluated in recent work by Greenberg and Copeland [9], is

$$K_{sp_1} = a_{Ca^{++}} a^2_{OH^-} \tag{1}$$

where a refers to the activity of each species. The activity of each ion, a_i, is equal to the product of the concentration c_i in moles/liter and the activity coefficient f_i. The concentration of each species is known from solubility data. The activity coefficients were calculated by means of the Debye-Hückel equation

$$-\log f_i = \frac{AZ_i^2 \mu^{\frac{1}{2}}}{1 + d_i B \mu^{\frac{1}{2}}} \tag{2}$$

where A and B are constants, d_i is the diameter of the ion, Z_i is the valence of the ion, and μ is the ionic strength. It is apparent that the activity coefficient f_i may be evaluated if the ionic strength of the solution is known.

The value of K_{sp_1} for calcium hydroxide is 9.1×10^{-6} (pK 5.04, where $p\text{K} = -\log \text{K}$) at 25 °C. It is well known, however, that supersaturated solutions of calcium hydroxide will be stable for relatively long periods of time [10].

TABLE 1. *Reactions at early stages*

Early reactants of portland cement	Solution	Products
C_3S C_3A $CaSO_4 \cdot \frac{1}{2}H_2O, CaSO_4 \cdot 2H_2O$ Na_2SO_4, K_2SO_4 CaO, Na_2O, K_2O	Ca^{++}, OH^- $H_4SiO_4, H_3SiO_4^-, H_2SiO_4^{--}$ $H_3AlO_3, H_2AlO_3^-, HAlO_4^{--}$ SO_4^{--} K^+, Na^+	$3CaO \cdot 2SiO_2 \cdot 3H_2O$ $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$ $4CaO \cdot Al_2O_3 \cdot 13H_2O$ $Ca(OH)_2$ $CaSO_4 \cdot 2H_2O$

Gypsum—$CaSO_4 \cdot 2H_2O$

The K_{sp_2} for gypsum,

$$K_{sp_2} = a_{Ca^{++}} a_{SO_4^{--}} \qquad (3)$$

was found to be 4.43×10^{-5} (pK 4.35) at 25 °C from solubility data [11] (2.06 g $CaSO_4$/1000 g H_2O) and an evaluation of the activity coefficient. Latimer [12] previously estimated the value to be 2.5×10^{-5} from thermodynamic data. The first value will be used since it is based primarily on experimental data.

Hydrated Calcium Silicate

The solubility product of a hydrate prepared from calcium oxide, silica and water at temperatures below 100 °C

$$K_{sp_3} = a_{Ca^{++}} a_{H_2SiO_4^{--}} \qquad (4)$$

was evaluated [2, 13] to be 10^{-7} (pK 7.0) at 25 °C. However, the K_{sp_3} in hydrating C_3S-water mixtures exhibited values of $10^{-6.8}$ (pK 6.8). It is believed that the latter value is for the quasi-equilibrium existing in these systems. It may be proposed that the C_3S-water systems are slightly supersaturated with respect to calcium silicate. Perhaps, on the other hand, the thin crystals of hydrate formed in the C_3S-water mixtures are a little more soluble than the crystals prepared from calcium oxide, silica, and water, which exhibit a lower solubility.

Hydrated Calcium Aluminates

The nature of the aluminic acid in solution is not known. Usually we assume that aluminum oxides exhibit an octahedral structure, AlO_6. For the sake of convenience in this discussion, aluminic acid is given the arbitrary formula H_3AlO_3. The ions $H_2AlO_3^-$ and $HAlO_3^{--}$ are formed from this acid. The acidity constants for aluminic acid, $pK_1 = 9.3$ and $pK_2 = 11.9$, have been evaluated in this laboratory.

Table 2 gives solubility data for hydrated calcium aluminates as obtained by Wells, Clarke, and McMurdie [14]. For both types of hydrates, the aluminum concentrations are roughly inversely proportional to the calcium ion concentrations. Instead of attempting determinations of accurate solubility products, it was decided to investigate the constancy of the following ion products suggested by the experimental relationships.

$$K_{sp_4} = a_{Ca^{++}} a_{HAlO_3^{--}} \qquad (5)$$

$$K'_{sp_4} = a_{Ca^{++}} a^2_{H_2AlO_3^-} \qquad (6)$$

When all the aluminum in solution is assigned to each of the two anions, these equations give the K_{sp_4} and K'_{sp_4} values shown in table 2. It will be seen that the values for pK_{sp_4} are somewhat more constant than those for pK'_{sp_4}. On the basis of the approximate constancy of K_{sp_4}, this product will be used as an empirical guide in lieu of an accurate solubility product. Owing to its simplified nature, it increases somewhat with increase in the calcium hydroxide content of the solution.

TABLE 2. *Solubilities in system* CaO-Al_2O_3-H_2O *at 21 °C*

(Wells, Clarke, McMurdie [14])

Concentrations moles/liter×10³		Solid phase in equilibrium	pK_{sp_4} [a]	pK'_{sp_4} [b]
Al_2O_3	CaO			
1.37	3.38	Stable isometric, C_3A aq	5.42	7.86
1.28	3.70	Stable isometric, C_3A aq	5.42	7.90
0.881	3.96	Stable isometric, C_3A aq	5.55	8.19
.392	4.55	Stable isometric, C_3A aq	5.87	8.86
1.43	9.65	Metastable hexagonal cal. alum.	5.12	7.52
0.94	10.4	Metastable hexagonal cal. alum.	5.29	7.87
.656	12.4	Metastable hexagonal cal. alum.	5.41	8.14
.412	13.0	Metastable hexagonal cal. alum.	5.61	8.53
.274	14.5	Metastable hexagonal cal. alum.	5.75	8.85

[a] $K_{sp_4} = a_{Ca^{++}} a_{HAlO_3^{--}}$.

[b] $K'_{sp_4} = a_{Ca^{++}} a^2_{H_2AlO_3^-}$.

Hydrated Sulfoaluminates

Because the solubility product of a complex sulfoaluminate might be difficult to determine, for the sake of convenience K_{sp_4} was used as an index of the solubility. Table 3 lists the results of studies of the solubilities of the high sulfoaluminate phases by Jones [15, 16] and Takemoto and Suzuki [17]. Table 3 gives the concentrations in moles/liter of calcium, sulfate, aluminum, alkali (K+Na), and hydroxyl ions. The solid phases coexisting with the solutions are listed next. In the final columns, pK_{sp_1}, pK_{sp_2}, and pK_{sp_4} are given.

In table 3 it may be noted that the pK_{sp_4} values are relatively constant in the presence of alkali, and average 7.37. There is an indication from the earlier work of Jones [15] (rows 1 and 2, table 3) that the K_{sp_4} values are about ten times larger in the absence of alkali. No satisfactory explanation could be found for so great a difference.

In mixtures of the high sulfoaluminate, calcium hydroxide, and gypsum, the pK_{sp_1} and pK_{sp_2} values for the latter two compounds may be seen in table 3 to satisfy approximately the equilibrium conditions. In the presence of the relatively insoluble high sulfoaluminate the compositions of the solutions are fixed only by the solubilities of the calcium hydroxide and gypsum. This could be verified by comparing the data of Takemoto and Suzuki [17] with those of Hansen and Pressler [18] whose results are discussed in the next section.

Mixtures of Gypsum, Calcium Hydroxide, and Alkali Hydroxides

A very interesting set of data on the equilibrium solubilities of these mixtures was reported by Hansen and Pressler [18]. In table 4 the experi-

Table 3. *System* $CaO–Al_2O_3–CaSO_4–H_2O$ *and alkalies* (25 °C)

Reference	Concentrations, moles/liter x 10^3					Coexisting solid phases	$pK_{sp\_}$	pK_{sp_2}	pK_{sp_4}
	CaO	SO_3	Al_2O_3	2(K+Na)	2(OH)				
15	31.6	12.3	0.06	----	19.3	$C_3A·3CaSO_4aq$ Gypsum $Ca(OH)_2$	5.03	4.28	6.29[a]
15	1.91	0.18	.01	----	18.9	$Ca(OH)_2$ $C_3A·3CaSO_4aq$ C_3AH_6	5.09	----	6.16[a]
16	16.45	66.0	.02	89.1	39.5	$C_3A·3CaSO_4aq$ Gypsum $Ca(OH)_2$	4.86	4.12	7.34
16	0.293	0.656	.065	89.1	91.1	$C_3A·3CaSO_4aq$ $Ca(OH)_2$ C_3AH_6	4.82	----	7.49
17	18.6	30.1	.02	42.8	28.6	Gypsum $C_3A·3CaSO_4aq$ $Ca(OH)_2$	4.97	4.24	7.12
17	18.7	36.4	.03	47.2	30.0		4.94	4.19	6.98
17	14.9	71.6	.02	94.7	39.0		4.92	4.14	7.40
17	15.2	81.4	.03	108.6	40.7		4.90	4.12	7.25
17	15.1	118	.03	146.3	45.6		4.87	4.05	7.34
17	15.1	132	.03	159.3	47.6		4.87	4.02	7.37
17	4.3	0	.05	42.1	48.2	$Ca(OH)_2$ $C_3A·3CaSO_4aq$ C_3AH_6	5.07	----	7.27
17	2.0	0	.03	97.7	96.7		4.98	----	8.06
17	1.9	0	.15	146.2	147		4.74	----	7.52

Average (excluding first two values) 7.37

[a] Values for alkali-free solution.

mental data and the pK_{sp_1} and pK_{sp_4} values for calcium hydroxide and gypsum are listed. The values may be seen to be approximately the same as the equilibrium values of 5.04 and 4.35 for calcium hydroxide and gypsum, respectively.

Table 4.—*Solubilities at 30 °C of calcium hydroxide and gypsum in dilute alkali solution.*
(Hansen and Pressler [18])

Concentrations, moles/liter				Coexisting solid phases	pK_{sp_1}	pK_{sp_2}
CaO	SO_3	OH	K_2O+Na_2O			
0.0298	0.0141	0.0419	0.0053	$CaSO_4·2H_2O$ and $Ca(OH)_2$ in each case.	4.97	4.29
.0256	.0191	.0529	.0199		4.87	4.27
.0228	.0223	.0523	.0256		4.93	4.26
.0226	.0219	.0514	.0250		4.93	4.27
.0214	.0253	.0524	.0301		4.95	4.23
.0198	.0303	.0602	.0406		4.90	4.23
.0185	.0373	.0618	.0497		4.94	4.21
.0184	.0395	.0698	.0561		4.84	4.20
.0180	.0425	.0711	.0599		4.85	4.20
.0174	.0544	.0771	.0756		4.84	4.16

Portland Cement-Water Mixtures

Many investigations [17, 19–22] have been conducted of the compositions of the aqueous phases in contact with hydrating portland cement pastes of normal w/c ratios. In order to substantiate the reported data, a few experiments were performed in this laboratory on Type I cements. Several problems exist in such study and will be briefly discussed initially.

Two methods for separating the aqueous phase from the solids have been employed: (1) centrifugation and (2) pressure filtration. For various reasons the second procedure was adopted in this laboratory.

The methods used for the analyses of calcium, silicic acid, aluminic acid, sulfate, alkalies, and *p*H have not been clearly presented in many studies reported in the literature [20]. In the study conducted in this laboratory, standard methods are being followed. Calcium is determined by titration with versene [24]. The molybdenum blue method for silicic acid [25] is suitable for small concentrations of silicic acid. For the determination of aluminum, the photometric procedure with 8-hydroxyquinoline is followed [26, 27]. The *p*H values are measured with the glass and calomel electrodes.

Tables 5–7 summarize the results of several studies of the composition of the aqueous phases in contact with portland cements. Table 5 lists the data for clinkers alone. In table 6 the results for clinkers plus calcium sulfates are given. In table 7 may be found the data for mixtures of clinkers and several additives excluding calcium sulfates. In the tables the following data are listed in order: (1) time of hydration, (2) *p*H, (3)–(8) the concentrations of hydroxyl, sulfate, calcium, sodium plus potassium, aluminum, and silicon; in the last four columns are the pK_{sp_1}, pK_{sp_2}, pK_{sp_3}, and pK_{sp_4} values.

In the sections which follow, the compositions of the aqueous phases as a function of time are discussed with respect to the equilibrium solubilities of each solid species.

Calcium Hydroxide

In most cases the pK_{sp_1} values may be seen to be less than the equilibrium 5.04 value immediately after cement is mixed with water. These solutions continue to remain supersaturated thereafter.

Aeration of the clinker alone for 24 hours before mixing it with water causes the solutions to become unsaturated with respect to calcium hydroxide (table 5). Similar results (table 6) are found on the aeration of portland cement containing gypsum. The aqueous phases in contact with ground clinker to which hemihydrate was added may be seen in table 6 to exhibit slightly unsaturated solutions.

The addition of alkali carbonates to cement [17] (table 7) does not appreciably affect the pK_{sp_1} values. It is interesting to observe that additions of small amounts of calcium chloride and sucrose to clinkers do not reduce the degree of supersaturation of the solutions compared to normal cement solutions.

The ratio of concentrations of calcium to twice the hydroxyl ion concentration, $(Ca^{++})/2(OH^-)$, is affected by two factors. First is the amount of alkali present in the clinker and second is the addition of calcium sulfates to the clinker. Increased amounts of alkali decrease this ratio (see tables 5, 6, and 7 for data). The addition of calcium sulfates to clinker increases the above ratio appreciably. This can be best seen from the comparison of the results on the same clinkers in tables 5 and 6.

Gypsum—$CaSO_4 \cdot 2H_2O$

It may be observed in table 6 that the pK_{sp_2} values are initially less than the equilibrium value and constantly increase with time. Thus for the most of the early hydration time the solution after initial supersaturation is close to saturation. The solutions become supersaturated in the initial stages because of the presence of the calcium sulfate hemihydrate and, secondarily, alkali sulfates. Aqueous phases in contact with clinker alone exhibit unsaturated solutions, as shown in table 5 by the pK_{sp_2} values, which are much greater than the saturation value. In table 7 it can be seen that the addition of calcium chloride and sucrose to clinker produces the same results as with clinker alone.

Calcium Silicates

The pK_{sp_3} values should be about 6.8–7.0 under equilibrium conditions. It is apparent from the results that within experimental error the pK_{sp_3} values for aqueous solutions in contact with cements and clinker (tables 5–7) indicate that the solutions are essentially saturated with calcium silicate. The addition of calcium chloride or sucrose to ground clinker does not appreciably change this situation. Aeration (tables 5, 6) does not cause any noticeable difference in K_{sp_3} values.

Calcium Aluminates

The equilibrium pK_{sp_4} value of 7.37 for calcium aluminate when calcium sulfoaluminate is present was used as an indication of the equilibrium solubility. For cement aqueous solutions the values were slightly lower, showing supersaturation. Several reasons may be offered for this behavior. Perhaps supersaturation exists because C_3A dissolves more rapidly (to give a supersaturated solution) than the rate at which the sulfoaluminate precipitates from solution. Another reason may be that hydrated calcium aluminates are present which exhibit a higher solubility than the high sulfate sulfoaluminate.

TABLE 5. *Compositions of aqueous phases in contact with ground clinkers*

Time	*p*H	Concentrations, moles/liter×10^3						pK_{sp_1}	pK_{sp_2}	pK_{sp_3}	pK_{sp_4}
		$2OH^-$	SO_4^{--}	Ca^{++}	$2(Na+K)$	Al_2O_3	SiO_2				
Stein [22]—Normal consistency, 18 °C											
10 min	------------	78.8	0.512	4.7	74.6	0.324	0.266	4.72	6.57	6.89	6.48
Kalousek, Jumper, and Tregoning [19]—Clinker 1, w/c=0.35, 25 °C, low alkali											
7 min	12.68	31.5	0.25	30.8	1.45	0.020	------------	4.53	5.94	------------	6.75
120 min	12.72	34.5	.38	26.2	11.0	.039	------------	4.53	5.85	------------	6.53
Kalousek, Jumper, and Tregoning—Clinker 5, w/c=0.35, 25 °C, high alkali											
7 min	13.19	106	35.1	2.14	142	0.127	0.482	4.91	5.31	7.18	7.47
120 min	13.39	164	1.63	2.67	162	.049	.250	4.44	6.56	7.38	7.78
Takemoto and Suzuki [17]—w/c=0.27, 20 °C											
30 sec	13.38	120	8.7	1.7	137.1	------------	0.26	4.87	5.97	7.50	------------
3 min	13.45	140	0.4	1.7	138.3	------------	.25	4.74	7.32	7.52	------------
8 min	13.45	140	.5	1.4	138.3	------------	.23	4.74	7.31	7.64	------------
30 min	13.45	142	.6	1.8	138.3	------------	.18	4.70	7.12	7.64	------------
[a] 60 min	13.45	141	.9	1.7	143.2	------------	.18	4.73	6.97	7.67	------------
[b] 323 min	13.45	143	.6	1.5	143.2	------------	.24	4.78	7.20	7.59	------------
Takemoto and Suzuki—w/c=0.28, 20 °C, 24 hr aeration											
30 sec	12.80	31.4	57.3	9.1	75.5	------------	0.12	5.27	4.38	7.06	------------
3 min	12.96	45.6	29.6	1.5	75.5	------------	.20	5.67	5.37	7.54	------------
[a] 7 min	13.25	88.0	1.0	1.1	86.1	------------	.17	5.22	6.96	6.73	------------
[b] 40 min	13.29	98.4	0.4	0.3	91.0	------------	.15	5.70	7.94	8.37	------------

[a] Initial set. [b] Final set.

Table 6. *Compositions of aqueous phases in contact with clinker plus calcium sulfates*

Time	pH	Concentrations, moles/liter×10^3						pK_{sp_1}	pK_{sp_2}	pK_{sp_3}	pK_{sp_4}
		$2OH^-$	SO_4^{--}	Ca^{++}	2(Na+K)	Al_2O_3	SiO_2				
Stein [22]—Clinker+4% gypsum, normal consistency, 18 °C											
10 min	------------	47.6	69	16.5	99.8	1.10	0.266	4.81	4.13	6.42	5.63
60 min	------------	57.4	64.9	16.4	105.9	0.628	.266	4.65	4.16	6.55	5.88
Kalousek, Jumper, and Tregoning [19]—Clinker 1+gypsum (1.75% SO_3), w/c=0.35, 25 °C, low alkali											
7 min	12.62	27	12.0	39.6	1.29	0.029	0.033	4.63	4.24	6.80	6.55
120 min	12.66	30.5	13.1	41.0	5.5	.039	.033	4.51	4.20	6.79	6.42
Kalousek, Jumper, and Tregoning [19]—Clinker 5+gypsum (1.75% SO_3), w/c=0.35, 25 °C, high alkali											
7 min	12.91	55	97	17.1	137	0.049	0.083	4.64	4.05	7.12	7.05
120 min	13.04	74	93	19.4	150	.069	.067	4.34	4.03	7.18	6.87
Takemoto and Suzuki [17]—Commercial cement A (1.08% SO_3), w/c=0.24, 20 °C											
30 sec	12.73	27.1	149	27.5	141.1	------------	------------	4.88	3.73	------------	------------
3 min	12.88	38.0	115	25.4	142.1	0.09	0.3	4.81	3.83	6.41	6.64
8 min	12.89	39.0	111	11.7	143.1	------------	.1	5.11	4.16	7.21	------------
30 min	12.94	43.3	107	10.4	144.2	.10	.2	5.07	4.23	6.96	6.96
60 min	12.93	42.0	112	9.5	143.2	------------	.2	5.13	4.23	7.00	------------
[a] 88 min	13.08	59.8	91.1	6.3	149.5	------------	.2	4.99	4.49	7.15	------------
[b] 127 min	13.23	85.1	59.7	3.7	153.2	------------	.3	4.89	4.88	7.18	------------
Takemoto and Suzuki [17]—Commercial cement B (1.51% SO_3), w/c=0.26, 20 °C											
30 sec	12.82	31.6	119	29.4	116.9	------------	0.08	4.79	3.76	6.94	------------
3 min	12.91	40.7	94.9	15.0	118.7	------------	.12	4.94	4.09	6.99	------------
8 min	12.93	42.1	91.5	14.3	119.1	------------	.09	4.92	4.12	7.13	------------
30 min	12.97	47.0	88.9	14.4	120.2	------------	.08	4.83	4.14	7.18	------------
[a] 95 min	13.00	49.8	98.2	12.9	127.9	------------	.06	4.84	4.15	7.36	------------
[b] 170 min	12.96	45.6	99.0	12.3	133.2	------------	.08	4.94	4.17	7.26	------------
Takemoto and Suzuki—Cement A, 24 hr aeration w/c=0.25, 20 °C											
30 sec	12.59	19.6	142	38.4	126.3	------------	0.06	5.23	3.59	6.97	------------
3 min	12.61	20.2	142	30.9	129.9	------------	.06	5.29	3.68	7.05	------------
8 min	12.81	32.2	111	11.8	129.9	------------	.06	5.25	4.14	7.41	------------
30 min	12.89	38.7	107	11.3	133.1	------------	.06	5.11	4.18	7.43	------------
60 min	12.93	42.5	103	10.3	132.2	------------	.06	5.07	4.24	7.47	------------
[a] 250 min	13.11	64.6	73	2.78	134.6	------------	.08	5.24	4.90	7.86	------------
[b] 320 min	13.39	122	40.5	1.27	139.1	------------	.10	5.03	5.50	8.11	------------
Takemoto and Suzuki—Clinker + hemihydrate (1.5% SO_3), w/c=0.25, 20 °C											
30 sec	12.91	40.8	149	38.8	140.2	------------	0.09	4.60	3.59	6.81	------------
3 min	12.66	22.8	148	29.7	140.5	0.1	.22	5.21	3.69	6.52	6.56
8 min	12.79	31.0	124	12.6	141.3	------------	.18	5.28	4.10	6.93	------------
30 min	12.82	32.8	117	9.1	142.0	.1	.12	5.36	4.25	7.24	7.01
60 min	12.93	42.1	123	10.2	145.7	------------	.11	5.11	4.19	7.24	------------
[a] 110 min	12.95	44.7	123	10.4	157.4	------------	.14	5.06	4.19	7.14	------------
[b] 197 min	12.86	36.5	115	9.2	158.4	------------	.16	5.28	4.27	7.13	------------
Steinherz and Welcman [20]—Cement A (0.9% $CaSO_4$), cement B (2.9% $CaSO_4$), cement C (3.4% $CaSO_4$) w/c=1.5, 20 °C											
(A) 1 min	12.6	28.3	28.9	21.5	35.6	0.69	0.665	4.97	4.20	5.83	5.62
(B) 1 min	12.4	24.5	71.0	46.1	49.2	------------	.164	4.93	3.66	6.29	------------
(C) 1 min	12.5	19.9	68.5	65.0	23.4	.70	1.00	4.96	3.53	5.37	5.26
Portland Cement Assoc. [23]—Type I, w/c=0.5, 25 °C											
10 min	12.76	39	17.5	30.9	25.6	0.005	0.027	4.46	4.24	7.06	7.50
30 min	12.40	17.1	39.5	31.2	25.3	.006	.072	5.20	3.93	6.67	7.48
70 min	12.90	105	10.4	32.7	25.0	.005	.053	4.25	4.55	6.84	7.56

[a] Initial set. [b] Final set.

Discussion

The principal source for the presence of calcium in solution is C_3S. The C_3A produces in solution the same number of ions that precipitate out in the high sulfate sulfoaluminate. Since the aluminum concentration is low, it may be concluded that C_3A does not increase the concentration of calcium appreciably. In addition the calcium sulfates present in normal cements contribute to the presence of calcium in solution. Free calcium oxide would be expected to contribute very little to the solution since it is probably dead-burned and therefore even the available oxide will be slow to react.

The hydroxyl ions in solution are produced from the hydration of C_3S and alkali. The sources of sulfate in solution are gypsum, hemihydrate and alkali sulfates. It is apparent that the immediate supersaturation of the solution must be caused by hemihydrate which is many times more soluble than gypsum. Gypsum with clinker, or clinker alone, will not produce supersaturation.

Calcium may be removed from the solution by the formation of hydrated calcium silicates, calcium aluminates, calcium sulfoaluminates, calcium hydroxide, and calcium sulfate. Hydroxyl ions are removed as calcium hydroxide. Sulfate ions are precipitated from the solutions as sulfoaluminate. In the presence of hemihydrate, false or plaster set is occasionally noticed which is usually interpreted as an indication of the formation of gypsum crystals.

Relatively high alkali content cements, by increasing the hydroxyl ion concentration, will accelerate the crystallization of calcium hydroxide from solution. The alkali sulfates present in cement or clinker may cause the precipitation of gypsum by forming supersaturated solutions; the resultant decrease in calcium ion concentration permits a higher hydroxyl ion content in the solution. Therefore, cements high in alkali sulfates may exhibit false set because of the formation of gypsum crystals.

In the initial stages of hydration the *p*H values of the aqueous phases are from 12.6 to 12.9. In the presence of high alkali cements the *p*H values after one hour of hydration may rise to approximately 13.2. It is clear from the results of Takemoto and Suzuki [17] and Kalousek, Jumper, and Tregoning [19], that high alkali clinkers produce aqueous phases with *p*H values up to 13.45. Apparently calcium sulfate reduces the hydroxyl ion concentration of solutions by removing calcium hydroxide. Reduction in *p*H is much more noticeable when calcium chloride is added to clinker. Although the solutions are usually supersaturated with respect to calcium hydroxide, any increase in calcium or hydroxyl ion concentration will accelerate the precipitation of calcium hydroxide.

The results of the present study are in accord with the solution theory for the hydration of ce-

TABLE 7. *Compositions of aqueous phases in contact with ground clinker plus additives*

Time	*p*H	Concentrations, moles/liter×10^3						pK_{sp_1}	pK_{sp_2}	pK_{sp_3}	pK_{sp_4}
		$2OH^-$	SO_4^{--}	Ca^{++}	$2(Na+K)$	Al_2O_3	SiO_2				
Takemoto and Suzuki [17]—Commercial cement A+alk. carbonates (0.2% K_2O, 0.2% Na_2O) w/c=0.26, 20 °C											
30 sec	12.93	42.5	297	18.8	327	------------	0.04	5.02	3.78	7.65	------------
3 min	12.87	37.2	320	27.8	327	------------	.04	4.97	3.59	7.50	------------
[a] 8 min	13.78	301	67.1	0.3	357	------------	2.70	5.06	6.16	7.55	------------
[b] 12 min	13.81	323	63.4	.3	375	------------	.98	5.01	6.20	8.01	------------
Kalousek, Jumper, and Tregoning [19]—Clinker 1+$CaCl_2$ (1.46%), w/c=0.35, 25 °C											
7 min	12.03	41	0.125	366	4.84	------------	0.020	4.34	5.84	------------	6.35
120 min	12.16	50	------------	294	14.52	------------	.020	4.22	------------	------------	6.39
Kalousek, Jumper, and Tregoning—Clinker 5+$CaCl_2$ (1.46%), w/c=0.35, 25 °C											
7 min	12.24	24	0.50	204	152	0.069	0.050	4.41	5.44	6.44	5.99
120 min	12.29	23	.25	169	171	.059	.033	4.51	5.80	6.67	6.12
Kalousek, Jumper, and Tregoning—Clinker 1+sucrose (0.05%), w/c=0.35, 25 °C											
7 min	12.64	56	0.25	28.2	1.45	0.029	0.033	4.65	5.95	6.83	6.45
120 min	12.72	68	.38	25.3	12.1	.069	.037	4.55	5.85	6.86	6.29
Kalousek, Jumper, and Tregoning—Clinker 5+sucrose (0.05%), w/c=0.35, 25 °C											
7 min	13.31	154	1.88	0.714	155	2.78	0.466	5.06	7.06	7.66	6.59
120 min	13.43	183	1.00	2.32	184	0.127	.333	4.43	6.87	7.35	7.47

[a] Initial set. [b] Final set

ment first proposed by Le Chatelier. Apparently calcium hydroxide crystallizes from a very supersaturated solution. However, no gypsum crystallizes from the solutions supersaturated with calcium and sulfate ions, except perhaps in the very early stages. False set may be evidence for the formation of gypsum. Almost all of the sulfate is found eventually in the very insoluble sulfoaluminates.

Both the silicate and aluminate phases are in contact with slightly supersaturated solutions. This is evidence that both the highly soluble C_3S and C_3A, after initial rapid reaction, react slowly by a diffusion mechanism. It may be concluded from these results that the rate of crystallization from solution is much more rapid than the slow hydration reactions which proceed by a diffusion mechanism through the layer of hydration products deposited on the unreacted portland cement. Therefore, the later rate of crystallization is controlled by the slow hydration reactions.

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Closure

Kenneth T. Greene

Dr. Hansen's suggestion that the coherence of pastes of quartz powder may result primarily from chemical rather than physical forces is entirely appropriate and strengthens the present author's belief that an intensive study of particle surfaces and the manner in which they may influence the properties of fresh portland cement pastes would be very valuable. It seems likely that some of the variable behavior of cements which appear to be very similar chemically and physically when judged by our present analytical methods may stem from differences of surface condition which we are unable at present to detect or measure.

I am indebted to Mr. Carlson for providing more recent data on the problem of the existence of calcium silicoaluminates corresponding to the formulas $3CaO \cdot Al_2O_3 \cdot CaSiO_3 \cdot 12H_2O$ and $3CaO \cdot Al_2O_3 \cdot 3CaSiO_3 \cdot 30\text{-}32H_2O$. The best evidence at present thus indicates that the occurrence of $3CaO \cdot Al_2O_3 \cdot CaSiO_3 \cdot 12H_2O$ is unconfirmed, while the existence of $3CaO \cdot Al_2O_3 \cdot 3CaSiO_3 \cdot 30$-$32H_2O$ is more likely but not firmly established. A reexamination of some of the original preparations of Flint and Wells, described by Mr. Carlson, suggests that their needle-shaped "silico-aluminate" crystals contained significant amounts of CO_2 as well as SiO_2.

Mr. Powers' discussion deals with an important point which should have been clarified in my paper. I am sure that he is correct in his opinion that there is no conflict between the conclusions of Powers and Steinour from their bleeding experiments and the data of the Soviet investigators, who used a method which would naturally give a different value for surface area since it measures a different thing.

The conclusion which the Soviet scientists draw from their data—namely, that the large increase in measured surface area results from a breakdown of the cement grains into much smaller particles—is another matter, as Mr. Powers points out. It appears that although there is necessarily no conflict regarding the data, there is a fundamental difference in conclusions.

The discussion of Dr. Greenberg and Mr. Mehra is a valuable contribution to our knowledge of the composition of the aqueous phase in the early stages of cement hydration. Studies of this kind are needed for a more complete understanding of the very early reactions and the manner in which they may influence the course of the setting and hardening phenomena as well as other physical properties of the fresh and hardened pastes.

In my original paper I stated that data on the concentration of components in solutions separated from cement pastes less than one minute after mixing are generally lacking. I wish to correct this statement since some results at 30 sec were published by Takemoto and Suzuki (reference 17 of Greenberg and Mehra). It is interesting to note that they show generally about the same concentration of SiO_2 in solution at 30 sec as at 1 min. It may be that this is an indication that the SiO_2 concentration is not much higher immediately after water contact, or it may mean that 30 sec after mixing is still not soon enough to detect such a higher concentration if it actually exists.

These discussers state, "However, no gypsum crystallizes from the solutions supersaturated with calcium and sulfate ions except perhaps in the very early stages. False set may be evidence for the formation of gypsum." I believe that under some circumstances hemihydrate may convert to gypsum in cement pastes without being manifested in a tendency to false set. DTA results obtained in our laboratories have indicated that in some cements, hemihydrate present before mixing converts to gypsum over a period of 10 min or more. These cements often show no false set by standard tests. Perhaps gypsum sometimes forms by crystallization from supersaturated solution and thereby causes false set, whereas at other times it arises by hydration of solid hemihydrate and does not induce false set.

Mr. Gaskin's experience regarding the influence of gases such as SO_2 on the setting behavior of cements is most interesting. Although it may be unlikely, as he says, that sufficient exposure to SO_2 will occur under normal manufacturing operations to become significant, it appears that the effect of different gases in the atmospheres of both kilns and grinding mills needs to receive greater attention than it has. As with the disturbed surfaces, mentioned by Dr. Hansen, adsorption of small amounts of gases and vapors may account for some of the presently unpredictable setting behavior of certain cements.

Paper IV-2. False Set in Portland Cement*

W. C. Hansen

Synopsis

Investigators generally agree that the crystallization of gypsum from cement pastes is the principal cause of false set in commercial cements. This paper reviews the literature on this subject, on the system $CaSO_4 \cdot 2H_2O$–$CaSO_4 \cdot 1/2H_2O$–water vapor, and on the system $CaSO_4 \cdot 2H_2O$–$Ca(OH)_2$–$NaOH$–H_2O.

This review shows that methods based on the stiffening of cement pastes and mortars as measured by the Vicat apparatus and on the sedimentation of slurries in water or other liquids have been used with success in studying the causes of false set. Also, that extracts from a cement paste can be studied to reveal whether or not gypsum is likely to crystallize in that paste. The use of these methods has resulted in investigators concluding that many suggested causes of false set are rarely, if ever, the cause of false set in commercial cements. Results with these methods have also shown that a type of false set can be developed by aeration in cements that do not contain dehydrated gypsum. The action of aeration appears to be one of altering the surfaces of the crystals of the aluminate and the aluminoferrite phases so that the retarding effect of calcium sulfate on the rates of their reaction with water is reduced. This area of the problem of false set requires additional study.

Résumé

On se trouve généralement d'accord sur le fait que la cristallisation du gypse dans les pâtes de ciment est la cause principale de la fausse prise des ciments du commerce. Cet exposé passe en revue ce qui a été écrit à ce sujet, sur le système $CaSO_4 \cdot 2H_2O$–$CaSO_4 \cdot 1/2H_2O$–vapeur d'eau et le système $CaSO_4 \cdot 2H_2O$–$Ca(OH)_2$–$NaOH$–H_2O.

Ce compte-rendu indique que les méthodes basées sur le procès du raidissement des pâtes de ciment et des mortiers tel que l'appareil de Vicat la mesure, et sur la sédimentation des schlamms dans l'eau ou dans des autres liquides, ont été employées avec succès dans l'étude des causes de la fausse prise. Cette revue montre également qu'il est possible d'étudier des fractions de la pâte de ciment dans le but de découvrir si le gypse est susceptible ou non de cristalliser dans cette pâte. Grâce à l'emploi de ces méthodes on conclut que des nombreuses causes de fausse prise proposées sont rarement—peut-être jamais—la cause de fausse prise dans les ciments du commerce. Les résultats que donnent ces méthodes indiquent aussi qu'un type de fausse prise peut se développer par aération dans des ciments qui ne contiennent pas de gypse déshydraté. Il semble que l'aération ait pour effet de modifier les surfaces des cristaux des phases d'aluminate et d'aluminoferrite de telle façon que l'effet retardateur du sulfate de calcium sur les vitesses de leur réaction avec l'eau est réduit. Cet aspect du problème de la fausse prise exige de l'étude supplémentaire.

Zusammenfassung

Die meisten Forscher nehmen an, daß die Kristallisierung des Gipses in Zementmassen der Grund für das falsche Abbinden der Handelszementsorten ist. Der Vortragende bespricht die Literatur, die darüber erschienen ist, über die Systeme $CaSO_4 \cdot 2H_2O$–$CaSO_4 \cdot 1/2H_2O$–Wasserdampf und $CaSO_4 \cdot 2H_2O$–$Ca(OH)_2$–$NaOH$–H_2O.

Man kann sehen, daß die Methoden, die auf dem Steifwerden der Zementpasten und Mörteln beruhen, wie sie mit dem Vicatapparat gemessen werden, und die Sedimentationsmethoden unter Benutzung von Wasser und von anderen Flüssigkeiten, sehr erfolgreich in der Erforschung der Grunde fur das falsche Abbinden benutzt worden sind. Auch kann man Zementpastenextrakte benutzen, wenn man ausfindig machen will, ob Gips vermutlich aus der Masse auskristallisieren wird, oder nicht. Die Anwendung dieser Methoden hat gezeigt, daß viele der angegebenen Möglichkeiten für das Vorkommen der falschen Abbindung für Handelszemente gar nicht in Frage kommen. Man kann das Phänomen auch mit Hilfe einer Belüftung an Zementen hervorbringen, die gar keinen hydratisierten oder unhydratisierten Gips enthalten. Diese Belüftung verändert vermutlich die Oberflächen der Aluminatkristalle und der Aluminoferritphasen, sodaß der Verzögerungseffekt des Kalziumsulfats auf deren Reaktionsgeschwindigkeiten mit Wasser verkleinert wird. Diese falschen Erstarrungserscheinungen müssen noch besser erforscht werden.

Introduction

In recent years, cement technologists have attempted to distinguish between "flash set" and "false set." The first is believed to be a manifestation of the lack of the required amount of sulfate in the cement to repress the rate of reaction of $3CaO \cdot Al_2O_3$ and water sufficiently to give a satisfactory time of set. Usually, in this type of set, the cement paste heats up excessively and reworking of the stiffened paste does not restore the original workability.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Universal Atlas Cement Division of the United States Steel Corporation, Gary, Ind.

False set is generally believed to be a manifestation of the presence in the cement of either calcium sulfate hemihydrate or soluble anhydrite or both, which dissolve rapidly and precipitate as gypsum. In this type of set, the cement paste heats up very little and reworking of the stiffened paste largely restores the original workability.

Attempts have been made to develop tests which would detect quick-setting tendencies in cements. One of these (ASTM C–359 [1] [1]) includes a reworking of a mortar for the purpose of distinguishing between flash and false set. Tests with this method have shown quick stiffening for some cements which contained very little, if any, dehydrated gypsum. (In this paper, the term "dehydrated gypsum" will mean either calcium sulfate hemihydrate or soluble anhydrite or a mixture of the two.) It appears, therefore, that the restoration of workability by reworking does not necessarily show that the stiffening was caused by the precipitation of gypsum.

In the early days of the manufacture of portland cement, it was believed by many that it was necessary to use plaster of Paris to control the set. For example, Meade [2] states "In spite of Le Chatelier's experiments, it has been a theory generally held in this country that gypsum would not retard the set of cement but that the only form of sulfate of lime which would do this is plaster of Paris; and that, where gypsum is ground in with the clinker, this is transformed into plaster of Paris."

Meade made tests with finely ground gypsum, plaster of Paris and dead-burned gypsum added to a powdered clinker with the following results:

Calcium sulfate added	Water used in pats	Initial setting time, Gillmore needle, for type of calcium sulfate indicated		
		Gypsum	Plaster of Paris	Dead-burned gypsum
Percent	*Percent*	*hr:min*	*hr:min*	*hr:min*
0	25	0:02	0:02	0:02
0.5	23	----------	0:05	----------
1.0	23	0:02	0:50	0:06
1.5	23	----------	2:50	----------
2.0	22	2:40	3:00	1:45
3.0	22	2:50	1:45	1:47
4.0	22	----------	0:35	----------
5.0	22	3:15	0:16	2:00
10.0	22	3:00	0:16	1:50
20.0	22	3:20	0:09	2:20

An examination of this table shows that cements with 1 percent of calcium sulfate as gypsum and as dead-burned gypsum had initial setting times of 2 and 6 min, respectively; whereas a cement with that amount of SO_3 added as hemihydrate had an initial setting time of 50 min. This demonstrates what is well known today that, with certain clinkers, the sulfate must get into solution at a very rapid rate to prevent the $3CaO{\cdot}Al_2O_3$ from causing some stiffening of the cement paste. Small amounts of dehydrated gypsum can do this because of the rapid rate at which they dissolve. Larger amounts of gypsum and still larger amounts of natural anhydrite are required to provide sufficient surface for the rapid rate of solution needed to give what might be called a normal initial set.

It seems that it is necessary to recognize that the term "normal initial set" has no definite meaning. If the setting caused by the reaction of $3CaO{\cdot}Al_2O_3$ with water is called flash set, then it is possible to have flash set that varies from severe to very mild, depending upon the extent to which the rate of the reaction of $3CaO{\cdot}Al_2O_3$ with water has been modified. It seems logical to believe that the stiffening caused by mild degrees of flash set can be destroyed by reworking of the paste.

Returning to the data by Meade, one observes that the cement made with plaster of Paris became fast setting when large quantities of plaster of Paris were used. This is a demonstration of the ability of dehydrated gypsum to produce what is now called false set.

There is a third type of quick stiffening that appears to differ from flash set or false set as defined above. This develops when some cements are exposed to the air (aerated) for some periods of time. Some of these cements are known to have contained very little, if any, dehydrated gypsum. Generally, this stiffening can be destroyed by reworking the paste.

Lhopitallier and Stiglitz [3] listed the following suggested causes of false set:

1. $CaSO_4{\cdot}2H_2O+\text{heat}=CaSO_4{\cdot}\frac{1}{2}H_2O$.
2. Action of alkali carbonates contained in cements partially deteriorated by exposure to air.
3. Rapid hydration of a very high proportion of very fine particles of cement.
4. High content of $3CaO{\cdot}Al_2O_3$ in the latter.
5. Coating of gypsum by cement during grinding and the consequent neutralization of the gypsum (formation of lamellae).
6. Very high specific surface of the gypsum.

Lhopitallier and Stiglitz concluded from their experience that items 2 to 6 were not involved in false set. They measured false set by the penetration of the Vicat needle in pastes mixed to normal consistency.

Some of the items mentioned in this introduction will be discussed in more detail in the body of the report. The purpose of this introduction is to point out that this paper will deal with three types of quick stiffening in an effort to clear up one problem that was touched upon in the First International Symposium on the Chemistry of Cement. In his discussion of the papers, Cooper [4] made the following statement: "The question of the setting of cement is somewhat vexed, and I think that more disputes arise between the user, the engineer, and the manufacturer on questions of setting than on any other point. The manu-

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[1] Figures in brackets indicate the literature references at the end of this paper.

facturer tests his cement and gets certain results. A certificate is frequently issued to that effect but the first thing the manufacturer hears is that the cement which took two hours to set when it was tested at the works takes two minutes or two days on the job. In the result, the matter is referred to a third party, who usually obtains quite different results from those of the manufacturer, engineer, architect, or the party using it."

There seems to be no question about dehydrated gypsum being the principal cause of false set in commercial cements. Hence, this paper will be concerned primarily with this phase of the setting problem.

First Use of Calcium Sulfate With Portland Cement

According to Davis [5], portland cement as we know it today probably was manufactured by I. C. Johnson in the plant of White and Son in about 1845. He claims that France and Germany quickly followed Britain and that, by 1875, portland cement of fair quality was being produced on a fairly large scale.

Forsen [6] points out that Scott, in 1857, published a paper on the influence of sulfur-bearing fuels on the strengths of burned lime which resulted in an investigation by Schott (1871) of the influence of gypsum mixed with various kinds of lime. It would seem that Schott probably included something similar to portland cement in his study of limes.

Forsen states, "Berger claims that Scott was the first to suggest control of the setting of portland cement with gypsum, whereas this important discovery is attributed by Goslich to Michaelis." In this connection, Steinour [7] states, "Michaelis said in 1905 that for perhaps 25 years he had introduced wet gypsum into the grinding mills when otherwise the cement was flash setting."

It seems that the discovery of the retarding properties of calcium sulfate may actually have been made by masons who either accidentally or deliberately mixed plaster of Paris with their limes. According to Lesley [8], the first use of calcium sulfate in this country resulted from an observation of the addition of plaster of Paris to the batch when concrete was being mixed in Paris.

The work by Meade cited in the introduction was carried out to demonstrate that forms of calcium sulfate other than plaster of Paris could be used to prevent flash set. There has been some tendency to blame false set onto increases in the fineness to which a cement was ground which, in turn, increased grinding temperatures and resulted in the dehydration of the gypsum.

Bucchi [9] says that the first references in the technical literature pertaining to false set appeared with the widespread use of large compound mills, characterized by high output rate, with a low rate of heat dispersal, and of the tendency of the manufacturers to produce high strength cements by means of impact grinding. He suggested that this type of false set be called "false set of fine grinding" to distinguish it from other types of false set.

It seems that the problem of false set probably developed because of several changes in the manufacturing process. Among these are the following:

1. improvements in the burning of the clinker;
2. changes in the compositions of the kiln feeds, which resulted in clinkers with lower $3CaO \cdot Al_2O_3$ contents;
3. better quenching of the clinker, which decreased the amount of crystalline $3CaO \cdot Al_2O_3$;
4. increases in the amounts of SO_3 permitted in cements; and
5. increases in the fineness.

It seems very likely that most of the early clinkers actually required dehydrated gypsum to prevent flash set and combined with calcium sulfate at rates which permitted the crystallization of little, if any, gypsum in the paste.

The System $CaSO_4$–H_2O

The system $CaSO_4$–H_2O has been the subject of many investigations with some disagreement as to the nature of the compounds formed when gypsum ($CaSO_4 \cdot 2H_2O$) is dehydrated by heating in air. Weiser, Milligan and Ekholm [10] made a very thorough study of the dehydration of selenite at a constant vapor pressure of 23.6 mm (that of water at 25 °C). The products were studied by X-ray diffraction. They called the completely dehydrated product "dehydrated hemihydrate." They state, "the evidence seems conclusive that $CaSO_4 \cdot 2H_2O$ is dehydrated isobarically, a definite hydrate $CaSO_4 \cdot 1/2H_2O$ which adsorbs a small amount of water is first formed and this, in turn, dehydrates in a stepwise fashion to give dehydrated hemihydrate, calcium sulfate, which adsorbs water that is not completely removed at a vapor pressure of 23.6 mm until well above the decomposition temperature". "The X-radiograms of the two substances, calcium sulfate hemihydrate and dehydrated hemihydrate, are similar, showing that the structures are similar; but the existence of definite characteristic differences between the two patterns indicates that the water molecules in the hemihydrate occupy fixed positions in the lattice. These observations likewise support the view that calcium sulfate hemihydrate is a chemical individual and that the process of dehydration is not zeolitic in character."

Kelley, Southard, and Anderson [11] defined two forms of hemihydrate and the two forms of anhydrite as follows:

α-hemihydrate (stable) can be prepared in the presence of liquid water above 97 °C or in saturated steam. It loses water with formation of an anhydrous soluble anhydrite in one step and is to be considered nonzeolitic.

β-hemihydrate (metastable) can be prepared from the dihydrate by dissociation in a vacuum or in a nearly dry atmosphere, followed by annealing at 100 °C. It loses H_2O with formation of a soluble anhydrite containing several tenths of a percent of H_2O. From 0.9 percent H_2O down, the H_2O is removed with increasing difficulty. The two forms of soluble anhydrite are labeled α and β, depending on the variety of hemihydrate to which they are related.

Soluble α-anhydrite can be made by dissociation of α-hemihydrate in a vacuum or in a relatively dry atmosphere near 100 °C. It contains virtually no water.

Soluble β-anhydrite can be made by dissociation of β-hemihydrate in high vacuum at 100 °C and by rapid, nearly complete calcination of $CaSO_4 \cdot 2H_2O$ at 200 °C. It always contains several tenths of a percent of H_2O.

Gilliland [12] gives X-ray diffraction patterns that show very minor differences between the patterns of hemihydrate and soluble anhydrite. However, it appears from these X-ray diffraction patterns and those reported by Weiser, Milligan, and Ekholm that it would be extremely difficult by the use of such patterns to distinguish between β-hemihydrate and soluble β-anhydrite in portland cement.

From these studies, it appears that the cement technologists need consider only what Kelley, Southard, and Anderson class as β-hemihydrate and soluble β-anhydrite. They found that this type of hemihydrate did not lose all of its water when calcined at 200 °C (392 °F). Portland cement is rarely, if ever, either ground or stored at a temperature as high as 392 °F. Hence, any soluble anhydrite found in portland cement should contain a few tenths of a percent of water. (In this paper, the terms "hemihydrate" and "soluble anhydrite" will always refer to the β forms as defined by Kelley, Southard, and Anderson.)

Much has been written about the solubilities of the various forms of calcium sulfate and its hydrates. Gypsum ($CaSO_4 \cdot 2H_2O$) is the only one of these that has a true solubility in water at the temperatures at which portland cement concrete is placed, and in solutions of the compositions found in cement pastes. Hence, the cement technologist needs consider only the solubility of gypsum. He is, however, very much interested in the rates at which the other forms of calcium sulfate dissolve. Hemihydrate and soluble anhydrite dissolve very rapidly and produce solutions which are highly supersaturated for short periods of time with respect to gypsum. Natural anhydrite dissolves at a slower rate than does gypsum. Hansen and Hunt [13] give data that show differences between extracts of pastes of cements made with gypsum and with natural anhydrite.

One property of gypsum of great interest to the cement technologist is its stability with respect to temperature and water vapor. The following table was constructed from data by Mellor [14]:

Vapor pressure in the system $CaSO_4 \cdot 2H_2O$-$CaSO_4 \cdot 1/2H_2O$-*water vapor*

Temperature	Vapor pressure—ps	Vapor pressure of water—pw	Relative humidity ps/pw×100
°F	*mm*	*mm*	
32	1.17	4.57	25
50	2.78	9.14	30
68	6.24	17.4	36
104	26.3	54.9	48
110	91.4	149	61
176	272.4	355	76
212	710.8	760	93
230	1104	1075	------------

Since portland cements are usually ground at temperatures [15] in the range of 100 to 300 °F, the relative humidity of the atmosphere would, in all cases, have to exceed about 50 percent to prevent some dehydration of the gypsum during grinding and storage. However, the rate of dehydration of gypsum depends upon both the temperature and the relative humidity. Hence, it seems possible that cements might be ground at temperatures above 200 °F without extensive dehydration of the gypsum and, if cooled as discharged from the mill to some temperature below 200 °F, the rate of dehydration might be reduced to a very low value. That cooling is effective is supported by the following statement from Blanks and Gilliland [16]: "As far as it has been possible to learn, there is not a single reported instance where adequate cooling of the grinding mills and of the cement prior to storage failed to relieve stiffening."

In this connection, Wilsnack [17] heated —200-mesh gypsum in 10-g portions at 150 °F for 0, 1, 2, and 4 days and found, respectively, the following water contents: 21.10; 21.02; 20.22 and 17.98 percent. When heated for 1 day at 200 °F, the water content was 7.34 percent.

Takemoto, Ito, and Hirayama [18] studied the dehydration of gypsum by means of differential thermal analysis during grinding of clinker and gypsum in an experimental mill. Their data are shown in figure 1. According to the authors, these data show formation of hemihydrate at 85 °C (185 °F) when the batch was ground for 40 min and the formation of soluble anhydrite at 130 °C (266 °F) when the batch was ground for 80 min.

There has been speculation as to whether or not dehydrated gypsum in portland cement would be converted to gypsum by combining with water vapor from the atmosphere after removal from the storage silo. Wandser [19] gives the following data for a sample of gypsum dehydrated by heating (to a loss on ignition of 4.07 percent) and then stored in an atmosphere of 65 percent relative humidity:

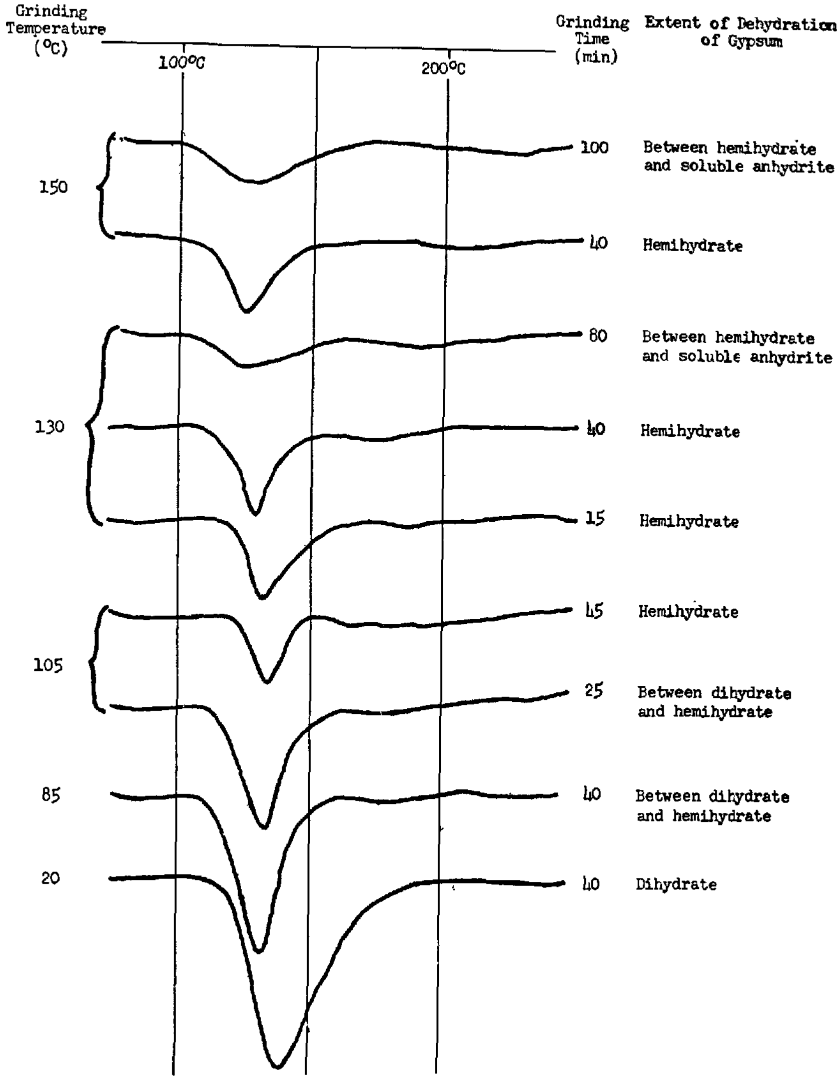

FIGURE 1. *Differential thermal analysis curves of cements ground with dihydrate (by Takemoto, Ito, and Hirayama).*

Heating rate: 5 °C/min, sensibility: 1/1.

Storage time	Water content
days	*percent*
1	7.11
2	7.41
28	7.42

The loss on ignition of pure hemihydrate is 6.2 percent.

Vikhter [20] exposed hemihydrate over solutions of sulfuric acid and found that, at relative humidities below 60 percent, the material adsorbed at the most about 1.3 percent H_2O and retained its activity practically indefinitely.

The small amount of water adsorbed by hemihydrate indicates that gypsum was not formed. The data by Mellor show that gypsum is converted to hemihydrate at a relative humidity of 61 percent and a temperature of 110 °F. It seems from these data that hemihydrate in cement would remain as hemihydrate during the handling of cement under the procedures which are normal to most projects in which cements are used.

As will be brought out later, some cements become false setting upon aeration. One explanation for this has been that the cement contained dehydrated gypsum but did not show false set until the cement was aerated because of the absence of gypsum crystals upon which to crystallize. From the above data, it seems unlikely that gypsum crystals would be formed under what might be considered normal conditions of aeration because it appears that soluble anhydrite hydrates in air to hemihydrate and that hemihydrate does not hydrate to gypsum under these conditions.

During the years 1929 to 1933, a number of reports were published in *Cement and Cement Manufacture* on false set. According to these reports, false set is caused by the following:

1. rapid absorption of water by finely-ground cement [21];
2. dehydration of the gypsum to an anhydrite with a rate of solution insufficient to prevent flash set [22, 23, 24];
3. partial or complete dehydration of the gypsum [25, 26, 27];
4. "balling up of bundles of tiny particles which become wetted on the outside of the bundle only and give a plastic mortar; but after a few minutes the water percolated into the interior of the bundles with an apparent stiffening of the pat which is mistaken for an initial set" [28];

   (a) "False set is due to insufficient gauging; that is, every particle of cement has not been brought into contact with gauging water".

   (b) "False set occurs chiefly when the clinker is of a soft nature and tends to clog and flake in the mill, a tendency which is aggravated by high temperature, whereas with hard gritty clinker high temperature does not produce false set"; and
5. improperly burned clinker [29].

Blank [30] describes tests made with wet clinker. Cement made from wet clinker was very fast setting and this could be corrected only by drying the clinker. Blank concluded that there was no "cut-and-dried explanation" for the causes of false set. However, it appears that he was dealing with a very unusual case which was different from the conditions under which most cases of false set were observed.

Data reported by Schachtschabel [27] are interesting in showing that some cements may require dehydrated gypsum to prevent flash set. His data are as follows:

Variation of setting time due to gypsum, hemihydrate, and soluble anhydrite

Water, 26 to 28 percent. Times of mixing, 1 and 3 min

Percent addition	Gypsum				Hemihydrate				Soluble anhydrite			
	Mix 1 min		3 min		1 min		3 min		1 min		3 min	
	Init.	Final	Init.	Final	Init.	Final	Init.	Final	Init.	Final	Init.	Final
	h. m.	h. m.	h. m.	h. m.	h. m.	h. m.	h. m.	h. m.	h. m.	h. m.	h. m.	h. m.
0.75	---	---	---	---	---	---	---	---	0 3	0 4	0 2	0 3
1.00	0 3	0 4	---	---	0 3	0 5	---	---	4 15	6 45	5 25	8 20
1.25	0 2	0 6	0 9	0 12	4 40	6 40	4 50	8 0	---	---	---	---
1.50	0 8	2 50	1 45	3 30	---	---	---	---	---	---	---	---
2.00	2 4	5 50	3 30	5 30	4 50	7 35	5 0	7 50	4 50	7 30	5 0	7 40
2.50	6 20	9 7	5 15	8 0	0 45	6 30	4 30	7 20	---	---	---	---
3.00	---	---	---	---	0 29	6 0	3 45	6 45	0 34	5 50	1 42	6 35
4.00	6 45	10 0	5 25	8 25	0 25	5 25	0 27	5 45	0 33	5 0	0 29	5 7
6.00	---	---	---	---	0 17	0 33	0 16	0 30	---	---	---	---
8.00	6 0	10 30	5 55	8 40	---	---	---	---	---	---	---	---

It required between 1.5 and 2.0 percent SO_3 as gypsum to prevent flash set with this clinker when freshly ground, whereas 1.0 percent SO_3 as soluble anhydrite and 1.25 percent SO_3 as hemihydrate were as effective as about 2.5 percent SO_3 as gypsum. Aging of the ground clinker in bags for 3 weeks reduced the amount of SO_3 as gypsum required for normal set to 0.5 percent.

These data also show that amounts of SO_3 above about 2.0 percent as either hemihydrate or soluble anhydrite produced a rapid initial set.

It appears from this review of the work reported between about 1928 and 1935 that investigators had clearly shown that dehydration of gypsum during either grinding or storage could cause false set in portland cement. Some investigators erroneously attributed false set caused by dehydration of gypsum to the formation of a relatively insoluble anhydrite.

Two investigators [21, 28] suggested that false set was due to rapid adsorption of water by the finely ground cement. The data by Schachtschabel indicate that some cases of fast stiffening might be classed as false set because of the rapid reaction of $3CaO{\cdot}Al_2O_3$ with water. For example, the clinker used by Schachtschabel when mixed with 1.5 percent SO_3 as gypsum gave an initial set of 8 min when mixed for 1 min and 105 min when mixed for 3 min. These results raise the question as to what is meant by normal setting. The cement paste mixed for 1 min probably would be classed either as flash or false setting whereas that mixed for 3 min probably would be classed as normal setting. It appears that the gypsum could not dissolve fast enough in the 1-min mixing period to prevent all traces of flash set. However, the additional mixing of the 3-min mixing period either maintained a higher rate of solution of the gypsum or else destroyed some of the set. If one were to class this cement with 1.5 percent SO_3 in the form of gypsum as false setting when mixed as a paste for 1 min, then one might be led to the conclusion that false set was caused by some factor such as rapid adsorption of water.

It has been a rather common belief that fast setting could be corrected by increasing the gypsum content of the cement. This was effective with this clinker as shown by the results for 1.5 and 2.5 percent SO_3 added as gypsum. However, when the SO_3 was raised from 2.0 to 2.5 percent by use of hemihydrate, the cement became fast setting. These results show why one practice might work satisfactorily in one cement plant and not in another.

The Liquid Phase of Cement Pastes

Studies on the constitution of portland cement have rather clearly defined the compositions of the crystalline phases in such cements. One such phase is a solid solution of K_2SO_4 and Na_2SO_4 which dissolves very quickly when the cement is mixed with water. Also, calcium hydroxide splits off very rapidly from the calcium silicates and aluminates. The liquid phase of cement paste, therefore, tends to satisfy the following equation within a very short time after the cement and water are mixed:

$$\underset{\text{Solid}}{CaSO_4\cdot 2H_2O} \rightleftharpoons CaSO_4 + 2MOH = M_2SO_4 + Ca(OH)_2 \rightleftharpoons \underset{\text{Solid}}{Ca(OH)_2},$$

where M equals either K or Na or both.

The solubility of $Ca(OH)_2$ and $CaSO_4\cdot 2H_2O$ in solutions of alkalies has been investigated by Hein [31] and by Hansen and Pressler [32]. The data by the latter authors are given in table 1.

In recent years, investigators in a number of countries have studied the problem of false set by means of extraction tests. Gilliland [12] used a test in which 250 g of cement was mixed in a Waring Blendor for 2 min with 125 ml of distilled water and filtered on a Buechner funnel. The extract was analyzed for CaO, $(OH)_2$, SO_3, K_2O and Na_2O. The quantity of SO_3 in such a solution at equilibrium was taken from the data by Hansen and Pressler. The following table gives data by Gilliland for four cements heated for 24 hr at various temperatures:

Penetration tests and extract compositions for heated cements

Cement No.	Heated 24 hr	Penetration test			Data for extracts—moles/liter			
		Water	½ min	5 min	Na_2O+K_2O	SO_3	Sat. SO_3	Excess SO_3
	°C	*Percent*	*mm*	*mm*				
9939		27.2	34	2	0.0271	0.0294	0.0227	0.0067
	128				.0250	.0510	.0216	.0294
	200	28.0	35	1	.0230	.0543	.0206	.0337
	300	26.0	38	0	.0240	.0543	.0211	.0332
	350	27.6	37	21	.0286	.0248	.0235	.0013
	650	29.2	37	30	.0343	.0202	.0268	.0066
9940		29.6	37	0	.0136	.0433	.0166	.0267
	128				.0138	.0461	.0166	.0295
	350	27.0	38	31	.0140	.0364	.0167	.0197
A–112		28.6	37	15	.0773	.0626	.0562	.0064
	128	29.0	35	0	.0739	.0906	.0537	.0369
	200	33.0	33	3	.0733	.0741	.0532	.0209
	300	28.0	37	0	.0707	.0946	.0514	.0432
	350	28.0	34	26	.0758	.0717	.0551	.0166
	650	28.2	36	28	.0823	.0533	.0600	.0067
A–215		28.0	33	17	.0472	.0424	.0346	.0078
	128	27.2	33	0	.0468	.0689	.0344	.0345

These data show that all of the extracts from the original cements contained SO_3 in excess of that required by a solution saturated with respect to gypsum. Small degrees of supersaturation might be accounted for by increased solubility of broken crystals. Hence, some of the original cements may have contained very little, if any, dehydrated gypsum.

Heating the cements at 300 °C generally increased the amount of SO_3 in the liquid phase. Heating at 350 °C appears to have converted some of the calcium sulfate to natural anhydrite and heating at 650 °C appears to have fairly well completed this conversion.

Gilliland used this extraction test to help prove that alkali carbonate does not cause false set during aeration as suggested by Bogue [33]. The results of his tests are as follows:

Treatment	Penetration Test		Data for extracts—moles/liter			
	½ min	5 min	K_2O+Na_2O	SO_3	Sat. SO_3	Excess SO_3
	mm	*mm*				
As received	33	15	0.0736	0.0658	0.0535	0.0123
Aerated 10 days at 50 percent RH	36	0	.0733	.0875	.0532	.0343
Heated to 350 °C for 24 hr after aeration	37	20	.0582	.0371	.0421	–.0050

Severe false setting was induced by aeration but heating at 350 °C, which is sufficient to convert gypsum and hemihydrate to natural anhydrite but insufficient to decompose alkali carbonates, destroyed the false set. This seems to demonstrate for this high-alkali cement that false set, upon

TABLE 1. *Solubility of* $Ca(OH)_2$ *and* $CaSO_4 \cdot 2H_2O$ *in solutions of* KOH *and* NaOH *at 25 and 30 °C (data by Hansen and Pressler* [32])

Composition of original solution moles/liter			Composition of solution in contact with solid $Ca(OH)_2$ and solid $CaSO_4 \cdot 2H_2O$—moles/liter				
K_2O	Na_2O	K_2O+Na_2O	CaO	SO_3	OH	Na_2O	K_2O+Na_2O Calc.[a]
DATA FOR 30 °C							
None	None	None	0.0319	0.0125	0.0387	--------------	0.0001
0.0050	None	0.0050	.0298	.0141	.0419	--------------	.0053
.0025	0.0025	.0050	.0294	.0141	.0393	--------------	.0044
.0150	.0050	.0200	.0256	.0191	.0529	0.0052	.0199
.0100	.0101	.0201	.0236	.0196	.0477	--------------	.0199
.0251	None	.0251	.0228	.0223	.0523	--------------	.0256
.0125	0.0125	.0250	.0226	.0219	.0514	--------------	.0250
.0150	.0151	.0301	.0226	.0236	.0585	--------------	.0302
.0251	.0050	.0301	.0231	.0241	.0587	0.0052	.0303
.0150	.0151	.0301	.0216	.0252	.0536	--------------	.0304
.0301	None	.0301	.0214	.0253	.0524	--------------	.0301
.0401	None	.0401	.0211	.0299	.0626	--------------	.0399
.0200	0.0202	.0402	.0198	.0303	.0602	--------------	.0406
.0150	.0252	.0402	.0195	.0303	.0589	0.0251	.0401
.0501	None	.0501	.0185	.0373	.0618	--------------	.0497
.0251	0.0252	.0503	.0188	.0376	.0633	--------------	.0502
.0251	.0252	.0503	.0194	.0363	.0672	0.0253	.0505
.0050	.0500	.0550	.0184	.0395	.0698	.0504	.0561
.0500	.0050	.0550	.0190	.0398	.0689	.0052	.0552
.0601	None	.0601	.0187	.0430	.0710	--------------	.0598
.0301	0.0302	.0603	.0180	.0425	.0711	--------------	.0599
.0150	.0504	.0654	.0175	.0468	.0734	0.0502	.0659
.0501	.0252	.0753	.0174	.0544	.0771	.0255	.0756
.1002	None	.1002	.0162	.0710	.0806	--------------	.0951
.1002	0.0050	.1052	.0167	.0783	.0884	0.0056	.1058
.1002	.0252	.1254	.0164	.0951	.0940	.0259	.1257
.1504	None	.1504	.0162	.1167	.0972	--------------	.1491
None	0.1448	.1448	.0150	.1151	.1024	--------------	.1513
0.1504	.0050	.1554	.0162	.1211	.1011	--------------	.1553
.1504	.0252	.1756	.0162	.1382	.1048	--------------	.1744
.2005	None	.2005	.0164	.1626	.1062	--------------	.1991
None	0.1930	.1930	.0149	.1586	.1146	--------------	.2010
0.2506	None	.2506	.0161	.2055	.1136	--------------	.2462 [b]
.1253	0.1250	.2503	.0169	.2040	.1188	--------------	.2465 [b]
.3750	None	.3750	.0094	.2121	.1455	--------------	.2555 [b]
None	0.3750	.3750	.0051	.2629	.2279	--------------	.3718
0.5012	None	.5012	.0093	.2083	.1386	--------------	.2683 [b]
1.0023	None	1.0023	.0034	.3662	.2752	--------------	.5000 [b]
DATA FOR 25 °C							
None	None	None	0.0331	0.0123	0.0414	--------------	0.0001
0.0100	None	0.0100	.0292	.0151	.0488	--------------	.0103
.0200	None	.0200	.0240	.0190	.0502	--------------	.0201
.0401	None	.0401	.0211	.0289	.0649	--------------	.0403
.0601	None	.0601	.0183	.0426	.0726	--------------	.0606
.1002	None	.1002	.0161	.0722	.0888	--------------	.1005
.2005	None	.2005	.0165	.1562	.1164	--------------	.1979 [b]

[a] Calculated from determined values for CaO, SO_3 and OH.
[b] $CaSO_4 \cdot K_2SO_4 \cdot H_2O$ probably formed as a solid phase.

aeration, is not caused by forming alkali carbonates.

It is now well known that, generally, a fairly large part of the alkalies in cement clinkers exist in these clinkers as the sulfates. The remaining alkalies probably exist as a solid solution of $23CaO \cdot K_2O \cdot 12SiO_2$ with $2CaO \cdot SiO_2$ and as a solid solution of $8CaO \cdot Na_2O \cdot 3Al_2O_3$ with $3CaO \cdot Al_2O_3$. It seems very unlikely that any significant amount of alkalies can be released from these phases as carbonates during normal exposure to air and, of course, alkali sulfates will not be converted to carbonates by exposure to air. Hence, it appears that the formation of alkali carbonates by aeration cannot be a cause of false set. However, when alkali carbonates are added to cement pastes, they precipitate $CaCO_3$, which might in itself cause stiffening of the paste just as the precipitation of gypsum does. Also, it seems that calcium sulfate requires the presence of some $Ca(OH)_2$ to prevent $3CaO \cdot Al_2O_3$ from reacting at a sufficient rate to cause some stiffening of the paste. Hence, it appears that the early stiffening of a cement paste observed by a number of investigators when they added alkali carbonates to a cement is a type of stiffening that would not be obtained in practice.

Schachtschabel [27] attributed the action of alkali carbonates added to the cement to the changing of the calcium sulfate to alkali sulfate by precipitation of $CaCO_3$.

The data by Gilliland indicate that the cement used in his study contained dehydrated gypsum as received because, at equilibrium, a solution containing 0.0736 moles K_2O+Na_2O should contain 0.0535 moles SO_3 instead of the 0.0658 moles which it contained. Aeration increased the SO_3 content to 0.0875.

Hansen [34] performed a somewhat similar experiment in which 200 g of cement was shaken with 150 ml water for 1 and 3 min. The cement was tested as received and after aeration in laboratory air for 24 and 48 hr. The results of these tests were as follows:

Treatment	Time of shaking	Composition of extract—moles/liter					
		SO_3	$(OH)_2$	CaO	Na_2O	Sat. SO_3	Excess SO_3
	min						
As received	1	0.0245	0.0279	0.0286	0.0238	0.021	0.004
	3	.0157	.0433	.0279	.0311	.025	−.009
Aerated 24 hr	1	.0523	.0238	.0589	.0172	.019	.033
	3	.0401	.0239	.0458	.0182	.020	.020
Aerated 48 hr	1	.0533	.0232	.0621	.0144	.018	.035
	3	.0431	.0234	.0512	.0153	.018	.025

This sample of cement must have contained dehydrated gypsum as received but, in the unaerated sample, the $3CaO \cdot Al_2O_3$ combined with the calcium sulfate at a rate such that, at 3 min, the solution was not saturated with respect to gypsum. When the cement was aerated, the solution was highly supersaturated at 3 min with respect to gypsum. This indicated that aeration reduced the rate at which $3CaO \cdot Al_2O_3$ reacted with calcium sulfate.

Hansen demonstrated that aeration reduced the rate of reaction of $3CaO \cdot Al_2O_3$ with calcium chloride by grinding the clinker without added calcium sulfate and then making extraction tests in which 200 g of the powdered clinker was shaken for 1, 5, 15, and 30 min with solutions of calcium chloride. The extracts were analyzed for chloride and the amounts combined during the shaking period were calculated with the following results:

Treatment	Grams Cl_2 combined with 100 g clinker for minutes indicated			
	1	5	15	30
As received	0.22	0.28	0.34	0.36
Aerated 24 hr	.08	.14	.22	.24
Aerated 48 hr	.03	.11	.22	.26

These data show that aeration retards the rate at which the cement combines with $CaCl_2$.

Manabe [35] showed, by studies with calcium sulfate made with radio-isotope sulfur-35, that aeration decreased the rate at which calcium sulfate combined in cement pastes.

Returning to the data by Gilliland, it is seen that these data also indicate that the rate at which $3CaO \cdot Al_2O_3$ reacts with the calcium sulfate has been decreased by aeration.

The presence of excess SO_3 in extracts from cement pastes does not always indicate the presence of dehydrated gypsum in the cement. If cements contain relatively large amounts of alkali sulfates, these sulfates may dissolve very rapidly to give solutions from which $CaSO_4 \cdot 2H_2O$ will precipitate by the reaction of the alkali sulfate with $Ca(OH)_2$ to give the equilibrium of eq (1). Hansen and Pressler [32] give the following data for the liquid phases of slurries of four cements after reaction periods of 3 min:

Cement No.	Composition of liquid phase			Composition of solution at equilibrium for given M_2O content		
	Moles/liter			Moles/liter		
	SO_3	CaO	M_2O	SO_3	CaO	M_2O
1	0.0127	0.0417	0.0018	0.0130	0.0310	0.0018
2	.0151	.0412	.0028	.0140	.0320	.0028
3	.0777	.0259	.0879	.0640	.0162	.0879
4	.0883	.0481	.0705	.0490	.0170	.0705

From these data, it is seen that the extract from

1. Cement No. 1 is slightly supersaturated with $Ca(OH)_2$;
2. Cement No. 2 is slightly supersaturated with $CaSO_4 \cdot 2H_2O$;
3. Cements Nos. 3 and 4 are supersaturated with respect to $CaSO_4 \cdot 2H_2O$ and unsaturated with respect to $Ca(OH)_2$. Hence, they will have to dissolve more $Ca(OH)_2$ and precipitate gypsum to attain equilibrium.

It appears that these cements contained large quantities of alkali sulfates that dissolved at very rapid rates.

Bucchi [9] developed a method of studying the rate at which SO_3 combined in the cement paste. In this method, samples of the paste after various periods of reaction were mixed with a sufficient amount of saturated $Ca(OH)_2$ solution to dissolve all of the SO_3 in the cement if it still remained as gypsum. The solutions were filtered and the filtrates were analyzed for SO_3. The results showed a very rapid combination of SO_3 in the first few minutes. Bucchi determined by this method the quantity of $SO_4^=$ remaining uncombined in the paste at the end of this initial rapid reaction. This value he called Q' and the original total $SO_4^=$ content of the paste he called Q. Then, $Q-Q'=X$, the amount of SO_4 combined during the first few minutes. According to Bucchi, if a cement shows rapid set when Q is equal to or less than X, the rapid set will be flash set. Generally, rapid set that occurs when Q is greater than X will be false set.

Bucchi prepared a number of cements by grinding the clinker separately and then blending them with either powdered gypsum or plaster of Paris or mixtures of the two. Results for one clinker, which are typical of those for all clinkers studied, are as follows:

SO_3 content of cement—percent				Time of set Vicat needle		$SO_4^=$ ion concentration [a] in the paste—percent		
SO_3 in clinker	SO_3 added as gypsum	SO_3 added as hemihydrate	Total	Init.	Final	Q	Q′	Q−Q′
0.52	0.66		1.18	0:08	0:18	1.09	0.00	--------
.52	1.37		1.89	2:35	4:25	1.75	0.42	1.33
.51	2.17		2.68	2:35	4:25	2.48	1.16	1.32
.50	3.00		3.50	2:34	4:17	3.23	1.90	1.33
.48	3.92		4.40	2:20	4:10	4.06	2.71	1.35
.48	4.97		5.45	2:41	4:30	5.03	3.71	1.32
.52		0.69	1.21	0:10	0:19	1.12	0.00	--------
.52		1.17	1.69	2:34	4:26	1.56	0.23	1.33
.52		1.66	2.18	2:35	4:29	2.01	0.69	1.32
.51		2.19	2.70	2:33	4:21	2.49	1.16	1.33
.51		2.56	3.07	1:59	4:22	2.84	1.50	1.34
.50		2.99	3.49	0:15	4:20	3.22	1.86	1.36
.49		4.22	4.71	0:12	0:27	4.35	2.99	1.36
.48		4.91	5.39	0:12	0:30	4.97	3.64	1.33
.52		0.42	2.19	2:31	4:30	2.02	0.69	1.33
.52		0.83	2.18	2:30	4:41	2.01	0.70	1.31
.52		1.16	2.18	2:00	3:50	2.01	0.70	1.31
.52		1.50	2.19	1:00	3:00	2.02	0.68	1.34
.52		1.58	2.18	0:40	2:31	2.01	0.72	1.29

[a] Q is initial concentration as calculated from $SO_4^=$ content of the cement and Q′ is the concentration at the end of the initial rapid reaction.

These results show that, for this clinker, gypsum and hemihydrate produced similar initial setting times until 2.56 percent SO_3 as hemihydrate was added. A very fast set was obtained with 2.99 to 4.91 percent SO_3 as hemihydrate.

Lhopitallier and Stiglitz [3] made an extensive study of false set by grinding clinkers with gypsum and then heating the cements to form dehydrated gypsum. They analyzed extracts from pastes for K_2O, Na_2O, CaO, SO_3, and $(OH)_2$ and compared them with the data published by Hein and by Hansen and Pressler and used the penetration of the Vicat plunger to indicate false set. The following conclusions were reached:

1. "The set of hemihydrate, formed by dehydration of gypsum in overheated grinding mills, suffices by itself to explain the phenomenon of false set of cements."
2. "The intensity of false set is a function of the absolute content of hemihydrate present in cement."
3. "In the case of partial dehydration, the fraction of non-dehydrated gypsum acts as seed for crystallization and accelerates the set of the hemihydrate."
4. "If mixing is continued beyond the set of the hemihydrate, the skeleton formed by the crystals of gypsum is broken and the paste becomes plastic again without further addition of water. The period of mixing necessary to break up false set is shorter the higher the proportion of particles of gypsum."
5. "Analysis of cement liquors taken at intervals of time allows one to ascertain the beginning of the phenomenon and to estimate the minimum time of mixing needed to break up the stiffening."

Murakami [36] found that false set due to hemihydrate could be explained by determining the chemical compositions of extracts from pastes taken immediately and 10 min after mixing with the amounts of water required for normal consistency. Takemoto and Suzuki [37] also studied extracts from neat pastes.

Manabe [35] added powdered clinker to solutions of $CaSO_4$ in which the $CaSO_4$ had been made with sulfur 35. By measuring the specific activity of the S in the original solution and in extracts made at various periods of time, he was able to study the rate at which SO_3 combined with the cement. As pointed out previously, he found that aeration decreased the rate of combination of SO_3 with the cement.

The development of methods based on the flame photometer for the determinations of alkalies has made it relatively easy to analyze the extracts from cement pastes. However, one can calculate the alkali contents of these extracts with sufficient accuracy for use in deciding whether or not an extract is supersaturated with respect to gypsum. These extracts are essentially solutions of alkali and calcium hydroxides and sulfates. Hence

$$\text{Moles } SO_3 + \text{Moles } (OH)_2 - \text{Moles CaO} = \text{Moles } M_2O.$$

The extremely small amounts of Al_2O_3, SiO_2, and other oxides present in such extracts do not seriously interfere with these calculations. The results of many tests in our laboratories show good agreement between determined and calculated values.

These extraction methods have made it possible for investigators to determine whether or not a cement could produce false set by precipitating gypsum. This has led most, if not all, recent investigators to conclude that dehydrated gypsum is the principal cause of false set. The knowledge that mixing of the paste can destroy false set has led them to the realization that the mixing period in the tests designed to test for false set should be short if the maximum amount of stiffening is to be determined.

Methods of Testing for False Set

An anonymous [38] investigator appears to have been the first to publish a method designed principally to detect false set. The proposed method was based on the sedimentation of slurries of the cement with water and with white spirit of turpentine. The results obtained were as follows:

	Spirit		Water		Vicat set		
Sample	Time taken to settle	Volume after settlement	Time taken to settle	Volume after settlement	Init.	Final	Volume after settlement [a]
	min.	cc	*min.*	cc	*min.*	*min.*	%
Fine sand	20	14	20	14¾	--------	--------	6.2
Fine emery	20	10	20	10½	--------	--------	5.0
Cement 1	100	13	45	17¼	90	210	32.7
Cement 2	65	12¾	3	39½	--------	5	209.8
Cement 3	165	13½	55	17½	45	120	29.6
Cement 4	80	12¾	3	38½	--------	5	201.9
Cement 5	100	13¼	40	16½	105	220	24.5
Cement 6	75	12¾	35	17½	30	110	37.2
Cement 6 (after ignition)	65	12	16	19¼	--------	--------	60.4
Cement 7	80	13	50	16½	115	230	26.9
Cement 7 (after ignition)	85	12	21	18¾	--------	--------	56.2

[a] Increase in water over that in spirit.

At about this time (1929), the U.S. Bureau of Reclamation began to work on a test method and a specification by which false setting cements could be rejected. It appears that the difficulties with false set became acute for this user primarily from the use of cements with low potential $3CaO{\cdot}Al_2O_3$ contents and the necessity of transporting the concrete some distance from the mixer before placing it in the forms.

In March 1937, the U.S. Bureau of Reclamation printed Specification No. 898D which developed into the present Federal Method 2501—"Early Stiffening of Cement, Paste Method" [39]. In No. 898D, 500 g of cement was kneaded for 3 min with 26 percent water in accordance with ASTM Designation C 77–32 [1]. The paste was molded into the Vicat ring and tested for depth of penetration of the 1-cm plunger of the Vicat apparatus. The cement was considered to be false setting when the plunger failed to penetrate 2 mm below the original surface 2½ min after mixing was completed.

Experience with this method showed that some cements required more than 26 percent water to produce workable pastes. The method was therefore changed to permit the use of the amount of water required to give a penetration of 35±2 mm. Also, the time at which the final penetration was determined was changed from 2½ to 5 min after mixing was completed. Cements may be rejected by specifications based on this method when the difference between the initial and final penetrations is less than 17 mm.

The State of Washington Department of Highways [40] checks all cements used in their work for stiffening characteristics and warns the resident engineer on construction that additional work may be required in placing concrete made with certain cements. In their method, which was revised in 1950, they mix a mortar of one part cement and two parts graded Ottawa sand with sufficient water to give a flow of 101 to 110 percent, ASTM Method C 109 [1]. They mix the water and cement for 30 sec in a bowl with a spoon. The sand is then added and the mortar is mixed for 60 sec. The Vicat mold is then filled and the depth of penetration of the Vicat plunger is measured 5 min after completion of the mixing. If the depth of penetration is less than 30 mm, the cement is considered to be false setting.

In 1955, the State of Nebraska [41] included a method of determining false set in a specification for portland cement. This method of test consists of determining the depth of penetration of the 1-cm plunger of the Vicat apparatus in a neat cement paste of normal consistency, ASTM Designation C 187 [1]. Penetrations are determined at 3, 4½, and 8 min after the water is added to the cement. The paste is remixed and remolded after the third reading and a final reading is taken at 10¼ min after the initial contact with water. A cement is classed as false setting when either the second or third penetration is less than 50 percent of the first penetration, and the fourth penetration is 90 percent or over, of the first penetration.

The American Society for Testing Materials [1] adopted a method in 1955 known as ASTM Designation C 359, "Tentative Method of Test for False Set of Portland Cement". This has been adopted in slightly modified form as Federal Method 2511 [39], "Tentative Method of Test for Early Stiffening of Portland Cement, Mortar Method".

This method, which was patterned after the Nebraska method [41], measures the depth of penetration of the 1-cm plunger of the Vicat apparatus in a 1:1 mortar. The mortar is mixed by machine and placed in a mold in slightly less than 3 min. Penetrations are determined at 3, 5, 8, and 11 min after mixing is started. After the 11-min reading is taken, the sample is remixed and remolded and the penetration is measured to determine whether or not the original workability of the mortar can be restored.

It appears that no other country has either adopted a standard method of test for false set or included limits for false set in their specifications for portland cement. However, many investigators in other countries have studied the problem of false set and some have introduced methods of testing for false set.

Manabe [42] used a method in which 10 g of cement was shaken with 15 ml of water in a 30-ml graduated cylinder for a prescribed period of time. The rate of sedimentation was measured and the results were correlated with results obtained by Federal Method 2501.

Sulikowski and Ziarno-Czamarska [43] used an electrical conductivity method to show false setting in cements which had been heated to dehydrate the gypsum. They found that the slurry of the unheated cement showed a rapid and then progressively slower decrease in electrical resistance whereas the slurry of the heated cement showed a pronounced maximum on the curve.

Bucchi [44] distinguished between false and flash set by an extraction test. In this test, two 5-g samples of the initial setting pat are weighed to the nearest 1 mg at the moment the pat shows initial set by the Vicat needle. One sample is extracted in saturated lime water and analyzed for SO_3, which is called S and expressed as percent of paste. The other sample is ignited at 950 °C to obtain loss on ignition, called Pa. Then, the SO_3 content in terms of anhydrous cement is

$$\frac{S}{100-Pa}\times 100$$

In the case of flash set, the extract gives only a faint opalescence when treated with $BaCl_2$ to precipitate $BaSO_4$, whereas, with false set, a measurable amount of $BaSO_4$ is precipitated.

Steinour [7] and Blanks and Gilliland [16] discuss some methods of testing for false set which they obtained by personal communications with the investigators.

A number of investigators have demonstrated the ability of small amounts of dehydrated gypsum to produce stiffening in pastes of inert powders. Typical of these are the results obtained by Hansen [34]. In these studies, quartz was ground in a cold mill to about the fineness of portland cement. One sample was ground without any additions; one was ground with gypsum equivalent to 2.0 percent SO_3; and one was ground with molding plaster equivalent to 2.0 percent SO_3. These were blended to give mixtures with varying SO_3 contents and the mixtures were tested for false set by ASTM Method C 359. The results were as follows:

False set in quartz paste as determined by ASTM Method C 359

	Paste containing gypsum penetration—mm					Paste containing molding plaster penetration—mm				
SO_3	Initial	5 min	8 min	11 min	Re-mix	Initial	5 min	8 min	11 min	Re-mix
%										
0	50+	45	46	44	50+	50+	45	46	44	50+
0. 25	47	43	42	42	47	49	40	38	30	50+
0. 50	46	44	40	48	46	46	38	27	20	50+
1. 00	46	45	41	43	47	48	10	8	7	50+
1. 50	47	47	42	40	46	47	5	0	0	50+
2. 00	48	44	41	41	48	41	0	0	0	50+

These results indicate that about 0.5 percent SO_3 as dehydrated gypsum could produce a mild stiffening in a cement paste provided the cement did not combine with more than traces of SO_3 during the test period. However, the cements that combine with SO_3 at very rapid rates during the first few minutes might not show false set, except when most or all of the gypsum has been dehydrated.

False Set Produced by Aeration

Swayze [45] demonstrated that certain clinkers which do not require calcium sulfate to prevent flash set may develop quick-stiffening tendencies when the powders are aerated. The clinker used had the following calculated compound composition—percent by weight:

$3CaO\cdot SiO_2$	73. 9	Free CaO	0. 6
$2CaO\cdot SiO_2$	9. 9	MgO	. 6
$3CaO\cdot Al_2O_3$	None	SO_3	. 01
$4CaO\cdot Al_2O_3\cdot Fe_2O_3$	11. 2	Na_2O+K_2O	. 04
$2CaO\cdot Fe_2O_3$	3. 7	Loss on ignition	. 08

This was ground in a laboratory mill to specific surfaces of about 2700 cm^2/g without calcium sulfate, with sufficient gypsum, and with sufficient natural anhydrite to give 2.5 percent SO_3. Each grind was made without and with either 0.5 or 0.2 percent water added to the mill. The results obtained by Swayze are as follows:

False set in cold ground laboratory cements, ASTM Method C 359: 32 percent water in mortar

Sample condition	Penetration—mm					Penetration—mm				
	Init.	5 min	8 min	11 min	Remix	Init.	5 min	8 min	11 min	Remix
	Clinker Only—Dry Grind					Clinker Only—0.5% Water				
Fresh sample	50	50	50	47	50	50	50	50	50	50
Aerated 16 hr	50	1	0	0	50	50	50	49	12	50
Heated 260—7 da [a]	50	1	0	0	50	50	50	42	5	50
Aerated 16 hr	50	11	0	0	50	50	50	33	2	50
	Clinker+Gypsum—Dry Grind					Clinker+Gypsum—0.5% Water				
Fresh sample	50	50	50	50	50	50	50	50	50	50
Aerated 16 hr	50	3	0	0	50	50	2	1	1	50
Heated 260—7 da [a]	50	0	0	0	50	50	0	0	0	50
Aerated 16 hr	50	0	0	0	50	50	0	0	0	50
	Clinker+Anhydrite—Dry Grind					Clinker+Anhydrite—0.2% Water				
Fresh sample	50	50	5	2	50	50	50	50	50	50
Aerated 16 hr	50	50	2	0	50	50	50	2	0	50
Heated 260—7 da [a]	50	39	3	0	50	50	50	38	3	50
Aerated 16 hr	50	50	2	0	50	50	50	50	35	50

[a] Fresh sample.

Swayze points out that it was difficult to grind the clinker plus anhydrite mixture because of ball-coating and that, accordingly, the powdered clinker was aerated before grinding was completed. The cements produced in all of the other grinds showed no quick-stiffening tendencies in this test until they had been aerated. Then, all developed quick-stiffening tendencies.

The fresh samples of all grinds when heated to 260 °F for 7 days in an open can and cooled in a closed can developed quick-stiffening tendencies. Aeration of these samples produced no changes in them as determined by the method of testing.

Swayze supplied the writer with a sample of the clinker ground dry without calcium sulfate. This was tested as received and after aeration in laboratory air for 48 hr. The latter was tested with 2 percent SO_3 added as powdered gypsum and with 2 percent freshly burned CaO. The results were as follows:

Sample	Additions	Water	Penetration—mm				
			Init.	5 min	8 min	11 min	Remix
		%					
A—As Received	None	32	50+	50+	37	2	50+
B—Aerated 48 hr	None	32	50+	6	1	1	50+
C—Aerated 48 hr	2% SO_3	32	50+	11	1	0	50+
D—Aerated 48 hr	2% CaO	32	50+	37	3	1	50+

The A and B samples were tested to determine the rate at which they combined with $CaCl_2$ by shaking 200 g with 150 ml of a 3 percent $CaCl_2$ solution. The results were as follows:

Sample	Grams Cl_2 combined for 100 g of clinker in time indicated	
	1 min	3 min
A—As Received	0.003	0.002
B—Aerated 48 hr	.002	.002

Swayze concluded from his studies that aeration increased the reactivity of the crystals of $3CaO \cdot SiO_2$ toward water. The results of the tests with the reaction toward $CaCl_2$ indicate that the aluminate phase combined with this salt at a very slow rate. It is believed that this cement should react with $CaCl_2$ because Swayze (personal communication) says that this cement combines with about 2.5 percent SO_3 in 24 hr.

Following this work by Swayze, tests were made in our laboratories with a number of clinkers. The clinkers were collected so that most of them did not come in contact with any water. These were then ground in a cold laboratory mill with gypsum. The freshly ground and aerated cements were tested by the extraction test for an indication of whether or not gypsum would precipitate from the liquid phase of the cement pastes, and for false set by ASTM Method C 359. The results for false set are given in table 2.

The results of the extraction tests did not indicate presence of either dehydrated gypsum or of excessive amounts of alkali sulfates in any of these cements. There is no reason to believe that more than traces of dehydrated gypsum could have formed during the grinding of these cements.

The results of the false set test show that some of the freshly ground samples stiffened somewhat during the test. For example, the penetration at the 11-mm period was 28 mm for sample B–1. It is believed that some stiffening in this test can be classed as normal stiffening for some cements.

A number of the cements show some stiffening during aeration. In some cases, the stiffening produced in 24 hr of aeration was not present in the cement which was aerated for 48 hr. Swayze and others claim that this happens frequently.

In this study, this type of false set was obtained with Types I, II, and III cements. Hence, it does not appear to be characteristic of any one type of clinker.

One must remember that grinding at temperatures below about 200 °F is never done commercially and that results similar to those obtained with cements ground at low temperatures may never be obtained in practice. This might be particularly true if the clinker contains some water. Many people have felt that water released from gypsum during grinding and storage has an influence on the behavior of the cement.

Takemoto, Ito, and Hirayama [18] obtained the data given in table 3 for cements aerated for 0, 5, and 15 hr.

A general statement by these authors regarding gypsum is as follows: "Gypsum shows a remarkable effect as a grinding aid. It seems to reduce cement coating on grinding media, flakes in cement, and total grinding time at temperatures below 105 °C (221 °F)."

They found that cements ground below 105 °C with gypsum, as compared with cements ground above 105 °C had many more medium size particles (between 15 and 40μ), less tendency to false set by aeration, and greater mortar strength.

Regarding false set, they state "Generally, cement ground at 20 °C had slight tendency to false setting, and even cement ground at 20 °C with hemihydrate showed normal setting after aeration for 15 hr. Cement ground at 20 °C with dihydrate had scarcely any tendency to false set by aeration. These cements ground at 85 or 105 °C with dihydrate had a tendency to false set by aeration, but the tendency disappeared after aeration for 15 hr. Cement ground at 130 or 150 °C with natural gypsum had a remarkable tendency to false set by aeration. The tendency to false set when ground at 85 or 105 °C with hemihydrate was similar to that of cement ground above 130 °C with gypsum."

"The poorer the particle size distribution of cement, the greater the tendency to false setting by aeration, even for cement ground at 20 °C

TABLE 2. *Data for clinkers ground in a cold mill with gypsum to give SO_3 contents of approximately 2.0 percent*

Data for clinker						Data for penetration test penetration—mm [b]				
Sample [a]	Type	SO_3	K_2O	Na_2O	Loss on ignition	Initial	5 min	8 min	11 min	Remix
		%	%	%	%					
A-1	I	0.03	0.41	0.13	0.30	50 50 50	50 47 38	50 46 31	50 43 16	50 50 50
A-2	II	0.17	0.36	0.09	0.39	50 50 50	50 50 50	50 50 50	50 50 44	50 50 50
A-3	III	0.10	0.28	0.10	0.72	50 50 50	50 13 50	50 7 45	50 5 38	50 50 50
B-1	I	0.53	0.56	0.10	0.12	50 50 50	50 42 38	32 15 15	28 8 5	50 50 50
C-1	I	0.35	0.63	0.36	0.75	50 45 50	43 24 41	40 10 28	39 5 12	50 24 44
C-2	II	0.63	0.79	0.22	0.36	50 50 50	50 45 46	50 12 34	45 8 10	50 50 50
D	I	0.49	0.11	0.10	0.03	50 50 50	50 50 50	50 41 50	50 39 50	50 50 50
E	I	0.09	0.39	0.24	0.22	50 50 50	50 50 45	45 43 42	44 41 38	50 50 50
F	I	0.11	0.46	0.11	0.53	50 3 16	50 1 8	50 0 7	42 0 5	50 50 50
G	I	0.48	0.08	0.14	0.05	50 50 50	44 50 50	40 50 44	37 48 44	50 50 50
H-1	I	0.87	0.49	0.10	0.10	50 33 50	50 5 50	50 2 50	50 1 50	50 50 50
H-2	II	0.90	0.47	0.08	0.26	50 4 50	50 2 50	50 1 50	50 1 39	50 50 50
I	III	0.46	0.77	0.25	0.54	50 50 50	50 50 50	50 50 47	50 50 34	50 50 50

[a] Letter indicates plant.

[b] First line original cement; second line cement aerated 24 hr; third line cement aerated 48 hr. Types I and II cements tested with 30 percent water; type III cements tested with 32 percent water.

with gypsum. Therefore, we must conclude that not only the extent of the dehydration of gypsum but also the size composition of the cement affects its tendency to false set by aeration."

It appears that it is not possible to predict what aeration might do. In an experiment in our laboratories, a clinker was ground without water in a mill at about 200 °F with natural anhydrite equivalent to 2.0 percent SO_3 (cement A). A similar grind was made, except that 2.0 percent water was added to the mill as grinding was started (cement B). These were tested for false set as follows:

1. A as ground
2. A+2.0 percent SO_3 as gypsum
3. A aerated 48 hr
4. B as ground
5. B+0.5 percent SO_3 as plaster of Paris
6. B aerated 48 hr

The results with ASTM Method C 359 were as follows:

Cement	Water	Penetration—mm				
		Initial	5 min	8 min	11 min	Remix
	%					
A — No water in mill						
As ground	30	27	12	3	3	10
2.0% SO_3 as gypsum	30	50+	41	30	15	50+
Aerated 48 hr	30	([a])	----	----	----	----
B — 2.0% Water added to mill						
As ground	30	40	9	3	2	6
0.5% as plaster	30	50+	50+	50+	50+	50+
Aerated 48 hr	30	([a])	----	----	----	----

[a] The mortar became dry and crumbly in the mixer and the temperature rose from 71 to 95 °F and from 71 to 84 °F for cements A and B, respectively.

These results indicate that the original cements were flash setting because the anhydrite could not dissolve fast enough to react with the $3CaO{\cdot}Al_2O_3$. The addition of 2.0 percent of SO_3 as gypsum to cement A almost eliminated the flash setting and the addition of 0.5 percent SO_3 as plaster of Paris

TABLE 3. *Data from paper by Takemoto, Ito, and Hirayama*

Cement No.[b]	W/C	Penetration—mm			Aeration[a] 5 hr				Aeration 15 hr			
					W/C	Penetration—mm			W/C	Penetration—mm		
		Init.	5 min	10 min		Init.	5 min	10 min		Init.	5 min	10 min
	%				%				%			
1	23.9	35	29	26	24.5	34	1	1	24.2	35	25	15
2	23.6	33	6	6	24.8	34	2	2	25.0	34	6	5
3	24.3	35	8	4	25.0	15	1	1	25.0	34	2	1
4	23.5	36	21	8	24.3	34	3	1	24.3	35	1	1
5	23.1	36	23	24	23.9	34	1	1	24.0	37	1	1
6	25.8	35	31	33	27.0	35	28	32	27.8	36	30	18
7	24.5	35	32	29	25.8	34	6	5	26.5	36	31	23
8	25.5	36	35	36	26.8	7	3	4	25.0	35	27	15
9	24.3	34	14	14	26.0	8	4	5	24.2	34	1	1
10	24.0	36	12	16	25.5	9	4	4	24.5	34	0	0
11	28.5	32	8	2	29.5	38	17	9	29.5	8	3	2
12	26.0	33	1	0	28.0	35	0	0	27.8	30	3	2
13	25.0	34	30	30	26.3	33	15	14	26.0	35	29	24
14	24.2	35	16	12	24.5	6	0	0	25.0	34	1	0
15	24.2	34	30	20	25.3	34	11	7	26.0	37	31	26
16	23.7	36	16	4	23.0	35	0	0	24.0	35	1	0
17	26.3	34	33	30	27.4	33	27	23	28.3	35	33	28
18	24.2	22	12	12	25.0	15	1	0	25.8	25	6	5

[a] Aeration layers 2 mm thick exposed at temperature of 20 °C and relative humidity of 85 percent.
[b] Blaine surfaces varied between 3500 and 3400 cm²/g.

to cement B did eliminate the flash setting. Aeration appears to have greatly increased the reactivity of the $3CaO{\cdot}Al_2O_3$ toward water in both cements.

The composition of this clinker was as follows:

Complete oxide analysis—percent									Free CaO—percent
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	SO_3	Loss on ignition	Total	
22.9	6.0	2.5	64.3	3.0	0.54	0.23	0.11	99.58	0.88

Calculated compound composition—percent					Alkalies—percent			
C_3S	C_2S	C_3A	C_4AF	$CaSO_4$	K_2O	Na_2O	Total	Na_2O Equiv.
43.0	33.3	11.7	7.6	0.4	0.33	0.17	0.50	0.39

Clinker of similar composition was ground in a commercial mill under conditions that were expected to dehydrate some or all of the gypsum. This cement was tested as received and, then, a sample was aerated for 24 hr. Samples of the aerated cement were stored in sealed containers for tests at later ages to determine whether or not the false set would disappear with age when not exposed to air and moisture. The cements were tested for false set by ASTM Method C 359 and extracts of slurries of 200 g of cement in 150 ml of water shaken for 1-, 3-, and 10-min periods were analyzed for SO_3, CaO, and $(OH)_2$, and the equivalent Na_2O content was calculated. The results of these tests are shown below.

The liquid phase of the paste of the cement as received was highly supersaturated with respect to gypsum at the 1-min period but only slightly, if at all, at the 3- and 10-min periods and the cement showed no false setting tendencies. The liquid phase of the pastes made with the cement after aeration for 24 hr and with the aerated cement stored for periods up to 4 weeks was highly supersaturated with respect to gypsum at both the 1- and 3-min periods. These results indicate that aeration decreased the rate at which the cement could combine with SO_3. Storage of the aerated cement in sealed containers up to 4 weeks did not change the cement with respect to its ability to combine with SO_3.

Sample[a]	Storage, weeks	Extraction data for period indicated—moles/liter						Penetration data—mm			
		1 min		3 min		10 min		Initial	5 min	8 min	Remix
		SO_3[b]	Na_2O	SO_3[b]	Na_2O	SO_3[b]	Na_2O				
C	None	0.0347	0.0163	0.0210	0.0127	0.0188	0.0172	50	50	50	50
D	None	------	------	------	------	------	------	3	0	0	50
E	1	.0442	.0141	0.457	.0170	.0207	.0175	2	0	0	50
F	2	.0419	.0150	.0376	.0177	.0210	.0193	3	0	0	50
G	3	.0432	.0153	.0380	.0169	.0214	.0182	3	0	0	50
H	4	.0430	.0155	.0373	.0171	.0208	.0186	3	0	0	50

[a] C=Sample as received; D is C aerated 24 hr; E to H are D stored for weeks indicated.
[b] SO_3 at equilibrium should be about 0.019 moles/liter.

When a cement shows flash set, it is generally assumed that this is the result of a rapid reaction of $3CaO \cdot Al_2O_3$ with water. However, the tests by Gilliland, Hansen, and Manabe indicate that the reactivity of the $3CaO \cdot Al_2O_3$ with calcium sulfate and chloride is decreased when the cement is aerated. This, of course, does not necessarily show that the reactivity of the $3CaO \cdot Al_2O_3$ with water has been decreased by aeration. Swayze showed that aeration caused flash set with a clinker that contained no calculated $3CaO \cdot Al_2O_3$ and assumed that aeration increased the reactivity of the $3CaO \cdot SiO_2$.

The fact that pastes of cements A and B made with clinker and natural anhydrite after aeration for 48 hr became extremely hot and crumbly, whereas the pastes of the cements before aeration showed milder flash set indicates that aeration increased the reactivity of the $3CaO \cdot Al_2O_3$ toward water. Actually, the reactivity of the $3CaO \cdot Al_2O_3$ toward water may not have been increased but the ability of the natural anhydrite to retard the reaction of $3CaO \cdot Al_2O_3$ with water probably was decreased. These results indicate that, in the cases cited, where the rates at which the cements combine with sulfate and chloride were decreased, the ability of the $3CaO \cdot Al_2O_3$ to react with sulfate and chloride had been decreased.

Hansen [34] concluded from work reported in 1958 that aeration by reducing the rate at which the cement combined with calcium sulfate permitted the dehydrated gypsum to precipitate as gypsum and produce false set. Actually, the precipitation probably was largely responsible for the rapid stiffening but its effect may have been augmented by a rapid reaction of the $3CaO \cdot Al_2O_3$ with water.

This raises the question as to why aeration either increases the reactivity of $3CaO \cdot Al_2O_3$ towards water or decreases the ability of calcium sulfate to combine with $3CaO \cdot Al_2O_3$ and prevent flash set. Hansen [46] has postulated that Ca^{++} and O^{-} ions in the surfaces of $3CaO \cdot Al_2O_3$ crystals can chemisorb water molecules from which H^+ and OH^- ions migrate into the crystals and split off $Ca(OH)_2$ and rearrange the ions in the crystals to form $2CaO \cdot Al_2O_3 \cdot xH_2O$. It is conceivable that these partially reacted crystals cannot chemisorb $SO_4^{=}$ and Cl^- ions and, accordingly, cannot react with calcium sulfate and calcium chloride. It is also conceivable that these partially reacted crystals can chemisorb H_3O^+ and OH^- ions and, in that way, react rapidly with water. In general, cement appears not to become very badly flash setting upon aeration and, since prolonged aeration often destroys the flash setting tendencies developed by shorter periods of aeration, it appears that the reaction with H^+ and OH^- ions either from water vapor or from liquid water tends to form a layer of hydrated material on the surfaces of the crystals that retards further reaction.

Swayze suggested that the reactivity of the $3CaO \cdot SiO_2$ with water is increased by aeration. However, it seems from these new data that the reactivity of the calcium aluminoferrite phase may have been increased by aeration and that the fast stiffening was caused by a rapid reaction of this phase with water and not by increased reactivity of the $3CaO \cdot SiO_2$. The data from our laboratories given in table 2 show that some Type II cements develop false set when aerated and indicate that both $3CaO \cdot Al_2O_3$ and the calcium aluminoferrite phase can be modified by chemisorption of water vapor so that their reactions with water cannot be retarded by calcium sulfate.

Cement technologists have long known that aeration produced false set in some cements. It seems that the scarcity of data bearing on the mechanism of this behavior probably resulted from the lack of methods of detecting what might be called mild cases of either flash or false set. ASTM Method C 359 appears to be able to detect very mild degrees of fast stiffening and has given investigators a tool by which the stiffening characteristics of cements can be studied in more detail.

There is a need for additional work to determine the exact mechanism by which aeration causes false set. However, it seems from a practical standpoint that the false set that causes trouble in the field is produced by dehydrated gypsum, because it appears that cements will seldom be aerated sufficiently to become false setting from the aeration reaction. It should be pointed out, however, that there is a great need for the samplers and testers to handle their samples in ways that do not permit aeration to develop false set in samples when the cements are not false setting.

Summary

Since the time of the First International Symposium on the Chemistry of Cement, progress regarding false set seems to have been as follows:

1. Rapid stiffening of cement pastes has been separated into (a) flash set produced by rapid reaction of $3CaO \cdot Al_2O_3$ with water; (b) false set produced by crystallization of gypsum.
2. A number of suggested causes of false set such as rapid absorption of water by clusters of cement particles, formation of alkali carbonates during aging, and so forth, have been considered and discarded.
3. Several methods of testing for false set have been developed.

4. Most evidence points to the conclusion that false set in commercial cements is almost entirely the result of dehydrating gypsum to either or both hemihydrate and soluble anhydrite during either or both grinding and storage.
5. A new problem has been created by the finding that aeration produces a false set that is not connected with dehydrated gypsum.

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Discussion

Toshio Manabe

Cement chemists may be interested in the problem of false set in cement, not only because it causes troubles in the field, but because it gives many important suggestions to study the reaction of the initial hydration period of cement.

I agree with Dr. Hansen in considering that "the crystallization of gypsum from cement paste is the principal cause of false set in commercial cements." However, as to the consideration of mechanism of false set, there are some questions on which I cannot agree. Especially I would not support Dr. Hansen's theory that in fresh cement C_3A combines with calcium sulfate at a rate which permits the crystallization of little, if any, gypsum in the paste, whereas aeration retards the rate of combination and consequently increases the amount of crystallization of gypsum.

In my experiments [1], it was found that a fair amount of calcium sulfate was rapidly combined with cement in the first few minutes and then the rate of combination became very slow. The time at which the rapid combination of calcium sulfate with cement began was delayed a few minutes by aeration, but the amount of calcium sulfate rapidly combined was nearly equal to that in the unaerated cement, as shown in figure 1. That is, by aeration, the time at which the rapid combination of calcium sulfate with cement occurs is shifted, but the amount of calcium sulfate rapidly combined within the first 10 min or so is scarcely decreased.

It seems that these results are considerably different from that obtained with $CaCl_2$ by the author. It is probable that the reactivity of aerated clinker compounds towards calcium sulfate may be much greater than that towards calcium chloride.

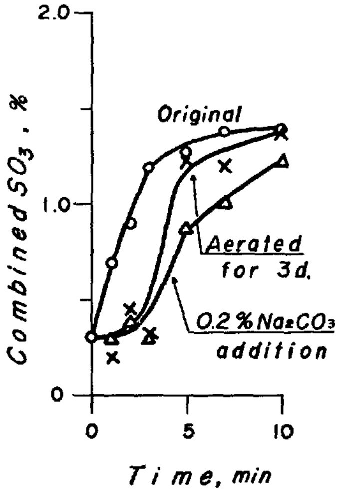

FIGURE 1. *Amount of SO_3 combined as sulfoaluminate during the initial hydration period.*
(Total SO_3 of the cement, 2.22%; W/C = 50%)

Now, let us consider a cement which contains 2.0 percent SO_3, for example. When the unaerated cement is mixed with water, 0.6–1.0 percent SO_3 would be rapidly combined with cement in a few minutes, and the rest, 1.0 percent or more SO_3, may be precipitated as dihydrate, if all SO_3 is present as dehydrated gypsum. Therefore, even in the fresh cement, a tendency to false setting would be expected. But in practice the cement probably would not show any false-setting tendency. What can be the reason?

If the gypsum in cement is only partly dehydrated during grinding and about 1.0 percent of SO_3 is present as gypsum, and if the dehydrated gypsum preferentially combines with cement, false set would not appear in the unaerated cement. As will be mentioned later, however, if gypsum remains partly unchanged in cement, it acts as crystal nuclei and effectively accelerates the rate at which the dehydrated gypsum converts to dihydrate. In this case, it seems that the precipitation of gypsum takes place during mixing, and then false set would not appear even if the cement is aerated.

From the data reported by Takemoto, Ito, and Hirayama [2] and Murakami [3], it is conceivable that gypsum in commercial cement is nearly completely converted to hemihydrate and, in some cases, even to soluble anhydrite during grinding. However, since soluble anhydrite has a very strong hygroscopic property, it reconverts easily to hemihydrate when exposed to air. Accordingly, it may be regarded as pretty certain that in most commercial cements, almost all calcium sulfate may be present in the form of hemihydrate.

From results of many penetration tests I came to the following conclusion:

Almost all commercial portland cements have a tendency to stiffening caused by dehydrated gypsum at a certain period after contact with water, and the stiffening is fully developed within a few minutes. The rate of development of stiffening may be pictured as in figure 2. If the paste is mixed until the time denoted by "e" in the figure, the stiffening tendency does not appear, because the structure formation which causes

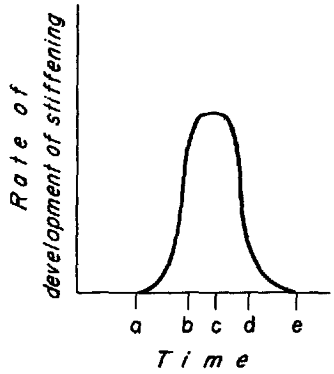

FIGURE 2. *Rate of development of stiffening.*

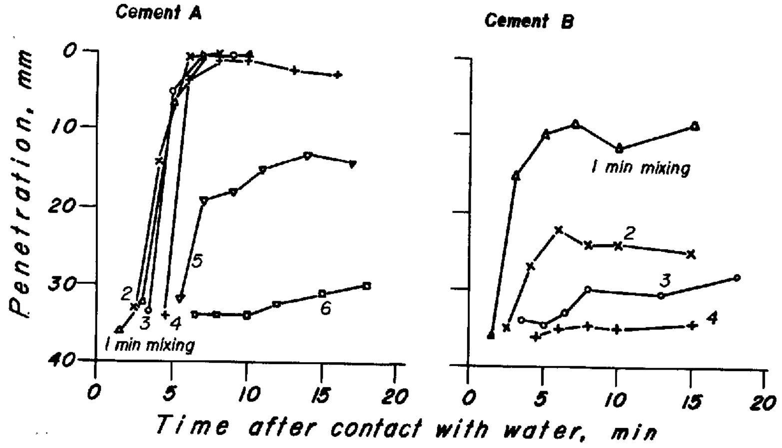

FIGURE 3. *Effect of mixing time on development of stiffening.*

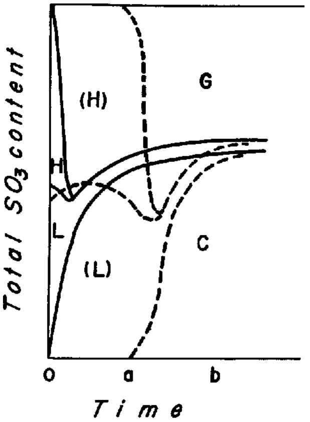

FIGURE 4. *Distribution of* SO_3 *among the various forms.*
Solid line, fresh cement; broken line, aerated cement; H, hemihydrate; G, gypsum; C, calcium sulfoaluminate; L, liquid phase.

the stiffening of the paste is destroyed by mixing. If the paste is mixed until "a", the stiffening is fully developed and if mixed until "b", "c", or "d", the stiffening is partly developed.

Figure 3 shows examples of the results of penetration tests which were carried out in neat cement pastes of approximately normal consistency by varying mixing time. In the case of cement A, "a" in figure 2 corresponds to 1 min, "e" corresponds to 6 min, and "b"–"d" correspond to 2–5 min. In cement B, the stiffening was developed immediately after mixing with water, and 3-min mixing corresponds to "e".

Further, the results of experiments on the chemical compositions of extracts from paste and also on the amount of SO_3 combined with cement permitted the drawing of a diagram, figure 4. This figure shows the distribution of SO_3 among the various forms in paste. When unaerated cement is mixed with water, the combination of SO_3 with cement immediately takes place, and the precipitation of gypsum follows at once; this process is shown by the solid line in the figure. But the time taken for this rapid combination and precipitation to begin ("a" in the figure) is progressively increased by aeration, as shown by the broken line. In comparison with the results of the penetration test, it is found that the time at which the stiffening occurs corresponds to that at which the combination and the precipitation rapidly appear.

Therefore, even if all the gypsum is converted to dehydrated gypsum, in the unaerated cement, the precipitation of gypsum takes place completely during mixing, the structure formation does not develop in the paste, and a tendency to false setting is not observed. If the precipitating time is delayed by aeration, however, the precipitation of gypsum occurs partly or wholly after mixing is completed, and the stiffening appears.

From these considerations it seems important to know when the precipitation of gypsum occurs after mixing with water. In the case of commercial plaster of Paris, the precipitation of gypsum usually occurs at about 15 min after contact with water. Plaster of Paris is commonly manufactured by the "kettle process", in which gypsum is almost converted to soluble anhydrite during heating and then reconverted to hemihydrate by the process of aging. However, it was found that when gypsum was converted only to hemihydrate or partly to soluble anhydrite by heating at rather lower temperature, the dehydrated gypsum reconverted to gypsum 4 or 5 min after contact with water. If gypsum was almost completely converted to soluble anhydrite, the reconversion to gypsum was retarded progressively, and even if the soluble anhydrite was converted to hemihydrate by exposing to air, the time at which the precipitation of gypsum occurred was almost unchanged, as in the case of commercial plaster of Paris.

By adding pulverized cement clinker, the setting time of plaster of Paris is considerably accelerated. This result indicates the ability of the clinker to accelerate the precipitation of gypsum. This could be the reason why fresh cement in which all of the gypsum is converted to dehydrated gypsum does not manifest false-setting tendency.

When the cement is aerated, the accelerating ability of clinker is weakened, so that the precipitating period of gypsum is delayed and false set appears.

Then, what part of the clinker acts as the accelerator? It is likely that the formation of the high-sulfate form of calcium sulfoaluminate gives rise immediately to the precipitation of gypsum. The author has postulated that $2CaO{\cdot}Al_2O_3{\cdot}xH_2O$ is formed by aeration and that it cannot react with calcium sulfate. In this connection it would be interesting to note some results obtained in my experiments. A portion of cement which did not manifest false set was exposed to air which had been passed through dilute sulfuric acid solution to regulate the humidity. (The relative humidity was about 60 percent.) Another portion of the cement was exposed to air which was passed through potassium hydroxide solution first to remove carbon dioxide and then through the sulfuric acid solution. The results of penetration tests with these aerated cement were as follows:

	Aerated with air containing CO_2 penetration—mm			Aerated with air not containing CO_2 penetration—mm		
	Init.	5 min.	10 min.	Init.	5 min.	10 min.
As received	35	34	35	-------	-------	-------
Aerated 12 hr	34	1	2	36	35	35
Aerated 24 hr	35	3	1	34	35	35

These results show that if the air does not contain carbon dioxide, false set does not appear by aeration. Therefore, it is probable that the products formed by hydration and subsequent carbonation play an important role in the false-setting phenomena caused by aeration.

It is well known that an addition of a small amount (0.1 percent or less) of alkali carbonates to a cement produces early stiffening of the paste. The author states that alkali carbonates precipitate calcium carbonate which might, in itself, cause stiffening of the paste just as the precipitation of gypsum does. But it seems to me that the amount of calcium carbonate precipitated is too little to make the paste stiffen.

Murakami [4] showed that addition of chemicals which acted as retarders of setting of dehydrated gypsum produced a tendency to false setting in cement paste, and concluded that alkali carbonates which retarded the precipitation of gypsum were formed in cement by aeration, and early stiffening resulted.

When alkali carbonates were added to cement paste, the rate of combination of SO_3 with the cement was decreased as in the case of aeration (fig. 1). But this similarity does not necessarily indicate that alkali carbonates are formed in cement by aeration. As mentioned by the author, it is probable that very little, if any, alkali carbonate is formed by aeration. Then I would rather consider that the addition of alkali carbonates and aeration act similarly only in the retardation of the rate at which SO_3 combines with the cement.

When a small amount of calcium lignosulfonate, which is often used in the field as dispersing agent or retarding agent, was added to cement pastes, a tendency to false setting appeared as shown in figure 5. In this case it was also found from the results of extraction tests that the rate of combination of SO_3 with cement was reduced by addition of calcium lignosulfonate and the precipitation of gypsum was retarded.

Another experiment on the ability of C_3A to accelerate the precipitation of gypsum also showed that the ability was reduced by aeration. The C_3A used in the study was prepared from reagent-grade calcium carbonate and aluminium oxide and, consequently, contained only a trace of alkali. Hence, it is clear that the reduction of the accelerating ability of C_3A is not caused by the formation of alkali carbonates.

Accordingly, it seems that the following conclusion could be drawn, that is, any conditions which retard the combination between calcium sulfate and cement have a tendency to produce false set.

In the next place, I should like to consider the degree of early stiffening of the paste. If

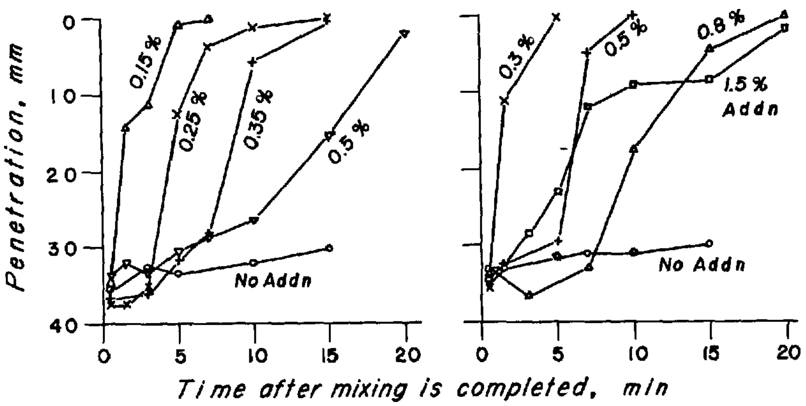

FIGURE 5. *Effect of addition of calcium lignosulfonate.*

the precipitation of gypsum causes the early stiffening, the degree of stiffening may be proportional to the amount of gypsum precipitated after mixing is completed.

The case of cements in which gypsum is completely dehydrated will be first considered. In these cases it is conceivable that if the precipitation of gypsum wholly occurs after mixing is completed, the degree of stiffening is at its maximum for the cement and may depend on the amount of SO_3 which does not rapidly combine with cement at the initial hydration period and precipitates as gypsum. This hypothesis may be confirmed by the following experiments.

Two grinds were made with a commercial portland cement clinker and a natural rock gypsum. The first one had an SO_3 content of about 0.7 percent, the second about 2.0 percent. The cements were then blended to obtain the desired intermediate SO_3 contents. Six cements thus obtained were heated to 140 °C for 2 hr to completely dehydrate the gypsum, then they were aerated for 2 days in small paper bags. Penetration tests were carried out for these cements using the Vicat apparatus. For the purpose of determining the maximum degree of stiffening, the pastes were mixed for 1½ min and then molded into the Vicat ring and tested for depth of penetration of the 10-mm plunger and the 5-mm plunger.

The results are given in figure 6.

Cement No. 1 showed a quick set accompanied by the evolution of considerable heat. Cement No. 2 did not manifest a tendency to false set. Cement No. 3 and the rest manifested the tendency to stiffening, and the degree of stiffening increased with the SO_3 content.

The amount of SO_3 which does not rapidly combine with the cement during the initial hydration period can be estimated by extracting the paste with lime solution. The results of the extraction tests on the pastes at the age of 20 min were as follows:

Cement No.	1	2	3	4	5	6
SO_3 content in cement percent of cement	0.70	0.79	1.00	1.21	1.56	2.13
Extracted SO_3 percent of cement	0.07	0.08	0.25	0.51	0.84	1.40
Combined SO_3 as sulfoaluminate percent of cement	0.64	0.71	0.75	0.70	0.72	0.73

The amount of SO_3 precipitated as gypsum can be estimated by subtracting the amount of SO_3 present in the liquid phase of the paste from the amount of extracted SO_3. The amount of SO_3 present in the liquid phase depends on the concentration of alkali in the liquid phase. In the case of the clinker used in the study the amount of SO_3 present in the liquid phase was estimated to be about 0.08 percent. These values represent the amount of SO_3 at the time "b" in figure 4.

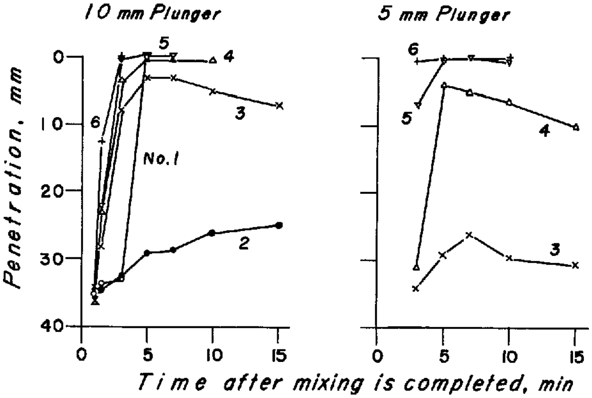

FIGURE 6. *Effect of calcium sulfate content.*
(Numerals in figure represent number of cement in table.)

From the table, it seems that the clinker used required about 0.75 percent of SO_3 for normal set. Hence the quick set shown in cement No. 1 was caused by the lack of SO_3. It also was clearly found that in cement No. 2 which did not show the stiffening, there was precipitation of little, if any, dihydrate, and that in cement No. 3 and the rest, the degree of stiffening increased nearly proportionally to the amount of precipitation of gypsum. Furthermore, it seems that the depth of penetration of the 10-mm plunger in paste is considerably prevented by the precipitation of gypsum equivalent to only 0.2 percent of SO_3.

When gypsum in cement is not completely dehydrated, that is, the calcium sulfate is a mixture of gypsum and dehydrated gypsum, the manner in which the dehydrated gypsum may behave during the first few minutes of the initial hydration period will be considered with an example.

A cement was prepared from a commercial clinker, gypsum, and hemihydrate labeled with S-35. The cement contained 2.32 percent of SO_3, which was made up of 0.14 percent from the clinker, 1.02 percent from the gypsum, and 1.06 percent from the labeled hemihydrate. The specific activity of SO_3 of the hemihydrate used in the study was 212.5 reg/min (register of 256 scaler), and the specific activity of the SO_3 in the cement was calculated to be 97.1 reg/min. One g of the cement was mixed with 0.5 ml of distilled water, and after 10 min it was shaken with 100 ml of lime solution for 4 min. Then the slurry was filtered on a Buchner funnel, and from 20 ml of the filtrate SO_3 was determined and from 70 ml the specific activity of SO_3 was determined. The activity of SO_3 in the filtrate was 84.2 reg/min, and the amount of SO_3 extracted was 1.70 percent. Consequently, the amount of SO_3 rapidly combined with cement within 10 min was 0.62 percent. From these data, it was calculated that 0.23 percent SO_3 from the gypsum and 0.39 percent SO_3 from the hemihydrate were combined with the cement within 10 min and also that the amount of hemihydrate preferentially combined with cement was only 0.23 percent as SO_3. Since the alkali content (R_2O) of the liquid phase at the age of 10 min was about 60 mM/l, 43 mM SO_3 should be contained in the liquid phase, corresponding to 0.17 percent of the cement.

From the result it is probable that when the cement comes in contact with water, the dehydrated gypsum preferentially dissolves but immediately transforms to dihydrate owing to the coexisting gypsum which acts strongly as crystal nuclei, and after that, the cement reacts at first with the SO_3 left in the liquid phase, which comes from dehydrated gypsum, and then the successive reaction occurs with the gypsum which is composed of gypsum present from the first and dihydrate precipitated from dehydrated gypsum. When the cement is not aerated, the reactivity of the cement is so strong that the amount of hemihydrate preferentially combined with the cement may be somewhat increased.

The effect of gypsum as crystal nuclei, of course, depends on the proportion of gypsum to dehydrated gypsum. If the proportion of gypsum is less than 25 percent of the total SO_3, the effect of the gypsum is obviously reduced.

The foregoing considerations about false set caused by the dehydrated gypsum may be briefly summed up as follows:

Gypsum in cement is usually dehydrated, during grinding, almost all to hemihydrate or even partly to soluble anhydrite. Such a dehydrated gypsum ought to reconvert to dihydrate in about 5 min after contact with water. But in case of cement, clinker, probably the aluminate phase, accelerates the precipitating period of gypsum to within 3 min. Hence, the structure developed by the precipitation of gypsum is destroyed by mixing, and the false-setting tendency does not appear. However, by aeration the accelerating ability of clinker is reduced and the precipitation of gypsum wholly or partly occurs after 3 min. Consequently, the structure formation develops after mixing is completed and the stiffening appears. If almost all the gypsum in the cement is dehydrated to soluble anhydrite owing to the high grinding temperature, it would be expected in some cases that clinker could not accelerate the precipitating period of gypsum to within 3 min; then even a fresh cement would manifest the false-setting tendency. If the grinding temperature is so low that 25 percent or more of the gypsum remains undehydrated, the undehydrated gypsum acts as crystal nuclei and accelerates the precipitation of gypsum. Hence, even the aerated cement does not manifest the false-setting tendency.

Therefore, in consideration of the false-setting phenomenon, the time at which the precipitation of gypsum occurs and the amount of gypsum precipitated are the important factors. The former depends on the degree of dehydration the gypsum is subjected to during grinding or storage and also the accelerating power of clinker for the precipitation of gypsum.

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Discussion

P. Seligmann and N. R. Greening

The purposes of this discussion are to confirm and to extend certain portions of the interesting line of reasoning developed in the discussion by Mr. Manabe.

The State of Hydration of Calcium Sulfate in Cement

Mr. Manabe states ". . . it is conceivable that gypsum in commercial cement is nearly completely converted to hemihydrate and, in some cases, even to soluble anhydrite during grinding." Data obtained at the Portland Cement Association Laboratories indicate that, because of the effectiveness of clinker as a dehydrating agent, this conclusion is more likely to be valid than might usually be supposed.

The technique used in these studies was the determination of the evaporable and nonevaporable water by the method of Copeland and Hayes [1],[1] involving drying at a water vapor pressure of 0.5 μ (over ice at the temperature of solid CO_2). As a standard for comparison, the room temperature dehydration of gypsum was studied; a sample of Mallinckrodt Analytical Grade gypsum (fine powder) was dried by this procedure and then successively equilibrated at 36 and 50 percent relative humidity. As shown in table 1, the gypsum loses well over 90 percent of its water at 0.5 μ water vapor pressure; consequently, if a cement containing calcium sulfate dihydrate were subjected to this drying procedure, most of the hydrate water would be classed as evaporable.

Table 1. *Room temperature dehydration of gypsum*

The mole ratio H_2O/SO_3 in the following table was computed on the assumption that the material after ignition at 950 °C was pure anhydrite.

Condition	Mole ratio H_2O/SO_3
As received	1.964
Dried at 0.5 μ water vapor pressure	0.083
Equilibrated at 36% relative humidity	.649
Equilibrated at 50% relative humidity	.663

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[1] Figures in brackets indicate the literature references at the end of this paper.

Evaporable water, nonevaporable water, and carbon dioxide were determined on 26 of the cements used in the Long-Time Study of Cement Performance in Concrete [2]. These values were then used in an analysis of the ignition loss of each cement, which was also measured. Since the SO_3 in the clinker is known for these cements [3] the contribution of the water and SO_3 by the added calcium sulfate could be accounted for separately. Table 2 shows, for each cement, the total loss on ignition and the mole ratios H_2O/SO_3 for the evaporable water and total water in the cement based both on the total sulfate present and on the added calcium sulfate. It is apparent that in all cases the mole ratio for the evaporable water is considerably less than 1.8–1.9, the range of values expected for dihydrate, and in many cases is less than that expected for the hemihydrate.

For reference, the last two columns of table 2 show the average and maximum temperatures of the cements in the streams from the finishing mill systems at the commercial plants where they were prepared [4]. No definite relationship between grinding temperature and water content is apparent.

The cements of table 2 had been stored in sealed containers for about 20 yr; it could be argued that this storage provided an abnormally favorable environment for the dehydration of gypsum by the clinker.

Further evidence on this point was obtained from tests made on four cements purchased from commercial sources in the Chicago area. For these cements, neither the grinding temperature nor the SO_3 content of the clinker was known. The results, shown in table 3, do not differ appreciably from those previously obtained.

X-ray diffraction patterns of the four commercial cements were made. Hydration products were detectable only in the pattern for cement 19737. In addition to the lines for the clinker compounds in this cement the diffraction pattern had a line at 3.50A, attributable to the anhydrite, and a line at 4.90A, presumably due to calcium hydroxide. These assignments were verified when a pattern of the cement after heating at 600–650 °C for 12 hr showed a disappearance of the 4.90A line, an intensification of the 3.50A line, and the presence of other anhydrite lines.

The same four commercial cements were examined petrographically.[2] In all four samples, the predominant form of calcium sulfate was the hemihydrate. In addition, traces of anhydrite and gypsum were found in cement No. 19737 and small quantities of calcium hydroxide in cements No. 19737 and No. 19738. The petrographic and X-ray examinations of No. 19737 thus appear to be relatively consistent. In the interpretation of these results, it must be pointed out that the crystal structure associated with calcium sulfate hemihydrate can be maintained by calcium sulfate over a considerable range of moisture contents without any appreciable change in optical or X-ray diffraction characteristics [5, 6].

Attempts have been made to measure the rate of dehydration of gypsum by ground clinker or by cement directly. The process appears to be very slow unless ball-milling is used. Thus, a sample of gypsum stored in a desiccator over ground clinker lost 0.1 percent of its water after 64 days at 70 °F.

TABLE 2. *Water content of the long-time-study cements*

Cement No.	Loss on ignition	Mole ratio H_2O/SO_3 based on				Cement temperature, °F	
		SO_3 in gypsum		Total SO_3		Average	Maximum
		Evap. water	Total water	Evap. water	Total water		
	Percent						
11	0.89	0.63	2.80	0.47	2.09	222	236
11–T	.86	1.14	2.95	.84	2.18	222	226
12	.37	0.00	0.56	.00	0.49	209	230
12–T	.58	.46	1.08	.43	1.01	229	245
13	1.60	.88	3.92	.88	3.92	240	248
14	0.83	.67	2.10	.51	1.62	228	245
15	.95	1.20	2.10	1.13	1.99	192	200
16	.70	0.62	2.02	0.44	1.43	[a] 209, 215	[a] 226, 232
16–T	.75	.83	2.05	.60	1.50	[a] 209, 215	[a] 226, 232
17	.37	.00	0.47	.00	0.41	[b] 247–264	[b] 278–292
18	1.04	1.62	2.80	1.26	2.18	183	225
18–T	0.83	1.56	2.50	1.19	1.90	[c] 187, 125	[c] 200, 130
21	.69	0.68	2.40	0.57	2.01	191	214
21–T	.65	.54	2.16	.45	1.82	209	221
22	.48	.41	0.85	.38	0.79	216	235
23	.42	.34	1.03	.30	.89	211	227
24	1.26	.85	3.45	.61	2.46	107	113
25	0.35	.42	1.03	.26	0.64	325	370
31	1.17	.35	1.83	.34	1.75	221	224
33	1.20	.00	2.34	.00	2.04	[a] 235, 209	[a] 254, 225
34	1.34	.56	2.95	.49	2.61	178	225
41	1.05	.39	2.43	.29	1.82	214	185
42	0.67	.98	1.71	.85	1.49	168	242
43	.77	.50	1.86	.33	1.25	273	284
43A	.71	.49	1.95	.36	1.42	259	274
51	.66	.23	1.33	.21	1.19	193	198

[a] Values for 2 mills used.
[b] Range of values for 3 mills used.
[c] The second value is for a regrind.

TABLE 3. *Water content of recently purchased cements*

Lot No.	Mole ratio H_2O/SO_3 based on	
	Evaporable water	Total water
19737	0.64	3.06
19738	.70	1.17
19739	.55	1.48
19740	.79	2.04

The Role of Carbon Dioxide in Cement Aeration

Recent work at these laboratories on the properties of calcium carboaluminate hydrate provides a possible mechanism for the inactivation of the surface of tricalcium aluminate during aeration of cement and also for certain effects of carbonate ion in solution that have been previously discussed.

Results obtained with an X-ray technique indicate that calcium carboaluminate is a material

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[2] The petrographic examinations were made by J. E. Cox and B. Erlin of the Portland Cement Association Petrographic Laboratory, whose assistance is gratefully acknowledged.

of exceedingly low solubility which can be formed preferentially when tricalcium aluminate is hydrated in a solution containing both sulfate and carbonate ions. The phenomenon has also been observed in hydrating cement paste at a normal water-cement ratio. Consequently, it is to be expected that a chemical reaction of tricalcium aluminate with carbon dioxide and moisture in the atmosphere would produce a carbonated coating that would be unreactive toward sulfate ions in solution. The experimental details are as follows.

Calcium carboaluminate hydrate, $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 10.5H_2O$ has an X-ray diffraction pattern with a very intense line at 7.60 A which is easily identified in carbonated samples of hydrated cement paste. This intense line persists during drying and has been observed in samples equilibrated over calcium chloride dihydrate. This diffraction line therefore provides a means for determining the presence of the calcium carboaluminate phase.

Recently, several observers [7, 8] have noted the formation of calcium carboaluminate hydrate during the hydration of tricalcium aluminate in the presence of solid calcium carbonate. It appears, consequently, that calcium carboaluminate hydrate is less soluble than calcium carbonate.

In the present work, a mixture of equimolar quantities of tricalcium aluminate and calcium carbonate in a sodium sulfate solution was agitated continuously on a rotating wheel. After 10 days, an X-ray pattern of the solid phase showed the presence of a large quantity of calcium carboaluminate hydrate and no indication whatever of the calcium carbonate or tricalcium aluminate originally present. Lines also appeared for both forms of calcium sulfoaluminate hydrate and for tetracalcium aluminate hydrate, but all these lines were quite weak. It may therefore be concluded that the carbonated compound forms in preference to the other reaction products and is definitely less soluble than calcium carbonate.

In order to study this phenomenon in relation to cement hydration, a paste was made with Long-Time-Study cement No. 18 (C_3A: 13.2%; SO_3: 1.8%) with 5 percent calcium carbonate at 0.50 water-cement ratio. This paste was moist cured. At intervals up to 6 months, the superficial layer was removed and X-ray diffraction patterns were made of the underlying material. Experience has shown that in the absence of the calcium carbonate, the X-ray diffraction patterns of pastes prepared in this manner would not include the line for the calcium carboaluminate hydrate. In the presence of the carbonate, however, the line was quite intense. The pattern also contained the main line for the high form of calcium sulfoaluminate hydrate, rather than that for the low form which would have been expected in this case in the absence of the carbonate. The result obtained verifies that the added calcium carbonate reacted with the tricalcium aluminate in the cement, but indicated that the specific conditions were favorable for production of a sulfoaluminate as well.

Finally, it can be seen that if larger amounts of carbonate ion were present in solution, a rapid reaction of these ions with the tricalcium aluminate phase in cement would account for the retardation of the reaction of cement with sulfate ion that was postulated by Mr. Manabe.

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Discussion

Jean Laneuville

I think Dr. Hansen's paper has shown that the fundamental mechanism by which some cements become fast setting upon aeration is still obscure. This problem is undoubtedly a real challenge to the initiative of cement chemists for the coming decade.

I wonder why some valuable contribution could not be derived by tackling the problem under another angle, say, the search for conditions under which false-setting tendency cannot be developed.

In our laboratory, we have made a few experiments on this matter by using selected rotary-kiln clinkers made under determined burning conditions. Clinker A was made under normal burning conditions. Clinker B, of a very high SO_3 content, was lightly burnt with a large excess of air prevailing in the rotary kiln. These clinkers were ground at 70 °F in a laboratory ball mill to a Blaine fineness of 2750 cm^2/g. Four percent of gypsum was added to clinker A before grinding, and the chemical composition of the resulting cement A is given in table 1. The lightly burnt clinker was ground without gypsum to give "cement" B. The fast-stiffening properties of these cements were tested according to the ASTM method C359 on the fresh samples, on the samples heated in closed tin cans to 293 °F during 6 hr, on samples aerated in the laboratory air in one-half-inch layers for different periods of time, and on samples heated 6 hr at 293 °F and subsequently cooled and aerated for periods of 10 and 19 days.

The data shown in the table indicate that under the test conditions, it was possible to produce fast stiffening by heating or aerating cement A, but it was impossible to develop the least stiffening either by heating or aerating cement B. Although the discrepancy between the oxide analysis of the two cements is not large, their stiffening properties are very dissimilar.

Of course, as cement B contained no gypsum and all the SO_3 was presumably bound in the form of potassium sulfate, sodium sulfate, and dead-burnt anhydrite, it seems normal that no false set could be induced by heating this cement. The fact that cement B could not be made fast stiffening by aeration under the same conditions which rendered cement A false setting is somewhat intriguing.

We came to the fact that two cements of quite similar oxide composition, made from clinkers burnt in the same kiln, with the same raw materials, thereafter ground in the same mill, aerated under the same conditions do develop very dissimilar fast-stiffening properties.

I wonder if these properties would not originate to a large extent in the conditions prevailing in the rotary kiln and cooler during the process of burning and cooling the clinker.

I would appreciate the author's comments on this topic.

Table 1. *Chemical composition and false-set test of two cold ground laboratory cements*

Cements	Oxide analysis—%										Calculated compound composition—%			
	Ign. loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	Free CaO	C_3S	C_2S	C_3A	C_4AF
A	1.14	21.68	4.95	3.38	62.49	3.05	2.30	0.67	0.34	0.39	45	28	7	10
B	0.13	21.58	4.79	3.68	63.47	3.08	2.50	0.68	0.33	0.73	49	25	6	11

ASTM method C359—30% water in mortar

Cement	Condition	Penetration—mm				
		Init.	5 min	8 min	11 min	Re-mix
A	Fresh	50	50	50	50	50
A	Heated 293 °F, 6 hr	50	0	0	0	50
A	Aerated, 3 days	50	50	50	48	50
A	Aerated, 5 days	50	40	39	10	50
A	Aerated, 10 days	5	2	0	0	50
A	Heated 290 °F, 6 hr, and aerated 10 days	38	0	0	0	50
B	Fresh	50	50	50	50	50
B	Heated 293 °F, 6 hr	50	50	50	50	50
B	Heated 293 °F, 22 hr	50	50	50	50	50
B	Aerated, 5 days	50	50	50	50	50
B	Aerated, 18 days	50	50	50	50	50
B	Aerated, 31 days	50	50	50	50	50
B	Heated 293 °F, 6 hr, and aerated 19 days	50	50	50	50	50

Discussion

Renichi Kondo

The valuable paper presented by Dr. W. C. Hansen explained systematically the causes of false setting. I can agree with him that false setting is generally due to the existence of dehydrated gypsum in cement, and that the false set induced by aeration is partly due to inactivation of the C_3A which increases the amount of effective dehydrated gypsum. I like to think, however, that aeration reduces the reactivity of the C_3A not only toward sulfate but also toward water, and that before aeration the paste of cement containing C_3A can be kneaded down almost to the texture produced by the immediate hydration during mixing, while after aeration the cement hydrates a little after the mixing period and, accordingly, the rapid setting may be brought about. Then the expression, "Increasing of the reactivity of C_3A with water by aeration", seems to be rather superficial.

In addition, the results of the determination of setting time of the components of cement showed that $C_{6.2}A_{2.2}F$, C_4AF, and the glass phase in clinker and its devitrified product set almost as rapidly as C_3A [1].

Furthermore, he concluded that the formation of alkali carbonate during aging is to be discarded as the cause of false setting. It is considered possible, however, that the alkali carbonate produced by aeration behaves as a retarder, under the influence of calcium hydroxide, on the plaster setting even if the amount of the carbonate is very small. Decreasing the amount of alkali sulfate in cement by aeration also retards the plaster setting. If retarding action undesirably prevents the setting of the plaster from taking place during mixing, as mentioned by Messrs. T. Yoshii and Y. Murakami [2], then false set should appear. Of course, I believe as Dr. Hansen does that the alkali carbonate itself is not the main factor of false setting through the formation of calcium carbonate.

The false setting on aeration can hardly be explained by a single mechanism, because there seem to exist so many factors and complicated mutual interactions, for instance, some cements give rise to complexity, showing the cycles found by Mr. Miyatake [3] along with the progress of aeration. The degree of false setting is changed successively with aeration, i.e., in the first stage it is very weak, in the second, intensive, in the third, decreased, in the fourth, strengthened, and finally the hardenability is lost.

Moreover, I have verified [4] that the velocities of moisture absorption of the cement components decrease in the following order: portland cement clinker$>$dehydrated gypsum$>C_3A\gg C_4AF$, glass phase in clinker, anhydrite, et cetera, especially in the initial stage.

In some cases, sodium carbonate in such a small amount as less than 0.1 percent remarkably intensified the false setting, while the further addition of about 5 percent of powdered C_3A weakened it to some extent. From the above results, therefore, the effect of carbonation seems to be much stronger than that of the aeration of C_3A, and also the moisture absorption of C_3A is unexpectedly low.

An accelerated test can be performed by means of the penetration test in which alkali carbonate is added in amounts up to 0.1 percent or 0.1–0.3 percent to the cement, the former amount being selected in order to detect the latent property of false setting due to the existence of dehydrated gypsum, and the latter amount to cause possible rapid setting of C_3A in some conditions.

On the other hand, it was also ascertained that portland blastfurnace cement did not set rapidly, even when it contained no gypsum. Then the addition of insoluble anhydrite was preferable, to reduce the tendency of false setting due to gypsum for this kind of cement as mentioned by L. Blondiau and Y. Blondiau [7]. In this connection, the high-slag type of portland blastfurnace cement had very low 3-day strength, but it could be about doubled without reducing the long-time strength by the further addition of 5 to 10 percent of anhydrite which simultaneously increased the expansion due to hydration until it just compensated the amount of drying shrinkage.

As for the measures taken to reduce the trend of false setting of portland cement, water is usually sprayed into the grinding mill for the purpose of lowering the temperature of the cement; however, the air-tight paper bag has been successfully used by a cement manufacturer in Japan. It is also believed to be efficacious to minimize the amount of gypsum so that normal initial setting would just take place, and at the same time, to make a further addition of insoluble anhydrite, i.e., dead-burnt gypsum, natural, or byproduct anhydrite, up to the optimum SO_3 content for improving the other characteristics of cement, such as strength, shrinkage, and chemical resistivity.

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Discussion

R. R. Hattiangadi

Dr. Hansen's valuable paper on false set in cement touches a very important, yet illusive, field of cement technology. From talks with several fellow members during the last 2 or 3 days, I am led to believe not only that the phenomenon of false set is a matter of anxiety to many cement manufacturers and cement chemists, but also that the understanding of the subject is undoubtedly obscure. There are apparently a very large number of situations where false set is encountered. I am aware that in narrating our own views based on observations, and a certain amount of fragmentary experimentation, I may only be contributing further confusion to the subject.

In two of our factories in India, situated more than 800 miles apart, employing limestone and other raw material of dissimilar geological and physical characteristics, but using similar wet process kilns, false set in plant cement used to occur spasmodically. The clinker in one factory was fairly high in lime and high in C_3A, whereas the other could be regarded as normal average portland clinker. The composition of the clinker at these two factories was approximately as follows:

	I	II
	Percent	*Percent*
CaO	65.0–66.0	63.0–64.0
Free CaO	1.0– 2.0	1.0– 2.0
C_3A	11.0–13.0	7.0– 9.0

The shortening of the initial and final setting times of the cement and slight stiffening were first observed at these two factories, in perfectly good mill samples of cement after they were left out in layers of ½ in. to 1 in. in open trays in a corner of the laboratory for periods of 24 to 48 hr. For want of a suitable expression, I am referring to this procedure, in my discussion hereafter, as "exposure" to the atmosphere. In other words, a freshly ground, normally setting cement at times acquired this peculiar characteristic within a day or so when kept exposed or aerated in the laboratory. The stiffened paste of the cement, showing false set, became normal setting on reworking. Also, the samples of cement became normal setting after further exposure to the atmosphere for about a week or so. This stiffening effect of the sample exposed for only short periods of 24 to 48 hr was observed, however, only during the dry winter months (less than 50 percent humidity), and even then, only occasionally, and never in the hot humid summer, nor in the rainy season. Then again, the samples showing false-set characteristics when later kept either in a 100 percent humid atmosphere and/or a CO_2 atmosphere for a few hours again became normal setting. Likewise, a freshly ground sample of plant cement when kept either in 100 percent humid atmosphere or a CO_2 atmosphere for the initial period of 24 to 48 hr at varying temperatures (between 5 °C and 40 °C) did not show any signs of stiffening or false set. While, thus, this erratic behavior of the cement was being observed in the laboratory, it was fortunate and remarkable that no complaints whatsoever reached us about this erratic setting-time behavior from any of the consumers. It would therefore appear that in actual field practice no false set was ever encountered. In fact, a large number of samples drawn from the field from various points and tested did not reveal any false-set characteristics; but—there was always the danger that any reference laboratory testing samples in accordance with the prevailing specifications might fail the cements in question. In this context, I am inclined to agree with one of the speakers who made a suggestion earlier somewhat to the effect that talk on this subject of false set might be kept in cold storage for some time, at least until one could write a specification which could boldly state that false set when encountered in laboratory testing should be ignored!

Reviewing the observations, the following common features could be listed in respect of both the factories cited above.

1. Exposure of the cement samples in layers ½ inch to 1 inch thick for only 24 to 48 hr in an atmosphere of low humidity and comparatively low temperature brought about false set in the cement.
2. Longer exposure for 8 to 10 days under the same conditions as above removed the false set.
3. Exposure for short or long periods, in atmospheres of (a) high humidity, (b) higher than normal CO_2 concentration and/or (c) higher temperatures (over 35 °C) did not impart false set to the cement.
4. The finer the cement was ground the greater was the proneness to false set.

The following experiments were carried out in a laboratory ball mill in an attempt to determine the principal factors which contributed to the development of false set.

1. Samples of clinker were ground in the laboratory ball mill with 4 percent of gypsum, but the resulting cement did not show any signs of false set, though the same clinker when ground in the plant mill with 4 percent of gypsum tended to show false set. This behavior indicated that the conditions of grinding in the plant were conducive to the occurrence of false set.
2. Ground gypsum was dehydrated, partially or completely, at various temperatures in a current of dry air, in a humid atmosphere, and also in an autoclave, and varying proportions of these samples of dehydrated gypsum were blended separately with ground clinker, but no false set was observed in any of the samples. In the above set of experiments, addition of larger proportions of partially dehydrated gypsum did give a permanent flash-set effect to some of the samples but not false set. The flash set or "plaster set" observed was quite different from false set as the samples with the flash-set effect did not normalize after prolonged exposure of 8 to 10 days. This result indicated that partial dehydration of gypsum was not necessarily the cause of the false set.
3. To simulate the conditions of plant grinding in the laboratory, samples of ground clinker were heated at temperatures of 100–120 °C in a current of steam for 10 to 20 min, and these samples were mixed with various proportions of gypsum and partially dehydrated gypsum. The sample of artificial cement so prepared showed signs of false set when exposed to dry cold atmosphere for 24 to 48 hr.

From the above it would appear that clinker and gypsum (cement) when ground under the conditions obtaining in a normal mill, i.e., in an atmosphere of comparatively high humidity (due to moisture present in the clinker and moisture evolved by dissociation of gypsum) and high temperature (say 100 °C or so) tends to show an effect of false set when exposed to dry cold atmosphere for 24 to 48 hours.

In trying to envisage the mechanism of the occurrence of false set, I have made two assumptions, which I believe are based on generally accepted theories regarding the retardation of setting time in cement. These assumptions are:

a. $Ca(OH)_2$ is the primary retarder of setting time in portland cement.

b. If the paste does not contain enough sulfate to produce calcium sulfoaluminates, which immediately envelop and protect the aluminate phase from water attack, rapid setting occurs due to quick hydrolysis and precipitation of most of the silica-alumina hydrogels.

Arguing from the above assumptions, it would appear that for a fresh plant cement ground under conditions of comparatively high humidity and temperature (100–120 °C) the cement grains would be covered with a thin layer of $Ca(OH)_2$ and, with the calcium sulfoaluminates in the contact solution, it would behave normally as to setting time.

As regards the temporary stiffening or false-set effect observed on exposed samples I would offer the following explanation, which may sound quite fantastic. When cement which is normal setting to start with is exposed to the atmosphere at temperatures of 5–10 °C for short periods, the grains of cement are perhaps coated by a continuous molecular layer of small crystals of $CaCO_3$ due to the combined action of the low atmospheric concentrations of CO_2 and H_2O. Such a sample of cement would show signs of false set because the cement grains are enveloped by a continuous layer of $CaCO_3$ crystals which does not permit the gaging water to come in contact with cement constituents to form $Ca(OH)_2$ in the contact solution immediately, but when this cement paste is worked vigorously for a longer time, the $CaCO_3$ film is broken and the required amounts of $Ca(OH)_2$ solution are formed and the cement paste regains normal set.

On the other hand when the cement is exposed to either (a) saturated atmosphere or (b) a higher concentration of CO_2 than that normally prevailing in the atmosphere, it does not show any signs of false set. In the first case (a), perhaps higher quantities of $Ca(OH)_2$ are formed on the surface of the cement grains, which go into solution immediately when the cement paste is prepared, and no effect of false set is observed. Perhaps in the second case (b), due to higher concentration of CO_2, comparatively larger crystals of $CaCO_3$ are formed on the surface of the cement grains, which perhaps concentrate themselves discontinuously, and this discontinuity permits more of the surface of the cement grains to be acted upon by the contact solution and produces more $Ca(OH)_2$ solution, giving normal set effect. A similar mechanism may seem to explain the fact that no false set starts to occur in these cements in the humid summer months or the rainy season, or when the cement is exposed for a period of a week or more even during the winter months. The spasmodic occurrence of false set in the plant cement could be explained by the fact that at times the dehydration of cement grains in the plant mill proceeds to such an extent that later aeration or exposure effect is not sufficient to cover the grains of cement with very fine crystals of $CaCO_3$ and the cement shows normal set even after 24 to 48 hr exposure.

Roller, Swayze, and others have worked on the effect of exposure of cement to humid atmosphere, but do not appear to have studied the problem from the angle represented in the above discussion. I would venture to suggest that if further work were to be done on determination of stiffening effect of cement exposed to the atmosphere at various temperatures and various periods of time under controlled conditions of humidity and CO_2 concentration and the composition of the contact solution within a few minutes of gaging were studied simultaneously, together with a study of surface reactions which seem to play an important part, a better answer to the reasons for false set might be obtained.

I take this opportunity to thank my associates, D. D. Murdeshwar, V. N. Pai, and R. Padmanabhan, in helping me carry out the various experiments.

Discussion

L. Santarelli

Dr. Hansen in his paper on false set illustrated the methods known till now to identify this phenomenon. I wish to add to Dr. Hansen's already complete documentation the results obtained by the use of an apparatus known as the "Automatic Penetrometer" which was presented at the XXXI Congrès de Chimie Industrielle [1][1].

The principle of this apparatus is as follows: if a rod with a conical head and loaded with a definite weight is sunk into a cementitious paste at a uniform rate, it will stop when the viscosity of the paste is such as to oppose the weight applied. If the total weight is regulated so that the stopping corresponds to the initial set shown by the Vicat needle, we can determine the setting times in concordance with the Vicat needle. This standard weight is equal to 320 g.

The same may be said for the final setting (standard weight 2200 g). It has been later ascertained that there is the following relation between the weight (P) and stopping time (T): $\log P=aT+b$. Hence, if the test data are plotted on a semilogarithmic diagram of weight vs. time the result is a straight line. Thus, the final setting time is readily extrapolated, if we have two points which characterize the straight line at lower stopping times.

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[1] Figures in brackets indicate the literature references at the end of this paper.

This apparatus, suitably modified, has been used with success to follow the hardening process of calcium sulfate hemihydrate in a cement in order to obtain useful information on the phenomenon of false set [2].

Since it was found that with a weight corresponding to the initial set of the Vicat needle it is often impossible to identify false set, it was decided to initially reduce the weight of the penetrometer to zero (by a special return spring) and to follow the course of the growing viscosity by loading the penetrometer with small weights as soon as the downward movement of the needle should come to a stop. At a certain point it can be seen that penetration can be continued by decreasing the weights instead of increasing them: this point corresponds to the appearance of the phenomenon of false set.

The results summarized in figure 1 clearly show the phenomenon: curve 1 corresponds to a normal setting cement, while the curves 2, 3, and 4 correspond to three cements with false set in which the phenomenon appears at 150 g, 280 g, and 550 g, respectively. If the measurement had been made with a penetrometer calibrated for "initial set", that is, having a weight of 320 g, it is evident that the cements which correspond to curves 2 and 3 would not show any anomalies.

The net difference between the curves 1 and 2, 3, 4 is characteristic. In fact, the three curves are made up of three distinct sections, the first very steep, which corresponds to the setting of the calcium sulfate hemihydrate. This short first period is followed by the phenomenon of recovery, due most probably to the destruction of the structure formed by the dihydrate crystals, due to the effect of alumina which reacts with $CaSO_4$ forming sulfoaluminate. This results in the formation of a distinct "knee" which is followed by the third section, which ends in a straight line and corresponds to the real setting of the cement.

With the above mentioned method it is possible to identify in a cement the hydration of the hemihydrate and the stiffening which is a consequence of this hydration. Furthermore, the method indicates the consistency reached by the structure formed by the dihydrate crystals formed during hydration and the time elapsed to obtain this structure.

I believe that the above is of interest toward a better knowledge of the phenomenon of false set.

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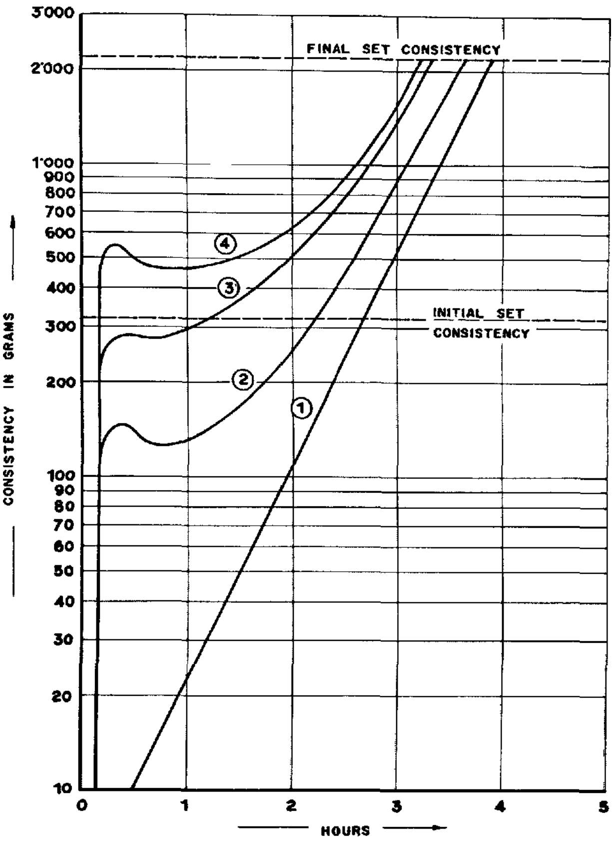

FIGURE 1. *Consistency curves obtained by automatic penetrometer on pastes of four cements.*

Curves 2, 3, and 4 are for cement showing false set

Discussion

Guenter Ahlers

Introduction

The purpose of this discussion is to report the results of some experiments which are believed to illuminate interestingly Dr. Hansen's paper, as well as the discussions of this paper by P. Seligmann and N. R. Greening, and by T. Manabe. The work to be presented here consists of quantitative analyses of cements for gypsum, and of a study of the gypsum precipitation in pastes by means of X-ray diffraction.

Gypsum Analyses

Quantitative analyses for gypsum by means of X-ray diffraction were carried out on 34 cements, chosen from 10 mills, most of which are located in the western United States. The analyses were performed on the 7.6-A line, without the use of an internal standard. The accuracy is estimated to be about 20 percent of the amount present, except at the very low concentrations, where it approaches ±0.3 percent gypsum. Of the cements examined 16 were found to contain less than 0.5 percent, 11 between 0.5 and 1.0 percent, 2 between 1.0 and 1.5 percent, 3 between 1.5 and 2.0 percent, and two cements contained 2.1 and 2.8 percent gypsum. The SO_3 contents of these cements ranged from 1.5 to 2.4 percent, corresponding to 3.2 to 5.2 percent gypsum. It is thus seen that it is the rule rather than the exception that almost all the gypsum has been dehydrated at least to the hemihydrate. The hemihydrate line at 6.0 A was always found, but no quantitative measurements were made on it. These results suggest that most cements contain enough hemihydrate to show stiffening due to gypsum precipitation, provided that this precipitation is not prevented by other factors. The occurrence of false set due to gypsum can thus be expected to depend primarily on factors which control the rate of precipitation of gypsum, and the rate of consumption of SO_3 by other reactions.

Gypsum Precipitation in Pastes

The precipitation of gypsum in pastes was observed as it occurred by measuring the 7.6-A line intensity in the paste as a function of time. Whereas these measurements could not yield quantitative results, because the surface of a paste cannot be expected to be representative of the entire sample, it is felt that they give an indication of the relative amounts of gypsum at different times. Such measurements were made on a cement paste which showed false set and on a mixture of finely ground Ottawa silica sand and 2.5 percent hemihydrate. The hemihydrate line at 6.0 A was also followed. In the cement paste the hemihydrate concentration began to drop immediately (the first measurement was made at 2 min after mixing), and gypsum began to precipitate. Both processes came to completion between 5 and 10 min after mixing. The sand sample behaved similarly, but the process was somewhat slower. It was completed after 20 min.

In order to relate gypsum precipitation to the degree of stiffening, a simple test was devised to measure relative stiffening. A 2.6-g rod with 0.3 cm^2 cross section was dropped onto the paste from such a height that it barely made an indentation. This height was taken as a measure of the stiffening. Such a simple test had the advantage that it could be performed repeatedly on the same paste. The stiffening as measured in this fashion on the cement reached a maximum after 8 min. For the sand-hemihydrate mixture this maximum was reached after 20 min. The agreement between the time at which maximum gypsum concentration and maximum stiffening were reached is believed to be a strong indication of a relation between the two processes.

A mixture of ground sand and 3 percent gypsum, and sand alone, showed no stiffening. The addition of 2 percent gypsum to the cement did not appreciably affect its stiffening characteristics. A sample of the cement was heated to 380 °C for 4 hr in order to convert all SO_3 to orthorhombic $CaSO_4$. After heating, 3 percent gypsum was added to the cement. The stiffening was then much less severe; however, other properties of the sample besides the hemihydrate contents may have been affected by this treatment.

Conclusions

It is believed that this work indicates that usually cements contain little or no gypsum. This finding might have been expected from the thermodynamic properties of gypsum and hemihydrate.[1] Most cements are ground at temperatures in excess of 100 °C, and at these temperatures gypsum is unstable. Especially in air-swept mills the dehydration should proceed with fair ease during grinding.

It is further felt that strong indications of a direct relation between gypsum precipitation and stiffening exist for the cement investigated here. The factors which determine whether or not excessive gypsum precipitation will occur seem as yet to be only partially understood. When gypsum precipitation does occur, it may or may not result in false set as measured by ASTM methods, depending on whether or not the precipitation is completed before the mixing is over.

Discussion

Myron A. Swayze

The purpose of this discussion of Dr. Hansen's paper is twofold: first to correct some of his present conclusions from my discussion of his 1958 ASTM paper on "Aeration Cause of False Set" (Hansen's references [34] and [45]); and second, to advance another explanation for development of false set due to aeration which I overlooked in 1958.

The corrections necessary in Dr. Hansen's present remarks on my 1958 discussion are as follows:

1.—Hansen's paper states, "Swayze showed that aeration caused *flash* set with a clinker that contained no C_3A". This is not correct. Both grinds of the zero-C_3A clinker alone had prolonged setting times compared with grinds containing gypsum or anhydrite. Clinkers of this type require no calcium sulfate to control set. The false set induced by aeration or heating and aeration of these grinds could, therefore, not be attributed to inactivation of C_3A or dehydrated gypsum, since both materials were absent.

2.—Hansen's paper states that only the grind of clinker plus anhydrite *without water* produced ball coating and thus became aerated during

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[1] K. K. Kelley, J. C. Southard, and C. T. Anderson, Bureau of Mines Technical Paper 625, 1941.

grinding from frequent opening of the mill. The grind with 0.2 percent water pulverized readily and displayed no false set in fresh condition.

The second part of this discussion deals with a new approach to the explanation of development of false set in cements due to aeration. Our experience with all commercial cements tested is that this property is always induced by relatively short exposures to moist air, and is worse in high C_3S cements than in low C_3S.

In an unpublished 1940 report on "Colloidal Aspects of Portland Cement Behavior" made by Dr. L. S. Brown to the Lone Star Cement Corporation, Brown recognized that the cement particles in a paste are from 100 to 1000 times larger than those found in typical colloidal suspensions, their concentration is much greater, and while the classic suspensions are of solids inert to the dispersion medium, the cement grains are reactive. Last, the composition of cement grains is complex, while the usual suspensions contain a single dispersed solid. Nevertheless, in freshly mixed pastes, the relatively enormous cement particles still follow the behavior of colloidal materials in reaction to forces that cause dispersion, flocculation, and peptization in colloidal suspensions.

In observations with a cataphoresis cell under the microscope, Brown found fresh suspensions of C_3S in water to be poorly dispersed and faintly electronegative. Calcium hydroxide suspensions could not be observed due to their strong electrolytic action. C_3A hexahydrate was well dispersed and strongly electropositive. Since gypsum had no electrolytic action, it should peptize cement grains, causing dispersion. While calcium hydroxide is sparingly soluble, that part in solution is about 90 percent ionized.

In a study of flash set, companion cements with and without gypsum were made from a fresh clinker containing 60 percent C_3S and 8 percent C_3A. Both cements had Wagner surface areas of 2150. Both were mixed rapidly with 25 percent water and made into setting-time pats. The paste without gypsum was stiff and dry, and had an initial set in 10 min. The paste with gypsum was smooth and fluid, with initial set in 3½ hr. After moist storage of the pats for 24 hr and in air for several days, thin sections were prepared. The sections showed only moderate but approximately equal hydration. The cement grains in the pat without gypsum were strongly flocculated, while those in the pat with gypsum were well dispersed.

The cement with gypsum was then aerated for a day and a third pat made with 25 percent water. The paste was materially drier and stiffer than that with the fresh cement, and study of the dried pat in thin section showed evidence of flocculation, although not as striking as in the case of flash set without gypsum.

Brown stated that the prehydration during aeration makes a certain amount of calcium hydroxide very quickly available to form a saturated solution on mixing with water, sufficient to cause flocculation of the cement grains. This flocculated structure did not have the strength and rigidity of that observed in the flash set pat, due to absence of hydrated C_3A, a product inhibited by the gypsum present.

This counteraction of the dispersing effect of gypsum in a cement paste by the electrolytic action of quickly available hydrated lime can easily be broadened to cover not only false set induced by aeration, but also false set in fresh cements in which gypsum has been converted to hemihydrate by the heat of grinding. From grinding tests we know that gypsum is a good grinding aid. Its action in this respect is very probably due to its dispersing action, with air as the dispersion medium. Hemihydrate, on the other hand, actually retards grinding beyond what is found for straight clinker grinds. Flocculation of cement grains is very evident by development of heavy coating on the mill and grinding media. We have no knowledge of the action of hemihydrate on cement particles in pastes, but the inference is strong that, if it flocculates them in air, it should show the same action in water. If this inference is correct, then we do not need the theory of "plaster" setting to explain the early gelling of cement pastes after mixing with water.

In modern cement grinding, temperatures are high enough to convert most of the gypsum to hemihydrate. The moisture liberated by this conversion can easily prehydrate C_3S grains if it remains in contact with them for an appreciable length of time, liberating very fine grained and quickly soluble calcium hydroxide. The combination of these two active agents in promoting flocculation may well be the principal sources of false set in freshly ground cements.

It is hoped that research on the electrostatic properties of hemihydrate and cement minerals will be stimulated by this discussion, so that a more logical explanation of false set can be derived by use of the principles of colloid chemistry.

Discussion

A. Rio and R. Turriziani

The observation made by several investigators that some cements show false set after air exposure, as detectable by ASTM method C359, has put in evidence a new type of phenomenon which seems to differ from the usual false set, appearing in freshly prepared cements after grinding, and due to the presence of dehydrated calcium sulfate in cement.

In Hansen's paper, false set by aeration is ascribed to the transformation which aluminates undergo after air exposure, by which they become less reactive towards sulfates and more towards water. According to this assumption, false set by aeration should be due to a precipitation and crystallization of gypsum, facilitated by a lower reactivity of aluminates to it, as well as to their more rapid reaction with water.

In his contribution to the discussion of false set, Manabe points out the fact that the aeration does not reduce the ability of aluminates to combine with calcium sulfate, but only affects the accelerating action of aluminates on the precipitation of gypsum.

Observations made in our laboratory, though confirming Hansen's and Manabe's conclusions that the false set by aeration is also essentially a false set by gypsum, suggest that the causes of the phenomenon are independent of the mineralogical compounds of clinker and therefore of any passivation of the aluminates.

Experiments carried out on cements of different origins showed the following:

1. When a cement gives false set after aeration, it also presents such a phenomenon before aeration, which may be seen by using a shorter mixing time (1 min, 10 sec) than the usual (3 min) (tables 1–2).
2. An addition of calcium sulfate to the cement giving false set (fresh or aerated) causes, generally, the disappearance of this phenomenon (tables 1–2).
3. False set remains in the cements which are reground 1 hr and this leaves out any action due to phenomena concerning films, or the surface of cement grains (table 2).
4. Generally, the extraction tests carried out according to Hansen and Pressler [1], but with the shaking time prolonged up to 10 min, confirm what has already been stated by Hansen and others, that the extracts of aerated cements show a larger $CaSO_4$ supersaturation than those of fresh cements (figures 1–2, table 1).

Furthermore, by observing the different types of commercial cements to be tested for false set, we noted as follows:

a. Some cements never presented false set, even after a long exposure to air.
b. On the contrary, other cements giving false set at the start lacked it completely after aeration.
c. Other cements showed false set after 24 hr aeration, while the phenomenon disappeared after 48 hr.

Experiments and observations we carried out suggest that the false set by aeration might depend on the different forms of calcium sulfate contained in the commercial cements.

In fact, according to what some authors [2, 3] have already shown, the precipitation rate of calcium sulfate is closely connected with the ratio that can be established between dihydrate and forms of dehydrated calcium sulfate occurring in cement.

At first the grinding conditions and later the aeration would affect the values of these ratios, varying the relative percentages of dihydrate and dehydrated calcium sulfate. Particularly the aeration by its action on the dehydrated forms of

TABLE 1. *Composition of extract and depth of penetration for fresh and aerated cements*

Sample condition	H_2O	Time of shaking	Composition of extract—moles/liter								Penetration—mm [c]					
			$(OH)_2$	SO_3	CaO	K_2O–Na_2O	Sat. CaO	Excess CaO	Sat. SO_3	Excess SO_3	1 min, 10 sec	3 min	5 min	8 min	11 min	Remix
	%	*min.*														
Cement A [a]																
Fresh	34	0.5	0.0250	0.1129	0.0166	0.1213	0.0164	0.0002	0.0905	0.0224	-------	48	48	48	48	48
		1	.0262	.1100	.0171	.1191	.0164	.0007	.0885	.0215	48	0	0	0	0	48
		3	.0337	.1087	.0215	.1209	.0164	.0051	.0895	.0192						
		5	.0367	.1062	.0151	.1278	.0164	−.0013	.0960	.0102						
		7	.0397	.1062	.0153	.1306	.0164	−.0011	.0980	.0082						
		10	.0385	.1062	.0131	.1316	.0164	−.0033	.0985	.0077						
Aerated 24 hr [b]	34	0.5	.0220	.1170	.0460	.0930	.0165	.0295	.0670	.0500	-------	48	17	0	0	48
		1	.0220	.1140	.0314	.1046	.0165	.0149	.0760	.0380	48	0	0	0	0	48
		3	.0237	.1180	.0301	.1116	.0164	.0137	.0822	.0358						
		5	.0280	.1180	.0207	.1253	.0164	.0043	.0935	.0245						
		7	.0320	.1110	.0143	.1287	.0164	−.0021	.0963	.0147						
		10	.0342	.1087	.0142	.1287	.0164	−.0022	.0963	.0124						
Aerated 24 hr +2% $CaSO_4 \cdot 2H_2O$	34	--------	--------	--------	--------	--------	--------	--------	--------	--------	-------	48	48	48	48	48
											48	4	0	0	0	48
Cement B [a]																
Fresh	34	0.5	.0295	.0885	.0153	.1027	.0165	−.0012	.0745	.0140	-------	48	48	48	48	48
		1	.0292	.0885	.0150	.1027	.0165	−.0015	.0745	.0140	48	48	29	15	9	48
		3	.0410	.0800	.0146	.1064	.0165	−.0019	.0775	.0025						
		5	.0415	.0745	.0117	.1043	.0165	−.0048	.0760	−.0015						
		7	.0412	.0745	.0093	.1064	.0165	−.0072	.0775	−.0030						
		10	.0450	.0745	.0097	.1098	.0164	−.0071	.0805	−.0060						
Aerated 24 hr	34	0.5	.0295	.0920	.0215	.1000	.0165	.0050	.0720	.0200	-------	48	48	0	0	48
		1	.0300	.0920	.0210	.1010	.0165	.0045	.0730	.0190	48	30	2	0	0	48
		3	.0310	.0885	.0185	.1010	.0165	.0020	.0730	.0155						
		5	.0355	.0863	.0171	.1047	.0165	.0006	.0760	.0103						
		7	.0410	.0800	.0141	.1069	.0165	−.0024	.0775	.0025						
		10	.0437	.0790	.0143	.1084	.0164	−.0021	.0795	−.0005						
Aerated 24 hr +2% $CaSO_4 \cdot 2H_2O$	34	--------	--------	--------	--------	--------	--------	--------	--------	--------	-------	48	48	29	4	48
											48	48	0	0	0	48

[a] Blaine surfaces varied between 3400–3600 cm²/g.
[b] Aeration layers 1.5 cm thick exposed at temperature of 20 °C and relative humidity of 85 percent.
[c] The penetration values were determined by A.S.T.M. Method C 359 after mixing time of 3 min or 1 min, 10 sec.

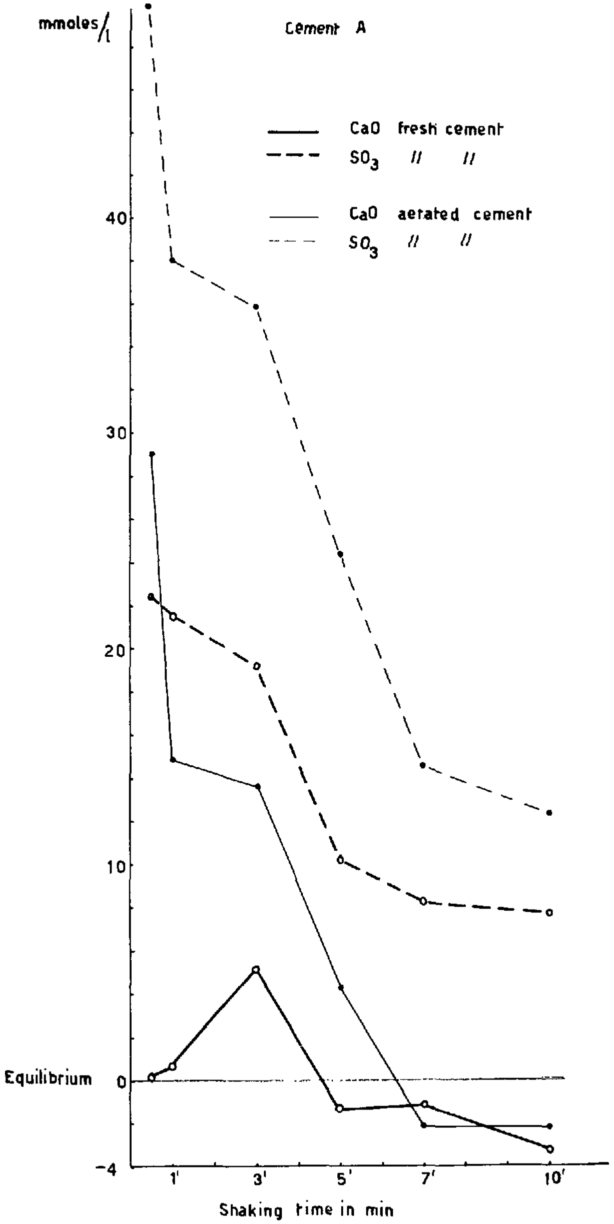

FIGURE 1. *Concentration of* CaO *and* SO_3 *in extracts from cement A after different periods of shaking.*

TABLE 2. *Depth of penetration for fresh and aerated cements*

Sample condition	H_2O	Penetration—mm [a]					
		1 min, 10 sec	3 min	5 min	8 min	11 min	Re-mix
Cement C	%						
Fresh	34	------	48	48	48	48	48
	34	48	48	48	25	15	48
Aerated 24 hr	34	------	48	48	48	45	48
	34	48	48	48	45	43	48
Aerated 24 hr and reground 1 hr	34	------	48	48	40	35	48
Aerated 24 hr + 2% $CaSO_4{\cdot}2H_2O$	34	------	48	48	48	48	48
	34	48	48	48	48	46	48
Cement D							
Fresh	34	------	48	48	48	48	48
	34	48	48	48	48	48	48
Aerated 24 hr	34	------	48	48	48	48	48
	34	48	48	48	48	48	48
Aerated 24 hr and reground 1 hr	34	------	48	48	48	48	48
Aerated 24 hr + 2% $CaSO_4{\cdot}2H_2O$	34	------	48	48	48	48	48
	34	48	48	48	48	48	48
Cement E							
Fresh	34	------	48	48	48	48	48
	34	48	48	31	16	7	48
Aerated 24 hr	34	------	48	48	29	19	48
	34	48	0	0	0	0	48
Aerated 24 hr and reground 1 hr	34	------	48	45	20	15	48
Aerated 24 hr + 2% $CaSO_4{\cdot}2H_2O$	34	------	48	48	48	48	48
	34	48	48	1	0	0	48
Cement F							
Fresh	34	------	48	48	46	46	48
	34	48	48	3	0	0	48
Aerated 24 hr	34	------	48	45	42	44	48
	34	48	21	0	0	0	48
Aerated 24 hr and reground 1 hr	34	------	48	36	30	48	48
Aerated 24 hr + 2% $CaSO_4{\cdot}2H_2O$	34	------	48	48	48	48	48
	34	48	48	4	0	0	48
Cement G							
Fresh	34	------	48	48	42	42	48
	34	48	48	25	2	0	48
Aerated 24 hr	34	------	48	3	0	0	48
	34	48	0	0	0	0	48
Aerated 24 hr and reground 1 hr	34	------	48	0	0	0	48
Aerated 24 hr + 2% $CaSO_4{\cdot}2H_2O$	34	------	48	48	43	39	48
	34	48	0	0	0	0	48

[a] The penetration values were determined by ASTM Method C 359 after *mixing time of 3 min or 1 min, 10 sec.*

calcium sulfate would tend to transform the latter into the stable form of dihydrate. During this process it would be possible to pass through stages where these ratios become such as to give rise to false set and of the supersaturation in SO_3 in the contact solutions.

On the basis of our supposition we should have a clear interpretation of the phenomena treated in sections 1, 2, 3, 4 and a, b, c.

Moreover, the smaller supersaturation values of fresh cements, which we attribute to a greater precipitation rate of calcium sulfate, are not only confirmed by the penetration tests after a mixing time of 1 min and 10 sec, but also agree with the combination rate of sulfate with aluminates, measured according to Bucchi [4, 5].

Actually, in agreement with Manabe, we do not find a difference between the combination rates of aerated and fresh cement. Therefore, the lower sulfate concentrations measured by extraction tests can be attributed only to a higher precipitation rate of the calcium sulfate, rather than to the lower ability of aluminates to combine with sulfates, as Hansen asserts.

Ultimately, the aeration, at least under the time and exposure conditions usually considered, would cause a variation in the relative quantities of dihydrated and dehydrated calcium sulfate

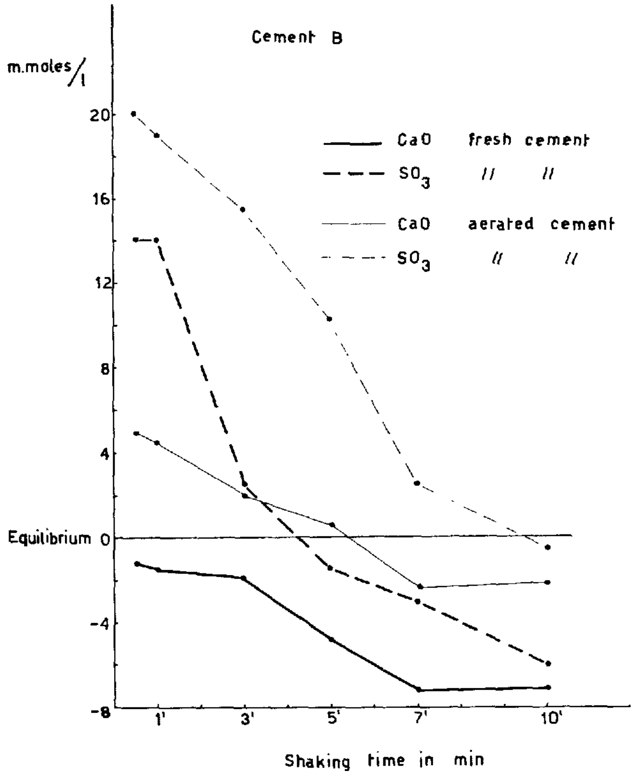

FIGURE 2. *Concentration of* CaO *and* SO_3 *in extracts from cement B after different periods of shaking.*

bringing about a different precipitation rate of gypsum which, since it occurs after the mixing, produces the characteristic stiffening of the paste. Of course, at the stage of our present experience, we cannot exclude the existence of concomitant effects due to phenomena of colloidal nature or of different type, as has already been pointed out by other authors, although such phenomena do not agree with the results of our experiments

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Discussion

A. J. Gaskin and J. K. McGowan

In general we agree with Hansen in ascribing the phenomenon of false set to the crystallization of gypsum in cement pastes, but we find that our views on the mechanism involved accord more with those expressed by Manabe [1][1] and by Seligmann and Greening [2].

During the past few years, examination of the behavior of 10 different cements of Australian origin has left us with the impression that the presence of more or less dehydrated remnants of gypsum in commercial cements must be regarded as a typical feature, that this material inevitably crystallizes as gypsum at a very early stage of paste preparation, and that most false-set effects are due to delays in this crystallization stage, extending it beyond the standard 3-min mixing period into the subsequent rest period.

Whether false set will be found in any given paste then becomes a question of the time at which gypsum crystallization begins, and the rate at which the crystallization of this phase proceeds, as well as a function of the amount of dehydrated material in the cement used.

These variables are separately influenced by various independent factors, and the resultant picture is quite complex. An ill-defined "flocculation" factor which temporarily increases the consistency of all cement pastes during the first few minutes of preparation, and the rare occurrence of a type of delayed "flash" set due to sulfate deficiency, are additional mechanisms which further confuse the main issue. Considering only the main process of gypsum crystallization, our broad view of the factors involved is as follows:

Commercial cement milling always appears to destroy the structure of gypsum to some extent. Mechanical as well as thermal action could be involved. The disordered product dissolves and crystallizes as gypsum during the mixing stage of paste preparation, the resultant stiffening effects being mixed out unless delayed for various reasons. In normal fresh cements, abundant nuclei for gypsum crystallization are present, and the onset and subsequent rate of the crystallization process can be accelerated by calcium ions supplied from C_3S and C_3A surfaces. Delayed crystallization resulting in false set can be caused by lack of sufficient nuclei, filming of accelerator sources, or by specific retardation effects of dissolved materials, principally carbonates. Adsorbed CO_2, released from clinker surfaces into the liquid phase of pastes, is the most potent retarder in practice, being supplied in sufficient quantities to the clinker surfaces during aeration.

Some of the experimental data from which this view has been evolved are given below.

The Nature of Gypsum in Cements

An X-ray study, made by Dr. J. Graham in this laboratory, of all commercial cements used in our investigation showed that the proportion of gypsum added during manufacture always exceeded that which we could recognize in the product. Results on laboratory cements did not show such discrepancies, and indicated that the technique of examination was sensitive and fairly precise.

Some commercial cements gave no indication that gypsum was present, most showed from 0.2

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[1] Figures in brackets, indicate the literature, reference at the end of this paper.

to 1.0 percent of recognizable gypsum, and a few gave higher values, ranging up to 60 percent of the amount originally added at the mill.

The proportion of gypsum preserved in any sample was generally characteristic of the plant of origin, but no correlation with mill temperatures could be found even though these varied from plant to plant over the range 100 to 125 °C.

Thermal effects could have been masked by variations in mill humidity, but no clear evidence was obtained in regard to the action of mill atmospheres. A mill with internal water addition, for instance, produced cement with no recognizable gypsum fraction.

Although some samples gave distinct patterns of the "hemihydrate-soluble anhydrite" type, suggesting that thermal dehydration had been occurring, it is possible that mechanical effects, which lead to similar types of dehydrated material, had also been operative.

It has been shown by Larsen and Bridgman [3] that gypsum may be dehydrated at room temperature by pressure alone, and Kiyama and Yanagimoto [4] demonstrated that the effect occurred below 65,000 psi, a pressure which could conceivably be applied to small particles caught between impacting balls in a large mill. The fact that gypsum may be dehydrated by ultrasonic vibration at 40 °C as shown by Zolotov and Kurochkin [5] is another aspect of the ease with which the water "sheets" may be encouraged to diffuse out of the gypsum structure.

If mechanical as well as thermal effects are important in large mills, it will not generally be possible to correlate the results of commercial cement milling with those from small laboratory mills run at equivalent temperatures. Closer correspondence would be expected when the small mills are run at higher than equivalent temperatures. This may account, in part, for the results of Takemoto, Ito, and Hirayama [6], who found little false-set tendency in cement ground at 105 °C in a small mill. Large mills at this temperature, however, can produce cements developing severe false set.

The nature of the "cement gypsum" components will probably be determined, therefore, not by mill temperature alone, but by such factors as the size of the mill, the size and type of grinding media, and the nature of the circuit, particularly as it affects the residence time of the finest particles.

In this connection it is of interest to note that open-circuit mills, loaded with a large proportion of small balls and fed with a hard clinker, gave cements with least recognizable gypsum, and worst false set, in our study, whilst the cement with the highest proportion of "retained" gypsum, and least false set, came from a carefully compartmented closed-circuit mill with a very high power efficiency, running at as high a temperature as the open-circuit mill.

The practical implications seem to be that the "cement gypsum" component will be in a more critical state when it is mechanically disorganized and dehydrated by overgrinding, particularly if the clinker components, which we believe to be accelerators of gypsum crystallization, are not also overground. By "critical" we mean having a slightly delayed setting time, through lack of nuclei or impairment of rate of solution. There seems to be no way of estimating these nucleation and solution factors except by paste trials. A "cement gypsum" or even a gypsum heated at 120 °C, may show no trace of dihydrate structure by X-ray diffraction, but may still be highly nucleated.

Particles of "gypsum" large enough to be picked out of cements for microscopical examination appeared to be of composite structure, with a mosaic appearance, due to variable birefringence, when viewed in polarized light using crossed Nicols, and showed a higher refractive index than gypsum. It is probable that this component of commercial cements contains fragments of the dihydrate structure intimately associated with material in all states of dehydration down to anhydrite. It cannot be simply described as "soluble anhydrite" or "hemihydrate," and may best be referred to as "cement gypsum" or some such arbitrary term.

Crystallization of Gypsum in Pastes

Although "cement gypsum" is more heterogeneous than most normal products of purely thermal dehydration of gypsum, some of its properties may be approximated by partially dehydrating very fine crystalline gypsum at 105–140 °C, to obtain materials in various "states of nucleation." Structurally, these thermal products are well organized and nucleate gypsum crystallization immediately when made into pastes. The nuclei may be progressively destroyed by more severe thermal treatments, and the solubility reduced by exposure to water vapor, both effects resulting in the development of induction periods and consequent setting delays when the materials are incorporated in pastes.

Commercial plasters of all types show long-delayed set compared with that of interest in false-setting cement systems. Some samples can be accelerated by addition of very fresh clinker, or mixtures of clinker and gypsum, to such an extent that the resultant pastes pass through the stiffening stage during mixing and hence do not exhibit false set, but we found such great variations in this respect even for consecutive samples from the same source that the use of this type of material was discontinued.

The most significant features of the gypsum crystallization process are the intensity of stiffening which can be caused by a small amount of material and the short time in which the setting reactions can be completed.

As little as 0.5 percent, by weight, of a well-nucleated dehydrated gypsum when added to a pure silica-water paste, can produce severe stiffening if mixing is stopped at 2 min. At 3 min, if mixing is resumed for a few seconds, the paste softens and remains soft on standing.

Replacement of the ground silica by larger proportions of highly nucleated dehydrated gypsum does not change the picture in respect to time of set and effect of mixing, but simply increases the intensity of the stiffening. Pastes made from all proportions of these two components will set rapidly enough to pass a false set test of the ASTM C 359 type.

By varying the nature of the "gypsum" component through more or less severe thermal treatment, but keeping the amount constant at 4 percent, a series of model paste systems exhibiting a range of stiffening periods from 2 to 5 min was prepared and used as a standard from which to deduce the efficiency of accelerating or retarding additives.

Accelerators in Model Pastes

In theory, high concentrations of calcium and sulfate ions in solution should accelerate gypsum crystallization. The particle size and solubility of dehydrated gypsum must therefore be important factors in determining the rate of attainment of suitable concentrations of these ions to initiate and promote the rate of growth of gypsum crystals in pastes.

External sources of calcium or sulfate ions will tend to overcome any delays due to inactivity of the dehydrated components, for reasons discussed by Schierholtz [7] and by Ridge [8].

Cement pastes contain ample sulfate in solution from the first moments of mixing, because of the presence of alkali sulfates. Conditions affecting the supply of calcium ions, therefore, become the main rate-determining features.

The clinker components C_3S and C_3A both supply calcium ions to solution rapidly and in quantity, and as expected, proved to be efficient accelerating agents, when added in a freshly ground condition to our model pastes.

Poorly nucleated pastes, incapable of passing a false-set test, were changed, by accelerating the stiffening stages, into normal-setting systems by addition of C_3A or C_3S in quantities as small as 5 percent by weight of the total paste solids.

Increasing the amount of dehydrated gypsum greatly in excess of the amount of added C_3A did not change the behavior of such pastes markedly, except to reduce the degree of acceleration slightly. If an initial period of sulfoaluminate crystallization preceded that of gypsum, it was not apparent in the form of a lengthened induction period. Nor did the stiffening phase of a paste containing equal quantities of C_3A and dehydrated gypsum appear to differ in any characteristic from the same phase in a paste, without C_3A, accelerated to the same extent with extra nuclei. No evidence could be obtained to show that sulfoaluminate formed rapidly enough to prevent the usual gypsum crystallization stage from occurring at the usual time.

Aged samples of C_3A and C_3S lost accelerating power, presumably by losing surface solubility through the buildup of hydrate and carbonate films.

Retardation in Model Pastes

Agents which reduce the surface solubility of dehydrated gypsum, block the activity of nuclei, or temporarily drive the ionic concentration of calcium or sulfate in solution to low levels so as to extend the induction period or decrease the rate of growth of gypsum crystals, retard set.

Surface solubility or the activity of nuclei seems to be impaired by traces of water vapor taken up during cooling, storage, or grinding of gypsum dehydration products made in the temperature range 105–120 °C. The effect, in model pastes, appears as the addition of up to an extra minute to the stiffening period. In ordinary cement pastes it appears to be overcome by the accelerating action of clinker. It is not likely to be a major variable controlling the incidence of false set in ordinary cements.

Carbonate ion in solution, however, is a very potent retarder, and is considered to be the main activator of false set in all ordinary commercial cement pastes containing dehydrated gypsum.

In the absence of C_3S and C_3A accelerators, model pastes could be changed from "normal" to "false" setting by the addition of as little as 0.001 percent, by weight, of CO_2 to the system. The gas was either introduced into the mixing water, or "adsorbed" on a small amount of an additive such as calcium hydroxide.

Pastes in which fresh finely ground clinkers rich in C_3S and C_3A were substituted for the ground silica component tolerated more carbonate in the form of CO_2, or equivalent alkali carbonate, because of the more rapid restoration of the calcium ion concentration.

With the most active clinker particles available, the limit of tolerance of pastes for CO_2 was 0.03 percent by weight, when 4 percent of poorly nucleated dehydrated gypsum was present, before false set appeared.

Commercial Cement Pastes

The combined thermal and mechanical effects of milling were found in the X-ray study of our plant samples to give as much as 4 percent of a dehydrated gypsum component in the worst-affected cements.

From the model-paste results, such samples could be expected to tolerate 0.03 percent by weight of CO_2, if very well nucleated, or less if deficient in nuclei, before developing false set. This was found to be so experimentally. The requisite quantities of CO_2 were taken up by the cements when exposed to the pure dry gas at atmospheric pressure, within a few minutes.

Samples which contained smaller amounts of dehydrated gypsum and a moderate proportion of recognizable dihydrate, remained normal setting until larger quantities of CO_2 were taken up during longer exposure periods. The best sample required 10 min exposure, taking up 0.15 percent of CO_2, before false set could be induced.

The behavior of the cements on aeration corresponded generally with the effects of exposure to CO_2. Those which failed after exposure periods of 1 to 3 min in the gas, failed the ASTM C 359 test after 2½ hr aeration, and those which survived longer periods in CO_2 survived aeration.

Carbonate added to pastes as sodium carbonate in quantities equivalent to the amounts of CO_2 found critical did not appear to be as effective in causing false set as "adsorption" of the gas. It is not proposed that alkali compounds in cements enter into the CO_2-adsorption or aeration processes to any major extent.

The mechanism of the "adsorption" of CO_2 on clinker compounds rich in lime is rather obscure. The gas must be retained at the surfaces in some state from which it can be released into solution rapidly. It is held as well on analytical reagent grade calcium hydroxide as it is on pure C_3S or C_3A, or commercial clinker. Grinding does not remove it, nor is its effectiveness as a retarder decreased by prolonged storage as long as water vapor is absent.

Flocculation Due to Carbonation of Clinker

Pastes containing only clinker and pure precipitated $CaSO_4 \cdot 2H_2O$ can be made to exhibit false set by exposure to CO_2, or even by long aeration. This is not the severe false set typically associated with dehydrated gypsum, but it is probably a minor component of false set in many cements.

The mechanism appears to involve delays in the attack of water on clinker surfaces, and consequent attainment of the normal state of "slight" flocculation. Cements generally pass through an initial stage of "severe" flocculation during mixing, but hydration effects at clinker surfaces and the stabilization of electrolyte concentration in the solution, then result in a weakening of the floc structure, although not to the point of dispersion.

If the rheological equilibrium normally established within 3 min is delayed by the presence of blocking films of carbonate on clinker particles, the intensity of flocculation may still be increasing during the subsequent rest period, so causing false set. Centrifuge sedimentation volumes were used to show that floc strengths reached maxima in periods of 1 to 3 min after addition of water when fresh cements containing the pure dihydrate were used at 0.6 water/cement ratio. With increasing exposure to CO_2, or aeration, these maxima were progressively displaced towards the 7-min mark on curves relating the sedimentation volumes (at "10 g") to time of mixing.

Dehydrated gypsum added to fresh-clinker systems intensified the floc strength at an early stage, if well-nucleated. If severely retarded by soluble carbonate in the system, or by deficiency of nuclei, such additions could produce a second floc-strength maximum at a later time than the "flocculation-effect" maximum.

Prevention of False Set

False set primarily caused by dehydrated gypsum retarded with carbonate is difficult to treat. Water vapor is the only agent, in our experience, which will reduce the effect of CO_2, once it has been adsorbed on cement. Carbonated cements stored over water in CO_2-free air in sealed containers revert towards normal set after 12 hr storage or longer. This behavior may be linked with the amelioration of milder degrees of false set commonly observed on prolonged aeration, particularly if humidity is high.

If cement contains dehydrated gypsum but has not already taken up CO_2, later adsorption of the gas may be blocked to some extent by treating the cement for a few minutes with a gas which is strongly "adsorbed" but otherwise innocuous, such as SO_2 or acetic anhydride. Cement takes up 0.1 percent of these gases rapidly, and this is sufficient to reduce the amount of CO_2 it will take up to the 0.03 percent level or even less. In favorable instances, this removes the tendency towards false set. The treatment may cause severe retardation of initial and final set, though it has little or no effect on 7-day strengths.

Prevention is better than cure where false set is concerned, and this implies attention to all factors promoting dehydration of gypsum and CO_2 adsorption. These include high mill temperatures, long residence times for fine gypsum particles in mills, low C_3S and C_3A contents, and exposure to excessive amounts of air or to any flue or exhaust gases during transport of the milled cement or subsequent storage.

If no plant changes can be made conveniently, improvement may be possible through a change in the source and type of gypsum used. This raw material varies to some extent in stability, as Wiedmann [9] has shown.

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Closure

W. C. Hansen

The written discussions of my paper give many new data and ideas that should be of great value in future studies pertaining to the overall problem of describing the mechanism of setting and hardening of cement pastes. It seems that many of these discussions require no comments, and, accordingly, I shall not attempt any extensive review of them. Instead, in this closure, some new data from our laboratories will be presented, and an attempt will be made to explain what happens when cements are aerated.

In the paper, I stated, "There is need for additional work to determine the exact mechanism by which aeration causes false set." Our work in this field was continued, and, with the results of that work, with a more thorough review of the literature, and with data and suggestions supplied by the written discussions, it appears that we can now explain what happens from the standpoint of stiffening when cements are aerated.

Portland cement clinkers vary with respect to the contents and compositions of the aluminoferrite phase and to the contents of C_3A, alkalies, and SO_3. Also, it seems that cements must vary widely with respect to the extent to which the gypsum has been dehydrated during grinding and storage. Because of these variations, one cannot be certain how any particular cement will respond under a given set of conditions, but it seems that we can now predict the general reactions of cements to aeration.

When speaking of false and flash or quick set, one is thinking of fast stiffening of a cement paste, either by itself or as a component of mortar or concrete, which occurs during the first 10 to 15 min after the paste comes in contact with water. It seems unquestionable that there are only two causes for this stiffening. One is the rapid reaction of C_3A and the aluminoferrite with water, and the other is the crystallization of gypsum. The first produces what is commonly known as flash or quick set and the other what is commonly known as false set. Normally, one associates the term flash or quick set with pastes that become relatively hot and unworkable. However, as pointed out in the paper, there should be all degrees of stiffening from mild to severe, caused by the reaction of C_3A with water. Hence, I propose using the expression "quick set" to indicate stiffening caused by C_3A and aluminoferrites. It seems that it is known beyond question that C_3S and C_2S cannot cause quick set.

It was pointed out in the paper that gypsum might crystallize from pastes made from cements that contained relatively large amounts of alkali sulfates. This, it seems, could be a cause of false set although the presence of dehydrated gypsum in cement appears undoubtedly to be the principal cause.

It seems that the general belief has been that quick set is caused only by C_3A. Professor Kondo, in his discussion, calls attention to work by Kondo, Tsukamato, and Yamauchi which showed that $C_{6.2}A_{2.2}F$ and C_4AF set about as rapidly as C_3A. Table 1 gives data by Yamaguchi, Takemoto, Uchikawa, and Takagi [1][1] obtained by X-ray quantitative analysis which show that C_4AF reacts rapidly with water. In the paper, I gave data obtained by Swayze with a cement that theoretically contained no C_3A which, it seems to me, show that the aluminoferrite phase in that cement caused quick set.

Table 1. *Data by Yamaguchi, Takemoto, Uchikawa, and Takagi* [1] *obtained by X-ray quantitative analyses of pastes*

Sample No.	Composition of sample—%				H_2O	Percent hydrated at 3 min		
	C_3S	C_3A	C_4AF	SO_3		C_3S	C_3A	C_4AF
					%			
S-3-0	------	100	------	------	50	------	27	------
S-3-20	------	100	------	20	50	------	28	------
S-5-0	80	20	------	------	45	5	13	------
S-5-5	80	20	------	5	36	4	13	------
S-4-0	------	------	100	------	33.6	------	------	7
S-4-20	------	------	100	20	25.6	------	------	10
S-7-0	80	------	20	0	50	3	------	4
S-7-5	80	------	20	5	50	5	------	7

Table 2. *Data by Lerch* [4]

SO_3	Heat of hydration at hour indicated—cal/g				
	2	4	8	12	16
%					
1.5	6.6	9.0	24.8	28 2	32.4
1.9	6.3	9.3	20.9	35.8	39.7
2 4	6.1	9.5	21.5	31.1	45.9
3.0	5.9	9.2	20.9	28 8	33.7

Another general impression has been that calcium sulfate was the primary retarder of quick set in portland cement. Dr. Hattiangadi, in his discussion, states "Calcium hydroxide is the primary retarder of set in portland cement."

Roller [2] (in 1934) claimed that the role of calcium sulfate in cement was to react with alkali hydroxides to produce calcium hydroxide which was the retarding agent. He claimed that $Ca(OH)_2$ in solution combined directly with solid crystals of C_3A and coated them with hydrated C_4A which delayed their reaction with components of the solution.

The work of Bates [3] indicated that calcium sulfate was not an effective retarder in the absence of $Ca(OH)_2$ and C_3S. Heat-of-hydration studies by Lerch [4] (see table 2) showed that cement pastes developed what appeared to be a delayed quick set when most of the gypsum had combined with the aluminates. At that time, the solutions are primarily solutions of alkali hydroxides and contain very little calcium hydroxide.

The data of table 1 show that calcium sulfate did not retard the rates of hydration of C_3A and C_4AF. On the other hand, C_3S did retard the rates of hydration of these compounds, and cal-

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[1] Figures in brackets refer to the literature references at the end of this paper.

cium sulfate increased the retardation produced by C_3S.

This review of the literature seems to show very definitely that the aluminoferrites as well as C_3A can cause quick set and that high concentrations of $Ca(OH)_2$ in the solutions are required to prevent quick set by these compounds. It seems also that the principal purpose of calcium sulfate is to provide a high concentration of calcium ions in the solution.

As pointed out in the paper, Gilliland, Hansen, and Manabe have published data that show that the rate at which SO_3 combines with the aluminates is decreased by aeration of the cement. In his discussion, Manabe gives data that show that the rate of combination of SO_3 with the aluminates is only temporarily delayed by aeration.

Our data (shown in table 3) were obtained on a commercial cement ground with a blend of approximately 40 parts gypsum and 60 parts natural anhydrite. The grinding and storage conditions should have dehydrated all of the gypsum.

In this discussion, reference to extraction data will be to data obtained from slurries of 200 g of cement and 150 ml of water. These have a water-cement ratio of 0.75 whereas, in tests made with ASTM Method C359, this ratio is either 0.30 or 0.32. The compositions of the solutions in the slurry with $W/C=0.75$ and in the mortar with $W/C=0.30$ will not be identical. However, it is believed that conclusions from the former will apply to the latter.

The cement of table 3 showed slight stiffening in the false-set test, and the extraction data show that the solution, which, at equilibrium, should (on the basis of its Na_2O content) contain between 0.020 and 0.025 moles of SO_3, was saturated with respect to gypsum at 1 min but not at 3 min. These data show that, with about 40 percent of the SO_3 present as dehydrated gypsum, the calcium sulfate in this cement could not dissolve during the period between 1 and 3 min at a rate sufficient to maintain a saturated solution. Such a solution could not, of course, precipitate any gypsum to cause rapid stiffening. The drop in penetration from 50 to 37 mm during the 11-min period, it seems, may be classed as the result of what may be considered normal reactions in a cement with a satisfactory setting time. These reactions probably are mostly those that produce quick set when improperly controlled. Accordingly, one might visualize this cement as showing extremely mild quick-setting tendencies.

When the cement was aerated for 24 hr, it produced a slightly stiffer paste that showed very little stiffening during the 11-min period. The extraction data show that the solution in this paste was highly supersaturated with respect to gypsum at 1 and 3 min. These data show that the rate of combination of SO_3 was decreased by aeration. However, the drop from 0.052 to 0.040 moles/liter between 1 and 3 min shows that the rate of combination was still relatively high, and it appears that this rate was too high to permit much, if any, gypsum to crystallize in the paste.

Aeration for 48 hr produced a cement that stiffened relatively severely during the 11-min period. Tests on the clinker from which the cement was made showed that the rates at which it combined with chloride before and after aeration were as follows:

Sample and treatment	Grams Cl_2 reacted per 100 g of clinker for minutes indicated			
	1	5	15	30
As ground	0.22	0.28	0.34	0.36
Aerated 24 hr	.08	.14	.22	.24
Aerated 48 hr	.03	.11	.22	.26

These data indicate that the 48-hr aeration decreased the rate at which the aluminates reacted with SO_3 much more than did the 24-hr aeration. Hence, one would expect that gypsum could crystallize from this solution and produce false set.

Our first conclusion then is that, when the cements contain dehydrated gypsum, and possibly when they do not contain dehydrated gypsum but contain relatively large amounts of alkali sulfates, aeration can cause false set by decreasing the rates at which C_3A and aluminoferrites combine with SO_3 during the first few minutes of contact with water. Because of the wide variations in cements, it is not possible to give figures for the amounts of dehydrated gypsum and alkali sulfates required to produce this type of false set. Such figures would have to be determined for each cement.

Table 4 gives data for a cement ground with natural anhydrite at about 225 °F with 1 percent of water. The penetration data for the unaerated cement indicate no tendency toward rapid stiff-

TABLE 3. *Data for a commercial cement ground with a 40–60 blend of gypsum plus natural anhydrite*

Treatment	Penetration—mm (C359)				Minutes of shaking	Extract for $W/C=0.75$ Moles/liter			
	Init.	5 min	11 min	Remix		SO_3	$(OH)_2$	CaO	Na_2O
None	50+	45	37	50+	1	0.025	0.028	0.028	0.024
					3	.016	.043	.028	.031
Aerated 24 hr	47	47	46	50+	1	.052	.024	.059	.018
					3	.040	.024	.046	.018
Aerated 48 hr	46	27	10	50+	1	.053	.023	.063	.014
					3	.043	.023	.051	.015

TABLE 4. *Data for cement ground with natural anhydrite*

Cement	Penetration—mm					Minutes of shaking	Moles/liter			
	Init.	5 min	8 min	11 min	Remix		SO_3 [b]	$(OH)_2$	CaO	Na_2O
As ground	50+	50+	50+	50+	50+	1	0.018	0.022	0.023	0.017
						3	.017	.023	.022	.018
Aerated 48 hr	50+	0	0	0	0	1	.009	.013	.007	.015
						3	.001	.020	.002	.019
Aerated+0.5% SO_3 [a]	50+	43	34	20	50+	1	.044	.014	.050	.009
						3	.042	.012	.042	.011
Aerated+1.0% SO_3	50+	47	15	6	50+	1	.043	.015	.049	.009
						3	.046	.012	.048	.010

[a] Hemihydrate.

[b] SO_3 at equilibrium, 0.015 to 0.018 mole/liter.

ening in this cement, and the extraction data show that the solution, which should contain about 0.018 moles of SO_3 per liter, was saturated with respect to SO_3 at the 1-min period and remained close to saturation during the 3-min period. In other words, the natural anhydrite in this cement dissolved at about the rate at which SO_3 combined with the cement.

Aeration gave a cement that generally would be classed as quick setting because it was not possible to get a workable mortar by reworking. An examination of the extraction data shows that the rate at which this cement combined with SO_3 was markedly increased by aeration. At 3 min, the solution was almost devoid of both SO_3 and CaO and contained primarily alkali hydroxides.

The results in this table indicate that aeration reduced the rate at which C_3S, and perhaps other cement minerals, released $Ca(OH)_2$ to the solution. They also indicate that this deficiency in the $Ca(OH)_2$ content of the solution permitted the aluminates to combine with SO_3 at a relatively high rate. It seems that these results support the conclusions by various authors which were stated earlier to the effect that $Ca(OH)_2$ is the primary retarding agent.

When 0.50 percent of SO_3 as hemihydrate was added to the aerated sample, quick set was eliminated, but the cement showed some false set. The extracts show that the solution was highly supersaturated with respect to gypsum at the 1- and 3-min periods and, accordingly, would be expected to precipitate gypsum. This addition of hemihydrate provided CaO to maintain a high concentration of $Ca(OH)_2$ in the solution.

There seems to be no reason to expect that aeration would decrease the rate of solution of natural anhydrite. Also, from the results of table 3 and the results reported by Dr. Manabe, there is good reason to believe that the rate at which SO_3 would combine in the aerated sample should have been reduced. Since it appears not to have been reduced, one has to search for a cause of the acceleration produced by aeration. The data indicate that this acceleration was caused by the lack of $Ca(OH)_2$ in the solution. These data appear to lend very strong support to the theory that $Ca(OH)_2$ is the material that retards the rate of reaction of the aluminates and that the real purpose of calcium sulfate is to supply Ca ions to react with alkali hydroxides and maintain the supply of $Ca(OH)_2$.

Our second conclusion is that aeration may produce quick set in cements when the cements contain relatively small amounts of dehydrated gypsum. Because of the variability in cements, it is not possible to predict the amounts of dehydrated gypsum required by different cements to prevent quick set.

Our third conclusion is that aeration decreases, by chemisorption of either or both CO_2 and H_2O from the air, the rates at which the cement minerals react with water. Data presented by Dr. Manabe indicate that CO_2 is required. However, it seems likely that CO_2 must be accompanied by water vapor. If the cement contains dehydrated gypsum, the decreased rate of reaction of aluminates will cause the cement to develop false-setting characteristics. If the cement contains very little or no dehydrated gypsum, the reduced rate at which C_3S releases $Ca(OH)_2$ to water will develop a tendency for the cement to become quick setting.

After reaching these conclusions, a study was made with a commercial cement ground in a short mill in closed circuit with an air separator. The cement from the separator was immediately cooled to about 120 °F before going to storage. The data for a sample of this cement after being in storage for a few days are given in table 5.

TABLE 5. *Data for cement ground with gypsum and cooled to 120 °F*

Treatment	Penetrations—mm (C359)				
	Initial	5 min	8 min	11 min	Remix
A) As received	50+	50+	50+	50+	50+
B) 10 Weeks in a can	50+	45	38	22	50+
C) B+0.25% SO_3 [a]	50+	46	45	36	50+
D) B+0.50% $CaCl_2$	50+	50+	44	36	50+
E) B, aerated 24 hr	45	42	32	16	50+

[a] As hemihydrate.

X-ray diffraction data showed the presence of gypsum in this cement but gave no evidence for the presence of hemihydrate. Extraction data indicated a slight supersaturation with respect to gypsum at 1 min and no supersaturation at 3 min.

The penetration data show that the rate of stiffening of the cement increased during storage for 10 weeks in a covered can and that aeration for 24 hr caused a further increase. Additions of either hemihydrate or calcium chloride decreased the rate of stiffening, which was to be expected if the increased rates of stiffening produced by storage and aeration were the result of more rapid reactions of the C_3A and aluminoferrites caused by decreased reactivity of C_3S. These data support the conclusion that aeration will tend to produce quick-setting characteristics in a cement that contains little or no dehydrated gypsum.

Several of the discussers have raised the question of alkali carbonates. I still feel that very little, if any, alkali carbonate will be formed during aeration. However, if it is formed and dissolves quickly when the cement comes in contact with water, it should precipitate $CaCO_3$. In this way, it would rob the solution of $Ca(OH)_2$ and tend to produce quick set. Any reagent added to cement that tended to form an insoluble calcium salt would tend to produce quick set. This might be the explanation for the results obtained by Dr. Manabe with lignosulfonates.

Messrs. Rio and Turriziani suggest that the ratio of dehydrated gypsum to gypsum in the original cement might be changed during aeration. Results of a recent study by Razouk, Salem, and Mikhail [5] indicate that this is unlikely. These investigators studied the sorption at different temperatures of water vapor by soluble anhydrite produced in vacuo. They found that this product quickly sorbed sufficient water at very low vapor pressures to form the hemihydrate. Only very minor amounts of additional water were sorbed as the vapor pressure increased until the relative humidity was very close to 100 percent. The sorption of water vapor to form gypsum from a saturated atmosphere was very slow compared to the sorption at lower vapor pressures to form hemihydrate. The authors concluded that the formation of gypsum took place "only in the presence of the saturated vapor of water".

It seems from this work that, if the conditions in a mill could produce soluble anhydrite, this compound would be converted almost instantaneously to hemihydrate when the cement was discharged from the mill and contacted the colder air which always carries some water vapor. It seems also that, except for exposures to air of extremely high humidities, hemihydrate in cements would never be converted to gypsum. The results of this work indicate that only three forms of calcium sulfate will be found in commercial cements. These are natural anhydrite, gypsum, and hemihydrate. In many cases, the gypsum used in cement plants contains small amounts of anhydrite and, in recent years, some cement plants have adopted the practice of using mixtures containing relatively large amounts of natural anhydrite.

Messrs. Gaskin and McGowan point out that mechanical as well as thermal action could destroy the structure of gypsum. They visualize that some particles of calcium sulfate in cements are composites of gypsum, hemihydrate, and soluble anhydrite and propose the term "cement gypsum" for the product. This condition seems entirely possible, but the action of such a composite probably is similar to the action of a blend of small particles of gypsum and small particles of hemihydrate. They state what everyone probably accepts, i.e., "prevention is better than cure where false set is concerned".

It seems from many of these discussions that it is well established that false set is caused by dehydrated gypsum and that a manufacturer who produces a cement containing dehydrated gypsum may have problems that differ somewhat from those of another manufacturer producing a similar cement because of differences in grinding circuits, differences in compositions of clinker, etc. It appears, however, that it would be difficult to prevent all dehydration of gypsum in commercial grinding circuits. It also appears that the presence of small amounts of dehydrated gypsum might be helpful in preventing quick set that might tend to develop in a cement containing largely gypsum or natural anhydrite or a mixture of the two.

Several discussers have suggested that, in cements which contain both gypsum and dehydrated gypsum, the former acts as nuclei to speed up the crystallization of gypsum in the cement pastes. This possibility was studied by grinding quartz sand with 2.0 percent of SO_3 as gypsum and as hemihydrate and blending the two to obtain powders with 2.0 percent of SO_3. Quartz was also ground with 1 percent of SO_3 as hemihydrate to provide a few blends with less than 2 percent of total SO_3.

The original powders and blends were tested with 32 percent of water by ASTM Method C359, and some were tested by modifications of this method in which mixing was stopped midway in the mixing period for either 1, 3, or 5 min. The mortar was then mixed for 1 min after this waiting period. The data are given in table 6.

The total period of mixing and molding in C359 is 3 min. It is seen from this table that 1.0 percent of SO_3 as hemihydrate produced rather severe stiffening. The stiffening was much less when the powder contained 1.0 percent of SO_3 as gypsum as well as 1.0 percent as hemihydrate. This supports the contention by Dr. Manabe and others that more crystallization of gypsum will occur in the mixing period if the cement contains some gypsum crystals to act as crystallization nuclei. The data also show that the 1-min waiting period was very effective in decreasing the stiffening in this mortar and that the longer periods were less effective than the 1-min period. This

TABLE 6. *Data for quartz with blends of gypsum and hemihydrate*

Percent SO_3 as		Waiting period—min [a]	Penetrations—mm (C359)			
Gypsum	Hemihydrate		Initial	5 min	11 min	Remix
2.00	None	No	50+	47	46	50+
None	2.00	No	2	2	1	17
None	1.00	No	30	23	16	35
1.00	1.00	No	50+	43	32	50+
1.00	1.00	1	50+	50+	43	50+
1.00	1.00	3	50+	46	41	47
1.00	1.00	5	50+	44	41	50+
0.25	1.75	No	11	10	4	15
.25	1.75	1	16	16	10	30
.25	1.75	3	34	20	13	39
.25	1.75	5	30	25	13	34

[a] Waiting period midway during mixing, followed by 1 min mixing.

result was to be expected because the mortar should tend to stiffen gradually with time.

The data show that 0.25 percent of SO_3 as gypsum was not very effective in decreasing the stiffening caused by 1.75 percent of SO_3 as hemihydrate, and that the 3- and 5-min waiting periods were more effective than the 1-min waiting period in decreasing the stiffening.

Mr. Laneuville gives data for two cements ground in a cold mill. One (cement B) made with a lightly burned clinker containing 2.50 percent of SO_3 was ground without added SO_3, and the other (a normally burned clinker) was ground with 4.0 percent of gypsum and had an SO_3 content of 2.30 percent. These cements contained alkalies equivalent to 0.78 percent of Na_2O. Pure gypsum has an SO_3 content of 46.6 percent. Therefore, about 1.9 percent of SO_3 was added as gypsum and about 0.4 percent existed in the clinker, probably as alkali sulfates.

The 0.78 percent of Na_2O could combine with 1.01 percent of SO_3. Hence, the SO_3 in cement B might have existed as 1.00 percent in alkali sulfates and 1.50 percent in natural anhydrite. It seems perfectly normal for these quantities of alkali sulfates and natural anhydrite to give a cement without quick-setting tendencies as ground. Heating should not in any way increase the rate of solution of this SO_3 and, accordingly, should not produce a false-setting cement. It appears that this cement contained sufficient readily soluble SO_3 in the form of alkali sulfates to prevent quick set upon aeration.

Cement A, ground with 1.9 percent of SO_3 as gypsum in a cold mill should not be false setting as ground, and it should develop false set upon heating to 293 °F. The fresh cement showed slight stiffening when aerated for 5 days and severe stiffening when aerated for 10 days. One would expect a cement ground with gypsum in a cold mill to show a tendency to become quick setting upon aeration. Also, one would expect that the cement when heated to 290 °F and aerated would show false set just as it did when heated and tested without aeration. The behaviors of these cements seem to fit into the hypothesis proposed for the development of false and quick set upon aeration.

The method for determining evaporable water described by Messrs. Seligmann and Greening and the X-ray method used by Mr. Ahlers should be be useful in studying a grinding operation to determine the degree to which the gypsum is dehydrated during grinding and the rate at which it dehydrates during storage. It appears that the rate at which C_3S reacts with CO_2 and water vapor as well as the rates at which the aluminates react with these materials should be investigated.

Professor Santarelli offers a new method of studying the setting characteristics of cements. The use of these newer methods might be a way of learning more about the nature of the reactions that occur during the setting of cements.

Mr. Swayze suggests a new approach to the study of these reactions and also that a more logical explanation of false set is needed. He suggests that stiffening of cement pastes is a flocculation of the grains of cement. Those who support the crystallization-of-gyspum theory feel that the cement paste is stiffened by the interlacing of the gypsum crystals. No one seems to have been very specific as to forces that produce a coherent mass of quick-setting paste. I have visualized the rapid reaction of water with C_3A and aluminoferrites as converting the surfaces of the crystals to more or less amorphous materials that cement the grains of cement together. The mechanism of setting and hardening certainly needs additional study, and it appears that the methods that have been devised to study false set will be useful in that study.

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Paper IV–3. Chemistry of Hydration of Portland Cement*

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Synopsis

The results of recent investigations have provided evidence for the presence of several aluminates and sulfoaluminates in hardened portland cement pastes. For some of these, little evidence for their presence had been obtained previously. Some indications have also been obtained as to the nature of the iron-bearing hydrates.

Information as to the water contents of the various hydrates formed can be obtained for certain drying conditions by statistical analysis of nonevaporable water data as a function of the composition parameters of the cement.

Along with X-ray and statistical results, free-lime data obtained by X-ray quantitative analysis can be combined with the oxide composition of a cement so that an estimated composition of a hydrated paste of that cement can be calculated. Most of our concepts about the rate of hydration of cement in pastes or concrete have been based on the rate of increase of strength, heat of hydration, and fixed water. Inferences concerning the rates of hydration of the individual components have been made from considerations of rate of change in heat of hydration, and in related physical and chemical properties of the hydration products. Direct measurement of these latter rates show that the inferences are not always true.

Recent data are presented on the heats of hydration of the different ASTM types of cements at ages from 3 days to 13 years at 0.40, 0.60, and 0.80 water-cement ratio. The significant influence of water-cement ratio on the rate of hydration of cement can be interpreted in terms of physical parameters of the hydrating paste. The effect of temperatures in the range of 4.4 to 110 °C on the rate of hydration of cement can be expressed by the Arrhenius equation.

As a first approximation, the intrinsic hydration characteristics of cements can be expressed in terms of the compositions of the cements, by least squares analyses of heat evolution and chemically combined water. Secondary changes of the hydrated calcium aluminate are indicated. Some aspects of the roles of gypsum, alkalies, glass content, and ignition loss of the original cement on heat evolution are considered.

Résumé

Les résultats de recherches récentes ont fourni des preuves de la présence de plusieurs aluminates et sulfoaluminates dans les pâtes de ciment portland durcies. Pour certaines d'entre elles, cette présence n'était jusqu'à présent que peu évidente. Des indications ont été également obtenues quant à la nature des hydrates ferrifères.

Pour certaines conditions de séchage, on peut obtenir des informations concernant les teneurs en eau des différents hydrates formés, au moyen d'une analyse statistique des données de l'eau non-évaporable en fonction des paramètres de la composition du ciment.

Avec les résultats des rayons X et statistiques, les données de chaux libre obtenues par analyse quantitative des rayons X peuvent être combinées aux compositions oxydes d'un ciment de façon telle que l'on peut calculer une composition estimée d'une pâte hydratée de ce ciment. La plupart de nos concepts sur la vitesse d'hydratation du ciment dans les pâtes ou dans le béton ont été basés sur la vitesse de l'augmentation de la résistance, la chaleur d'hydratation, et l'eau fixée. Des déductions concernant les vitesses d'hydratation des composants individuels ont été tirées à partir de considérations sur la vitesse de changement dans la chaleur d'hydratation, et dans les propriétés physiques et chimiques, s'y rapportant, des produits d'hydratation. La mesure directe de ces dernières vitesses indique que les déductions ne sont pas toujours vraies.

Présentation est faite de données récentes sur les chaleurs d'hydratation des différents types de ciments selon les normes ASTM à des âges allant de 3 jours à 13 ans à un rapport eau-ciment de 0.40, 0.60, et 0.80. L'influence significative du rapport eau-ciment sur la vitesse d'hydratation du ciment peut être interprétée en fonction de paramètres physiques de la pâte qui s'hydrate. L'équation Arrhenius peut exprimer l'effet des températures allant de 4.4 à 110 °C sur la vitesse d'hydratation du ciment.

Comme première approximation, on peut exprimer les caractéristiques intrinsèques d'hydratation des ciments en fonction des compositions des ciments, par analyses aux écarts moindres quadratiques de l'évolution de la chaleur et de l'eau chimiquement combinée. Les changements secondaires de l'aluminate de calcium hydraté sont indiqués. Certains aspects du rôle du gypse, des alcalis, de la teneur en verre, et de la perte au feu du ciment original sur l'évolution de la chaleur sont considérés.

Zusammenfassung

Die Ergebnisse der neuesten Forschung haben gezeigt, daß mehrere Aluminate und Sulfoaluminate in gehärteten Portlandzementmassen vorhanden sind. Einige dieser sind früher nicht identifiziert worden, und man hat auch schon etwas über den Charakter der eisenhaltigen Hydrate ausfindig machen können.

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Man kann den Wassergehalt der verschiedenen Hydrate für gewisse Trocknungsbedingungen mit Hilfe einer statistischen Analyse, bei der das nichtverdampfungsfähige Wasser als Funktion der Zusammensetzungsparameter des Zementes ausgedrückt wird, bestimmen.

Durch eine Kombination der Röntgenbeugungsmessungen, der statistischen Resultate und der Werte für freien Kalk, wie sie durch quantitative Röntgenstrukturbestimmungen erhalten werden, und auch der Oxydzusammensetzungen kann man eine schätzungsweise Zusammensetzung der hydratisierten Paste eines solchen Zements errechnen. Die meisten unserer Ideen über die Hydratationsgeschwindigkeit des Zements in Pasten oder in Beton wurden durch ein Studium der Geschwindigkeit der Festigkeitszunahmen, der Hydratationswärme und des gebundenen Wassers erhalten. Die Hydratationsgeschwindigkeiten der einzelnen Verbindungen wurden von Betrachtungen, die sich mit den Hydratationswärmeveränderungen befassen, und auch mit verwandten physikalischen und chemischen Eigenschaften der Hydratationsprodukte, inter- und extrapoliert. Aber direkte Messungen dieser Veranderungen haben gezeigt, daß solche Inter- und Extrapolierungen manchmal zu Irrtümern leiten können.

Die letzten Messungen der Hydratationswärmen der verschiedenen ASTM-Typen der Zemente, die zwischen 3 Tagen und 13 Jahren alt waren, und mit Wasser/Zementverhältnissen 0,40, 0,60 und 0,80 angemacht worden waren, werden erörtert. Der bedeutungsvolle Einfluß des Wasser/Zementverhältnisses auf die Hydratationsgeschwindigkeit des Zements kann mit Hilfe der physikalischen Parameter der hydratisierenden Masse ausgedrückt werden. Der Temperatureffekt kann zwischen 4,4 und 110 °C für die Zementhydratationsgeschwindigkeit vermittelst der Arrhenius Gleichung ausgedrückt werden.

In erster Annäherung kann die körpereigene Hydratatationskenngröße als Funktion der Zementzusammensetzungen ausgedruckt werden, wenn man die Methode der kleinsten Quadrate auf die Warmeentwicklung und das chemisch gebundene Wasser anwendet. Das hydratisierte Kalziumaluminat zeigt sekundäre Veränderungen, die besprochen werden. Die Einflüsse des Gipses, der Alkalien, des Glasgehalts und des Gewichtsverlusts bei Rotglut des ursprünglichen Zements auf die Wärmeentwicklung werden besprochen.

Foreword

The difficulties encountered in the study of the chemistry of hydration of portland cement have been discussed many times, and are known only too well by all who work in this field. In spite of these difficulties progress is being made, even though the path to understanding may meander a bit.

The past work on the pure compounds found in cement has provided a foundation for the study of the hydration of cement itself, and the constant improvement in experimental techniques has made it possible to begin the study of hydration products in hardened pastes of portland cement. The chemistry of hydration of cement in hardened pastes has been emphasized in this review; perhaps it has been overemphasized. Many of the conclusions presented here are based on good evidence; others are admittedly tentative, but they are included in order to establish a basis for further discussion.

The paper is divided into three main sections: In the first section the composition of the hydration products of portland cement is discussed. In the second section the rate of hydration of cement, and the rate of hydration of each of the four major phases in cement is reviewed. In the third section the most recent information on the energetics of hydration is presented.

I. The Stoichiometry of the Hydration of Portland Cement

D. L. Kantro and L. E. Copeland

Status of the Problem as of 1952

By 1952, it had been established [1] [1] that the silica-bearing phases in portland cement react with water to form calcium silicate hydrates of two possible types, designated CSH(I) and $C_2SH(II)$. These hydrates were observed and discussed by Taylor [2], many of his observations being in good agreement with earlier work. The similarity between CSH(I) and the natural mineral tobermorite was pointed out by Claringbull and Hey [3] and discussed in detail by Bernal [1]. The $C_2SH(II)$, while not in the tobermorite composition range, showed many similar properties. The X-ray diffraction diagrams of these two calcium silicate hydrates are so much alike that to distinguish between them is quite difficult. Hence it could not be ascertained at the time of the 1952 London Symposium whether either or both of these calcium silicate hydrates occurred in hydrated portland cement.

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[1] Figures in brackets indicate the literature references at the end of this paper.

It had been surmised by a number of investigators that the 3:2 calcium silicate hydrate of the tobermorite series, that is, CSH(I), was the more likely product formed in the hydration of portland cements. That this is the case arises from the fact that it is this composition of solid which is in equilibrium with a saturated $Ca(OH)_2$ solution [4]. If $C_2SH(II)$ were to form, it would presumably be a metastable product. As far back as 1938, the 3:2 calcium silicate hydrate was considered to be the product of the hydration of the silicate phases of portland cement. For example, Bessey [5] arrived at this conclusion on the basis of free calcium hydroxide determinations on hydrated pastes.

Steinour, in his 1952 review [4], points out that the most probable reaction product of tricalcium aluminate, at least initially, is the tetracalcium aluminate hydrate, C_4AH_{13}. The cubic calcium aluminate, C_3AH_6, if it forms at all, forms only slowly. He points out also that the hexagonal hydrate that forms has at times been reported as an intergrowth of a dicalcium aluminate hydrate and the tetracalcium aluminate hydrate, such that the overall $CaO:Al_2O_3$ ratio of the phase is 3.0.

In their discussion of Steinour's paper, Nurse and Taylor [6] cite evidence from X-ray diffraction for the presence of C_4AH_{13}. They also cite X-ray evidence for the cubic C_3AH_6, but inasmuch as their observations were on a 22-year-old specimen, they concluded that the cubic hydrate was the result of a slow conversion of the tetracalcium aluminate hydrate.

There have been a number of investigations of calcium aluminoferrites and ferrites, and calcium ferrite hydrates have been prepared which are analogous to some of the calcium aluminate hydrates. The calcium ferrite hydrates form solid solutions with the corresponding calcium aluminate hydrates, but little experimental data had been found that these solid solutions occur in hydrated portland cement pastes.

One problem that has received a great amount of attention for many years from cement chemists is that of the sulfoaluminates, and, to a lesser extent, sulfoferrites. These complex compounds arise from the interaction of the appropriate component of clinker with gypsum, added as a retarder. In general, either of two calcium sulfoaluminates may form, these being the calcium monosulfoaluminate, $C_3A{\cdot}CaSO_4{\cdot}12H_2O$, and ettringite, $C_3A{\cdot}3CaSO_4{\cdot}31H_2O$. These compounds are also known as the low sulfate and high sulfate sulfoaluminate, respectively. As was pointed out by Steinour [4], equilibrium studies such as those made by Jones [7] indicate that ettringite forms during the early stages of reaction, but as further hydration of C_3A takes place, the low sulfate sulfoaluminate will form at the expense of the ettringite. Once all of the SO_3 has been used for this reaction, further hydration of aluminate should lead to a solid solution of tetracalcium aluminate hydrate and calcium monosulfoaluminate. However, at the time of Steinour's review, no direct observation of either sulfoaluminate in cement pastes had been made, and any conclusions drawn were strictly by inference. The ettringite observed in cracks and pores in old concrete or hardened paste was considered to be formed by secondary reaction due to exposure. More recently similar observations were made on old mortar exposed to air [8].

The calcium sulfoferrites corresponding to the low-sulfate and high-sulfate sulfoaluminates have been prepared individually [9]. The analogy of the sulfoferrites to the sulfoaluminates both in constitution and behavior has been pointed out. However, no identification of either of the sulfoferrites as a reaction product of cement, gypsum, and water under ordinary conditions of hydration could be made.

Methods of Investigation of the Chemical Reactions Occurring During the Hydration of Portland Cement

The qualitative and quantitative information concerning the hydration processes of portland cement have been obtained in several different ways. In general, however, regardless of what technique is being used, the cement paste may be treated in either of two ways. The observations may be made on the paste as a whole or the paste may be broken down into fractions such that one or more of these fractions may be enriched with respect to certain of the hydration products.

Nurse and Taylor [6] describe a method whereby the paste is ground to a powder and then ground in a suitable liquid such that a suspension of finest particles is formed. The suspension is removed from the coarse fraction and centrifuged to recover the fine fraction.

Differences in specific gravity of various constituents have also been used to effect separation. Taylor [10] separated several fractions from finely ground pastes by centrifuging the material in bromoform and bromoform-benzene mixtures. Turriziani [11] used a sedimentation apparatus in which the suspending agent was amyl alcohol. Several fractions of different finenesses were obtained and division of these into subfractions by the specific gravity technique using bromoform-benzene mixtures was then performed.

The separation methods have certain difficulties associated with them. It has not yet been possible to separate a fraction consisting of a single hydration product, nor has it been possible to separate a fraction which contained all of a given substance that occurs in the paste, e.g., if a given fraction is shown to be enriched with respect to the iron-bearing component, it still will not contain all of the iron-bearing phases in the original paste. Finally, there is the distinct possibility that the products of hydration may be altered by the separation process. Nurse and Taylor found C_3AH_6 in some of their fractions, but attach little importance to the result since the sample was heated at one stage of the procedure.

Perhaps the most fruitful investigations made of hydrated cement pastes, either whole or divided, are those using X-ray diffraction techniques. Most of the X-ray examinations of cement pastes made up to the present time have been by the Debye-Scherrer film technique. However, the recent development of the diffractometer now permits greater resolution and reveals important details heretofore unknown. It was with apparatus of this type that Kantro, Copeland, and Anderson [12] examined a group of well-hydrated portland cement pastes of various compositions. Although portions of these pastes were ground and dried, no treatment was given them to cause any unknown phase alteration. Fully hydrated pastes were used so that clinker lines would not interfere with the lines of the various hydrates. The hydrated pastes were examined both in saturated condition and in dried condition. The saturated specimens were small rectangular slices removed from the centers of the paste cylinders and polished smooth. The surfaces obtained contained no holes due to air bubbles inasmuch as the pastes were prepared by a vacuum-mixing technique [13] so that no air was entrained. Provisions were made to keep the specimen saturated during the entire X-ray observation. The remainder of the paste was ground to pass a 200-mesh sieve and dried either over $Mg(ClO_4)_2 \cdot 2\text{-}4H_2O$ or over ice at -78 °C (see below). These dried powders were packed in small sample holders and their diffraction patterns observed in the usual manner. Some dry powder specimens were brought to equilibrium at other relative humidities prior to X-ray examination. This was accomplished by placing the sample in a desiccator over an appropriate saturated salt solution, evacuating the desiccator, and allowing the sample to stand under these conditions for at least 2 weeks.

One of the difficulties encountered by many investigators attempting to identify the hydration products of portland cement by X-ray diffraction techniques is the alteration or decomposition of certain of the hydration products as the result of drying.

Lines of some substances disappear and others shift to new positions. In view of this type of behavior, observations of both wet and dry samples produce more useful information than either type of observation alone. The assignment of a diffraction line to a particular material is often complicated by the presence of a second substance having a line in the same vicinity. However, when the water content of the paste is changed, such that some of the lines may shift while others do not, the identification of a particular hydrate in portland cement paste may be made not only on the basis of the presence of lines at certain *d*-spacings, but also on the basis of the shifts the lines have when the paste is wetted or dried. Likewise, the lack of a line shift serves as a useful identifying feature in some cases.

Thermogravimetric and differential thermal analysis techniques have been applied to hydrated portland cement pastes. Taylor [10] used thermogravimetric analysis to show the relationship of the weight loss-temperature curve of a portland cement paste to those of various substances which may be hydration products. However, no definite conclusions may be drawn from the cement paste data, although they do indicate the type of result to be expected.

Recently Turriziani [11] used differential thermal analysis (DTA) in an investigation of the hydration products of portland cement. This method, however, like thermogravimetric analysis, in its present state of development suffers from certain shortcomings. Primary among these is that a number of possible cement hydration products have endotherms so close to the same position that, as Turriziani points out, ". . . the characterization of the individual components of the mixture is practically impossible." However, by observing samples under reproducible conditions, one can often derive information from the relative amplitudes of certain peaks.

Until recently, most of the investigations carried out with the electron microscope have been limited to the study of hydration products formed in a large excess of water. Such studies are subject to the "difficulties in verifying the indications relative to cement paste" mentioned by Steinour [4]. Surface replica techniques are now being used to study the structure of hardened pastes, and methods of sample preparation are being developed that may permit one to study the substances produced when cement hydrates as a paste. Selected area electron diffraction in conjunction with electron microscopy promises to be a most useful tool. Its greatest disadvantage is the inability to control the orientation of the extremely small crystallites found. Eventually electron diffraction patterns of crystals with known compositions will provide the information necessary to make certain the identification of the products of hydration of cement.

Although electron-optical investigations of the stoichiometry of portland cement hydration fall within the realm of this discussion, they have, for the most part, been omitted, inasmuch as the entire field of electron-optical investigations in cement chemistry is discussed elsewhere in this symposium.

Chemical analysis has and always will provide a great deal of necessary information in the study of cement hydration products. One of the techniques of chemical analysis widely used is the determination of free calcium hydroxide. The quantitative analysis for free calcium hydroxide by means of X-rays [14] provides an excellent means for determining the amount of crystalline calcium hydroxide present in a given paste. If amorphous calcium hydroxide is also present [15], needless to say, it is not detected by the method.

All free calcium hydroxide, both crystalline and amorphous, may be determined by solvent extraction techniques. The Franke method [16] using a mixture of isobutyl alcohol and ethyl acetoacetate as the extraction solvent has been modified recently [17, 18] so that the total calcium hydroxide extracted may be corrected for the amount of calcium oxide removed from other substances in the mixture, provided this decomposition has proceeded slowly relative to the rate of solution of free calcium hydroxide. If the decomposition is rapid, however, no such correction can be made, and it is impossible to distinguish between extractable and free calcium hydroxide by this technique alone.

It therefore is quite advantageous to compare results of X-ray and solvent extraction calcium hydroxide determinations in order to obtain useful information about the hydrated cement paste system. Some results obtained by this method will be discussed in a later section.

The interpretation of the data obtained by the methods described above in quantitative or semi-quantitative terms requires that other chemical data be available. Among these are the oxide composition of the original cement, the compound composition of the original cement and the bound water content of the hydrated paste.

The oxide analyses may be obtained by conventional analytical techniques. The potential compound composition of the cement may then be calculated according to the method of Bogue [19]. The determination of the actual composition of the cement may be carried out by means of X-ray quantitative analysis [20, 21]. This again, like the X-ray free lime determination, is an internal standard method.

The bound water content or nonevaporable water content of hydrated cement paste is a somewhat arbitrary value, depending upon the equilibrium water vapor pressure to which the material was dried. Although many methods of drying have been devised in the past only two will be considered in the ensuing discussions and these will be described here. The two methods differ mainly in the desiccant used, and hence in the equilibrium vapor pressure. One of the desiccants is a mixture of magnesium perchlorate dihydrate and tetrahydrate, which produces an equilibrium vapor pressure of 8 μ. The other is ice at the temperature of dry ice having an equilibrium vapor pressure of $\frac{1}{2}$ μ. The method of vacuum drying specimens to the $\frac{1}{2}$ μ level has been described in detail by Copeland and Hayes [22].

The Hydration Products of Portland Cement

The Calcium Silicate Hydrate

The results obtained from patterns of both wet and dry cement pastes [12] indicate that a calcium silicate hydrate of the tobermorite type is present, in agreement with the results reported by Taylor [10]. Only three diffraction maxima are observed for this substance. Bernal, Jeffery, and Taylor [23] report only two lines for the products of hydration of C_3S at room temperature. These were at 3.07 and 1.83 A. More recently, Brunauer, Copeland, and Bragg [24] reported lines at 3.03, 2.82, and 1.83 A from the products of the hydration of C_3S as paste at room temperature. It is possible that the 2.82 A line was missed in the older work because it is a peak superimposed on the broad high angle shoulder of the 3.03 A line, and as a result, would be difficultly detectable by a Debye-Scherrer technique. Brunauer, Kantro, and Copeland [15] have found that the calcium silicate hydrate produced by the hydration of C_2S as well as that by C_3S shows the same three diffraction lines.

The X-ray diffraction patterns of hydrated portland cement pastes have certain characteristics in common with those of hydrated C_3S and C_2S. The same three lines ascribable to calcium silicate hydrate in the pastes of the pure silicate compounds also appear in cement paste patterns. The characteristics of these lines in cement paste patterns are much the same as in the calcium silicate paste pattern. There is a broad hump with a maximum in the vicinity of 3.05 A. This peak is quite asymmetric, just as in the cases of C_3S and C_2S, falling off relatively sharply on the low angle side and much more gradually on the high angle side. In the wet slab patterns, the principal calcite line, at 3.03 A [25], is superimposed on this peak.

The line found at 2.82 A in calcium silicate hydrate patterns appears shifted to 2.78 A in cement paste patterns. This shift is due to the presence of lines from other hydration products at about the same spacing. Among the substances contributing to the 2.78 A peak is ettringite, with a line at 2.77 A [26]. This line, however, would not be present in dry powder patterns. Although the ettringite pattern disappears when the sample is dried, the 2.78 A line does not shift back to 2.82 A. The low sulfate sulfoaluminate has a line in the vicinity of 2.78 A [27, 28, 29]. Thus, the persistence, on drying, of the 2.78 A line in substances showing no low sulfate sulfoaluminate, but only ettringite, as well as in substances showing the simultaneous presence of both indicates that sulfoaluminates are not solely responsible for the shift.

The 2.78 A line in cement pastes appears to be somewhat stronger than that of the 2.82 A line in pastes of hydrated calcium silicates. The shape is also somewhat different and is that shape to be expected if a line from a well-crystallized hydrate were superimposed upon the 2.82 A tobermorite line.

The 1.82 A tobermorite line is easily distinguishable. The line appearing here is far too strong to be accounted for as the low sulfate sulfoaluminate line found by Midgley [27, 28] at 1.82 A, while Fratini, Schippa, and Turriziani [29] do not report a low sulfate sulfoaluminate line at this spacing. No known hydration product other than tobermorite can give a line strong enough to account for the 1.82 A spacing observed.

It can be seen from the above discussion that the same calcium silicate hydrate lines appearing in patterns of hydrated pastes of C_3S and C_2S are found in the patterns of hydrated portland cement pastes. Although these lines tend to characterize this hydrate as a tobermorite type, they constitute a set of data too meager in themselves to give any information as to the composition of this phase.

There are indications from other techniques as well that the calcium silicate hydrate in portland cement pastes is of the tobermorite type, e.g., the thermogravimetric curves of Taylor [10] and the differential thermal data of a number of investigators, most recent among these being Turriziani [11]. Finally, Gaze and Robertson [30] have identified tobermorite crystals as the product of hydration of a foamed mixture of portland cement and asbestos, using an electron microscope. The presence of tobermorite in this latter example is not conclusive that it is the product of ordinary paste hydration, however.

The calcium silicate hydrate which forms in portland cement pastes probably contains small amounts of impurities, primarily alumina. It was shown by Kalousek [31] that aluminum can be substituted for silicon in the tobermorite lattice without the substance losing its original identity. Compositions containing as much as 4 to 5 percent Al_2O_3 were prepared hydrothermally. A similar situation may exist in portland cement pastes during hydration at room temperature. Other substances such as alkali may also enter into the silicate structure [32].

The Calcium Sulfoaluminates

In the preceding paragraphs, several references were made concerning the presence of either the low sulfate calcium sulfoaluminate, the high sulfate calcium sulfoaluminate, or both. X-ray diffraction lines of both substances have been observed in hydrated pastes, sometimes separately and sometimes simultaneously. Table 1 lists the X-ray diffraction *d*-spacings observed with wet slabs of several cement pastes. Table 2 lists *d*-spacings observed with dried ground cement pastes.

The two strongest ettringite lines, at 9.73 and 5.61 A [26] occur in positions not interfered with by other possible products of cement hydration. It can be seen in table 1 that whenever the 9.73 A line appears in a hydrated cement, the 5.61 A line also appears. In most cement pastes where they appear, these lines are weak and the other ettringite lines are proportionately weaker so as to be obscured by normal background variation. However, in those patterns where the 9.73 A line is more intense, some of the weaker lines such as 4.69 and 3.48 A can be distinguished. The rather strong line occurring at 3.88 A is somewhat obscured by a calcite line. However, as this calcite line is weak relative to the principal calcite line, at 3.03 A, the 3.88 A line found in all cement paste patterns showing 9.73 and 5.61 A lines is easily seen to be too strong to be accounted for only as calcite.

As can be seen from table 1, the ettringite lines are found in pastes which have been cured for long periods of time. Thus the data for 10-year-old pastes made from cements of various compositions indicate the presence of a significant quantity of ettringite, except for those pastes made from cements high in C_3A. However, in pastes of one high C_3A cement, 15754, samples of which have been prepared under a variety of conditions, no ettringite is found except in the youngest paste observed, one which was hydrated for only 6 months. Thus it would appear that this cement behaves in the manner described by Taylor [10], in that ettringite forms at early ages, and then disappears. Taylor suggested that the disappearance of ettringite may be due to the formation of the low sulfate sulfoaluminate, which then dissolved in the C_4AH_{13} phase to form a solid solution.

On the other hand, ettringite has been observed in some cements, such as those mentioned above, even after long periods of curing. This type of behavior is in agreement with that observed by Turriziani [11], who found this material in pastes made from four different cement compositions, and hydrated at two different water-cement ratios, at ages from 7 days to 6 yr.

Considerably less success has been had in years past in identifying the low sulfate sulfoaluminate in portland cement pastes by X-ray diffraction techniques. Turriziani [11] was unable to find evidence for monosulfoaluminate in any of his specimens over the whole range of compositions, water-cement ratios, and times investigated. He concluded that if this material does form, it does so only at a very slow rate. Diffraction patterns for the compound $C_3A\cdot CaSO_4\cdot 12H_2O$ have been reported by Midgley [27, 28] and Fratini, Schippa, and Turriziani [29]. The results are in reasonably good agreement. The principal diffraction peaks for this material are at 8.9 and 4.45 A. The 8.9 A line has been observed in certain of the wet slab patterns, the data for which are given in table 1. The 4.45 A line appears in every one of these as well, but in addition, in patterns in which the 8.9 A line does not appear. As will be seen later, this arises from the fact that a strong line from another phase also appears at 4.4 A. The other lines of the calcium monosulfoaluminate are either too weak to be detectable in view of the difficultly distinguishable 8.9 A line, or else other substances have lines appearing in the same locations, such

TABLE 1. *X-ray d-spacings—hydrated cement wet slab and rewetted sample data*

Specimen	C-88	C-54	C-87	C-75	C-75 [c]	C-66-K	C-66-O	C-61-C	C-33-1	C-33-1 [c]	C-31-1	C-32-1
Cement	15754	15754	15754	15754	15754	15754	15754	LTS-17	15622	15622	15497	15669B
Type	I	I	I	I	I	I	I	I	II	II	III	IV
Nominal W/C	.40	.55	.40	.65	.65	.70	.57	.70	.60	.60	.60	.60
Age	11 yr	11 yr	7 yr	7 yr	7 yr	11 mo	6 mo	1 yr	10 yr	10 yr	10 yr	10 yr
Spacings, A							9.7	9.8	9.8	9.8	9.7	9.8
		8.9		8.9	9.0	9.0		9.0		8.8	9.0	
							8.7	8.6			8.3	
	7.8	7.8	7.8	7.7	7.8	7.8	7.8	7.8	7.8	7.8	7.8	7.8
								7.4	7.4	7.4		
							5.66	5.68	5.64	5.66	5.64	5.64
	5.09	5.06	5.09	5.09	(b)	5.09	5.11	[a] 5.08	[a] 5.06	(b)	5.08	
	4.94	4.92	4.93	4.93	4.93	4.94	4.92	4.94	4.93	4.94	4.92	4.92
									4.72	4.72	4.72	4.72
				4.49	4.48			4.48				
	4.41	4.38	4.43	4.39	4.40	4.41	4.39	4.41	4.39	4.40	4.41	
		4.27	4.27		4.28		4.27		4.26		4.26	4.29
	4.00	4.00	4.03	4.02	4.02			4.02	4.04		4.02	4.02
	3.88	3.86	3.86	3.87	3.86	3.88	3.88	3.88	3.88	3.88	3.88	3.88
	3.79	3.78	3.77	3.77		3.78		3.81			3.81	
					3.67				3.67	3.67		3.69
						3.50		3.50	3.48	3.48	3.49	3.49
		3.43		3.45	3.42		3.45					
	3.35	3.35	3.34	3.35			3.34	3.36	3.35	3.38	3.35	3.36
	3.31	3.30		3.31	3.32	3.32		3.31		3.32	3.31	
												3.26
	3.12	3.11	3.12	3.12	3.12	3.12	3.12	3.12	3.12	3.12	3.12	3.12
	3.05	3.04	3.05	3.05	3.04	3.05	3.05	3.05	3.05	3.05	3.05	3.05
		2.97			2.97		2.98					
	2.88	2.88	2.88	2.88	2.89	2.89	2.88	2.89			2.89	
				2.84		2.83						2.84
	2.78	2.77	2.78	2.78	2.78	2.78	2.79	2.78	2.78	2.78	2.77	2.78
						2.69	2.69		2.67	2.69	2.70	
	2.63	2.63	2.63	2.63	2.63	2.63	2.63	2.63	2.63	2.63	2.63	2.63
	2.60	2.58	2.59	2.59	2.58	2.59	2.59	2.59	2.57	2.58	2.56	2.56
	2.53	2.52	2.54	2.53	2.54		2.54	2.54	2.54	2.53	2.53	
	2.50	2.50	2.50	2.49		2.49	2.49		2.51		2.50	2.51
	2.47	2.45	2.46	2.47	2.46		2.46	2.46	2.46		2.45	2.45
	2.43	2.42	2.43	2.43	2.42	2.43	2.43	2.43	2.42	2.44	2.43	2.41
	2.37		2.37	2.36	2.36		2.36	2.37		2.35	2.36	
		2.31	2.31									
	2.29	2.29	2.29	2.29	2.29	2.29	2.29	2.30	2.29	2.29	2.29	2.29
	2.27	2.26	2.27	2.27	2.26	2.27	2.26	2.27	2.27	2.27	2.26	
			2.19	2.19	2.20	2.19	2.20	2.20	2.21	2.21	2.21	2.21
	2.14			2.14	2.14	2.14	2.14	2.14	2.15	2.16	2.14	2.16
	2.10	2.10	2.10	2.10	2.10	2.11	2.10	2.10	2.09	2.10	2.10	2.10
	2.07	2.06	2.06		2.07	2.07		2.04	2.06	2.06	2.06	2.06
	2.01	2.01	2.02	2.01	2.01	2.01	2.02	2.01	2.01	2.01	2.01	2.01
	1.96	1.96	1.97		1.96	1.96	1.96	1.96			1.96	1.97
	1.932	1.929	1.931	1.931	1.930	1.932	1.930	1.931	1.930	1.931	1.930	1.932
	1.912	1.912	1.912	1.912			1.912		1.912		1.912	1.912
	1.881	1.875	1.879	1.879	1.875		1.879	1.881	1.879		1.875	1.879
	1.826	1.819	1.824	1.824	1.823	1.827	1.823	1.828	1.823	1.824	1.823	1.826
	1.799	1.796	1.799	1.799	1.798	1.799	1.798	1.799	1.797	1.798	1.797	1.801
	1.722	1.714	1.723	1.719	1.717	1.719	1.723	1.723	1.722	1.720	1.717	
	1.690	1.688	1.689	1.690	1.688	1.690	1.688	1.690	1.689	1.689	1.688	1.689
			1.665				1.662			1.663	1.667	1.665
	1.660	1.658	1.660	1.660	1.658	1.662	1.652	1.661	1.657	1.656	1.654	
	1.639	1.635	1.638	1.638	1.638	1.635	1.638	1.639	1.636	1.638	1.638	1.634
			1.609				1.607					

[a] Shoulder on strong peak. Exact d-spacing not certain.
[b] Badly obscured by strong peak. Spacing cannot be estimated.
[c] Dried sample, rewetted in a saturated atmosphere.

that assignment of the diffraction maximum to a particular substance would be questionable.

However, the low sulfate sulfoaluminate lines do not behave in the same way as ettringite, when the material is dried. Instead, the basal reflections shift to lower *d*-spacings, while the other lines show no significant change. Roberts [33] points out that upon drying over anhydrous $CaCl_2$, the low sulfate sulfoaluminate basal spacing contracts from 8.9 to 8.2 A. When this material is dried in CO_2-free air at 115° or *in vacuo* at room temperature to the half-micron level, the 8.9 A line, assigned 001 by Fratini, Schippa, and Turriziani [29], contracts to 8.2 A, and the line at 4.45 A, assigned 002, contracts to 4.1 A [34]. The 8.2 A line appears in the patterns of those pastes for which the wet slab pattern showed the 8.9 A line. In the past, the 8.2 A line has been attributed to the tetracalcium aluminate hydrate [10], but the fact that it appears only in patterns of material which, when dry, shows the low sulfate sulfoaluminate line, indicates that it is this substance which is responsible for the line. Likewise, the 4.15 A line in dried powder patterns appears only when the 8.2 A line does. That the 4.4 A line does not disappear in dry powder patterns is due to the fact that another material, not affected by drying, contributes to it.

The lines of low sulfate sulfoaluminate appearing in dry powder patterns are strong and sharp, indicating that a significant amount of the material is present in the paste. This is true even for those pastes whose wet slab patterns gave low sulfate sulfoaluminate lines which were very weak. The weakness of the lines in wet pastes is due to the effect of carbonation.

Dried specimens of several of the pastes included in tables 1 and 2 were brought to equilibrium with various relative humidities. No significant changes were observed at humidities below 28 percent. However, in patterns of low sulfate sulfoaluminate-bearing samples, equilibrated at higher humidities,

TABLE 2. *X-ray d-spacings—hydrated cement dried powder data*

Specimen	C-75	C-49	C-61-C	C-33-1	C-33	C-33-1	C-31	C-32-1	C-32
Cement	15754	15754	LTS-17	15622	15622	15497	15497	15669B	15669B
Type	I	I	I	II	II	III	III	IV	IV
Nominal W/C	.65	.65	.70	.60	.60	.60	.60	.60	.60
Age	7 yr	5 yr	1 yr	10 yr	7 yr	10 yr	7 yr	10 yr	7 yr
Spacings, A	8.2	8.2	8.2			8.2	8.2		
	7.7	7.9	7.7	7.8	7.8	7.7			
			7.3	7.4	7.3				
	5.47	5.48	5.45	5.47	5.43	5.45		5.47	5.48
	[a] 5.06	(b)	(b)	[a] 5.06	5.06	5.07	[a] 5.06	(b)	(b)
	4.92	4.95	4.91	4.92	4.92	4.92	4.92	4.92	4.92
	4.41	4.41	4.41	4.41	4.39	4.39	4.39	4.40	4.39
	4.09	4.10	4.07			4.08	4.08		
					4.00				
	3.89	3.92		3.86	3.89	3.86			3.92
	3.62				3.66				
	3.31	3.32	3.31	3.32	3.35	3.31	3.30		3.30
							3.21		3.18
	3.12	3.12	3.12	3.12	3.12	3.12	3.12	3.12	3.11
	3.04	3.05	3.03	3.05	3.04	3.04	3.05	3.03	3.03
	2.92					2.92			
	2.88	2.88	2.88			2.86	2.86		2.87
	2.78	2.78	2.78	2.78	2.77	2.77	2.76	2.79	2.78
		2.70	2.71	[a] 2.67	2.68				
	2.63	2.63	2.63	2.63	2.63	2.63	2.63	2.63	2.63
		[a] 2.60	2.59	2.60	2.58	2.55	2.58		
	2.53	2.53	2.53	2.53	2.53	2.53	2.53	2.53	
	2.49		2.48						
	2.46	2.46		2.46	2.45	2.46	2.47		2.45
	2.43	2.43	2.43	2.44		2.43	2.42		
	2.35	2.35	2.35			2.35	2.35		
	2.31	2.30		2.30			2.30	2.30	
	2.26	2.26	2.26	2.26	2.26	2.26	2.28		
	2.08	2.10					2.08		
		2.05		2.06	2.05				2.05
	2.01	2.01	2.01	2.01	2.01	2.01	2.00	2.01	2.02
	1.93	1.93	1.93	1.93	1.93	1.93	1.93	1.93	1.93
	1.88	1.89							1.89
	1.82	1.82	1.83	1.82	1.82	1.82	1.82	1.82	1.82
	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80
	1.72	1.72	1.72	1.72	1.72	1.72	1.71		1.71
	1.69	1.69	1.69	1.69	1.69	1.69	1.69	1.69	1.69
	1.65	1.65	1.65	1.65	1.65	1.65	1.65	1.65	1.66
	1.64	1.64	1.64	1.64	1.64	1.64	1.64		1.64
	1.61	1.60			1.62				

[a] Shoulder on strong peak. Exact d-spacing not certain.

[b] Bably obscured by strong peak. Spacing cannot be estimated.

the 8.9 A line appeared. It showed only as a shoulder on the 8.2 A peak at 28.8 percent relative humidity, was about equal in intensity with the shrinking 8.2 A peak at 33 percent relative humidity, and at 42 percent relative humidity, the 8.2 A peak was a small shoulder on the 8.9 A peak. These features are illustrated in figure 1. At higher humidities, the patterns appeared quite like the wet slab patterns, except that no significant amount of carbonation had occurred. As a result, the low sulfate sulfoaluminate lines were of intensities comparable to those of the lines in the dried powder patterns. That is, they were strong and sharp. Because of this, it was easy to distinguish the 4.45 A sulfoaluminate line from a 4.40 A line due to another phase (see below). This resolution is illustrated in figure 1. Furthermore, it can be seen from results in tables 1 and 2 and in figure 1 that while the 4.1 A line in the dry material shifts to 4.45 A in the wet material, the line at 4.0 A reappears as well when the sample is rewetted. This corresponds to the line reported at 3.99 A by Midgley [27, 28] and at 4.02 A by Fratini, Schippa, and Turriziani [29].

Thus in figure 1, idealized patterns in the 9 A and 4 A regions are shown for pastes containing the dry form of low sulfate sulfoaluminate, the wet form, and an intermediate case (33 percent humidity) in which both forms appear simultaneously. The differences between wet slab and rewetted powder patterns show that low sulfate sulfoaluminate reacts with CO_2 just as does $Ca(OH)_2$.

The ettringite lines appearing in wet slab patterns at 9.8 and 5.6 A are absent in the dried powder patterns of these pastes. Rewetting these pastes at humidities up to 47 percent has no significant effect on the diffraction pattern. Rewetting at 100 percent relative humidity causes the ettringite lines to return. No significant amount of carbonation occurred with these rewetted samples, and yet the ettringite lines were of comparable intensities to those in the original wet slab patterns wherein considerably more carbonation occurred. Thus, if CO_2 reacts with ettringite, it does so sufficiently slowly so as not to affect the X-ray observations.

The low sulfate sulfoaluminate is found in pastes made from cements high in C_3A, but not in those made from cements low in C_3A. On the other hand, ettringite is the only sulfoaluminate found in pastes made from cements low in C_3A, while little if any of it is found in pastes of cements high in C_3A.

One of the cements low in C_3A discussed above is of especial interest in one respect, however. If the low sulfate sulfoaluminate were to have formed instead of ettringite, not enough Al_2O_3 would be present in the cement to react with all the SO_3. Under these circumstances, it is possible that a sulfoferrite might form. Malquori and Cirilli [35] have prepared calcium sulfoferrites analogous to

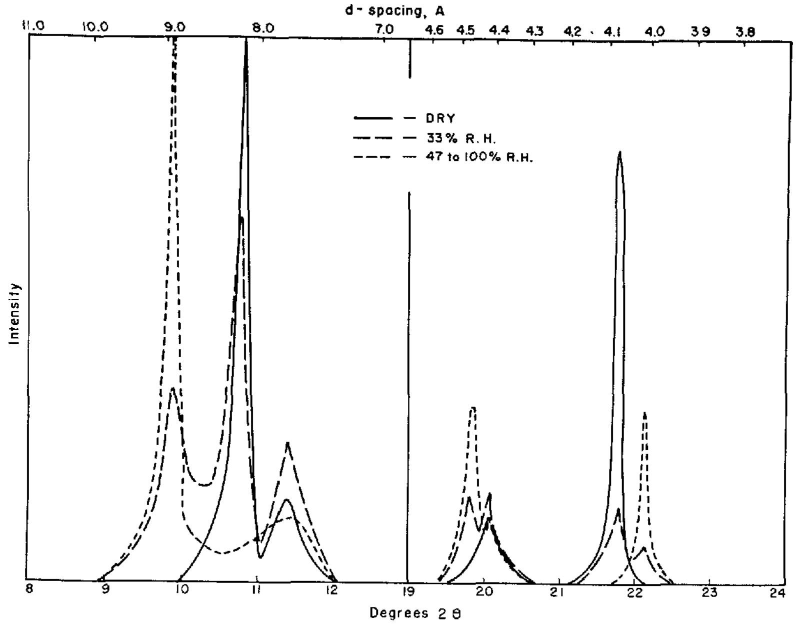

FIGURE 1. *Calcium monosulfoaluminate lines in X-ray patterns of portland cement paste at different relative humidities.*

the calcium sulfoaluminates which are found in hydrated portland cement pastes. The X-ray diffraction patterns of these sulfoferrites are, in general, very much like those of their sulfoaluminate analogs. As a result, the sulfoferrite compounds, were they present in portland cement pastes, would not be readily distinguishable from their aluminate counterparts. However, there is evidence that the iron-bearing phase in cement hydrates in a unique manner not involving SO_3. This will be discussed in the next section.

The Calcium Aluminate and Calcium Ferrite Hydrates

The calcium aluminate and calcium ferrite hydrates have been reported as existing in hydrated cements in two different forms: cubic and hexagonal. The cubic hydrates are represented by the compounds C_3AH_6 and C_3FH_6; the hexagonal hydrates are represented by the compounds C_4AH_{13} and C_4FH_{13}. It was shown by earlier investigators such as Wells, Clarke, and McMurdie [36] that C_3AH_6 is the stable calcium aluminate hydrate in contact with solutions saturated with respect to calcium hydroxide. On the other hand, in none of the discussions of the stoichiometry of the hydration of portland cement is much evidence given for the presence of the cubic tricalcium aluminate hydrate. On the basis of evidence available at the time, Steinour [4] stated that ". . . initial formation of C_4AH_{13} in clinker and water paste seems much more probable than formation of cubic C_3AH_6. . . . It is not impossible, however, that the cubic hexahydrate might form later." In recent X-ray investigations of portland cement pastes, Taylor [10] and later Turriziani [11] report only the hexagonal tetracalcium aluminate hydrate, C_4AH_{13}; they observed no cubic tricalcium aluminate hydrate in the pastes.

In the discussion to follow we shall review evidence that both cubic and hexagonal hydrates are present in hardened pastes and that the cubic phase at least is a solid solution of several substances. We shall discuss first the cubic and then the hexagonal hydrates.

It can be seen from the data in tables 1 and 2 that a group of lines appears distinctly in patterns of all cement pastes except the Type IV cement, which is quite low both in Al_2O_3 and in Fe_2O_3, and even in patterns of this cement paste there is evidence of these lines. This group of lines appears at 5.07, 4.40, 3.32, 2.26, 2.01, and 1.72 A, corresponding to six relatively strong C_3AH_6 lines reported at 5.14, 4.45, 3.37, 2.30, 2.04, and 1.75 A by Midgley [27, 28], and at 5.13, 4.45, 3.36, 2.30, 2.04, and 1.75 A by Burdese and Gallo [37]. The lines for the analogous iron compound, C_3FH_6, are reported at 5.20, 4.54, 3.40, 2.33, 2.07, and 1.77 A by Flint, McMurdie, and Wells [38] and at 5.18, 4.50, 3.41, 2.33, 2.07, and 1.77 A by Burdese and Gallo [37]. More complete *d*-spacing data for these materials are given in table 3. The reported C_3AH_6 lines are all higher than those observed in the hydrated cement pastes, and the C_3FH_6 lines are farther removed from the observed lines. The spacings observed in cement pastes would not be those expected from C_3AH_6, C_3FH_6, or a solid solution of the two.

Burdese and Gallo [37] also report spacings for a partially dehydrated cubic tricalcium ferrite, C_3FH_2. These spacings are 5.07, 4.38, 3.32, 3.10, 2.78, 2.53, 2.27, 2.01, and 1.72 A in very good agreement with those observed in cement pastes,

Table 3. *d-spacings reported for tricalcium aluminate and ferrite hydrates and corresponding spacings in some representative hydrated cement pastes*

hkl [38] [a]	C_3AH_6 [38]	C_3AH_6 [27, 28]	C_3AH_6 [37]	$C_3AH_{3.75}$ [44]	C_3FH_6 [38]	C_3FH_6 [37]	C_3FH_2 [37]	C–75	C–33–1
211	5.16(VS)	5.14(S)	5.13(MS)	5.03(VW)	5.20(M)	5.18(MS)	5.07(M)	5.09	5.06
220	4.47(M)	4.45(M)	4.45(M)	4.39(VW)	4.54(S)	4.50(S)	4.38(MW)	4.39	4.39
321	3.37(M)	3.37(M)	3.36(MW)	3.30(VW)	3.40(W)	3.41(MW)	3.32(W)	3.31	3.32
400	3.15(M)	3.15(M)	3.15(W)	3.09(VW)	3.19(S)	3.19(MS)	3.10(MS)	[b]	[b]
420	2.81(M)	2.82(MS)	2.81(MS)	2.77(VW)	2.85(S)	2.85(MS)	2.78(MS)	[b]	[b]
332	---	---	2.68(VW)	---	2.72(VW)	2.72(VW)	---	---	---
422	2.56(VW)	2.57(W)	2.55(W)	---	2.60(M)	2.61(MW)	2.53(M)	2.53	2.53
431	2.46(W)	2.47(MW)	2.47(W)	---	2.50(VW)	2.51(W)	2.44(WW)	2.43	2.44
521	2.30(VS)	2.30(VS)	2.30(MS)	2.26(VW)	2.33(M)	2.33(MS)	2.27(W)	2.27	2.27
440	2.22(VW)	2.23(VW)	2.23(W)	---	---	2.26(W)	---	---	---
611, 532	2.04(S)	2.04(S)	2.04(S)	2.01(VW)	2.07(M)	2.07(S)	2.01(S)	2.01	2.01
620	1.99(VW)	1.99(VW)	1.99(VW)	---	1.99(W)	2.02(W)	1.96(W)	1.96	---
444	1.81(VW)	1.82(VW)	1.82(VW)	---	---	1.84(WW)	1.79(VW)	[b]	[b]
640	1.74(W)	1.75(MW)	1.75(MS)	1.72(VW)	1.77(M)	1.77(M)	1.72(M)	1.72	1.72
633, 552, 721	1.71(W)	1.71(W)	1.71(W)	---	1.73(W)	1.74(VW)	1.70(VW)	---	---
642	1.68(M)	1.68(M)	1.68(S)	1.66(VW)	1.70(VS)	1.71(VS)	1.66(VS)	1.66	1.66
651, 732	1.60(VW)	1.60(M)	---	---	1.62(VW)	---	---	---	---
800	1.57(W)	1.57(VW)	1.57(W)	---	1.59(W)	1.60(W)	1.55(W)	---	---
840	1.40(W)	1.41(MS)	---	---	1.43(M)	---	---	---	---

[a] Numbers in brackets refer to literature cited at end of text.
[b] Probably present, but overlapped by line from some other component.

as can be seen in table 3. The lines at 3.10 and 2.78, of course, are overlapped by strong lines of $Ca(OH)_2$ [39] and the calcium silicate hydrate, respectively. (It is to be pointed out here again that the strength of the 2.78 A line is far too great to be accounted for on the basis of any aluminate or ferrite.) The compound C_3FH_2, however, is obtained by dehydration of C_3FH_6 at 250 °C [40]. It is difficult to imagine that a species normally formed by dehydration at relatively high temperatures should form at room temperature in a saturated aqueous system, unless some other substance were dissolved in it to stabilize it. Stabilization of solid phases under conditions far removed from equilibrium is not an unusual phenomenon, especially in cement chemistry; one merely need consider the case of β-C_2S. However, the more usual examples, such as β-C_2S, do not involve an aqueous solution phase.

From the kinetic data presented in another section of this discussion, it would appear that the ferrite phase in portland cement hydrates with no significant change in A/F ratio of the remaining unhydrated material. Hence, one might assume that the product of hydration may be a solid solution of a ferrite and an aluminate such that the A/F ratio of the solid solution is the same as it was in the original ferrite phase. Thus, if the original ferrite phase had an A/F ratio of unity, then the hydration product in question would presumably be an equimolar solid solution of a C_3F hydrate and a C_3A hydrate, the phase having the overall composition C_6AFH_x. On the basis of a statistical analysis of nonevaporable water data as a linear function of the composition parameters of a group of 27 cements (the water data being obtained from a group of well-hydrated cement pastes), the water content of such a phase is calculated to be 6 moles per mole of C_6AF; that is, the phase has the composition C_6AFH_6. This work, and the calculations leading to this result, will be discussed in detail in a later section. However, it is interesting to note that the water results obtained are such as to indicate that no pure ferrite phase can form, and that solid solution with an aluminate is probably necessary.

The composition C_6AFH_6 can be considered to correspond to a solid solution of C_3FH_2 with an aluminate of composition C_3AH_4. The lattice of C_3AH_6 shrinks in a regular manner as water is removed [41, 42, 43] but the lattice remains cubic as long as the H/A ratio is greater than 1.5. One might expect a composition C_3AH_4 to have almost exactly the same lattice parameter as C_3FH_2. Indeed, this appears to be the case, since Burdese and Gallo report the lattice constant of C_3FH_2 to be 12.39 A, and Köberich [44] gives the lattice constant of $C_3AH_{3.75}$ as 12.37 A. The X-ray *d*-spacings reported for this material are in reasonably good agreement with those of C_3FH_2 and those found in patterns of hydrated pastes as can be seen in table 3.

The estimation of the composition of this ferrite-aluminate solid solution phase is still a first approximation. The material is more likely to be a silica-containing member of the hydrogarnet series. The estimated water content would be expected to be low because it is replaced by silica as was described by Flint, McMurdie, and Wells [38]. Thus, if the estimated lattice spacing of 12.38 A is taken into consideration, and it is still assumed that the A/F ratio of the material is 1.0, then the material corresponds to a hydrogarnet having a composition in the vicinity of $C_6AFS_2H_8$.

The lines ascribed to the proposed solid solution phase appear in wet slab as well as dry powder patterns, as is indicated by the data in tables 1 and 2. However, in almost all patterns, wet or dry, the 5.07 A line is partly obscured by the 4.90 A calcium hydroxide line [39]. In many cases a shoulder appears sufficiently distinctly so that a reasonable estimate of the *d*-spacing at 5.07 A can be made. In a few other cases, however, the shoulder is not as distinct, and about all that can be said for such cases is that there is a line present, though fairly well hidden by the

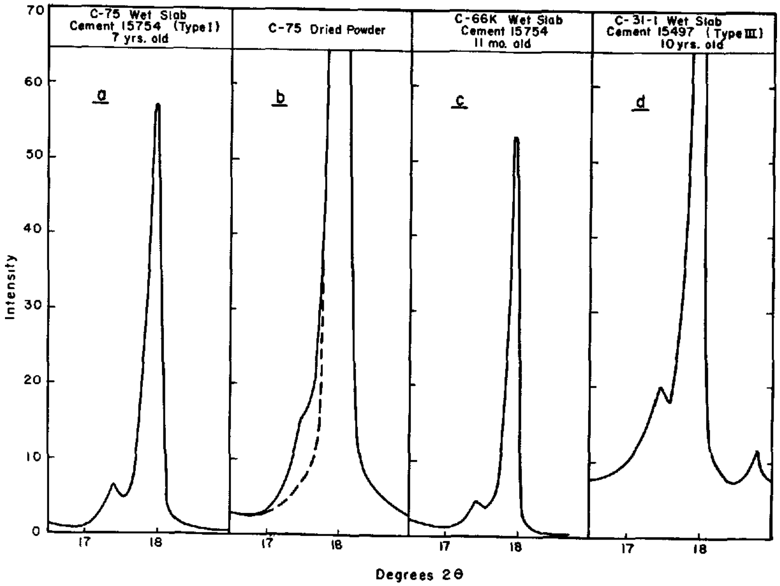

FIGURE 2. *The appearance of the 5.07 and 4.40 A lines in portland cement paste X-ray patterns.*

calcium hydroxide line. Examples of these types are given in figure 2.

The X-ray pattern of this solid solution phase obtained from a sample of a well-hydrated paste of cement 15754 from which most of the calcium hydroxide had been extracted by means of water was somewhat more distinct. The 5.07 A peak was almost completely undisturbed by the 4.90 A calcium hydroxide line. The 3.11 A line was too large to be accounted for by the remaining calcium hydroxide, and although little evidence for other substances containing aluminum or iron was found, the 2.78 A peak was still too large to be caused only by the calcium silicate hydrate phase.

There is little evidence to show either a growth or decrease of the solid solution hydrate lines as a function of time. The lines appear in the pastes of cement 15754 at all ages reported in table 1. Hence, there is no indication that this hydrate would only be a product of hydration of the C_4AF phase after long periods of time. On the contrary, whatever amount of this hydrate is found would appear to have been formed at some early age, and to have remained unchanged thereafter.

In his DTA investigation Turriziani [11] was unable to detect any cubic phase, either C_3AH_6, C_3FH_6, or a hydrogarnet. He observed decomposition temperatures in the vicinity of 375 °C for C_3AH_6 and two members of the solid solution series C_3AH_6-C_3AS_3. However, if the hydrogarnet had an A/F ratio of 1.0, then the decomposition temperature ought to be in the vicinity of 240 °C [38]. An endotherm at this temperature may be difficult to detect when an endotherm also appears at 220 °C due to the presence of tetracalcium aluminate hydrate.

Many investigators in the past have reported the presence of a hexagonal tricalcium aluminate hydrate. Schippa and Turriziani [45] state that it is impossible to form such a compound under conditions such as those that exist in a hydrating cement paste, and that the substance observed is actually calcium monocarboaluminate. All of the wet slab patterns show a line at 7.8 A, corresponding to the principal line of calcium monocarboaluminate [46]. Much of this carboaluminate may have resulted from the carbonation of the wet slabs during handling. However, the pastes of cements high in C_3A have a 7.8 A line with a pronounced asymmetry on the low-angle side, indicating the presence of another, weaker line at a higher *d*-spacing. In some high C_3A cement paste patterns, this asymmetry has developed into a shoulder such that the *d*-spacing of the peak causing it may be estimated. The value obtained, 8.3 A, is very close to the position of the strongest line of tetracalcium aluminate hydrate, C_4AH_{13}, reported by Schippa and Turriziani [45] as 8.4 A, and by Roberts [33] as 8.2 A. In the wet slab patterns, this line is sufficiently weak that it is not expected that any of the other C_4AH_{13} lines, all of which are weaker than the 8.4 A line, would be detectable. In some dried powder patterns, other lines are seen.

The principal peak of the iron analog of this aluminate, that is, C_4FH_{13}, occurs at 8.2 A [47]. Thus, a solid solution of this material with the corresponding aluminate could produce a line at 8.3 A. However, the determination of *d*-spacing from a shoulder of the type described is far too inaccurate to warrant any conclusion regarding the composition of the hexagonal phase.

In the dried powder patterns, the 7.8 A line is much weaker, since very little if any carbonation has occurred during handling. The fact that no shift is observed in this line when the specimen is dried is in agreement with results obtained on a sample of pure calcium monocarboaluminate which was dried to the half-micron level. The pattern of the dried pure compound showed no appreciable shift in line positions from those in the wet sample pattern [34], and was in reasonably good agreement with the spacings reported by Turriziani and Schippa [45, 46] and by Buttler, Dent Glasser, and Taylor [48]. The carboaluminate line in dried samples, and in rewetted samples as well, is weak, indicating that not much of the material is present. That little, if any, CO_2 has entered the dried pastes is indicated by the fact that the principal calcite line is not observable.

Buttler, Dent Glasser, and Taylor present diagrams of patterns of C_4AH_{13} after various drying treatments. These patterns indicate a shift in the basal reflection in the same way as was found for the monosulfoaluminate. When heated to 105 °C, the C_4AH_{13} line at 8 A shifted to 7.8 A. Drying at 105 °C is roughly equivalent to the vacuum drying condition described by Copeland and Hayes [22]. However, when C_4AH_{13} is dried *in vacuo* at room temperature [34], the basal line shifts from 8.4 A, the wet state position [45], to 7.8 A over a relatively short period of time. Continued drying for a much longer period of time (21 days) led to only a small weight loss relative to that in the first 3 days, but the basal reflection shifted to 7.4 A, in agreement with the value reported by Roberts [33]. X-ray patterns of this material revealed only the 7.8 A line unless special precautions were taken to eliminate all traces of water vapor, this being done by passing a dry nitrogen stream over the sample while the pattern was being obtained. Hence, it appears that very little water need be taken up by the well-dried C_4AH_{13} before the basal reflection shifts from 7.4 A to 7.8 A, so that in many cases, the line observed at 7.8 A may represent either carboaluminate, C_4AH_{13}, or both. The reversibility of the hydration-dehydration process in C_4A hydrate was also noted by Roberts. However, there is always a small amount of CO_2 in any paste, most of which was present in the cement prior to hydration. If all this CO_2 were in the form of carboaluminate, there would, in most cases, not be enough present such that all of the tetracalcium aluminate hydrate potentially in the paste would be in the form of carboaluminate.

The diffraction maximum observed at 7.8 A is not a strong, sharp peak, but rather a low, broad hump. This spacing is the basal reflection of the pseudohexagonal crystal [48], regardless of which of the two compounds it represents. The fact that this reflection is poorly developed indicates that the crystals may be quite small and disordered, a condition somewhat akin to that of the CSH(I) produced by reaction of CaO and SiO_2 at room temperature. (The calcium silicate hydrate produced by the hydration of C_3S, of course, shows no basal reflection whatever [15, 24].)

There is some evidence that tetracalcium ferrite hydrate may also have a diffraction line at 7.8 A. Various investigators have reported different basal reflections for C_4FH_x, presumably because each investigated material with a different moisture content. Greening and Seligmann [47] found the basal spacing to be 8.2 A for material in the saturated state. Watanabe and Iwai [49] report a value of 7.96 A for somewhat drier material. Taylor [50] has X-ray data for a hydrate of the composition C_4FH_{10} which includes a basal reflection of 7.8 A. However, even this material would presumably lose water on further drying to the $\frac{1}{2}$-μ level, and as a result, undergo further layer contraction. This would result in a downward shift of the basal reflection toward the 7.4 A value reported for dried tetracalcium aluminate hydrate. There is no information available at present as to how rapidly this dried ferrite hydrate would pick up moisture.

In some of the dried powder patterns, other lines of the hexagonal calcium aluminate hydrate are seen. The most important among these is at 3.9 A, the 002 reflection. The carboaluminate has no line at 3.9 A, but rather, one at 3.8 A. This latter spacing appears in many wet slab patterns, along with a line at 3.9 A caused by the presence of calcite. In the dry powder patterns, no calcite lines appear, and no line at 3.8 A. However, a small line at 3.9 A is found indicating that the hydrated aluminate is primarily C_4AH_{13}. The spacing at 3.9 A is also one found with C_4FH_{10} [50]. Lines appear at 2.46 and 2.10 A in the dried powder patterns, but these also contain contributions from other compounds, such as calcium monosulfoaluminate. The similarity of the pattern of this latter compound with that of tetracalcium aluminate hydrate is quite marked, with the exception of the locations of the basal reflections.

There remains the distinct possibility that the cement paste pattern lines attributed to monosulfoaluminate are in truth those of a solid solution of this material with the tetracalcium aluminate hydrate, but this would not obviate the fact that the evidence obtained indicates the presence of this latter material by itself.

The Dependence of Water Content on Cement Composition

Nonevaporable water data have been obtained on a group of cements hydrated for times up to 13 yr [51, 52]. The cements used were those prepared for use in the "Long Time Study" project at the Portland Cement Association Research and Development Laboratories. The oxide compositions and the potential compound compositions of these cements were published by Lerch and Ford [53].

It was assumed that both nonevaporable water and surface area were dependent on linear functions of the cement composition parameters. Thus:

$$w_n/c = k_1(\text{alite}) + k_2(\text{belite}) + k_3(C_3A) + k_4(F_{ss}) + k_5(CaSO_4) \quad (1)$$

where the k_i are constants and w_n/c is the nonevaporable water content in grams of water per per gram of cement. The quantities (alite) and (belite) refer to the C_3S and C_2S phases as they occur in portland cement, each containing minor quantities of other oxides, primarily Al_2O_3, as has been discussed by Jeffery (in the case of alite) [54], and in some recent publications on the quantitative analysis of portland cements by means of X-rays [20, 21]. The symbol F_{ss} represents the ferrite solid solution phase. All cement compound quantities may be expressed in grams per gram of cement.

It was shown in the quantitative cement analysis work that the compositions obtained from X-ray analysis did not differ significantly from those obtained from the potential compound calculation devised by Bogue [19] except in the case of C_3A. The C_3A values were lower in the X-ray determination because of the Al_2O_3 in the alite and belite phases; the alite phase was correspondingly higher because of this Al_2O_3. Inasmuch as the ferrite solid solutions had A/F ratios near unity for the most part, the X-ray and potential values were in good agreement.

For the purposes of the calculations, it proved expedient to use potential rather than X-ray values because X-ray values were not available for all of the cements. Since the Al_2O_3 in the alite and belite phases probably behaves during the hydration process in much the same manner as the Al_2O_3 in C_3A, it is likely that no significant error is introduced by the use of potential data. Expressed in terms of the potential compound compositions, eq (1) becomes

$$w_n/c = a_1(C_3S) + a_2(C_2S) + a_3(C_3A) + a_4(C_4AF) + a_5(CaSO_4) \quad (2)$$

where the a_i are again constants in the equation.

Since the quantity w_n/c in eq (2) is a linear function of the potential compound quantities, which, in turn, are linear functions of the oxides [19], it follows that w_n/c is also a linear function of the oxides. Thus

$$w_n/c = b_1(CaO) + b_2(SiO_2) + b_3(Al_2O_3) + b_4(Fe_2O_3) + b_5(SO_3). \quad (3)$$

The coefficients in eq (2) have been evaluated by the method of least squares from data obtained from the "Long Time Study" (LTS) cements hydrated for 1, 6½, and 13 yr, at water:cement ratios of 0.4, 0.6, and 0.8, and dried to approximate equilibrium with the vapor pressure of water over a mixture of $Mg(ClO_4)_2 \cdot 2H_2O$ and $Mg(ClO_4)_2 \cdot 4H_2O$ (8 μ), or that of water over ice at −78.5 °C (½ μ). The parameters of eq (2) were evaluated including the $CaSO_4$ term (5-parameter system) or omitting this term (4-parameter system). The results are shown in table 4. In this table, the age of the specimen is given in column 1, the water:cement ratio and method of drying in column 2, the number of parameters evaluated in column 3, the number of cements in the data set in column 4, the values of the parameters in columns 5, 7, 9, 11, and 13, and the standard errors of these parameters in columns 6, 8, 10, 12, and 14.

Investigations of the stoichiometry of the hydration of C_3S and C_2S [15, 24] have shown that the hydration reactions may be represented by the equations

$$2C_3S + 5H = C_3S_2H_2 + 3CH \quad (4)$$

$$2C_2S + 3H = C_3S_2H_2 + CH \quad (5)$$

the composition of the calcium silicate hydrate being given as that of the half-micron material. From these equations, it is seen that each gram of C_3S reacts with 0.197 g of water, and each gram of C_2S with 0.157 g of water. The constants, a_1, in eq (2), obtained from the least squares treatment of the various sets of half-micron sample data, range from 0.199 to 0.208. It would therefore appear that in 6.5-year-old pastes, hydrated at relatively high water:cement ratios, for which these values were obtained, the C_3S is completely hydrated.

The constants, a_2, obtained from these same data, range from 0.147 to 0.152. The fraction of C_2S hydrated, estimated as the ratio of the calculated value of a_2 to the theoretical value based on eq (5) is 0.951, on the average, for a

TABLE 4. *Least squares coefficients from nonevaporable water data*

Age	w_0/c & drying [a]	No. of parameters	No. of cements	a_1	σ_1	a_2	σ_2	a_3	σ_3	a_4	σ_4	a_5	σ_5
13 yr	0.4(P)	5	27	0.226	0.017	0.194	0.014	0.510	0.066	0.097	0.065	0.149	0.312
"	"	4	27	.230	.015	.196	.013	.522	.060	.109	.058		
6½ yr	0.8(P)	5	23	.228	.022	.193	.020	.478	.097	.151	.097	0.317	0.460
"	"	4	23	.234	.020	.197	.018	.509	.085	.184	.083		
"	0.8(D)	5	23	.201	.020	.154	.017	.571	.086	.190	.086	−0.120	0.410
"	"	4	23	.199	.018	.152	.016	.561	.075	.178	.073		
6½ yr	0.6(P)	5	24	.228	.020	.188	.018	.412	.090	.091	.079	0.607	0.409
"	"	4	24	.238	.020	.198	.017	.477	.081	.142	.074		
"	0.6(D)	5	24	.204	.019	.147	.016	.470	.083	.129	.074	0.243	0.380
"	"	4	24	.208	.017	.151	.015	.496	.072	.149	.065		
6½ yr	0.4(P)	5	27	.223	.018	.170	.015	.463	.070	.117	.069	0.503	0.333
"	"	4	27	.234	.017	.178	.015	.504	.066	.158	.065		
1 yr	0.4(P)	5	27	.212	.020	.155	.016	.363	.076	.067	075	0.786	0.360
"	"	4	27	.228	.019	.168	.016	.429	.074	.132	.073		

[a] (P)—dried at 8μ vapor pressure; (D)—dried at ½μ vapor pressure.

6.5-year-old paste hydrated at a water:cement ratio of 0.6, and 0.974 for pastes of the same age hydrated at a water:cement ratio of 0.8. These latter values, however, must be considered as maximum values, inasmuch as there is usually somewhat more water in the calcium silicate hydrate phase than the two moles per mole of SiO_2 indicated by the two eqs (4) and (5), [15].

For 8-μ dried C_3S and C_2S pastes, the stoichiometric equations are [15]:

$$2C_3S+5.8H=C_3S_2H_{2.8}+3CH \qquad (6)$$

$$2C_2S+3.8H=C_3S_2H_{2.8}+CH. \qquad (7)$$

These equations predict the values of a_1 and a_2 to be 0.229 and 0.199, respectively. The values obtained indicate that for pastes hydrated at water:cement ratios of 0.4, after 1 yr, the C_3S is over 95 percent hydrated and after 6½ yr, it is completely hydrated. The C_2S is not so well hydrated, however, being, on the average, 81.4, 87.6, and 98.2 percent hydrated at 1, 6½, and 13 yr, respectively.

Inasmuch as the cements used in the least squares analysis are of widely different compositions, it must be pointed out that such a treatment is valid only for relatively well-hydrated pastes, wherein the effect of dependence of hydration rate on cement composition is no longer important.

Interpretation of the aluminate, ferrite, and sulfate nonevaporable water results is more difficult. In the first place, there are several possible products of hydration, and as has been shown, evidence has been obtained for the presence of some of them. Others may be present for which no evidence has as yet been obtained. As can be seen from the standard errors, the least squares parameters for the ferrite and sulfate are far less certain than are the C_3S and C_2S parameters. Furthermore, while there is no significant difference between the 4- and 5-parameter C_3S and C_2S results, the other parameters are strongly affected. The contribution of the sulfate in the 5-parameter calculation is absorbed primarily by the aluminate and ferrite parameters in the 4-parameter calculation.

The least squares results may be expressed in terms of oxides, according to eq (3). The parameters may then be converted to moles of water per mole of oxide. When this is done, the results for half-micron dried samples at a water:cement ratio of 0.8, rounded to whole numbers (except in the case of SiO_2) are $H/C=1$, $H/S=-0.5$, $H/A=5$, $H/F=-5$, and $H/SO_3=-2$. These values may be used to predict the water contents of the various possible products of hydration. For instance, a calcium silicate hydrate with a C/S ratio of 3/2 would have the composition $C_3S_2H_2$, just as was indicated from the potential compound parameters and the stoichiometric equations for the hydration of the pure silicates. Tetracalcium aluminate hydrate would have the composition C_4AH_9, which is to be compared with the compositions reported by Roberts [33] for tetracalcium aluminate hydrates dried under various conditions. Roberts gives H/A values of 11 for material dried over solid NaOH or anhydrous $CaCl_2$, and values of 7 for material dried over P_2O_5 or at 120 °C.

The calcium ferrite hydrate case is not so simple. A tetracalcium ferrite hydrate would have a negative water content, which is, of course, absurd. However, if the aluminates and ferrites were in solid solution, physically possible, and not unreasonable, water contents are predicted.

The predicted water contents of the sulfoaluminates are, as was pointed out above, quite uncertain. The water-to-oxide ratios given above lead to the compositions $C_3A{\cdot}CaSO_4{\cdot}7H$ and $C_3A{\cdot}3CaSO_4{\cdot}5H$. Lerch, Ashton, and Bogue [55] found water contents for these materials, dried at 110 °C, to be 6H and 7H, respectively. Roberts' recent work [33] indicates a value for the low sulfate sulfoaluminate of about 8H. If the least squares H/SO_3 value were -1 instead of -2, the predicted compositions of the sulfoaluminates would be $C_3A{\cdot}CaSO_4{\cdot}8H$ and $C_3A{\cdot}3CaSO_4{\cdot}8H$. Thus, on the basis of experimental evidence, it appears that the H/SO_3 ratio should be somewhere between -1 and -2. Both these values fall well within the uncertainty limits determined statistically.

The evidence from the least squares calculations combined with the evidence obtained from the X-ray diffraction studies provides a strong indication that the alumina in C_3A reacts in a different manner from that in the ferrite phase. The cements low in C_3A shown in tables 1 and 2 both contain ettringite. On the other hand, those cements high in C_3A when hydrated contained the low sulfate sulfoaluminate. Thus, it appears that only when the A/F ratio in the cement is relatively high, does the low sulfate sulfoaluminate form. Steinour points out, in his recent discussion of the setting of portland cement [56], that when the molar A/F ratio in a cement is less than 1.0, no retarder is needed. He also attributes flash set to the formation of a hexagonal calcium aluminate. Under the conditions obtained with the use of the high C_3A cements whose compositions are given in table 5, the presence of gypsum

TABLE 5. *Oxide compositions of four portland cements*

Cement type	15754 I	15622 II	15497 III	15669 IV
	Percent	*Percent*	*Percent*	*Percent*
SiO_2	20.67	22.44	19.83	27.51
CaO	63.03	63.81	63.41	63.73
Al_2O_3	6.13	3.88	5.21	1.95
Fe_2O_3	[a] 2.20	4.20	[a] 2.59	1.92
MgO	2.05	1.36	1.28	1.64
SO_3	2.37	1.59	1.82	1.82
Total	96.45	97.28	94.14	98.57
Free CaO	0.93	0.49	3.14	0.15
Na_2O	.17	.05	0.30	.05
K_2O	.16	.17	.40	.22

[a] The total Fe_2O_3 includes a small amount of FeO expressed as Fe_2O_3.

prevents the formation of the hexagonal aluminate (presumably tetracalcium aluminate hydrate) by the formation of the sulfoaluminate. The first sulfoaluminate to form is ettringite, apparently, since of the X-ray patterns of pastes from cement 15754, only that of the youngest observed, a 6-month old specimen, showed ettringite. Taylor [10], too, studying a normal portland cement, observed initial formation of ettringite, with subsequent disappearance. It is interesting to note that a hexagonal phase ultimately does form, this however being the low sulfate sulfoaluminate. The molar A/F ratios in the two cements, 15754 and 15497, in which the monosulfoaluminate does form are 4.37 and 3.15, respectively.

On the other hand, the low sulfate sulfoaluminate does not form in cements 15622 and 15669 in which no significant amount of C_3A is present. The molar A/F ratios in these two cements are 1.45 and 1.59, respectively, or, when corrected for the alumina in the silicate phases, 0.81 and 1.34. It would appear from these results that no significant amount of alumina from the ferrite phase enters into a sulfoaluminate as long as enough alumina is available from other sources to combine with all of the SO_3 present to form at least the high sulfate sulfoaluminate.

Flint and Wells [57] observed that while C_3AH_6 was susceptible to attack by sulfate, hydrogarnets containing either iron or silica were quite resistant. It would appear from these considerations that the molar ratio of nonferrite alumina to SO_3 in a given cement would serve as an indication as to which sulfoaluminate forms ultimately. Thus, the high C_3A cements, which contain the low sulfate sulfoaluminate for the most part have SO_3 to nonferrite Al_2O_3 ratios of 0.7 and 0.6, respectively, while the low C_3A cements, which contain the high form for the most part have ratios 1.2 and 3.9.

It is therefore also likely that no sulfoferrites form in portland cement pastes, at least of cements within the wide composition range covered by those whose X-ray data are given in tables 1 and 2, and whose compositions are given in table 5. Furthermore, the least squares coefficients discussed above also indicate that there is no sulfoferrite, in that such a compound, either high form or low form, could not have a negative calculated water content, physically absurd. Of course, a solid solution of sulfoaluminate and sulfoferrite is possible as far as the least squares considerations go just as in the case of aluminates and ferrites.

II. Kinetics of the Hydration of Portland Cement

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Introduction

The purpose of this section of the paper is to review our knowledge of the kinetics of hydration. Mechanisms of hydration may at times be mentioned but a discussion of mechanisms is not a principal objective.

The first kinetic studies of the hydration of portland cement were concerned with determining the strength of concrete and mortars as a function of time of curing. Useful information can be obtained from such studies, but their value for theoretical purposes is limited because the development of strength in concrete and mortar is influenced by many factors other than the rate of hydration of the cement in the mix. Knowledge of the rates of hydration of cement is just one step toward understanding the mechanism of hydration and the development of strength, but it is an important one.

Three general methods have been used in studying the kinetics of hydration of portland cement: (1) microscopic examination of hardened neat cement pastes after known curing times, (2) observations of changes in the physical and chemical properties of hardened pastes as a function of time, and (3) X-ray diffraction analysis of unhydrated cement in hardened pastes.

In general, the microscopic studies can be, and in some cases have been, interpreted to support Michaelis' theory of the hardening of portland cement in that the unhydrated clinker particles are found embedded in a gel which has no structure visible in the light microscope. The presence of all four major phases has been observed in these particles—even after 20 yr.

The measurement of several physical and chemical properties of pastes as a function of curing times has been made. In some cases inferences concerning the rates of hydration of the individual components of cement have been drawn from these measurements. It will become evident that some of these inferences are not justified.

In recent years new techniques have been developed. One of these, X-ray diffraction, offers about our best tool for measuring directly the rates of hydration of the individual phases in portland cement. At the present time the experimental error is large when compared with the experimental error of standard chemical methods of analysis, but significant results can be obtained. Further experience with the method will bring improved results. Perhaps other new techniques can also be applied to the problems.

Direct Microscopic Observations

Most of the microscopic examinations have been made on polished sections, or sometimes upon thin sections, of hardened pastes. But Anderegg and Hubbell [58] chose to develop a different technique for their work. They first passed cement through an air separator to obtain several fractions of cement with particles with a narrow size range. They then prepared pastes of these sized fractions, $w_0/c=0.4$, and cured them in contact with a small quantity of water. At each of several selected ages a small fragment was broken from each paste and dried in an oven to stop the hydration reactions by removing the water. Each fragment was then ground until microscopic evidence showed the material to be subdivided into small and uniformly sized particles. Specimens for microscopic examinations were prepared by placing these particles on a microscope slide in an oil with a refractive index of 1.67. Thus it was possible for them to tell whether or not a particle was hydrated by its refractive index, for if it is hydrated its refractive index is lower than that of the oil and vice versa. They counted thousands of particles (weighting the count by the size of the particles) and determined the volume fraction of hydrated cement from the number of hydrated particles relative to the total number of particles. They obtained the weight fraction hydrated by using the densities of the unhydrated cement and of the completely hydrated cement.

To check their results they determined the fraction of cement hydrated in samples prepared by mixing completely hydrated cement with unhydrated cement in known proportions. They reported results accurate to about 2.5 percent.

They proceeded then to calculate the depth of penetration of the water into cement particles. To do this they assumed that the shape of the original cement particles was the same as that of the unhydrated particles remaining in the paste, and made microscopic measurements to determine the size and shape of a great many cement particles. Typical results, given in table 6, were estimated for a cement with a known particle size distribution using their results on depth of penetration of water in sized fractions of clinker particles. They noted that their Type III cement appeared to hydrate no more rapidly than did their Type I cement.

These experiments were repeated [59] using pure compounds and mixtures of pure compounds. Pure C_2S hydrated much more slowly than did pure C_3S, which hydrated much more slowly than did pure C_3A. The addition of 10 percent C_4AF to either C_3S or C_2S caused the mixture to hydrate much more rapidly than either component of the mixture would hydrate when pure.

Brownmiller [60] examined polished sections of neat cement pastes cured for various times. From this examination he estimated that about $\frac{1}{3}$ of the cement remained unhydrated at the end of the first day. He compared the sizes of the particles visible in the polished sections with the sizes of the particles of original cement and estimated that a 60μ particle decreased in size to about 45μ during the first day, that the depth of penetration was about $7\frac{1}{2}\mu$. At 7 days approximately 80 percent of the cement had hydrated, and at 28 days about 85 percent. Cements that were high in C_3S and C_3A were almost completely hydrated at the end of 7 days. He concluded that as hydration proceeds there is a uniform decrease in the size of the cement particles, and stated, "There is no microscopic evidence of the channeling of water into the interior of cement particles to selectively hydrate any single major constituent."

TABLE 6. *Depth of penetration of water in clinker particles and the degree of hydration of a typical portland cement*

Time (days)	Depth of penetration (μ)	Percent hydrated
1	10	24
7	47.2	42
28	78.1	51
90	----------------	60

However, he did observe that different phases at the boundary of a particle did not hydrate at the same rates: e.g., C_3S hydrates more rapidly than C_2S, and some interstitial material hydrates very slowly indeed.

Rexford [61] used thin sections. He pointed out that accurate rates of hydration from such microscopic examination were very difficult to obtain; one needs to examine many fields and measure accurately with a Wentworth micrometer stage. He confirmed Brownmiller's conclusions that hydration proceeded from the boundaries of cement particles inwards towards the center at a comparatively uniform overall rate, which affected all the constituents of that particle more or less simultaneously. He stated further, "No indication of completed hydration of any one compound was ever observed although incipient selectivity was often visible around the periphery of a cement particle." His conclusions were based upon the examination of hardened pastes cured up to 6 months, and upon examination of concrete up to 20 yrs old.

Ward [62] examined thin sections and came to somewhat different conclusions. He described two kinds of gel, one of which he called a "ground mass" gel that was interrupted by unhydrated clinker grains, calcium hydroxide crystals, and by small channels, and pores. Small crystalline particles of low birefringence were scattered throughout this gel. As the paste aged, a clear gel appeared to exude from the ground mass or to precipitate in the voids and channels.

He observed that C_2S and C_4AF were slow to hydrate and that many cement grains were shattered during the hydration. He identified the fragments as C_2S. He concluded that each clinker grain does not hydrate in such a manner as to develop an individual coating of hydrate with subsequent uniting of these coatings.

The overall rate of hydration of cement observed in these microscopic studies agrees qualitatively with expectations based upon the rate of strength development. Anderegg and Hubbell tacitly assumed a mechanism of hydration that was supported later by the independent observations of Brownmiller and of Rexford. In answering a criticism of their paper, Anderegg and Hubbell show that they were aware that this assumption was not universally accepted, but argued that it is true. Actually, it is supported by the theory of hardening advanced by Michaelis, just as Brownmiller interprets his results to support Michaelis' theory.

There is a small difference between the compositions of the finely ground part and the coarser part of a cement, but if hydration proceeds by a more or less uniform diminution in the size of the cement grains, then the finer fraction would disappear first—probably during the first day. After that time the composition of the unhydrated residue should change only slowly if at all.

Ward criticized the above views. He wrote of an apparent increase in the amount of C_2S in the hardened pastes and suggested that the individual phases react separately, then at a favorable concentration a general precipitation of gel occurs. But both concepts can be correct. The mechanism proposed by Ward could account for the initial setting of cement but by far the greatest amount of cement could be hydrated as Brownmiller and Rexford have described it. It is certainly true that if cement grains were "shattered" by hydration, this must have occurred before the paste hardened.

Ward observed shattering of C_2S grains in observing the hydration of the pure compound under the microscope. He noted that his pure C_2S showed a tendency to dust and suggested that perhaps the shattering was the result of the $\beta \rightarrow \gamma$ conversion. Is it possible that water could leach a soluble stabilizing agent out of the C_2S phase in portland cement, causing the same conversion with shattering of the cement grain?

Kinetics From Changes in Physical and Chemical Properties

Heat of Hydration

Many workers have determined the heat of hydration of portland cement as a function of time of curing. Woods, Steinour, and Starke [63, 64] were able to correlate such heats of hydration with the development of strength in mortars, and also found a good correlation between the rate of development of strength and the composition of the cement. Their primary motive was development of low heat cement, and therefore it was essential to their purpose to find a relationship between heat of hydration and composition of cement. For this they employed the method of least squares, assuming that at any given age each percent of each cement compound makes a fixed contribution to the heat evolution independent of the proportion of the compound in the cement. They were successful in accomplishing their objective. Other workers have generally followed their example. Davis, Carlson, Troxell, and Kelly [65] made similar studies of heats of hydration, and Verbeck and Foster [51] published initial results of an extensive investigation which is continuing. The latter authors included the effects of gypsum and both gypsum and glass in their computations.

By comparing the magnitudes of the respective "contributions" of each of the components to the heat of hydration, it can be inferred that the rates of hydration of the major components have the order C_3A, C_4AF, C_3S, C_2S. This order agrees with that obtained by comparing the rates of hydration of the pure components. The contribution of each component to the heat of hydration of completely hydrated cement paste is, within experimental error, the heat of hydration of the pure component.

Apparently no one working with heats of hydration has done more than draw qualitative conclusions concerning rates of hydration of the individual components from his data. If the assumption made tacitly in applying the principle of least squares to heat of hydration data is valid, the rates of hydration of the individual phases can be estimated. It will be instructive to consider this assumption.

Consider k cement pastes, each made with a cement different in composition from all the others. Let H_i be the heat of hydration of the paste made from 1 g of the ith cement and cured t days. Let X_{ij} be the weight fraction of component j in the ith cement, and $w_{ij}(t)$ be the weight of component j per gram of cement that has hydrated in t days. Let h_j be the heat of hydration of 1 g of component j. The heat of hydration of the paste can now be written:

$$H_i(t) = \sum_j w_{ij}(t) h_j. \tag{8}$$

The $w_{ij}(t)$ are unknown. In the application of the least squares principle to the k pastes, each hydrated t days, it is assumed that H_i can be written:

$$H_i(t) = \sum_j a_j(t) X_{ij}. \tag{9}$$

The coefficients $a_j(t)$ are called the contributions of the major components j to the heat of hydration. Eq (8) can be put into the form of eq (9) by multiplying and dividing each term on the right of eq (8) by X_{ij}, that is,

$$H_i(t) = \sum_j \frac{w_{ij}(t)}{X_{ij}} h_j X_{ij}. \tag{10}$$

Equations (9) and (10) are consistent if

$$a_j(t)=\frac{w_{ij}(t)}{X_{ij}}h_j. \tag{11}$$

In applying the method of least squares to eq (9), it must be assumed that the $a_j(t)$ are independent of the compositions of the cements; consequently, $\frac{w_{ij}}{X_{ij}}$, the degree of hydration of component j, must be the same in all cement pastes at the time t. Also, the time derivative of the degree of hydration, which we shall call the fractional rate of hydration, must be independent of the composition of the cement used in making the paste. A mechanism could be devised to account for this behavior, but the validity of the assumption must be shown by evidence independent of heats of hydration.

Heats of hydration have been used in other ways to obtain information concerning rates of hydration. Steinherz [66] has recently noted that Anderegg and Hubbell [58] oversimplified their calculations on the depth of penetration of water in cement grains by their assumption concerning the shape of their particles. He presents a different approach based upon the measurement of a mean volume and weighted mean diameter of the particles and the assumption that the shape of the particles corresponds more closely to flattened cylinders than to spheres. He used the heat of hydration of the fraction of clinker grains he studied to estimate the amount of cement hydrated, and calculated a depth of penetration. He obtained results similar to those of Anderegg and Hubbell.

The effect to be expected of assuming that the components hydrate at equal fractional rates in cement has been shown by zur Strassen [67]. He considers two different conditions: (1) the rate of diffusion of water through the gel layer is so high that sufficient water is always present in the reaction zone to bring about conversion, or (2) that the reaction is impeded by the rate at which water can diffuse through the gel film being formed. He assumed that the particle size distribution of the original cement could be represented by a Rosen-Rammler size distribution with exponent 1.05. Using Verbeck and Foster's heats of hydration as a measure of the amount of cement hydrated, he calculated the depth of penetration of water into the cement particles and found that the rate followed the diffusion law at times up to 28 days for Type I cement, and times up to 7 days for Type III cements. Thereafter the rate became slower.

He also used the data of Schwiete and Knoblauch [68] on the heats of hydration of pure C_2S and pure C_3S and concluded that for C_2S the rate of reaction is constant up to about 80 percent conversion. For C_3S, after a short period when the rate is linear, the rate follows the diffusion law. He suggests that in cement the expected initial retardation of the hydration of β-C_2S is so little reflected in the $\frac{V_m}{w_n}$ and $\frac{\Delta H}{w_n}$ ratios that the impression of a fully uniform rate of hydration is given. (V_m is the weight of water required to form an adsorbed layer one molecule thick.)

Nonevaporable Water

The nonevaporable water content (or any other good measure of fixed water) is a measure of the extent of hydration of cement in pastes, just as is the heat of hydration. As yet no extensive analysis concerning kinetics of nonevaporable water data has been made as has been done for heats of hydration. Actually there is little need to do so for it has been shown [51, 69] that there is a linear relationship between the two quantities. Least squares calculations based upon the same model as was used for heats of hydration would certainly give the same results.

The effect of the original water-cement ratio, w_o/c, upon the rate of hydration of cement can be seen by comparing nonevaporable water contents of pastes made from the same cement and cured under the same conditions, except for variations in w_o/c. Unpublished data from this laboratory show that w_o/c has little effect upon the rate of hydration during the first 3 or 4 days. After that, the smaller is w_o/c, the more rapidly the rate of hydration decreases. This effect is consistent with the widely accepted view that the rate of hydration is controlled in some manner by the rate of diffusion of reacting species through the gel.

Recently Taplin [70] has published similar, but more complete data, covering w_o/c ratios from 0.157 to 0.80. These data, figure 3, show the same effects when w_o/c is over 0.5, but in pastes where w_o/c is low, the rate of hydration for a short time is higher than in pastes where w_o/c is high. The slightly greater rate of hydration can probably be accounted for by the temperature of the pastes. The temperature of fresh pastes cast in molds and stored in a constant temperature room will rise several degrees above room temperature during the first 24 hr. The smaller the mass of the paste per gram of cement the greater will be this temperature rise, and the greater will be the effect upon the rate of hydration.

The effect of availability of water immediately after hardening is shown graphically in figure 4. The upper curve shows w_n/c for a paste with $w_o/c=0.6$ cured in contact with water at all times. The lower curve represents two samples of a paste made from the same cement with the same initial w_o/c, but cured under different conditions [71]. The pastes were placed under a bell jar for 48 hr after mixing. After that time, half of the paste was transferred to a sealed jar for the remaining curing time. The other half was wrapped with filter paper and placed in a covered tray in contact with a small amount of water. These two samples continued to hydrate at the same rate even though the total water content per gram of cement w_t/c, of the sample in contact with

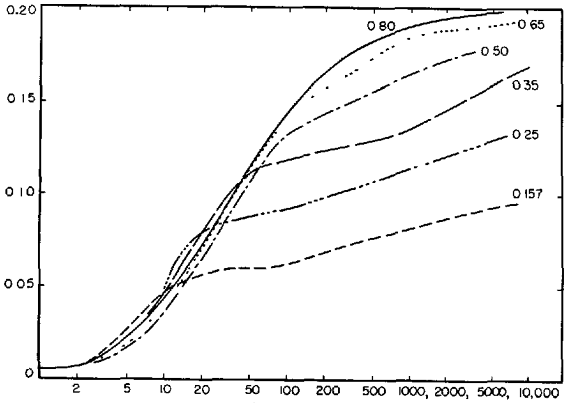

FIGURE 3. *Effect of w_o/c upon rate of increase of combined water in portland cement pastes.*

water increased to 0.64 at 200 days. The total water content of a sample cured continuously moist to the same nonevaporable water content, $w_n/c=0.20$, should be 0.652 [72]. The nonevaporable water content of 0.20 was attained in less than 28 days in the sample cured continuously moist.

The effect of the lack of an adequate supply of water during the first 2 days upon the rate of hydration was so great that the effect of w_o/c was almost eliminated. Pastes with $w_o/c=0.6$ hydrated only slightly more rapidly than pastes with $w_o/c=0.44$. It is important that the fresh paste has an adequate supply of water continuously if the maximum rate of hydration is to be maintained. Copeland and Bragg observed very little effect due to self-desiccation after the first 2 days, but their curing conditions missed the large effect shown in figure 4.

Specific Surface of Hardened Paste

In their study of the physical properties of hardened portland cement paste, Powers and Brownyard [73] observed that the specific surface of hardened paste was a linear function of the nonevaporable water content. The data were not quite precise enough to show that the line definitely passed through the origin, but if there is an intercept, it must be small. Further data, obtained later, confirmed the linear relationship for pastes made from cement with normal composition. In pastes made from cements with high C_2S contents, V_m did not appear to be exactly proportional to w_n.

Rate of Formation of Calcium Hydroxide

A part of the nonevaporable water of hardened pastes is in the calcium hydroxide. Pressler, Brunauer, Kantro, and Weise [18] determined calcium hydroxide in a number of hardened pastes. One series of pastes was made from a cement low in C_2S; another series was made from a cement high in C_2S. Pastes in each of these series were cured for intervals of time ranging from 1 day to several years. In the series made from the low-C_2S cement, the calcium hydroxide produced in hydration was found to be a linear function of the nonevaporable water content. The relationship between the calcium hydroxide and nonevaporable water formed by hydrating the high-C_2S cement was decidedly curvilinear.

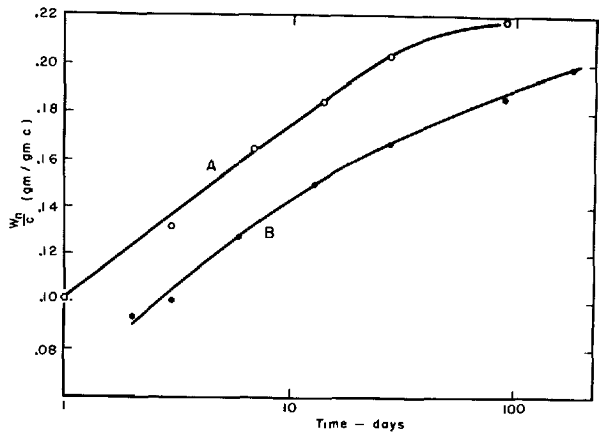

FIGURE 4. *Effect of self-desiccation of portland cement pastes upon rate of hydration of the cement.*

A—cured continuously moist, B—self-desiccated.

Discussion of Rates of Change of Physical Properties

Powers and Brownyard [73] pointed out that if V_m is proportional to w_n, then the ratio of colloidal to noncolloidal products should be the same at all stages of hydration. To simplify the handling of their data, they assumed that V_m/w_n was constant. The linear relationship [51] between the heat of hydration and nonevaporable water, and also V_m, seemed to confirm the idea that the same kinds of hydration products were being formed at all stages of hydration. One of the authors (Copeland) pointed out that these linear relationships would be observed if the components in cement hydrated at the same fractional rates. It was recognized that this assumption could not be true during the initial stages of the reaction, but it might be true after the first 24 hr.

Brunauer [74], after a careful examination of heat of hydration data, observed that the heat of hydration of cements high in C_2S was not a linear function of the nonevaporable water. It was pointed out above that V_m/w_n is probably not constant in pastes made from these same cements, so if the assumption is true at all, it is limited to cements comparatively low in C_2S.

The assumption of equal fractional rates of hydration of the components in cement is different from the assumption made in applying the principle of least squares to heat of hydration data. In the latter case it is assumed that the fractional rate of hydration of each component is independent of the composition of the cement. The results of the least squares calculation show that the fractional rates of hydration are not equal to each other, so one or both of these assumptions is incorrect.

The heat of hydration studies exemplify the difficulty of inferring rates of hydration from the rate of change in physical and chemical properties. Different assumptions have been made and rates calculated from the same data: (a) The interpretation of least squares coefficients as the contribution to the heat of hydration by that component requires that the fraction of a component hydrated in a given interval of time be always the same and independent of the composition of the cements and accordingly the composition of the gel. This assumption seems to require that all cements become completely hydrated in the same period of time—that time required by the component with the lowest fractional rate of hydration. (b) The assumption of a uniform depth of penetration of water in cement grains can also fit the data as has been shown by Steinherz [66] and by zur Strassen [67]. The concept of a uniform depth of penetration is consistent with the assumption that the components hydrate at equal fractional rates. It is not supported in detail by direct microscopic examination, for as pointed out above [60, 61], C_2S and some interstitial material hydrate more slowly than C_3S and C_3A. But it is just this effect of the slower hydrating components covering C_3S and C_3A regions and preventing water from getting to them that could account for equal fractional rates of hydration for all components.

X-Ray Diffraction Analysis

The rates of change in physical and chemical properties of portland cement pastes depend upon the rates of hydration of the components in cement, but the dependence is complex. The rates deduced from observing changes in properties depend upon the assumptions that are made in interpreting the data. The desire to find a method of measuring the rates directly prompted us to make our first attempts at X-ray analysis.

The first published attempt to use X-ray analysis to estimate rates of hydration directly is that of H. F. W. Taylor [10]. He prepared pastes of portland cement and hydrated them for periods of time up to 300 days. An attempt to separate the hydration products from the unhydrated cement with a dense liquid was not completely successful. Nevertheless, he examined Debye-Scherrer patterns of the fractions and concluded that C_3S hydrates much more rapidly in cement pastes than does C_2S, as is shown by his estimates of the weight fraction of C_3S in the silicates in table 7. He estimated that after 14 days curing, at least 50 percent of the cement had hydrated. The ignition loss indicated 61 percent hydration.

Table 7. *Weight fraction of C_3S in silicates of the unhydrated residue of cement in pastes*

Days	0	1	4	7	14	44	300
$\frac{C_3S}{C_3S+\beta\text{-}C_2S}$	60	50	30	25	20	<10	<5

At the same time attempts were being made in this laboratory to use X-rays to analyze portland cement pastes; but only recently has acceptable precision in cement analysis been attained [21]. The method has been applied [75] to the analysis of two series of pastes made from different cements, the first, a cement of average composition, 15754, the second a cement low in C_2S and C_3A, 15669.

The same method of analysis was used for analyzing these pastes as is used for analyzing cements with one exception: the 511 line for silicon (the internal standard) was used instead of the 111 line used in analyzing the cements. The advantage of using this line at smaller spacing in pastes is twofold: (1) there are no interfering lines from either the cement or the hydration products for this line, whereas the 111 line is affected to some extent by the broad 3.06 A line from the tobermorite and the adjacent 100 line from $Ca(OH)_2$; (2) after the pastes have hydrated a few days, the weaker 511 line matches better the strengths of the lines from the cement components. The intensity of this line relative to the 111 line of silicon is given as 0.17 by Swanson and Fuyat [25] and found by us to be 0.171 ± 0.002 for our sample of silicon.

The cement pastes were prepared with $w_o/c = 0.4$ and cured for intervals of time ranging from 2 hr to 6 months. The analyses of the four major phases unhydrated in each paste is given in table 8. The values reported are referred to the original weight of cement in the paste. Nonevaporable water contents are also given.

The degree of hydration of each component in the two series of pastes are compared in figure 5. Time is plotted on a log scale for convenience. Equal fractional rates of hydration for the components of a cement will be shown by coincidence of these curves. A cursory examination of the figures shows that the components of cement do not hydrate at the same fractional rate in either cement.

The degree of hydration of alite is plotted in figure 5(a). The alite in the normal portland cement does not hydrate at the same fractional rate as that in cement 15669, although probably this condition is realized within experimental error after about 28 days.

The degree of hydration of alite in cement 15669 increases more rapidly than in cement 15754, but the actual rate of hydration of alite in cement 15754 is more rapid than in cement 15669, as is shown in figure 6(a).

The results for belite are plotted in figures 5(b) and 6(b). The degree of hydration of belite at any time in cement 15754 is greater than in cement 15669, but again the actual rate of hydration is higher in the cement containing the more belite. The relatively large error in determining the amount of belite in the pastes made from cement 15669 makes the conclusion that the fractional rates are not equal somewhat less certain than for the case of alite.

TABLE 8. *Composition of unhydrated residue in portland cement pastes (g component/g cement)*

	Type I cement					Type IV cement				
Time hydrated	Alite	Belite	C_3A	F_{ss}	$\left(\frac{W_n}{c}\right)_{\frac{1}{2}}$	Alite	Belite	C_3A	F_{ss}	$\left(\frac{W_n}{c}\right)_{\frac{1}{2}}$
0	.531	.259	.069	.097	----------	.262	.627	.010	.058	----------
2 hr	.538	.248	.054	.064	.0108	.253	.605	.009	.068	.0000
6 hr	.416	.242	.060	.082	.0258	.194	.553	.007	.084	.0118
1 day	.308	.226	.025	.082	.0881	.105	.618	.003	.060	.0426
2 days	.222	.196	.021	.053	.1145	.063	.515	.004	.051	.0570
3 days	.179	.198	.016	.052	.1204	.052	.600	.005	.051	.0619
4 days	.150	.170	.012	.044	.1276	.054	.536	.007	.053	.0674
7 days	.119	.152	.013	.038	.1438	.041	.477	.009	.052	.0763
14 days	.079	.118	.008	.024	.1614	.031	.518	.001	.056	.0818
28 days	.059	.136	.001	.021	.1748	.025	.282	.000	.036	.1048
3 months	.023	.034	.001	.010	.1890	.006	.220	.000	.024	.1305
6 months	.008	.020	.000	.010	.1947	.004	.185	.000	.004	.1394

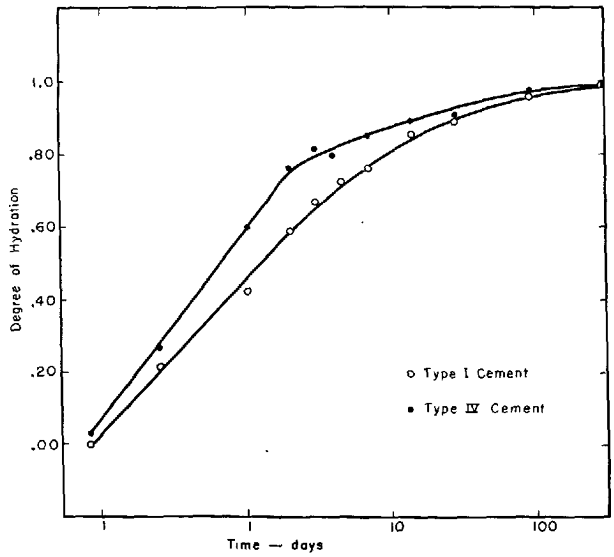

FIGURE 5a. *Degree of hydration of alite in the two series of pastes.*

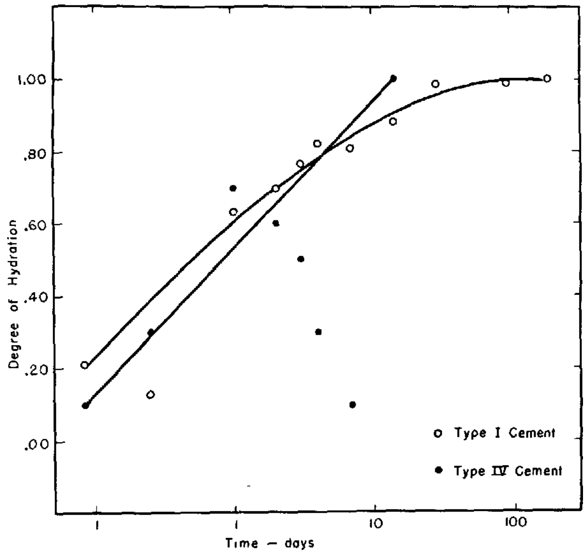

FIGURE 5c. *Degree of hydration of tricalcium aluminate in the two series of pastes.*

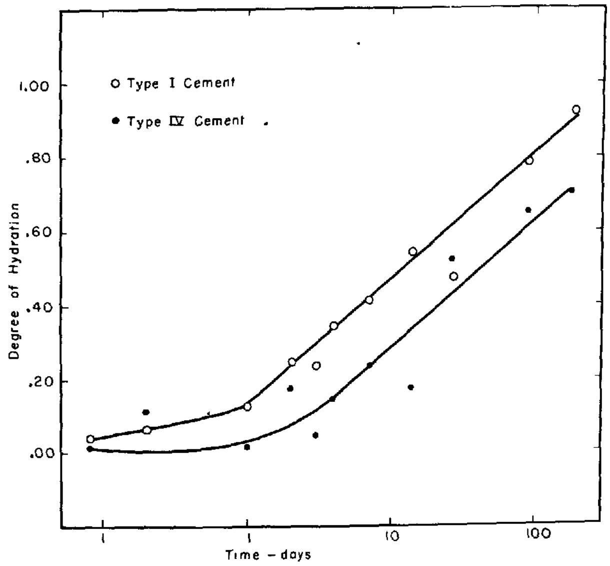

FIGURE 5b. *Degree of hydration of belite in the two series of pastes.*

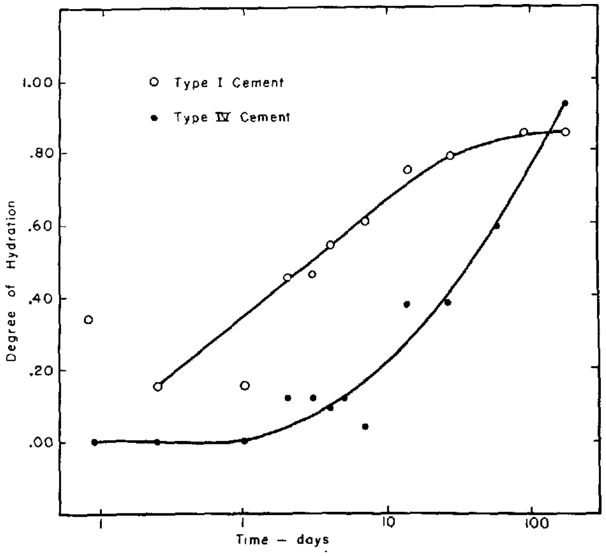

FIGURE 5d. *Degree of hydration of ferrite solid solution phase in the two series of pastes.*

The degrees of hydration of C_3A in the two cements are the same within experimental error, figure 5(c). There is only 1 percent C_3A in cement 15669, and this small quantity is difficult to determine precisely. The C_3A results for cement 15754 present a consistent trend, and most of the C_3A results on cement 15669 agree with the same trend. The screening of C_3A from water may be responsible for the fact that its absolute rate of hydration, figure 6(c), is so much lower than the rate of hydration of C_3S.

The greatest difference in the fractional rate of hydration of a component in these two cements is shown by the ferrite solid solution phases, figure 5(d). Perhaps a difference in the composition of the phase is partially responsible, although there is, as yet, no way of knowing how the composition of the ferrite phase affects its rate of hydration in cement. The A/F ratio of the F_{ss} phase in cement 15754 is 1.44. That in cement 15669 is 1.22. It was observed that the strongest ferrite line did not shift in position as hydration progressed; consequently, the composition of the unhydrated residue is the same as that of the original component. The absolute rate of hydration of the ferrite solid solution phase, as well as its fractional rate, is lower than that of any other component.

The X-ray analyses are certainly not as precise as one would like, and probably not as precise as will be obtained in subsequent studies. They are precise enough to show without question that the major phases in portland cement do not hydrate at equal fractional rates; but in the discussion to follow it will be seen that the observed rates of hydration are consistent with the empirical relations that formed the basis for the assumption of equal fractional rates of hydration for all the components.

One of these empirical relations was the proportionality between V_m and w_n, and another the proportionality between the heat of hydration and w_n. Powers and Brownyard [73] recognized that V_m might not be strictly proportional to w_n, but assumed proportionality to simplify the treatment of their data. The best straight line through the data does not pass through the origin, but has a small positive intercept on the w_n axis. This

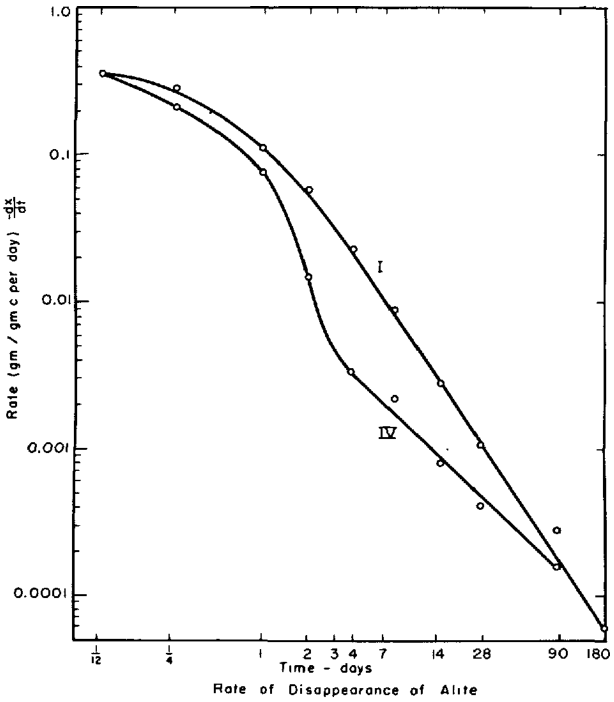

FIGURE 6a. *Rates of hydration of alite in Type I and IV cements.*

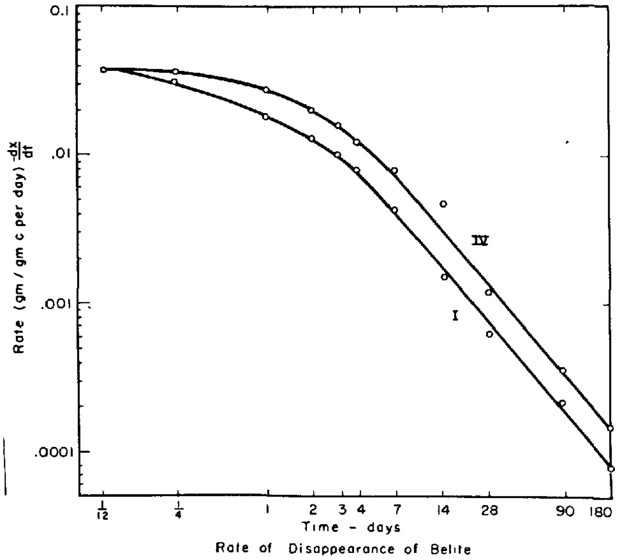

FIGURE 6b. *Rates of hydration of belite in Type I and IV cements.*

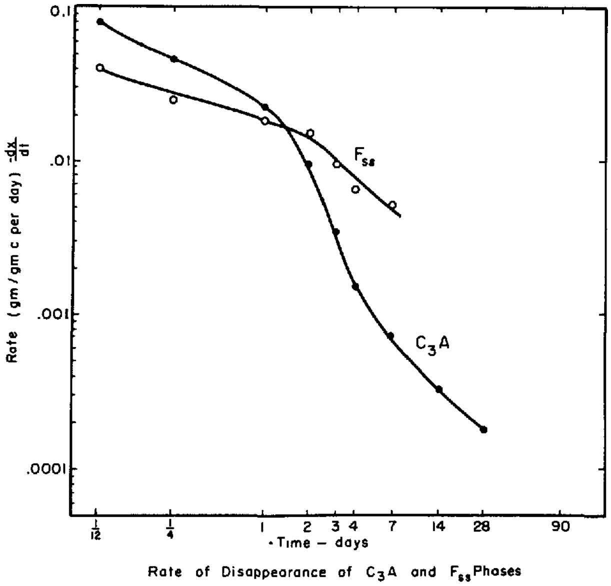

FIGURE 6c. *Rates of hydration of tricalcium aluminate and calcium aluminoferrite solid solution in Type I cement.*

relationship is discussed in detail in another paper in this symposium.

Calculations were made to compare the X-ray results with the data of Verbeck and Foster [51]. To do this, the least squares coefficients for the heat of hydration of cement at 6½ years were used with amounts of each component that had hydrated in each paste as determined from the X-ray analysis. Similarly, the nonevaporable water and the amount of water adsorbed at 36 percent relative humidity in pastes dried over $Mg(ClO_4)_2{\cdot}2H_2O$ were calculated from the respective least squares coefficients for fully hydrated pastes and the X-ray analyses. The data are plotted in figure 7. The two lines are the lines drawn by Verbeck and Foster in their figures 6–7. The calculated heats of hydration agree very well with the heat of hydration line for Type I cement. The calculated adsorptions are slightly below the line drawn by Verbeck and Foster, but well within the range for Type I and Type III cements as determined by them.

There is no equation relating V_m of a paste to the composition of the cement used in making the paste. Instead of calculating V_m, the water adsorbed at 36 percent relative humidity was calculated and is plotted as a function of the nonevaporable water for pastes dried at the vapor pressure of water at −78 °C in figure 8. The data fall on a line with a slight curvature, but if the observed values of w_n had been used, the scatter would have been great enough to obliterate the curvature. A straight line through the origin gives a pretty good fit to the points. The slope of the straight line has the value 0.42. This is a reasonable value since for this cement $V_m/w_n=0.31$. The best straight line through the data would not pass through the origin, but would give a small positive intercept on the w_n/c axis, as is observed experimentally.

The rates of hydration give satisfactory agreement with the empirical relationships between properties of hardened pastes. Since the major phases hydrate at fractional rates different from each other, one may question the significance of the expression "degree of hydration" as applied to cement and the meaning of terms such as "maturity factor" for pastes, mortars, or concrete. These concepts are important practically, even though they may not be precisely defined theoretically.

The ratio of the heat of hydration of a cement paste to the heat of hydration of a fully hydrated paste from that cement has been used as a measure of the "degree of hydration" of the cement in the paste. The ratio of the nonevaporable water to the maximum nonevaporable water has been used for the same purpose in our laboratories.

The "degree of hydration" of the cement in each of the pastes used in this investigation was calculated by adding together the amounts that had hydrated of the four major phases and dividing by the original cement content of the paste. In figure 9, the values are plotted as a function of the ratio of the observed w_n/c divided by the maximum w_n/c for the cement. The function is not quite linear, but the ratios give a fairly

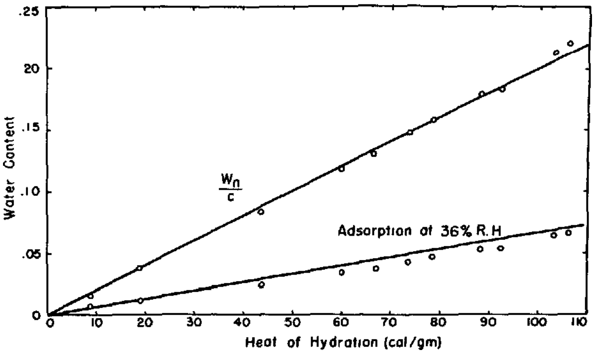

FIGURE 7. *Relationship between heat of hydration, nonevaporable water, and water sorption at 36 percent relative humidity.*

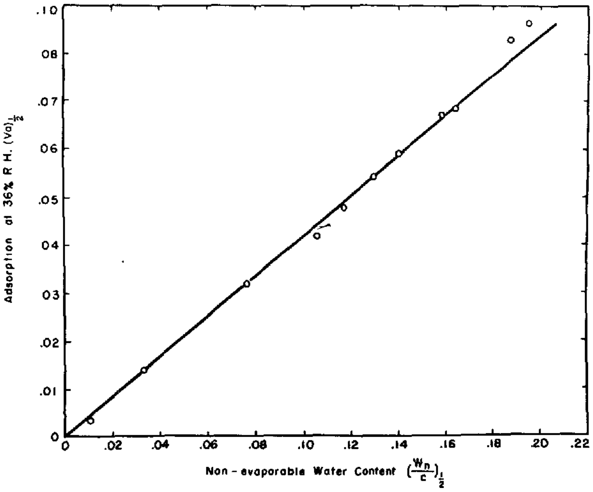

FIGURE 8. *Relationship between* $\left(\frac{w_n}{c}\right)_{1/2}$ *and water sorption at 36 percent relative humidity.*

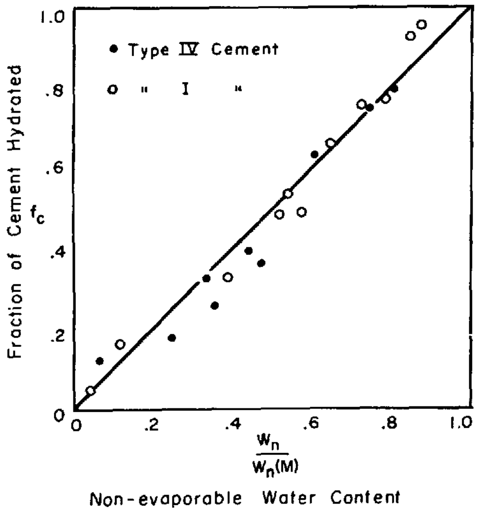

FIGURE 9. *Relationship between the degree of hydration of cement and* $\left(\frac{w_n}{c}\right)_{1/2}$ *in hardened pastes.*

reliable estimate of the degree of hydration, particularly when the cement is over 50 percent hydrated.

Because of near linearity between w_n and the heat of hydration, and also w_n and the surface area, any of these may be used as estimates of the degree of hydration of cement.

Analysis of pastes with X-ray diffraction promises to be a most useful tool for investigating rates of hydration of the individual constituents of cement. The preliminary work shows that the fractional rates of hydration of the four major compounds are not equal to each other. Further, the fractional rate of hydration of any chosen component, except possibly C_3A, is not the same, for all cements, but does depend upon the composition of the cement. The reliability of the X-ray analysis has been shown by calculating the heat of hydration, nonevaporable water, and the amount of water adsorbed at 36 percent relative humidity. The relationships between these calculated quantities were the same as has been observed from measurements of these properties on hardened pastes. Although these relationships are probably not exactly linear, they are sufficiently close to being linear that any of them may be used to estimate the "degree of hydration" of the cement in a paste.

Effect of Temperature

The study of the effect of temperature upon the rate of hydration of cement has been limited, for the most part, to the study of the effect of temperature upon either the heat of hydration or the development of strength in concrete. As a result of these studies, several functions have been proposed with which one may estimate the maturity of concrete after curing under prescribed conditions of time and temperature.

Saul [76] defined the maturity of concrete "as its age multiplied by the average temperature above freezing it has maintained," and concluded that concretes of the same mix will have approximately the same strength at the same maturity, whatever combination of time and temperature produce that maturity. Bergstrom [77] concluded that the base temperature should be −10 °C instead of the freezing point. Thus the maturity should be calculated from the temperature, θ, and the time, t, by the equation

$$M=\int_0^t(\theta+10)dt \qquad (12)$$

Plowman [78] found that concrete hydrated slowly at −10 °C, but that hydration ceased at −11.7 °C, and recommended this latter temperature as the base temperature.

Rastrup [79, 80, 81] examined heat of hydration data and assumed that the hydration of cement proceeded very much as most chemical reactions proceed. He concluded that the heat of hydration of a variable temperature process could be compared with the heat of hydration determined at a predetermined constant temperature, θ_a, by use of the time-temperature function

$$\tau_a=\int_0^t 2^{\left(\frac{\theta-\theta_a}{10}\right)}dt \qquad (13)$$

The Saul-Bergstrom function corresponding to Rastrup's use of a time-temperature function is

$$\tau_a=\int_0^t\left(\frac{\theta+10}{\theta_a+10}\right)dt \qquad (14)$$

Nykänen [82, 83] performed an extensive series of tests to determine a time-temperature function. He observed that a sharp decrease in the rate of hydration of concrete occurred as the temperature dropped below 0 °C, and that the composition of the cement affected the time-temperature function. He modified Bergstrom's function to

$$M=\Sigma k(\theta-\theta_b)\Delta t \qquad (15)$$

where θ_b is the base temperature at which hydration ceases, and k is a factor the value of which depends upon the temperature of the concrete and the composition of the cement.

For temperatures above 0 °C, $k=1$; for temperatures below 0 °C, $k=0.2$ to 0.4, depending upon the composition of the cement. The base temperature, θ_b, ranged between −10 and −15 °C, depending upon the composition of the cement.

These time-temperature functions serve for approximate calculations and are probably good enough for practical purposes. McIntosh [84] points out some of the shortcomings of these functions; when they are applied to concrete cured continuously at low temperatures, an estimate based on maturity calculated from −10 °C leads to an overestimate at low maturities and an underestimate at high maturities. The error at low maturities can be partly alleviated by calculating maturity from the time the concrete starts to gain strength instead of from the time of mixing. But the time-temperature functions cannot account for the fact that concrete cured initially at low temperature and later at normal temperature can develop a higher compressive strength than concrete cured continuously at a normal temperature. Bernhardt [85] shows that the maximum strength developed in a concrete is not independent of its temperature during curing.

Danielsson [86] points out that if a time-temperature function exists, the composition and morphology of the hydration products of cement must be independent of the temperature at which they were formed, but depend only upon the state of hydration or, what amounts to the same thing, upon the value of the heat of hydration, H. The value of dH/dt would depend upon θ and H alone, and would not depend upon the temperature-time path by which H was reached. Also, values of dH/dt for two different temperatures would have a fixed ratio for the same H. He found, experimentally, that at low H this last condition was approximately true, but that at high H the condition did not hold. Consequently, a time-temperature function should not be more than an approximation. He also found that dH/dt was not independent of the time-temperature path by which H was reached. This indicates that the composition and properties of the hydration products depend upon the temperature of the hydration process as do the findings of McIntosh and Bernhardt mentioned above.

III. Energetics of the Hydration of Portland Cement

George Verbeck

Introduction

Numerous studies have been made of the heat evolved when cement reacts with water and various methods of measurement of heat liberation have been used, depending upon the purpose of each investigation.

Where the primary interest is in temperature rise of concrete for use in massive structures, large adiabatic calorimeters have been used, thereby obtaining directly the information desired without assumptions as to the heat capacity of the paste and aggregate components of the concrete or the effect of temperature history of the concrete on the heat actually evolved. However, most studies of the energetics of cement hydration have involved measurements directly on cement paste.

For the study of the early stages of hydration, conduction calorimeters can be used most advantageously. Such devices permit the continuous and accurate recording of the rate of heat liberation from an age of about ½ hr to perhaps 3 days of hydration; this technique is usually supplemented by a simple "bottle" calorimeter for measurements prior to ½ hr. The magnitude, number, and times of appearance of the heat liberation "peaks" that are observed during this early period assist in the understanding of the various chemical reactions taking place and of the influence of various factors, such as hydration temperature, gypsum content, and accelerators and retarders on the properties of pastes and concrete at both early and later ages.

After the first few days of hydration, the rate of heat liberation becomes very low and direct measurement of heat evolution is difficult. The heat of solution method developed by Woods, Steinour, and Starke [63] is most useful for heat of hydration measurements for hydration periods from about 3 days to any desired age.

It is not the present purpose of this paper to consider studies of the heat evolution during the initial reactions. The discussion to follow will concern the various aspects of cement hydration as revealed by the heat of solution technique for hydration periods from 3 days to 13 yr.

Heat of Hydration at Ages of 3 Days to 13 Years

The data previously published by Verbeck and Foster [51] have been substantially augmented in a continuing study of the heat of hydration characteristics of cements. Data are now available for the heat of hydration characteristics of 27 plant-produced portland cements corresponding to ASTM Types I, II, III, IV, and V cements for hydration periods up to 13 yrs and at 0.40 0.60, and 0.80 water-cement ratios by weight. For the immediate purpose only the average results obtained for each of the different ASTM types of portland cement will be considered.

Data on the average heats of hydration of the different types of cement for ages from 3 days to 13 yr are presented in table 9 and figure 10. The cement pastes used in these tests were prepared at an initial water-cement ratio of 0.40 by weight and were hydrated in sealed vials until tested. In general, only small increments of heat were evolved between the 6½ and 13 year test ages. For the Type III cements very little, if any, heat was evolved during this period, the −0.1 cal/g observed being well within expected experimental error.

TABLE 9. *Average heats of hydration of the different ASTM types of cements*

0.40 water-cement ratio; cured at 21° C.

ASTM cement type	No. of cements averaged	Heat of hydration at age indicated, cal/g						
		3 days	7 days	28 days	3 mo.	1 yr	6½ yr	13 yr
I	8	60.9	79.2	95.6	103.8	108.6	116.8	118.2
II	5	46.9	60.9	79.6	88.1	95.4	98.4	100.7
III	3	75.9	90.6	101.6	106.8	114.2	120.6	120.5
IV	4	40.9	50.1	65.6	74.4	80.6	85.3	87.3

It should be noted that the average heat of hydration characteristics of the different ASTM types of cement are in keeping with the purposes for which each was designed. At early ages, the average heat of hydration of the Type III cements (high early strength) were significantly greater than the Type I cements (normal) although at 13 yr the heats of hydration are comparable. At all ages through 13 yr, the average heat of hydration of the Type IV cements (low heat) is significantly below the average of the Type II cements (moderate heat) which in turn evolves less heat at all ages than the Type I (normal) cements.

It should be emphasized that the particular plant-produced cements in this study were specifically selected to include cements possessing a wide range of characteristics within each ASTM type classification. The individual cements within each of the different ASTM types therefore show differences in heat evolution characteristics. The data shown in figure 11 represent the maximum, minimum, and average heats of hydration of the different ASTM types of cement at the various ages. These results show that each cement type has a reasonably separate and distinct range in heat of hydration at the various ages and that, in general, only moderate overlapping occurs between the various types The greatest range among the cements of any type occurs among the Type I cements, presumably in part because of the greater number of cements included in this classification and in part because the specifications for Type I cement (normal or general purpose portland cement) are purposefully less restrictive than for the other types of cements designed for more specific purposes.

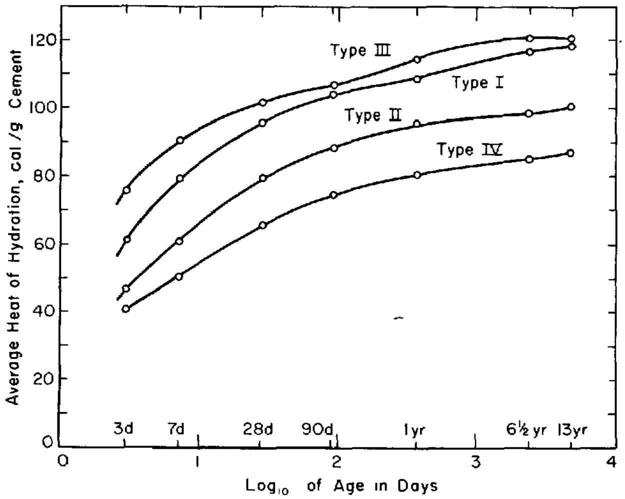

FIGURE 10. *Average heats of hydration of different ASTM types of cement at various ages.*

(0.40 water-cement ratio; cured at 21 °C.)

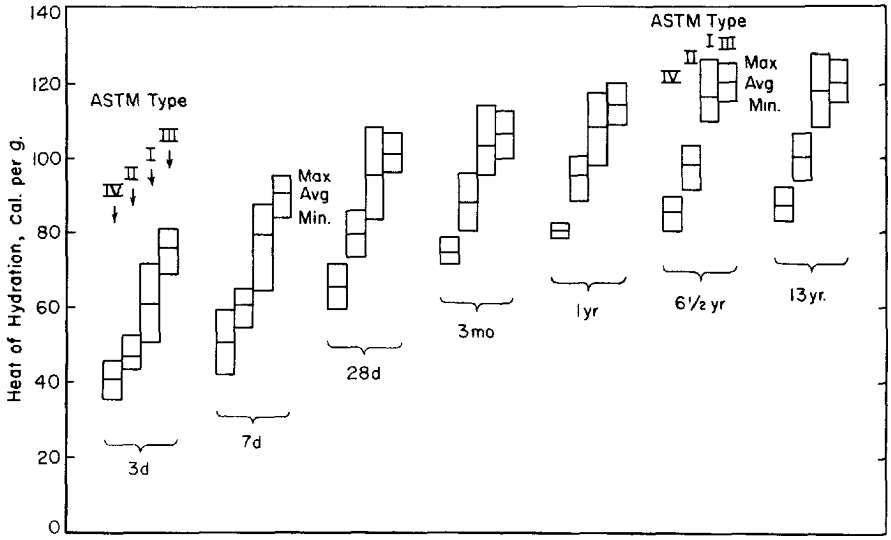

FIGURE 11. *Comparison of ranges in heats of hydration of the different ASTM types of cement.*

(0.40 water-cement ratio; cured at 21 °C.)

Effect of Water-Cement Ratio

The hydration of cement is accompanied by an increase in the volume of solids within the hydrating paste, the volume of the hydration product being greater than the volume of cement from which it was produced. The hydration product steadily increases in volume and fills the capillary void space within the paste, the initial volume of which is established by the original water-cement ratio of the paste. If the capillary void space originally present is small (low water-cement ratio) this space can become completely filled with hydration products and hydration will cease even though a substantial fraction of the cement remains unhydrated.

Some published information on the influence of water-cement ratio on heat evolution is available in the data of Carlson and Forbrich [87]. These data were limited to a single cement for ages ranging from 3 days to only 28 days. Their data indicate that the original water-cement ratio has a great influence on the heat of hydration of the cement as shown in table 10. An increase in water-cement ratio from 0.30 to 0.50 increased the heat of hydration by 14 percent at 3 days and 23 percent at 28 days.

The effect of water-cement ratio on heat of hydration might be expected to vary among cements having different hydration characteristics and compositions and in addition to become most pronounced at the later ages when the hydration of cement is more nearly complete. Because of the reported magnitude of the influence of water-cement ratio on heat of hydration and the practical and theoretical significance of such effects, the heat of hydration studies at 0.40 water-cement ratio presented in table 9 were extended to include measurements of pastes having water-cement ratios of 0.60 and 0.80 by weight.

In order to prepare hardened paste specimens having these high water-cement ratios it was necessary to prevent the segregation (bleeding) of water from the pastes while still plastic by slowly rotating the sealed vials containing the paste until setting occurred. To determine whether rotation of the fresh paste altered hydration of the cement as suggested by Carlson and Forbrich, redeterminations were made of the heat evolutions of five different cements at 0.40 water-cement ratio using this rotation technique for comparison with the previously obtained "static" results.

Such comparisons have since been made for hydration periods from 3 days to 6½ yr. The initially rotated vials were hydrated at 23 °C as compared to 21 °C for the earlier static vial tests. The average difference between results obtained by these two methods was ±2.8 cal/g when comparing each cement at each age and averaged −0.2 cal/g for all cements at all test ages. This is considered to be a satisfactory agreement. The rotated vial tests were initiated several years after the static vial tests. Because of this lapse of time, the five cements were resampled and their heats of solution and ignition losses redetermined when the rotated vial tests were begun. The average deviations of the heats of solution and ignition losses of the cements were ±2.1 cal/g and ±0.06 percent respectively. Thus it may be concluded that rotation of the specimen vials and hydration at the slightly elevated temperature did not significantly affect the heat evolutions of the cements. The differences that were observed in heats of hydration can be considered to be due to experimental errors and to differences in the heats of solution of the unhydrated cements caused by differences in the ignition losses of the two samples of each cement used.

TABLE 10. *Effect of water-cement ratio on heat of hydration*

Carlson and Forbrich [87]

Water-cement ratio, wt.	Heat of hydration at age indicated cal/g		
	3 days	7 days	28 days
0.30	45.7	58.3	74.3
.40	49.2	61.8	82.9
.50	52.3	69.8	91.4

Comparisons will now be made of the effect of water-cement ratio on the heat of hydration of cements representing different ASTM types at ages up to 6½ yr. Such data are shown in table 11.

It is readily apparent from the data that heat evolution is significantly influenced by water-cement ratio. During the early stages of hydration, an increase in water-cement ratio from 0.4 to 0.8 had only a slight effect on hydration and heat liberation of the Type IV cements, but produced a significant effect, an increase of 14 percent, in the heat of hydration of the Type III cements at 3 days. The greatest differences in heat of hydration occur at intermediate hydration ages, the exact age for the maximum difference depending upon the type of cement and occurring at earlier ages for the more rapidly hydrating cements. The increase in heat of hydration resulting from an increase in water-cement ratio from 0.4 to 0.8 was a maximum of 19.5 cal/g for the Type III cements at 90 days, and was a maximum of 14.2 cal/g for the Type IV cements at 1 yr, a very substantial effect which should be considered when evaluating cements for mass concrete. These increases in heat evolution exceeded the heat yet to be evolved from those ages to the 13-yr test age for the 0.4 water-cement ratio pastes.

TABLE 11. *Effect of water-cement ratio on average heats of hydration of different ASTM types of cements cured at 21 °C*

ASTM cement type	No. of cements averaged	Water-cement ratio	Heat of hydration at age indicated, cal/g						
			3 days	7 days	28 days	90 days	1 yr.	6½ yr.	13 yr.
I	8	0.40	60.9	79.2	95.6	103.8	108.6	116.8	118.2
		.60	65.8	87.7	107.1	114.7	120.0	123.1	----
		.80	66.3	89.4	111.6	119.5	122.2	125.0	----
II	5	.40	46.9	60.9	79.6	88.1	95.4	98.4	100.7
		.60	49.6	61.3	83.5	94.8	102.1	104.6	----
		.80	49.3	64.3	84.7	99.2	106.8	106.1	----
III	3	.40	75.9	90.6	101.6	106.8	114.2	120.6	120.5
		.60	86.1	103.6	119.9	124.4	127.3	127.2	----
		.80	86.7	105.0	121.0	126.3	130.0	130.6	----
IV	4	.40	40.9	50.1	65.6	74.4	80.6	85.3	87.3
		.60	43.2	53.5	66.6	78.7	90.4	92.5	----
		.80	41.7	52.8	69.8	82.5	94.8	96.4	----
All	20	.40	55.65	70.52	86.50	94.44	100.54	106.47	107.99
		.60	60.28	76.64	95.02	103.98	110.70	112.97	----
		.80	60.19	78.14	97.92	108.20	114.04	115.40	----

Although at the 6½-yr test age the average heat of hydration of all cements at 0.8 water-cement ratio was 8 percent greater than at 0.4 water-cement ratio, it should be noted that the rate at which heat was evolved at the later ages was greatest for the low water-cement ratio pastes; between the 1- and 6½-yr test ages, the 0.4 water-cement ratio pastes on the average liberated 5.9 cal/g while the 0.8 water-cement ratio pastes liberated only 1.4 cal/g. These differences indicate that the major effect of water-cement ratio in the range of 0.4 to 0.8, is not primarily to limit the maximum degree of hydration and hence heat liberation, but rather to influence the rate of hydration.

Interesting comparisons of the effect of the different water-cement ratios on the corresponding rates of hydration can be made if it is assumed: (1) that the heat of hydration observed at 6½ yr for the 0.8 water-cement ratio paste represents complete hydration of the cement, a very reasonable assumption and, (2) that the rate or degree of hydration of the 0.8 water-cement ratio pastes at the various ages represents hydration of cement as unimpeded by surrounding reaction products as can be expected at rational water-cement ratios. With these assumptions, at each of the test ages and water-cement ratios, the amount of unhydrated cement present can be estimated from the difference between the heat of complete hydration and the heat of hydration at each test age. The fraction of this unhydrated cement which was actually hydrated during the subsequent test interval can be calculated from the increment of heat evolved during the subsequent test interval. Such fractions when compared to the fraction of hydration for the 0.8 water-cement ratio paste for the corresponding age increment yield the relative rate of hydration during the various test age intervals of the 0.4 and 0.6 water-cement ratio pastes compared to the assumed ideal at 0.8 water-cement ratio.

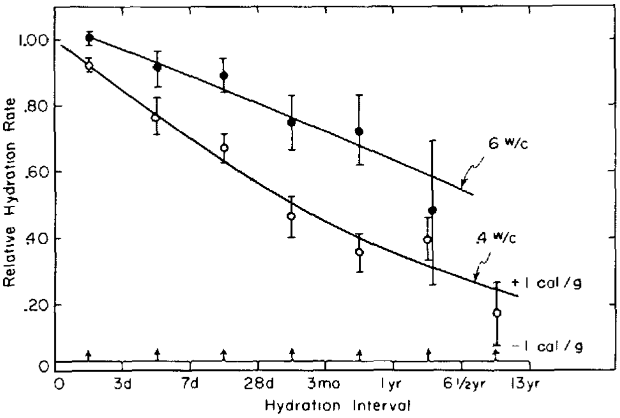

FIGURE 12. *Average effect of water-cement ratio on rate of hydration at various ages.*

Such comparisons for the average of all 20 cements are made in figure 12 for the various test periods. For presentation an arbitrary time scale has been used and the essentially linear nature of the relationships that appears with the use of this scale is not significant. The influence of a calorimetric error of ±1.0 cal/g in heat of hydration on the comparisons at the various ages is shown and emphasizes the sensitivity of the calculated relative hydration rate, particularly at the later ages.

It is apparent that the water-cement ratio significantly affects the inherent rate of hydration of the cements. The 0.6 water-cement ratio pastes hydrated more slowly than the 0.8 water-cement ratio pastes and this retardation became more pronounced at the later test ages. During the 1- to 6½-yr test interval to 0.6 water-cement ratio pastes hydrated only 50 to 60 percent as fast as the 0.8 water-cement ratio pastes. The 0.4 water-cement ratio pastes were retarded at all ages to an even greater extent and during the 6½- to 13-yr test interval, hydrated only about 25 percent of the remaining unhydrated cement, whereas in the 0.8 water-cement ratio pastes any unhydrated cement would have been completely hydrated.

The influence of water-cement ratio on rate of hydration appears readily interpretable. The hydration of cement requires the diffusion of water through the hydration products to the surface of the unhydrated cement and the diffusion of reacted material away from the reaction site. The hydration product which is laid down in the liquid surrounding the unhydrated cement serves to retard the diffusion of these materials and hence retard the hydration of the cement. At a particular water-cement ratio the ratardation of hydration should increase as hydration proceeds due to the increasing amounts (concentrations) of hydration product present. Such effects can be seen in figure 12. As the original water-cement ratio of the paste is reduced, the concentration of hydration product is increased; this increased concentration further retards the hydration of the cement.

The effects of progressive hydration and of water-cement ratio can be combined to express this concept of retardation due to increasing concentrations of hydration product in a manner similar to the "gel-space" ratio used by Powers [88]. The relative rates of hydration of cement at 0.4 and 0.6 water-cement ratio previously shown in figure 12 at the various test intervals are compared in figure 13 with their corresponding average gel-space ratios. It can be seen that this concept approximately expresses the retarding effects observed. A second approximation to the relationship could be made by a correction for the moderate retardation that must have occurred at the later stages of hydration of the 0.8 water-cement ratio pastes for which a maximum gel-space ratio of 0.59 is calculated.

It should be kept in mind that although the gel-space ratio may approximately express the concentration of hydration gel for any particular cement or average of cements, it would not be expected to quantitatively express the gel concentrations when comparing different cements since the amount of gel produced per unit of heat evolved depends to some degree on the composition of the cement. Additional empirical correlations between the relative hydration rates and other fundamental parameters of the hydrated paste can also be obtained.

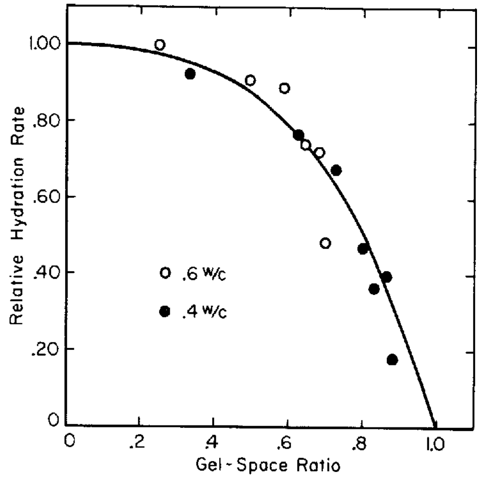

FIGURE 13. *Average effect of gel-space ratio on rate of hydration of pastes of different water-cement ratios and ages from 3 days to 13 yr.*

Effect of Temperature

The information available on the influence of temperature on degree and rate of hydration is not as extensive as desired, particularly as regards the higher water-cement ratios for extended hydration periods. However, the available data very satisfactorily reveal the effect of a wide range of temperatures on hydration rate of pastes of 0.4 water-cement ratio.

Heat of hydration data obtained by Carlson and Forbrich [87] using a "standard" cement at 0.4 water-cement ratio cured at temperatures of 4.4, 23.3, and 40 °C for ages from 3 to 90 days are shown in figure 14. The large increase in heat evolution during the early stages of hydration produced by increase in temperature is evident. It would appear from these data, for pastes of 0.4 water-cement ratio, that the temperature affects only the rate of hydration, the results obtained at the 28 and 90 day test periods suggesting equal ultimate heats of hydration at some later age.

It is interesting to quantitatively compare the early rates of hydration at the different temperatures; these rates may be taken as relative to the heat of hydration at one day and estimated from the curves in figure 14. For most chemical reactions the dependence of the kinetic reaction rate, K, upon reaction temperature T°_K, is expressed by the Arrhenius equation, $\ln K = -\frac{E}{RT} + \text{const.}$, in which E represents the "activation energy" and R is the gas constant. As may be noted in figure 14, the observed relationship between log K and $1/T$ is essentially linear and hence the relative reaction rates observed at the different temperatures are related in the manner required by the Arrhenius equation.

Additional information of a somewhat different nature is available from the studies in this laboratory [52] over the temperature range of 4.4 to 110 °C. Two different cements, ASTM Type I and Type IV, were hydrated at the preselected temperatures for the lengths of time required to produce approximately the same degree of hydration in the pastes of each cement, as estimated from heat of hydration and nonevaporable water measurements. The relative rates of hydration at the different temperatures are inversely related to the time required at each temperature to reach the equivalent degree of hydration. Such data are shown in table 12. Although the degrees of hydration attained for the various tests of each cement are not identical, they are believed to be sufficiently alike to permit the direct calculation of rate of hydration as shown in the table. Evaluation of these results on the basis of the Arrhenius equation is shown in figure 15. It may be observed

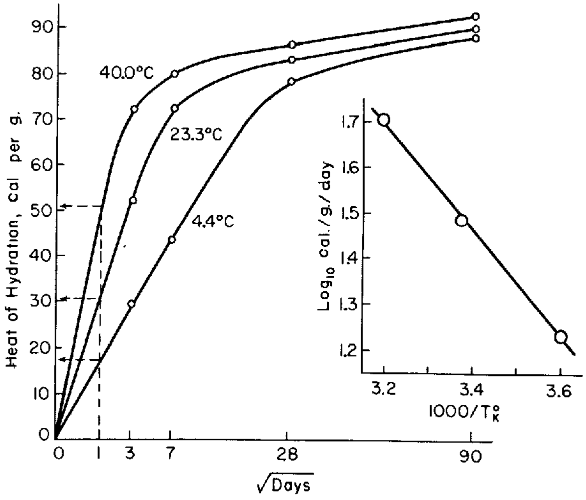

FIGURE 14. *Effect of temperature on hydration of cement*

Data from Carlson and Forbrich [87].

that an acceptably linear relationship is obtained for each cement over this wide temperature range. The relationship for the Carlson and Forbrich data shown in figure 14 is reproduced in figure 15. It is important to note that all three of the linear relationships obtained are essentially parallel, indicating that these cements do have the same "activation energy" although they have a very wide range in calculated potential compositions and inherent rates of heat liberation.

TABLE 12. *Effect of temperature, on rate of hydration, of cement.*

0.40 water-cement ratio.

ASTM cement type	Hydration temp. °C	Hydration period, days	Heat of hydration cal/g	Hydration rate cal/g/day	Log_{10} hydration rate	$\frac{1}{T°_K}$
I	110.0	1	92.35	92.35	1.965	0.00261
	71.0	2	98.02	49.01	1.690	.00290
	43.4	3	93.05	31.02	1.492	.00316
	21.0	9	96.43	10.71	1.030	.00340
	4.4	11	83.22	7.57	0.879	.00360
IV	110.0	1	56.51	56.51	1.752	0.00261
	71.0	2	56.49	28.24	1.451	.00290
	43.4	3	49.44	16.46	1.216	.00316
	21.0	8	47.48	5.93	0.773	.00340
	4.4	11	41.89	3.81	0.581	.00360

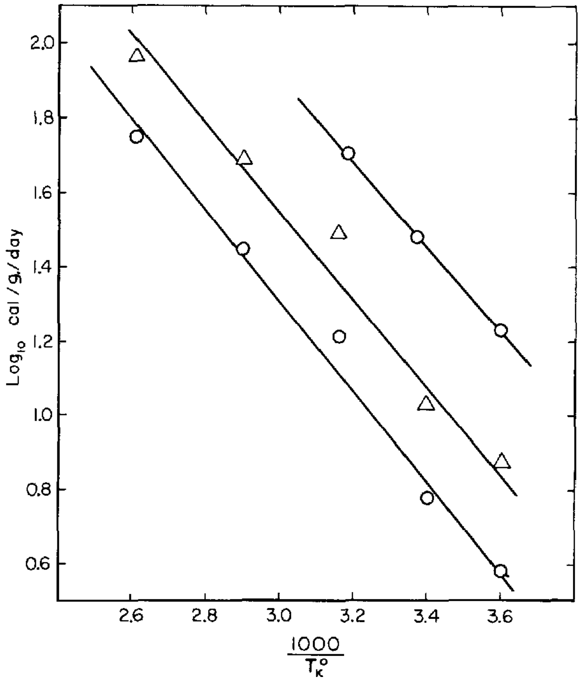

FIGURE 15. *Relationship of log "reaction rate" and* $1/T°_K$ *for cements over temperature range from 4.4 to 100° C.*

Effect of Moisture Content—Heats of Adsorption and Wetting

The heat of hydration of a cement, as normally measured, represents the total heat evolution that is usually of direct practical interest. However, this heat consists of two separate factors representing the energy change due to chemical reactions and the heat of the simultaneous adsorption of water on the colloidal hydration product. For a well hydrated cement, perhaps 80 percent of the energy released is due directly to the chemical reactions, i.e., the formation of "hydrates," while 20 percent of the energy represents the "wetting" of the large surface area of this colloidal product, this "wetting," of course, being necessary for the continuation of hydration. The relative amounts of these energies depend to some degree upon the chemical composition of the cement. The heat of adsorption of the hydration product is of considerable practical and theoretical interest.

In its most practical aspect, it appeared possible that unevaluated heat of adsorption effects could influence the heat of hydration measurements of cement with resulting errors in estimation of the degree of hydration of the cement from such data. Copeland and Bragg [71] have shown that hydrating past specimens, sealed to prevent uptake of water, become "self desiccated," the relative humidity within such pastes decreasing as the cement hydrates, with the decrease being most pronounced for pastes of low water-cement ratio. The lowest relative humidity they observed was 94 percent in a paste of 0.44 water-cement ratio at 1 yr. It would appear probable that pastes of 0.40 water-cement ratio cured 6½ or 13 yr might have relative humidities significantly below this value. In addition to self desiccation, a cement paste can lose further increments of moisture during the crushing, grinding, screening, and weighing procedures required in the preparation of paste samples for heat of solution measurements. These considerations suggest that the relative humidity of 0.40 water-cement ratio pastes at the later test ages, such as shown in table 9, might be as low as 80 or 90 percent. The heat of solution of a paste at 80 percent relative humidity is greater than that of a more nearly saturated paste, the additional increment representing the heat of wetting of the surface from perhaps 80 to 100 percent relative humidity. This greater heat of solution of the hydrated but partially dried paste reduces the apparent heat of hydration of the paste. Powers and Brownyard [69] report the heat of wetting of paste equilibrated by adsorption to 80 percent relative humidity to be as great as about 6 to 7 cal/g cement. An "error" of this magnitude in determination of the heat of hydration of low water-cement ratio pastes at later ages if neglected could introduce a significant error in estimation of degree of hydration of the cement from such data.

The heat of wetting was determined at the 13-yr test age for all pastes of 0.40 water-cement ratio reported in table 9. In addition to the customary determination of the heat of solution of the partially desiccated paste, a sample of the paste was wetted and equilibrated and then introduced into the calorimeter using a specially designed capsule for heat of solution measurements. For the cements of 0.40 water-cement ratio at the 13-yr test age, the average heat of wetting was determined to be only 0.9 cal/g cement. Since even smaller heats of wetting could be anticipated in tests at higher water-cement ratio and earlier ages further use of this special technique was not considered necessary.

In addition, the heats of adsorption and desorption of hydrated cement paste are of considerable theoretical interest. Unfortunately, only a modest amount of information is available on the heat of adsorption. The data obtained by Powers and Brownyard [69] regarding heat of adsorption of hydrated pastes is most instructive and also serves to reveal the need for additional information.

These data, shown in figure 16, were obtained by the heat of solution method for pastes dried to the nonevaporable water state (magnesium perchlorate) and then equilibrated at various relative vapor pressures. It can be observed that the relationships obtained for these two cements are similar and that each relationship appears to consist of two discrete portions each of which is a linear function of water content. These data imply that two different classes of water are sorbed on hydrated paste, the types of water having distinctly different "heats of adsorption" but yet each type having a constant differential heat of adsorption over the entire range of water contents in which it operates. In addition, there appears to be a rather abrupt discontinuity in the relationships observed, which would not be anticipated if only simple surface adsorption were involved. It should be further noted that the total heat of adsorption, taken as the difference between the heat of solution of the pastes at the nonevaporable water state and the heat of solution extrapolated from the observed relationships to the total water content at 100 percent relative humidity, is approximately 30.4 cal/g for cement 16186 and 30.8 and 30.9 cal/g for cement 16189, A, B, and C rounds respectively. This apparent equality in the total heat of adsorption of these pastes is of considerable significance since the degrees of hydration of the two pastes were materially different; the original water-cement ratios of the pastes being the same.

These observations of the "heat of adsorption," are analogous to recent observations in this laboratory of the drying shrinkage of cement pastes in the absence of carbonation. These shrinkage studies of hydrated pastes yield similar implications; the shrinkage-moisture content relationships of pastes between 100 and 0 percent relative humidity consistently demonstrated that there are two distinctly different types of water desorbed, each type of water having a constant shrinkage-water loss ratio over its operative range.

It is well established that various hydrated compounds in cement, the calcium aluminates and calcium sulfoaluminates, at least, will dehydrate and lose chemically combined water in this general range of relative vapor pressures. These results indicate the importance of the energy changes which accompany adsorption and desorption, particularly in their contribution to a full understanding of the volume changes of cement paste.

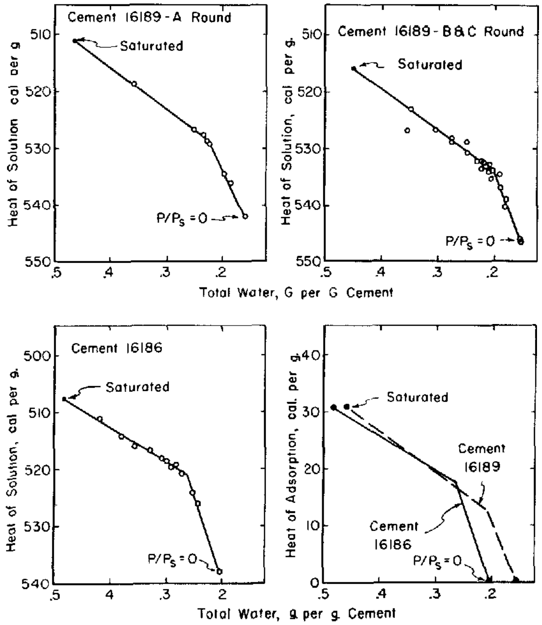

FIGURE 16. *Heats of solution and adsorption of pastes containing various amounts of adsorbed water.*

Data from Powers and Brownyard [69].

Intrinsic Characteristics of Cement

It is apparent from the data presented in figures 10 and 11, and from numerous other studies of the heat of hydration of cement, that cements differ significantly in heat evolution characteristics, both as to total ultimate heat evolution and the rate at which this heat is liberated. It is believed that the causes of these different heat evolution characteristics in cements are understood, at least to a semiquantitative degree. Factors causing these differences include the composition of the cement, the fineness of the cement, partial prehydration of cement, glass content, and alkali and gypsum contents. The influence of some of these factors will now be discussed.

Cement Composition

As a first approximation it is apparent that the heat liberated by a cement during complete hydration is approximately the sum of the heats of com-

TABLE 13. *Heats of complete hydration of individual compounds*

Anhydrous compound	Product	Heat of hydration, cal/g anhydrous compounds	
C_3S	C_3S+3H_2O	120	Lerch & Bogue [89]
C_2S	C_2S+2H_2O	62	Lerch & Bogue [89]
C_3A	$C_3A \cdot 6H_2O$	207	Lerch & Bogue [89]
C_3A	$C_3A \cdot 6H_2O$	214	Thorvaldson, Brown & Peaker [94]
C_3A	$C_3A \cdot 8H_2O$	235	" " " "
C_3A	$C_3A \cdot 10 \cdot 2H_2O$	251	" " " "
C_3A	$C_3A \cdot 11 \cdot 6H_2O$	261	" " " "
C_3A	$C_3A \cdot 3CaSO_4 \cdot 32H_2O$	347	Lerch & Bogue [89]
C_4AF		100	Lerch & Bogue [89]
CaO	$Ca(OH)_2$	278. 9	Thorvaldson, Brown & Peaker [95]

plete hydration of the individual compounds present or calculated to be present in the cement. The individual chemical compounds have significantly different heats of complete hydration as is shown in table 13. The heat evolved by C_2S is only 62 cal/g whereas the heat of hydration of C_3A is at least 207 cal/g, with C_3S and C_4AF having intermediate values. Cements having high C_3A (and C_3S) contents have significantly higher heats of complete hydration than cements low in these constituents and high in C_2S content.

The various compounds differ not only in heat of complete hydration but also in rate at which they hydrate; it has been generally observed that those compounds with high heats of complete hydration, C_3A and C_3S, also hydrate much more rapidly than C_2S, which has a low heat of hydration.

It is of interest to interpret the observed heats of hydration of different cements at various periods of hydration in terms of the composition of the cements. Various investigators [63, 65, 51] have used the method of least squares for this purpose. The coefficients obtained by such least squares analyses need to be interpreted with considerable care because of the several assumptions that are involved. Least squares analyses can be performed on the basis either of calculated compound composition or of oxide analysis. Since the calculated compound composition can be expressed by linear relationships with the oxide composition, least squares analyses on both bases are mathematically equivalent. Therefore, a least squares analysis in terms of calculated compound composition that produces heat coefficients that correspond to the heats of hydration of the individual compounds, and that collectively will closely reproduce the heats of hydration of the cements, does not require that the assumed or calculated compounds in reality exist. In addition, the least squares method assumes that the various compounds hydrate independently as has been discussed in the second main section of this paper.

Since it is not expected that the inherent hydration characteristics for any particular compound or phase would be identical in the various cements because of differences in actual composition and grain size of that phase among the different cements, the coefficients obtained for the various compounds will represent only the average coefficient for that compound among the different cements.

The results of least squares analyses of heat of hydration results at various ages obtained by Woods, Steinour, and Starke [63] with laboratory prepared cements are shown in table 14 and are compared with the heats of complete hydration for the pure compounds as reported by Lerch and Bogue [89]. The coefficients obtained for the compounds at the later ages acceptably correspond to the heats of complete hydration of the individual compounds. In addition, the coefficients obtained at the early ages conform qualitatively, at least, to the intrinsic reactivity of the individual compounds in that C_3S and C_3A react rapidly whereas C_2S reacts slowly. Therefore, the heat of hydration coefficients obtained by least squares analyses appear to have a real significance in relation to both the rate of hydration and the total heat evolutions of the individual compounds. These cements were laboratory ground with a constant amount of gypsum from laboratory prepared clinker having a very low alkali content.

TABLE 14. *Results of least squares analysis of heats of hydration of cements*

From Woods, Steinour, and Starke [63, 64]

Compound	Least squares coefficients. Heats of hydration, cal/g compound						Heats of complete hydration, (Lerch & Bogue [89]) cal/g compound
	3 days	7 days	28 days	3 mo	6 mo	1 yr	
C_3S	98	110	114	122	121	136	120
C_2S	19	18	44	55	53	62	62
C_3A	170	188	202	188	218	200	207
C_4AF	29	43	48	47	73	30	100

The least squares analyses previously reported by Verbeck and Foster [51] for commercially prepared cements at 0.40 water-cement ratio hydrated up to 6½ yr have now been extended to include analyses of results obtained after 13 yr of hydration and new results obtained for pastes of 0.60 and 0.80 water-cement ratio. Results obtained at 0.40 water-cement ratio are shown in table 15 and are compared with the data of Lerch and Bogue [89] for the heats of complete hydration of the pure compounds. The heat coefficients obtained for C_3S, C_2S, and C_4AF with these commercial cements are in close agreement with the reported heats for complete hydration. However, the coefficient obtained for C_3A is considerably

Table 15. *Results of least squares analysis of heats of hydration of cements*

Compound	Least squares coefficients, heat of hydration at water-cement ratio and age indicated							Heats of complete hydration (Lerch & Bogue [89]) cal/g compound
	cal/g compound—0.40 W/C and 21 °C.							
	3 day	7 day	28 day	90 day	1 yr.	6½ yr.	13 yr.	
C_3S	58	53	30	104	117	117	122	120
C_2S	12	10	25	42	54	53	59	62
C_3A	212	372	329	311	279	328	324	207
C_4AF	69	118	118	98	90	111	102	100

greater than that obtained for the formation of C_3AH_6, 207 cal/g, but approximates the heat of hydration of C_3A, 347 cal/g of C_3A, to form $C_3A{\cdot}3CaSO_4{\cdot}32H_2O$, as reported by Lerch and Bogue.

Analyses by least squares can be based on various models and many have been evaluated. The coefficients shown in table 15 were derived on the following assumption:

(1) $H_t = a\ (\%\ C_3S) + b\ (\%\ C_2S) + c\ (\%\ C_3A) + d\ (\%\ C_4AF)$

in which H_t=heat of hydration at a given age.

However, and particularly in view of the high coefficient that was obtained for C_3A, additional postulations were made as follows:

(2) Formation of $C_3A{\cdot}CaSO_4{\cdot}12H_2O$
$H_t = a\ (\%\ C_3S) + b\ (\%\ C_2S) + c\ (\%\ C_3A - 1.125\%\ SO_3) + d\ (\%\ C_4AF) + e\ (\%\ SO_3)$ and

(3) Formation of $C_3A{\cdot}3CaSO_4{\cdot}32H_2O$
$H_t = a\ (\%\ C_3S) + b\ (\%\ C_2S) + c\ (\%\ C_3A - 3.375\%\ SO_3) + d\ (\%\ C_4AF) + e\ (\%\ SO_3)$

The results of such analyses are shown in table 16, where it may be noted that these additional assumptions did not assist in revealing further details of the nature of the hydration reactions and the accompanying heat evolutions.

Table 16. *Results of least squares analyses of heat of hydration data including the formation of calcium sulfoaluminates*

Compound	Least squares coefficients—cal/g compound, 0.8 W/C—1 yr		
	eq (1)	eq (2)	eq (3)
C_3S	124	128	125
C_2S	76	91	81
C_3A	325	396	384
SO_3	------------	−602	672
C_4AF	95	152	121

Of the various assumptions evaluated, perhaps the most instructive concerned the role of clinker alkalies on heat evolution. Newkirk [90] has reported that K_2O and Na_2O in portland cement clinker form the compounds $KC_{23}S_{12}$ and NC_8A_3. Least squares analysis based on calculated potential compound compositions, including the formation of these alkali substituted compounds produced the coefficients shown in table 17.

Table 17. *Comparison of least squares coefficients for alkali substituted compounds at early and late ages*

Compound	Least squares coefficients, cal/g compound, 0.8 W/C—16 cements		
	3 days	1 yr	6½ yr
C_3S	92	130	134
C_2S	22	73	76
$KC_{23}S_{12}$	57	62	74
C_3A	127	310	325
NC_8A_3	4	322	288
C_4AF	−17	88	71

Comparisons of the coefficients obtained at 1 yr and at 6½ yr for C_2S and $KC_{23}S_{12}$ or for C_3A and NC_8A_3 suggest that at complete hydration the heat contributions of the presumed alkali substituted compounds are similar to the heat contributions of the unsubstituted compounds. However, at the age of 3 days the heat contributions of the substituted and unsubstituted compounds appear significantly different, suggesting a significant effect of alkalies, directly or indirectly at early ages.

Further elucidation of the nature of the reactions by least squares studies based on such relatively direct postulations may not be possible; Lerch [91] has shown that heat evolution depends in part and in a rather complicated way upon the mutual effects of C_3A content, fineness, alkali content, and gypsum content of the cement.

There is evidence indicating that the heat contribution coefficients of the individual compounds derived by the method of least squares have an additional significance. The amount of combined water (the nonevaporable water content) in a hydrated cement paste, can be used as a further index to the degree of hydration of cement. The nonevaporable water content, w_n/c, was determined for all the cements at all test ages and for all water-cement rations, simultaneously with the heat of hydration measurements previously discussed. Least squares analysis of this information in a manner similar to that used with the heat of hydration results is most instructive. The number of moles of water associated with each mole of the clinker compounds can be derived by such analysis and compared with the heat contributions derived for the same test conditions, as is shown in figure 17. These relationships reveal that the derived coefficients for heat contributions and for moles of combined water for both C_3S and C_2S approximate as a limit a point closely corresponding to the ultimate heat of hydration and water content of the products C_3S+3H_2O and C_2S+2H_2O respectively. For less than complete hydration, it can be observed that both the derived heat coefficients and the combined water coefficients indicate

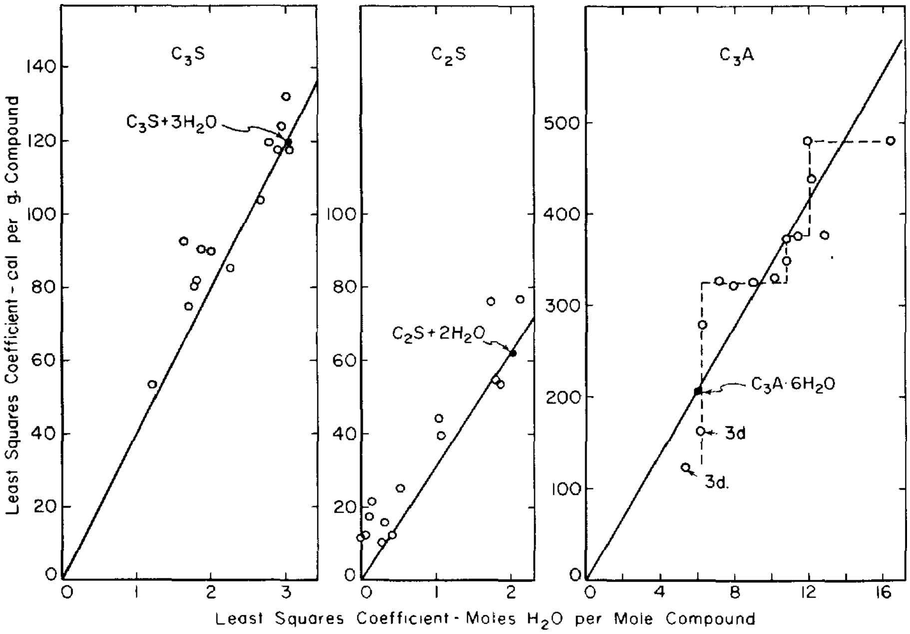

FIGURE 17. *Comparison of least squares coefficients for heat evolution and combined water of C_3S, C_2S, and C_3A.*

approximately the same degree of hydration of the compound, in further support of the significance of heat contributions derived by least squares.

The relationship obtained for C_3A indicates that both the derived heat contribution and combined water for this compound exceed the ultimate heat of hydration and water content of $C_3A{\cdot}6H_2O$ except at the earliest test age, 3 days. The relationship obtained suggests an irregular relationship (dashed line) corresponding to hydrates higher than $C_3A{\cdot}6H_2O$. More detailed study suggests that higher hydrates are formed which slowly reconvert to lower hydrates as the cement continues to hydrate with time. Such a relationship as shown in figure 18 supports the possibility of slow secondary changes in the C_3A hydrated product, where it can be seen that both the heat coefficients and combined water coefficients reflect similar changes with time.

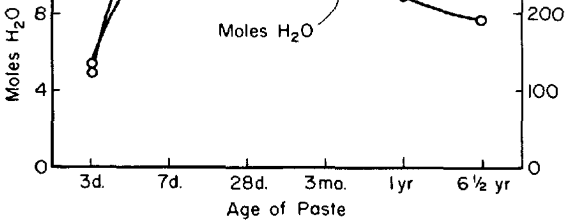

FIGURE 18. *Least squares coefficients for heat evolution and combined water of C_3A at various ages.*

0.80 water-cement ratio pastes.

It is believed that the degree to which the derived heat coefficients and combined water coefficients permit equal estimates of the degree of hydration and of observed secondary changes serves to support the significance of such derived coefficients. However, there are several other factors which can contribute to or alter heat evolution and which are not normally included in least square analysis. Cement constituents such as free calcium oxide and magnesium oxide will hydrate with evolutions of heat that usually are not considered in least squares analysis. In addition, the glass content of the clinker and the ignition loss of the original cement, which represents a degree of partial prehydration and carbonation of the clinker minerals have not usually been considered but do have a significant effect on the heat of solution of the original cement.

The effect of glass content on heat of solution and heat of hydration as reported by Lerch [92, 93] and shown in table 18 is most interesting. The average increase in heat of hydration observed with an increase in glass content is 7.9 cal/g at the 28-day test age. This increase corresponds within experimental error with the 6.8 cal/g increase in heat of solution of the original cement. These data suggest that the observed increase in heat of hydration is due solely to the increased energy content of the clinker with an increase in glass content and that although the glass phase during hydration eventually attains the same state as the corresponding crystalline phase, the glass phase hydrates less rapidly than the crystalline phase.

TABLE 18. *Effect of glass content on heat of solution and heat of hydration*

Average heat of solution [92] cal/g				Average heat of hydration [93] cal/g		
Orig. cement	3 days	7 days	28 days	3 days	7 days	28 days
638.8	564.2	552.4	544.9	74.6	86.4	93.9
641.9	567.2	555.0	546.0	74.7	86.9	95.9
645.6	570.9	554.7	543.8	74.7	90.9	101.8

The heats of solution of the original cements and hence the observed heats of hydration also depend significantly upon the partial prehydration of the original cement. Studies at this laboratory [52] have shown that the ignition loss of a cement represents loss of chemically combined water and CO_2 and loss of evaporable water, the latter presumably associated with the calcium sulfate in the cement. The amounts of CO_2 and of these different classes of water vary appreciably among cements and as shown in table 19 significantly affect the heats of solution of the cements and hence the observed heats of hydration. An approximate correction can be made to the heats of solution of cements from measurements of the CO_2 content and the content and distribution of the water within the cement assuming that the combined water and CO_2 have reacted with calcium oxide and that the original cement should have an evaporable water content corresponding to the dihydrate of the $CaSO_4$ in the cement. Approximate corrections calculated on this basis for 26 cements are significant in amount and variability as shown in table 19.

TABLE 19. *Range and analysis of losses on ignition and the corresponding corrections to heats of solution of 27 commercial cements*

Range	Ignition loss	Combined water	CO_2	Evaporable water	Correction to heat of solution of original cement, cal/g
	%	%	%	%	
Maximum	1.60	1.11	0.33	0.49	+9.5
Average	0.82	0.45	.17	.19	+3.5
Minimum	.35	.13	.08	.00	+0.4

Results of a least squares analysis based on a selected group of these cements in which the correction for heats of solution of the original cements ranged from +0.7 to +4.9 are compared in table 20, with results of a similar analysis based on the uncorrected heats of solution.

TABLE 20. *Results of least squares analyses based on uncorrected and corrected heats of solution of original cements*

Basis of analysis	Least squares coefficients heats of hydration, cal/g compound 0.80 water-cement ratio, 6½ yr			
	C_3S	C_2S	C_3A	C_4AF
Uncorrected heats of hydration	132	77	321	73
Corrected heats of hydration	137	81	325	62

It is observed that the coefficients for C_3S, C_2S, and C_3A were higher for the corrected heat analysis, indicating that the chemically combined water and CO_2 do not react primarily with either the C_3S or C_3A component of the cement. Other studies indicate some relation between the amounts of free CaO and alkali in the various cements and the amounts of combined water and CO_2 which they contain.

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Discussion

J. H. Taplin

Copeland and Kantro discuss the effect of W_0/C on the kinetics of the hydration of portland cement paste. They quote some data of mine for a cement A2 which, in the early part of the reaction, reacted more rapidly at the lower water-cement ratios. They propose an explanation in terms of the greater temperature rise to be expected during the first 24 hr in pastes of higher cement content. This explanation was not given by me because the effect was not found in similar experiments with other cements. The effect of W_0/C on the hydration rate at 25 °C is shown for three of these cements in figure 1. It seems safe to conclude that, with some cements, W_0/C does have an appreciable effect on the rate during the first 3 or 4 days.

As a further test of the temperature-rise explanation for the behavior of cement A2, some of the experiments were repeated, and the temperature of the paste relative to the curing cabinet was obtained by means of a thermocouple in the paste and a recording potentiometer. For paste with a W_0/C ratio of 0.35, cured at 25 °C in a six-gang steel mold which was wrapped in polyethylene sheet, the greatest temperature difference between the paste and the curing cabinet was attained at 15 hr, and amounted to only 0.7 °C, whilst the mean difference during the period 5 to 22 hr was less than 0.25 °C. Assuming an apparent activation energy of 10 kcal, an increase of 0.25 °C will increase the rate by only 1.3 percent. For a 0.25 W_0/C paste which was cured at 25 °C in a single polyvinyl chloride mold in a stoppered glass tube, the maximum temperature rise was 0.85 °C at 15 hr, and the mean rise between 5 and 22 hr was 0.5 °C, which corresponds to a rate increase of 2.5 percent. These temperature rises are too small to account for much of the rate increases of up to 20 percent actually observed for cement A2 at low W_0/C.

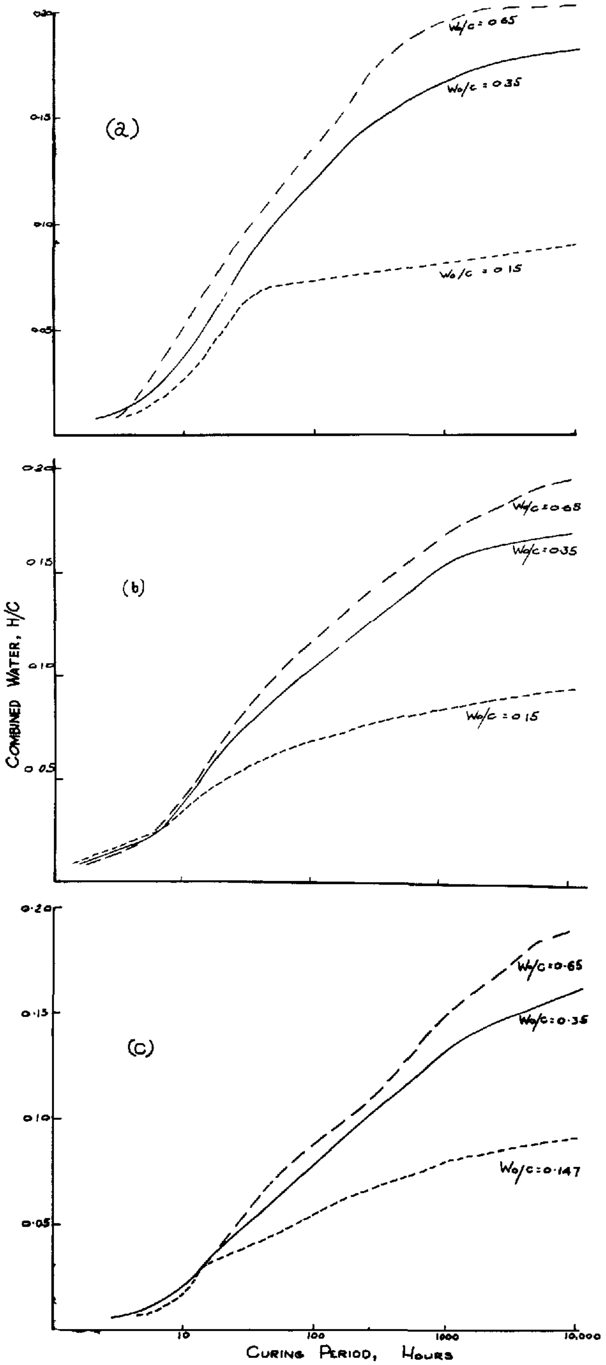

Figure 1. *Effect of* W_o/C *on rate of increase of combined water in portland cement paste. The* W_o/C *is marked on each curve. (a) Cement B1, (b) Cement C1, (c) Cement D1.*

Copeland and Kantro also describe a large increase in hydration rate for paste which is cured continuously saturated. As we had not observed this effect we carried out the experiment described below.

Two six-gang ebonite molds for 4 x ½ x ½-in specimens were filled from the same batch of 0.35 W_0/C paste. The cement, A3, was a different batch of the same brand as A2, i.e., an ordinary portland cement with a high alkali content. One mold was half immersed in a dish of water in such a way that the paste made contact with the water through the lower joints of the mold. The upper surface of the mold was sealed by a polyethylene sheet in contact with the paste. After 2½ hr it was observed that a pool of solution had collected above the paste, between it and the polyethylene. This osmotic flow proves that the paste and water were in contact through the mold joints. The other mold was simply wrapped in a polyethylene sheet. Both molds were stored side by side in a large constant-temperature room at 21 °C and stripped after 19 hr. The specimens from the continuously saturated mold were placed in stoppered glass tubes containing a few ml of water. Those from the self-desiccated mold were placed in dry tubes.

Table 1. *The effect of curing condition on the hydration of an 0.35* W_o/C *paste at 25 °C*

10^4 H/C

Curing period	Saturated	Self-desiccated	Mean difference
hr 19. 5	412 423	438 432	−17. 5
26	538 575	570 562	−9. 5
43	802 796	865 831	−49. 0
68	1100 1148	1072 1042	+67. 0
144	1171 1160	1107 1136	+44. 0
237	1260 1313	1249 1240	+42. 0
646	1403 1382	1317 1332	+68. 0
1730	1505 1485	1367 1412	+105. 5
Mean	1029. 6	998. 3	+31. 3

After various curing periods, samples were taken in duplicate from both sets of specimens, and measurements were made of the combined water [1], H/C, with the results shown in table 1. The mean difference in H/C of 0.0031 between saturated and self-desiccated specimens is significant at the 95 percent probability level and corresponds to the hydration of about 1.5 percent of the cement. (Copeland and Kantro, in their figure 4, show a difference which corresponds to the hydration of about 15 percent of the cement.) The mean negative difference in table 1, for curing times less than 48 hr, is not significantly different from zero. It must be concluded that, for this cement at least, the difference in hydration between continuously saturated and self-desiccated paste is very small for the first 48 hr and corresponds to the hydration of only 5 percent of the cement after about 10 weeks.

Copeland and Kantro briefly discuss possible reaction mechanisms for portland cement. The structure of cement clinker is such that the more reactive major components tend to be surrounded by thin shells of the less reactive minor components. This makes it very difficult to analyze experiments designed to show the effect of particle size, depth of reaction, or mineral composition on the hydration rate. It seems probable that the inner and outer products [1] are different in composition and/or structure, but as yet, there is little evidence about this.

Verbeck discusses the effect of curing temperature on the rate of hydration of portland cement. The apparent activation energy obtained from his Arrhenius plots is less than the 10 kcal obtained in this laboratory [2]. However, the apparent activation energy obtained from Verbeck's figure 14 should be doubled, because if one assumes a square-root law, one must use the square of the slope, heat of hydration against the square root of time, as an estimate of hydration rate.

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Discussion

H.-G. Smolczyk

The following discussion is for the purpose of contributing a new idea to the most interesting paper by the gentlemen of the Portland Cement Association. Throughout cement chemistry, X-ray investigation is a valuable means of determining clinker components as well as of observing the hydration of cements. For very many cases the procedures using an internal standard, as described in detail by Copeland and Bragg [1], and more recently by Brunauer, Copeland, Kantro Weise, and Schulz [2], and by Midgley, Rosaman, and Fletcher [3], are the best and most exact methods of quantitative X-ray analysis.

There are cases, however, for which the method of direct X-ray analysis without a standard (or with an external standard serving only as a control of intensities) is to be preferred. One example is the X-ray investigation of the rate of hydration of minerals in a cement as dependent on the time of hydration. Hereby the absolute amounts of these minerals in percentage of the hydrated cement are of minor interest, for the results can be compared only if these values are expressed as percentage of the original dry cement. The major interest is not in the absolute amount of newly produced hydrates expressed as percentage of the hydrated matrix, but in the percentage of the formerly unhydrated cement that is combined with water.

The method using an internal standard will measure only absolute amounts obtained as percentage of the hydrated matrix, so the loss on ignition has to be determined first before the wanted relations between the dry components can be calculated.

On the other hand use of the method of direct analysis permits neglecting the influence of the water on the X-ray intensities, because of the very low mass absorption coefficient of H_2O. By direct analysis the results will also be obtained as percentage of the original dry cement. The error arising from neglecting the influence of the water is so small, compared with the other errors of X-ray analysis, that it is of no importance at all, as demonstrated by the following two examples:

1. *Hydration rate of alite in portland cement.*

Suppose the 50 percent of alite in the cement to be 80 percent hydrated and the cement paste to have an H_2O content of 25 percent. Then the dry paste without water content will contain 10 percent of alite, and the hydration rate of the alite will be

$$HR=\frac{50-10}{50}=0.80$$

The matrix with water content, however, contains 7.5 percent of alite and 25 percent of water.

Now let us calculate the X-ray line intensity for the alite that can be expected. The following rough values are introduced:

μ_C = the mass absorption coefficient of the original dry cement $=100$
μ_H = the mass absorption coefficient of $H_2O= 10$
μ_A = the mass absorption coefficient of the alite $=100$
I°_A = the X-ray line intensity for 100 percent of alite $=160.$

In the unhydrated cement containing x_1 fraction of alite, the intensity is:

$$I_{A1}=I^\circ_A x_1 \frac{\mu_A}{\mu_C}=160\cdot 0.50\cdot\frac{100}{100}=80$$

After the cement has taken in 25 percent of water, the mass absorption coefficient of the matrix is $\mu_M=75+2.5=77.5$. Therefore the intensity for the 7.5 percent of alite in the matrix will be:

$$I_{A2}=I^{\circ}_{A}x_{2}\,\frac{\mu_A}{\mu_M}=160\cdot 0.075\cdot\frac{100}{77.5}=15.5$$

If now the calculation is performed without paying regard to the mass absorption coefficients, and if only the measured absolute intensities of the alite in the two X-ray diagrams of the cement before and after hydration are introduced in the equation, the rate of hydration will be

$$HR=\frac{80-15.5}{80}=0.806$$

So the neglect of the mass absorption coefficients has caused an absolute error of only +0.6 percent. The other errors of X-ray investigation methods exceed by far the one introduced by this procedure, for 10 percent of alite cannot in any case be determined exactly to ±0.3 percent.

2. *Determination of the percentage of original cement bound in ettringite.*

In order to perform such a determination the measuring of intensities alone will not be sufficient, but it will be necessary to know the I°_{E} and the μ_E of ettringite as well as the μ_C of the dry original cement.

Suppose 10 percent of the original cement changed into ettringite, and the cement to have taken in again 25 percent of water. Let the mass absorption coefficient of the dry cement μ_C be again 100, then that of the set cement, μ_M, will be again 77.5. For the ettringite the following values have to be introduced:

μ_E=the mass absorption coefficient of ettringite=50

I°_{E}=the X-ray line intensity for 100 percent of ettringite=500.

The matrix contains 7.5 percent of $C_3A\ (Cs)_3$ where $s=SO_3$, equivalent to 13.9 percent of $C_3A\ (Cs)_3 H_{32}$, and the intensity for the ettringite in the matrix will be

$$I_E=I^{\circ}_{E}x\,\frac{\mu_E}{\mu_M}=500\cdot 0.139\cdot\frac{50}{77.5}=44.9$$

If this measured intensity is introduced in the equation

$$x=\frac{I_x}{I_0}\cdot\frac{\mu_G}{\mu_x}$$

and the mass absorption coefficient of the dry cement is applied in place of μ_G, the content of ettringite in percentage of the dry cement may be calculated as follows

$$x_E=\frac{I_E}{I^{\circ}_{E}}\cdot\frac{\mu_C}{\mu_E}=\frac{44.9}{500}\cdot\frac{100}{50}=0.18$$

Now the hydration water of the ettringite (46 percent) has to be subtracted from the 18 percent of ettringite, and the value 9.7 percent of $C_3A\ (Cs)_3$ is obtained.

In this determination, too, an error of only −0.3 percent has been introduced, which is of no importance compared with the well-known inaccuracy of the X-ray analysis of hydrates.

By applying this method the hydrated percentages of the original cement can be determined directly with only a very small error and without the necessity of knowing the water content of the matrix. Hereby a very careful preparation of the samples is of great importance. As the method of avoiding preferred orientation, described by Copeland and Bragg [1], cannot be applied here, only those hydrates can be determined the preferred orientation rates of which are fully known and reproducible.

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Paper IV–S1. Role of Gypsum in the Hardening of Hydraulic Cements*

P. P. Budnikov

Synopsis

On the basis of his investigations, the author has shown that the high-sulfated form of calcium hydrosulfoaluminate that forms in cement as a result of interaction of calcium sulfate with aluminates is under proper physicochemical conditions a structurally useful compound in the hardened cement.

The addition of an elevated amount of gypsum (or anhydrite) to high-C_3A portland cement increases the resistance to the action of water solutions of Na, Mg, and Ca sulfates; this is explained by the formation of hydrosulfoaluminate. The greater the amount of C_3A bound with calcium sulfate at early hardening periods (under 28 days), the higher is the sulfate resistivity of the hardened cement. The optimum content of gypsum in portland cement is that binding the C_3A to calcium hydrosulfoaluminate in the early period of hardening of the cement.

In sulfate-slag (clinkerless or low-clinker) cements based on acid and basic granulated blast furnace slags, in presence of a liquid phase (water) and of a small amount of alkali ($Ca(OH)_2$ or $Mg(OH)_2$) and of calcium sulfate there forms calcium hydrosulfoaluminate. The latter, jointly with other new formations—calcium hydrosilicate, $3CaO{\cdot}2SiO_2{\cdot}aq$, and calcium hydroaluminate, $2CaO{\cdot}Al_2O_3{\cdot}7H_2O$, and in the case of acid slag, $2CaO{\cdot}Al_2O_3{\cdot}7H_2O$ and $2CaO{\cdot}SiO_2{\cdot}aq$—determines the hardening and durability of the cement stone.

In aluminous cement the addition of about 30 percent of gypsum in presence of a liquid phase interacts chemically with calcium aluminates forming hydrosulfoaluminate which influences positively the properties of this cement. When hardening occurs under moist conditions, an expanding cement is obtained which possesses a high water impermeability, without any decrease of strength at elevated temperature conditions due to exothermy or external heating. If about 25 percent of insoluble anhydrite is added to aluminous cements, a non-shrinking cement is obtained, hardening normally under conditions close to adiabatic. Concrete with that cement has an increased resistivity in aggressive media containing NaCl, $MgCl_2$, Na_2SO_4, $MgSO_4$ and $CaSO_4$.

Résumé

Comme suite de ses recherches l'auteur a démontré que la forme de hydrosulfoaluminate de calcium à haute teneur de sulfate qui ce forme dans le ciment à cause de l'interaction du sulfate de calcium avec les aluminates, sous des conditions physico-phimiques correspondantes, présente une liaison structurellement utile dans la pierre de ciment solidifié.

L'addition d'une quantité élevée de gypse (ou d'anhydrite) au ciment portland à haute teneur d'aluminate augmente la résistibilité de la pierre de ciment à l'action de solutions d'eau de sulfates de Na, Mg et Ca, ce qui s'explique par la formation de hydrosulfoaluminate. Le plus de C_3A entre en liaison avec le sulfate de calcium dans les termes de début de la solidification du ciment (avant 28 jours), la plus haute est la résistivité aux sulfates de la pierre de ciment. La quantité optimale de gypse dans le ciment portland doit être celle qui lie le C_3A à former l'hydrosulfoaluminate de calcium pendant la période de début de durcissement du ciment.

Dans les ciments sulfate-laitier (sans clinker ou avec peu de clinker), obtenus sur la base de laitiers granulés acides ou basiques, en présence d'une phase liquid (eau) et d'une petite quantité d'alcalis ($Ca(OH)_2$ ou $Mg(OH)_2$) et de sulfate de calcium, est formé l'hydrosulfoaluminate de calcium, lequel, ensemble avec d'autres nouvelles formations—silicate hydrocalcique $3CaO{\cdot}2SiO_2{\cdot}aq$ et aluminate hydrocalcique $2CaO{\cdot}Al_2O_3{\cdot}7H_2O$ et dans le cas de laitier acide $2CaO{\cdot}Al_2O_3{\cdot}7H_2O$ et $2CaO{\cdot}SiO_2{\cdot}$ aq.,—stipule la solidification et la longévité de la pierre de ciment.

Dans le ciment alumineux le gypse additionné à celui-ci dans une quantité d'à peu prés de 30% en présence d'une phase liquide entre en interaction chimique avec les aluminates de calcium en formant l'hydrosulfoaluminate qui influence positivement les propriétés de ce ciment:on obtient un ciment dilatable se solidifiant sous des conditions humides avec une haute imperméabilité sous des conditions de températures élévées pour le compte d'exothèrmie ou d'échauffement externe. En additionnant au ciment alumineux près de 25% d'anhydrite insoluble, on obtient un ciment incontractable se solidifiant normalement sous des conditions s'approchant aux adiabatiques. Le béton avec ce ciment possède une stabilité élevée dans les milieux agressifs contenant des sels de NaCl, $MgCl_2$, Na_2SO_4, $MgSO_4$ et $CaSO_4$.

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Zusammenfassung

Auf Grund seiner Untersuchungen hat der Verfasser gezeigt, daß die hoch-sulfatische Form von Calciumhydrosulfoaluminat, die sich im Zement infolge der gegenseitigen Wirkung von Calciumsulfat mit Aluminaten bildet, unter entsprechenden physikalisch-chemischen Bedingungen eine strukturell nützliche Verbindung im erhärteten Zementstein ist.

Die Zugabe einer erhöhten Menge von Gips (oder Anhydrit) zu hochaluminatigem Portland-Zement erhöht die Beständigkeit von Zementstein der Einwirkung von wässerigen Lösungen von Na, Mg und Ca gegenüber, was sich durch die Bildung von Hydrosulfoaluminat erklärt. Je größer die Menge des in frühen Bindezeiten des Zements (unter 28 Tagen) mit Calciumsulfat gebundenen C_3A ist, desto höher ist die Sulfatbeständigkeit des Zementsteines. Die optimale Menge von Gips im Portland-Zement soll die sein, die C_3A in Calciumhydrosulfoaluminat während der Beginnungszeit des Zementhärtens bindet.

In Sulfatschlackenzementen (klinkerlosen oder wenig Klinker enthaltenden), die ausgehend von sauren oder basischen granulierten Hochofenschlacken beim Vorhandensein von einer flüßigen Phase (Wasser), in Anwesenheit einer kleinen Menge von Alkali ($Ca(OH)_2$ oder $Mg(OH)_2$ und Calciumsulfat, erhalten werden, wird Calciumhydrosulfoaluminat gebildet, das zusammen mit anderen Neubildungen—Hydrocalciumsilikat $3CaO{\cdot}2SiO_2{\cdot}aq$ und Hydrocalciumaluminat $2CaO{\cdot}Al_2O_3{\cdot}7H_2O$, und im Fall einer sauren Schlacke $2CaO{\cdot}Al_2O_3{\cdot}7H_2O$ und $2CaO{\cdot}SiO_2{\cdot}aq.$,—das Härten und die Beständigkeit des Zementsteins verursacht.

Im Aluminatzement tritt der ihm in einer Menge von etwa 30% zugegebene Gips in Anwesenheit einer Flüßigen Phase in eine chemische Zusammenwirkung mit Calciumaluminaten ein unter Bildung von Hydrosulfoaluminat, das die Eigenschaften dieses Zements günstig beeinflußt—es wird ein expandierender Zement beim Härten unter feuchten Bedingungen erhalten, der eine hohe Wasserdichtigkeit, ohne Einbüßen seiner Dauerhaftigkeit unter Verhältnissen hoher, durch Exothermie oder äußere Erwärmung hervorgerufener, Temperaturen besitzt. Bei einer Zugabe von etwa 25% unlöslichen Anhydrits zum Aluminatzement wird ein volumbeständiger Zement erhalten, der unter den adiabatischen nahen Bedingungen normal erhärtet. Beton mit diesem Zement besitzt eine erhöhte Beständigkeit in agressiven, NaCl-, $MgCl_2$-, Na_2SO_4-, $MgSO_4$-, und $CaSO_4$- Salze enthaltenden Mitten.

Introduction

The role of gypsum and other forms of calcium sulfate (hemihydrate, insoluble anhydrite) varies in different binding materials. Gypsum is used in the cement industry as an addition controlling the setting time. In some cases it slows the rate of setting (portland cement); in others it accelerates the hardening of the cement (for instance of slag portland cement) and increases its strength.

About 2.5 percent, computed as SO_3, is usually reckoned to be an admissible amount of gypsum in portland cement.

Many investigations have been devoted to the influence of gypsum on the properties of different cements. But the optimum percentage of gypsum in cement is expressed in different papers by different values.

Some investigations show that the optimum amount of gypsum in portland cement favorably influencing the strength of hardened cement paste is that quantity bound with C_3A in the initial period of hardening. A further increase of gypsum content can lead to a decrease of strength of the cement paste and even to its disintegration during further hardening.

The C_3A of portland cement enters speedily into a reaction with gypsum under suitable physicochemical conditions, especially if calcium hydroxide is contained in the liquid phase, forming a complex calcium hydrosulfoaluminate compound, $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}30\text{–}31H_2O$. The formation of this salt, crystallizing in the shape of thin needles or prisms, is accompanied by a considerable increase in volume.

If hydrosulfoaluminate has formed at early stages of hardening, i.e., during the formation of the structure of cement paste, it is a structurally useful compound increasing the strength of the paste. The formation of crystalline sulfoaluminate in hardened cement paste, however, is accompanied by a disintegration of the paste because of the growth of the crystals and the considerable inner strains arising as a result.

Thus in some cases the formation of hydrosulfoaluminate in concrete structures based on portland cement can lead to their destruction, and in others it is a useful factor contributing to an increase of strength of the concrete.

The amount of gypsum to be added to portland cement depends principally on the amount of C_3A present and on the velocity with which it combines with gypsum [1].[1]

It is known that gypsum combines not only with C_3A to form calcium hydrosulfoaluminate, but also with C_4AF; but the rate of reaction with C_4AF is very much slower than that of the reaction with C_3A.

In order to study the rate of reaction of gypsum with tricalcium aluminate, we synthesized the latter by burning a mixture of fine powders of reagent-quality CaO and Al_2O_3. Out of a moistened mixture of these components (three equivalents of CaO and one of Al_2O_3) were pressed at 300 kg/cm^2 bricks subsequently fired to sintering at 1380 °C. This temperature was maintained for 3 hr. The fired bricks were crushed to pass completely the 4900 mesh/cm^2 sieve. Bricks were again pressed from the moistened powder and refired at the same temperature. After the fourth

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[1] Figures in brackets indicate the literature references at the end of this paper.

firing, free lime was absent in the product. A chemical analysis showed a CaO content of 62.25 percent. Petrographic investigation showed that the fired product was formed of irregularly shaped fine isotropic crystals with refractive index $N=1.710$.

A photomicrograph of isometric $C_3A \cdot 6H_2O$ crystals obtained as a result of hydration of C_3A in water for two days is shown in figure 1.

Amounts of 10, 20, and 30 percent of gypsum were added to the C_3A. To determine the amount of unreacted gypsum, we used a method based on the different solubilities of gypsum and calcium sulfoaluminate in a saturated $Ca(OH)_2$ solution.

The results of determination of the rate of reaction of gypsum with tricalcium aluminate are shown in table 1.

The results showed that with 10 percent of gypsum in the mixture only 0.80 percent of unbound SO_3 remained after 6 hours and that SO_3 was absent in the solution after 24 hr. With 20 percent of gypsum, SO_3 disappeared from the solution in 7 days, and with 30 percent, in 28 days.

The time of binding of C_3A lengthened when gypsum dihydrate was introduced, and with 10 percent of gypsum the period of binding diminished.

TABLE 1. *Rate of reaction of gypsum with tricalcium aluminate*

Amount of gypsum in mix		Amount of unreacted SO_3 in:					
Gypsum	Calculated as SO_3	6 hrs	24 hrs	3 days	7 days	16 days	28 days
Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
10	5.88	0.80	0	--------	--------	--------	--------
20	11.76	3.44	1.80	0.32	0	--------	--------
30	17.64	6.60	4.93	2.63	1.18	0.64	0

An investigation of the interaction of C_3A with gypsum (saturated solution) showed the formation of characteristic calcium sulfoaluminate needles with refractive indices $N_g=1.462 \pm 0.002$ and $N_p=1.458$.

In figure 2 we see calcium sulfoaluminate crystals formed in 6 hr as a result of interaction of C_3A with gypsum in the liquid phase. In figure 3 are shown calcium sulfoaluminate crystals formed in the liquid phase in 6 hr as a result of interaction of gypsum with cement clinker containing 11.04 percent of C_3A.

In investigations on the influence of different amounts of gypsum on portland cement with different C_3A contents, three clinkers were taken whose mineralogical composition is shown in table 2.

TABLE 2. *Mineralogical composition of clinkers (in %)*

No. of clinker	C_3S	C_2S	C_3A	C_4AF	MgO	$CaSO_4$	Free CaO
I	56.21	19.00	5.00	16.00	1.70	0.49	0.60
II	41.15	32.20	8.45	15.25	1.31	.68	96
III	49.58	23.91	11.04	10.20	3.30	.71	1.03

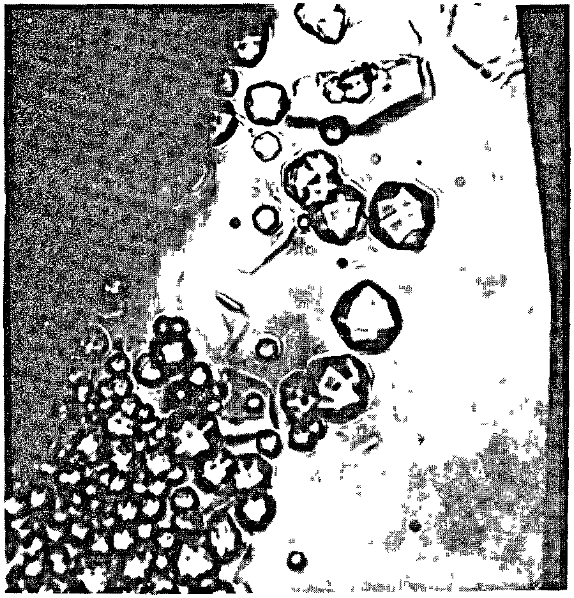

FIGURE 1. *Photomicrograph of isometric* $C_3A \cdot 6H_2O$ *crystals obtained as a result of hydration of* C_3A *in water for two days.*

Photograph made with the aid of a green light filter. Magn. 800 times.

FIGURE 2. *Calcium sulfoaluminate crystals formed by the interaction of* C_3A *with gypsum.*

Photograph made under electronic microscope. Magn. 4000 times.

FIGURE 3. *Calcium sulfoaluminate formed by interaction of cement clinker with gypsum.*

Photograph made under electronic microscope. Magn. 4000 times.

The clinkers were ground to a specific surface of 3,200 cm^2/g. Hemihydrate was added in proportions of 3.5 and 10 percent, reckoned as anhydrous calcium sulfate.

The determinations of the rate of binding of gypsum as a function of the content of C_3A in portland cements showed that cement containing 5 percent of C_3A bound the 3 percent of added gypsum completely in 24 hr. The same phenomenon was noted also in cement with 11.04 percent of C_3A, to which 3 and 5 percent of gypsum had been added. A slower interaction takes place in the case of cements containing 10 percent of gypsum. Thus, in a high-C_3A portland cement containing 6.30 percent of SO_3 at 6 hr after mixing, the percentage of unbound gypsum in the cement was 2.9, at 24 hr 1.87, at 3 days 1.10, at 7 days 0.441, and at 28 days 0.10.

The retarding of the binding of gypsum can take place because of the formation of a large amount of hydrated compounds covering the particles of cement and thus hampering the access of calcium sulfate molecules to the unreacted part of the cement. Obviously this factor plays the largest part in the case of the high-C_3A portland cement.

Cements with a different C_3A content without any addition of gypsum, in contrast to synthetic C_3A, as would be expected, set quickly; if 3 percent of gypsum is added to the same cements, the setting takes longer.

With an increase of the percentage of gypsum the term of binding shortens, leading to a reduction of the interval of binding.

The influence of gypsum as a retarder of setting of portland cement can be explained by the fact that in the presence of the liquid phase the gypsum reacts quickly with the calcium aluminate hydrate, forming submicroscopic hydrosulfoaluminate crystals; the latter, settling on the surface clinker particles, envelop them and thus retard the hydration of cement, i.e., its setting. These deposits are voluminous, because of a simultaneous formation of a gel of calcium silicate hydrates, and draw off the water from the cement particles.

The strength of cement samples as a function of gypsum content was determined for the bending strength on prisms measuring 1 x 1 x 3 cm and for the compressive strength on cubes measuring 1.41 x 1.41 x 1.41 cm prepared from a 1:3 plastic mortar with sand (sand passing the 144 mesh/cm^2 sieve and remaining on the 256 mesh/cm^2 sieve was used).

It was found that in the cases of 3 and 5 percent content of gypsum in high-alumina portland cement (C_3A—11.04%) the intensity of growth of strength[2] was rather regular up to 28 days of hardening [3]. In the case of the same cement with 3 percent of gypsum after 28 days and especially after 90 days hardening a considerable slackening of the rate of increase of strength took place; at the same time, the strength of samples of the same cement with 7 and especially with 10 percent of gypsum grew considerably only after 28 days of hardening. The slackening of the increase of strength before 28 days in the case of high-C_3A portland cement with 7 and 10 percent of gypsum is to be explained by a continuous breaking up of the structure because of the formation of sulfoaluminate. After 28 days hardening, when practically all gypsum was bound, the strength of cement paste sharply increased.

The bending strength of samples from high-C_3A portland cement was determined for 3, 5, 7, and 10 percent of gypsum.

The investigations showed that in the case of cement with 10 percent of gypsum the increase in bending strength was continuous, in contrast to cement with 3 percent of gypsum whose increase in strength ceased after 2 months.

When investigating the sulfate resistance of cements with different C_3A contents as a function of the amount of gypsum added, we prepared samples from a 1:3 plastic cement mortar. After 28 days hardening in water the samples were immersed in 5-percent Na_2SO_4 and 1-percent $MgSO_4$ solutions and in a saturated gypsum solution. The salt solutions were replaced every month.

It was found that in the case of storage of samples in a Na_2SO_4 solution the highest strength was shown by high-alumina portland cement (C_3A—8.45%) containing 7 and 10 percent of gypsum, and the greatest lowering of strength was observed in the case of cement containing 3 percent of gypsum.

Complete disintegration of cement (C_3A—11.04%) with a 3-percent gypsum content took place first with samples stored in a sodium sulfate solution, then with those stored in a magnesium sulfate solution, and lastly, in 12 months, in a saturated gypsum solution (fig. 4).

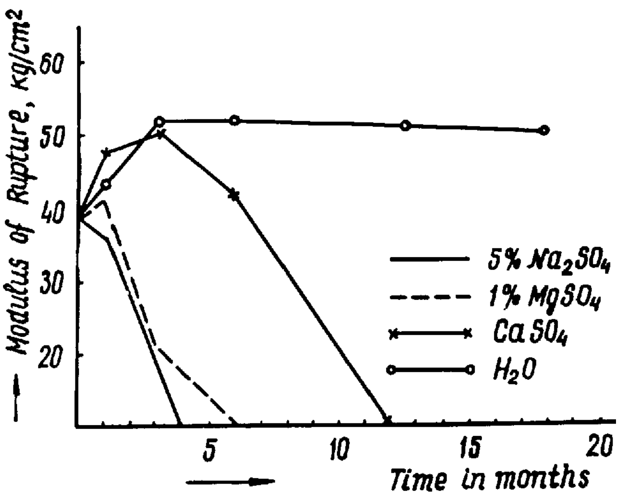

FIGURE 4. *Bending strength of cement samples stored in sulfate solutions* (C_3A *in cement, 11.04%; gypsum, 3%*).

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[2] By intensity of growth of strength is understood the percentage relation of strength at a given age to that at 3 days.

Samples of high-alumina portland cement (C_3A—11.04%) containing 10 percent of gypsum showed the highest bending strength when stored in a 5 percent sodium sulfate solution and the lowest in a saturated gypsum solution (fig. 5).

Aluminous cement presents another example in which gypsum influences essentially the properties of cement.

Many investigators have studied the processes of hydration and hardening of aluminous cement. In the process of hydration of the $CaO{\cdot}Al_2O_3$ and $5CaO{\cdot}3Al_2O_3$ contained in aluminous cement there is formed a colloidal phase that gradually takes the shape of a fine-grained mass. The finest hexagonal crystals of $2CaO{\cdot}Al_2O_3{\cdot}7H_2O$ speedily grow in size, forming a firm crystalline network, and the cement hardens in 5–6 hr, the mortar with sand attaining a strength of about 200 kg/cm^2 and higher; in 10–15 hr, 400–500 kg/cm^2; and on the third day of hardening about 600 kg/cm^2 and more. Thereafter the strength of the cement increases slowly and insignificantly. But this hardening process, as is known, takes place under normal temperature conditions, i.e., at 5–25 °C.

As has been shown by many investigations and in practice, an increase in the temperature from 30 to 70 °C influences unfavorably the strength of this cement, the strength of the cement stone falling more than 50 percent.

The unfavorable influence of elevated temperatures of the medium on the strength of aluminous cement is explained by the formation of Thorvaldson aluminate in the shape of fine cubic crystals of $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$.

The formation of these cubic crystals in the mass of the $Al_2O_3{\cdot}nH_2O$ gel and the absence of a crystalline network are the fundamental causes of the low strength of aluminous cement hardened at elevated temperatures.

The possibility is not excluded that the strength of aluminous cement depends not only on the shape of the crystalline components, but also on the amount of alumina hydrate that forms in the earliest stages of hardening, in the shape of a gel-like mass, and, filling up all voids, creates a dense structure.

When the temperature increases, the alumina gel forms in a considerably smaller amount than at 18–20 °C which presumably is insufficient for the creation of high density and strength.

As has been shown by our investigations, it is possible to avoid this negative phenomenon by introducing gypsum or anhydrite into the batch of aluminous cement. The calcium aluminates in aluminous cement, $CaO{\cdot}Al_2O_3$ and $5CaO{\cdot}3Al_2O_3$, dissolving in water, begin to interact with calcium sulfate with the formation of the complex compound calcium hydrosulfoaluminate, $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31H_2O$. The temperature increase accompanying the hydration of aluminous cement contributes to this process. The binding of calcium sulfate as hydrosulfoaluminate takes place at the first stage of hardening, when the cement paste does not yet have a stiff skeleton, and the volume changes of the system connected with the lower density of this new product (calcium hydrosulfoaluminate), do not influence negatively the mechanical strength of the hardened cement paste obtained as a result of these chemical and physical processes.

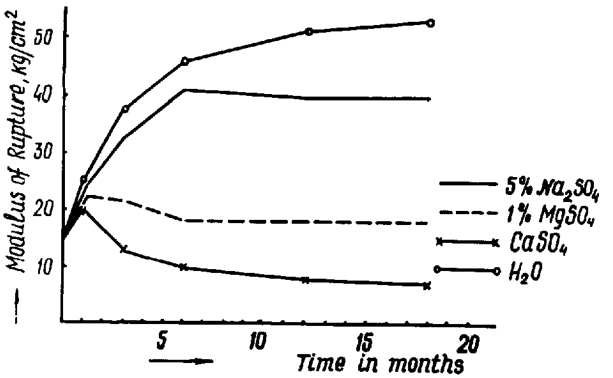

FIGURE 5. *Bending strength of cement samples stored in sulfate solutions* (C_3A *in cement, 11.04%; gypsum, 10%).*

We took an aluminous cement of the following chemical composition (in %):

SiO_2	10.36	Fe_2O_3+FeO	1.85
Al_2O_3	47.25	MgO	0.39
CaO	38.91	SO_3	.38
		S	.81

It was shown by the investigations that the most active addition to aluminous cement is anhydrite obtained by firing gypsum at about 600–700 °C.

If aluminous cement showed a crushing strength amounting in 3 days to 525 kg/cm^2 and in 7 days to 550 kg/cm^2, the same cement with an addition of 25 percent of artificial insoluble anhydrite showed at the same ages 580 and 660 kg/cm^2. The packing of anhydrite-aluminous cement into molds at 2 hours after mixing did not influence negatively the mechanical strength of the cement. The addition of artificial insoluble anhydrite to aluminous cement accelerates the setting of the cement, and of natural anhydrite retards it.

Characteristic properties of aluminous cement in the case of an addition of calcium sulfate to it are: high early strength, expansion when stored in moist conditions, high water impermeability, and an increased mechanical strength when hardening under high-temperature conditions (when the whole mass of the mixture or concrete is being equally warmed up from 35 to 80 °C because of exothermal self-heating or of external heating). Hydrosulfoaluminate formed during the hydration of anhydrite-aluminous cement is not only an excellent structural element of hardened cement paste, lending it a high mechanical strength, but also changes the character of the heat evolution curve in the process of cement hydration.

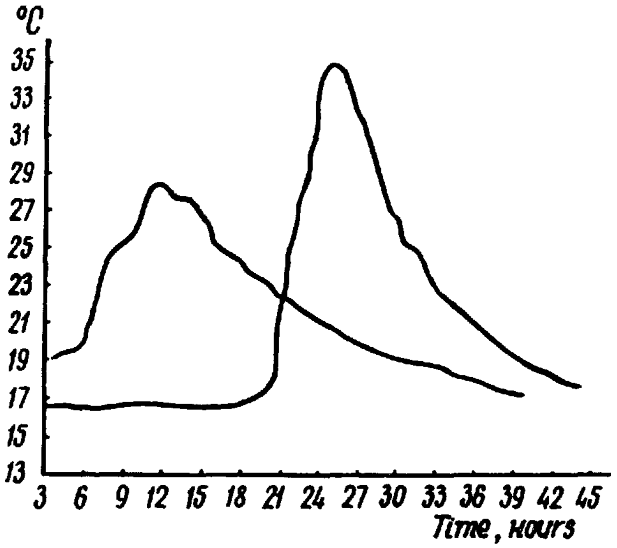

FIGURE 6. *Time-temperature curves of cements in concrete.* 1—aluminous cement; 2—anhydrite-aluminous cement.

The total amount of heat evolved during the hardening of anhydrite-aluminous cement is somewhat lower than in the case of aluminous cement of equal strength. When the strength is about 600 kg/cm^2, the heat evolution of aluminous cement equals about 100 cal/g and of anhydrite-aluminous cement about 70 cal/g. In the velocity and character of heat evolution anhydrite-aluminous cement differs from aluminous cement. Self-heating of anhydrite-aluminous cement begins much earlier, but the interval between the beginning of self-heating and the temperature maximum is much longer, though the latter comes somewhat earlier than in the case of aluminous cement. Thus the evolution of heat and the increase of temperature in the case of anhydrite aluminous cement occurs more regularly than in the case of aluminous cement; with the latter this process is somewhat retarded at first but is greater later on. Figure 6 illustrates the character of the exothermic processes of hydration of both cements [6].

The character of the heat evolution in the case of anhydrite-aluminous cement has a positive importance for its practical use: firstly, the self-warming taking place soon after mixing and laying of concrete is advantageous to the hardening process; secondly, the inner temperature strains in bulk concrete will be somewhat lower; and, thirdly, an early self-warming better preserves the concrete mass from freezing under conditions of winter concrete-laying.

A specific peculiarity of anhydrite-aluminous cement is the considerable increase of its mechanical strength when self-heating of the hardening mortar and concrete takes place or when warmth is applied from outer sources; on the contrary, the strength of aluminous cement is considerably lowered under these conditions.

Thus, if at 3 days normally cured aluminous cement had a compressive strength of 560 kg/cm^2, when hardening under adiabatic conditions at 60 °C its strength was lowered to 132 kg/cm^2. Under the same conditions the strength of anhydrite-aluminous cement (with 25 percent of anhydrite) increased from 490 to 520 kg/cm^2 and in 28 days to 650 kg/cm^2. These cements conduct themselves similarly in concrete.

It is known that among binding materials, aluminous cement is the most resistant in aggressive media, if a temperature of the medium not exceeding 20–25 °C is maintained during the building of structures.

In this respect anhydrite-aluminous cement is of interest; concrete made with this cement has a good resistance in aggressive media containing soluble $NaCl$, $MgCl_2$, Na_2SO_4, $MgSO_4$, and $CaSO_4$. In solutions of these salts the tensile strength of one-year samples did not decrease.

The adhesiveness of aluminous and anhydrite-aluminous cements to iron is equal under normal temperature hardening conditions; on the other hand, under nearly adiabatic conditions of hardening the adhesiveness of anhydrite-aluminous cement to iron is nearly twice that of aluminous cement.

The anhydrite-aluminous cement is non-shrinking and under certain circumstances expanding under moist conditions. The phenomenon of expansion of cement during hardening takes place because of the formation of calcium hydrosulfoaluminate.[3]

The expansion of aluminous cement manifests itself especially well if 30 percent of gypsum is added to it [7].

In the case of water curing of samples of aluminous cement containing 30 percent of gypsum (1:0 mortar), about a half of the combined linear expansion takes place during the first day. Samples of 1:3 mortar with the same regime of hardening showed an expansion of 0.08 percent in one day and 0.09 percent in 3 days, further expansion ceasing afterwards.

The expanding gypsum-aluminous cement is characterized by a high water impermeability. Cylindrical samples 230 mm in diameter and 50 mm in length were prepared from a 1:2.5 by weight cement mortar, as well as concrete samples 100 mm in length of the following composition for 1 m^3 of concrete: cement—280 kg, water—170 l, building sand—690 kg, crushed granite of 30 to 5 mm size—1300 kg.

At three days, samples of expanding cement proved to be sufficiently impermeable to water under 8 atm. pressure.

It was found that gypsum-aluminous cement in rich mortars of 1:2 and 1:2.5 (by weight) compositions and in concrete with 377 kg/m^3 of cement and a water-cement ratio of 0.45 is frost resistant; in mortars and concretes of the consistency and

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[3] On the influence of temperature conditions on the stability of calcium sulfoaluminate and sulfoferrite see P. P. Budnikov and V. S. Gorshkov. Reports of Academy of Sciences of U.S.S.R., 1959, vol. 126, No. 2, p. 337.

composition shown it withstands over 200 cycles of alternate freezing (at −17 to −22 °C) and thawing for 16 hr in water at 17±3 °C.

Trial determinations of the adhesion to reinforcing steel of concrete made with expanding cement were undertaken by the method of pressing down steel bars 14.4 mm in diameter and 125 mm in length. The concretes tested had a *w/c* ratio = 0.60. The concrete cubes measures 100×100×100 mm. In the case of air curing the average value of adhesion proved to be 64 kg/cm², and in the case of water curing, 40 kg/cm².

The temperature rise during the hardening of expanding cement does not influence its strength. Tests showed that at 60–65° with alternate drying and saturating with water the expanding cement was stable.

Crushed granulated blast furnace slags when mixed with water, as is known, possess very feeble binding properties or do not possess them at all. In order to call forth a reaction between slag and water, an addition of an alkaline stimulator is needed. The presence of an inconsiderable amount of alkali is sufficient to establish on the surface of slag particles an extensive formation of hydrated products bringing about a binding and hardening of granulated slag similar to cement. An addition of sulfate to the slag in the presence of an alkaline stimulator, as was demonstrated by our investigations, intensifies the process of hydration and hardening [2, 8, 9, 10, 11].

When studying the phenomena taking place in the liquid phase of hardening slag cement paste, we found that $CaSO_4$, whose content in cement as gypsum amounted to about 20 percent, disappeared from the liquid phase in 25–45 hr when the blast furnace slag contained about 20 percent of Al_2O_3 and in 70–115 hr when the content of Al_2O_3 amounted to about 10 percent. When $CaSO_4$ is present in the liquid phase, alumina does not appear in the solution or appears in quite inconsiderable amounts. Alumina appears in the liquid phase only after the disappearance of $CaSO_4$. Simultaneously there takes place also an increase of the calcium oxide content of the solution.

When finely divided basic granulated blast furnace slag interacts with calcium sulfate (different modifications) in the liquid phase in the presence of a small amount of alkali, there form calcium hydrosulfoaluminate $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31H_2O$, calcium hydroaluminate $2CaO{\cdot}Al_2O_3{\cdot}7H_2O$, and calcium hydrosilicate of the composition $3CaO{\cdot}2SiO_2{\cdot}$aq. and, in the case of acid slag, calcium hydrosulfoaluminate and calcium hydrosilicate $2CaO{\cdot}SiO_2{\cdot}$aq. When the calcium oxide content of the liquid phase is not high and there are present large amounts of alumina in the slag, the formation of $2CaO{\cdot}Al_2O_3{\cdot}7H_2O$ is also possible.

The formation of calcium hydrosulfoaluminate in sulfate-slag cement paste during mixing exhibits also in this cement a positive action creating the initial strength of the cement, and by its formation there develops the process of formation of other new compounds—calcium hydroaluminates and hydrosilicates—that stimulate a further growth of the strength of cement paste.

The character of the hardening processes of sulfate-slag cement depends on the concentration of free lime in the solution, the presence of magnesium hydroxide, and the amount of calcium sulfate added.

An alkaline medium is necessary for the normal hardening of sulfate-slag cements. In this respect the best addition is magnesium hydroxide, which corrodes the slag particles and thus communicates to them an increased activity. Practically, dolomite fired at 800–1100 °C is used for this purpose [12, 13]. In the case of basic slag the amount of lime introduced must be the least and therefore the dolomite is fired at about 800–900 °C, but in the case of acid slags it must be fired at 1,000–1,100 °C in order to attain also the decarbonation of calcium carbonate.[4]

The free lime from the dolomite in the latter case is necessary to supply calcium hydroxide for the reaction with the active silica of granulated blast furnace slags taking place during the mixing of the cement with water, leading to the formation of calcium hydrosilicate [14, 15, 16].

For the fulfilment of this condition it is necessary that not more than 3 percent of lime or about 7 percent of portland cement be present in the mixture of crushed granulated blast furnace slag and calcium sulfate, for calcium hydroxide is split off by the slag in a very inconsiderable amount and is quickly absorbed to form calcium hydrosulfoaluminate. This mechanism is confirmed by the experimentally established dependence of the crushing strength of sulfate-slag cement paste on the percentage of calcium oxide contained in the liquid phase (fig. 7).

Curve 1 corresponds to the crushing strength in kg/cm² of standard samples after 7 days hardening in water, curve 2 to that after 27 days under the same conditions of hardening.

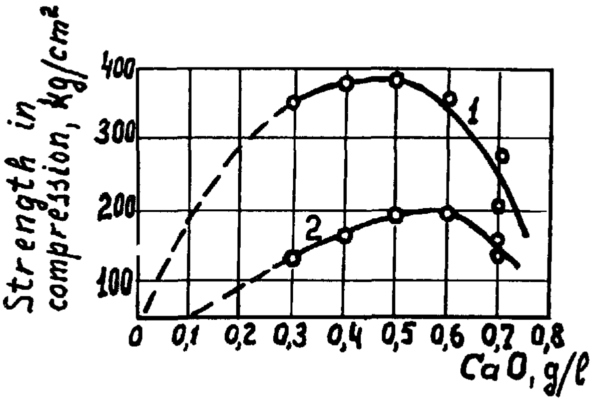

FIGURE 7. *Dependence of the crushing strength of sulfate-slag cement paste on the percentage of calcium oxide present in the liquid phase.*

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[4] $CaCO_3$ of dolomite fired at about 800–900 °C is not only a microfiller of cement, but in the hydration process it can react with C_3A with the formation of $C_3A{\cdot}CaCO_3{\cdot}11H_2O$, which promotes the increase of strength of sulfate-slag cement (P. P. Budnikov, V. M. Kilbasov, A. S. Panteleev, Reports of the Acad. Sci. U.S.S.R., 1959, v. 129, No. 5, 1104; Silikattechnik 1960, No. 6, p. 271–272).

Because the velocity of binding of calcium oxide during the formation of calcium sulfoaluminate and hydrosilicate exceeds the velocity of dissolution of calcium hydroxide, the concentration of CaO in solutions decreases quickly, and the aluminates, when dissolving, form the hydrosulfoaluminate without swelling. As has been shown by our investigations, a higher solubility of calcium aluminates is attained at a calcium oxide concentration of 0.4–0.5 g/l [17].

The rate of increase of strength of cement paste depends on the chemical composition of the slag and the potential energy supply—the faster the molten blast furnace slag is cooled and the more calcium oxide and alumina it contains, the greater is the strength of sulfate-slag cement.

The chemistry of the hardening process of slag cements is influenced by the composition of the cement, its specific surface, the amount of water added for mixing, and the temperature of the medium.

In order to study the properties of sulfate-slag cement, two slags were taken whose chemical composition is shown in table 3.

TABLE 3. *Chemical composition of granulated blast furnace slags (in %)*

Oxides	Slag samples		Oxides	Slag samples	
	I	II		I	II
SiO_2	35.21	36.96	MnO	2.56	2.02
Al_2O_3	9.35	20.20	Fe_2O_3	1.43	1.26
CaO	46.41	34.10	SO_3	2.05	0.32
MgO	2.43	3.45	S	------------	0.21

To form cements, slag I was ground with 5 percent of dolomite burnt at 800 °C and 5 percent of anhydrite (gypsum burnt at 700 °C): and slag II was ground with 7 percent of dolomite burnt at 1,100 °C and 5 percent of anhydrite.

The fineness of grinding of the cements: residue on sieve 900 mesh/cm^2—0.2-0.3 percent and on sieve 4,900 mesh/cm^2—6-7 percent. The setting time of cement I: beginning 45 min, end, 1 hr 40 min; of II: beginning 2 hr 10 min, end, 3 hr 42 min.

In table 4 are shown the test data of the sulfate-slag cements in rammed samples (7.07×7.07×7.07 cm) from a 1:3 mortar when stored in water.

TABLE 4. *Crushing and tensile strength of sulfate-slag cements (mortar 1:3), kg/cm^2*

Age	Cement I		Cement II	
	Crushing	Tensile	Crushing	Tensile
4 days	185	16.0	98	7.8
7 days	281	26.8	121	11.3
28 days	333	30.3	341	22.4
3 months	363	35.2	435	37.3
6 months	396	37.4	464	39.5
1 year	406	38.8	532	45.3
5 years	458	39.4	------------	------------
12 years	509	41.4	------------	------------

When acid blast furnace slags with an increased alumina content [5] was used, with 10 percent of anhydrite and 10 percent of burnt (at 900 °C) dolomite jointly ground, sulfate-slag cement was obtained that had the following strength characteristics in kg/cm^2 (numerator—tensile strength, denominator—crushing strength):

in 4 days	19.9/184
in 7 days	23.3/277
in 28 days	32.8/425
in 3 months	37.1/431.

Investigation data show that granulated blast furnace slags can be successfully used to obtain sulfate-slag cement of the 300–400 strength class [18].

For plastic mortars the strength characteristics of sulfate-slag cement are higher than for other cements.

In the case of wet grinding of blast furnace slags jointly with calcium sulfate or with 5 or 10 percent of lime in a ball mill, as the investigations have shown, a very plastic workable mass is obtained. The trial of the cement obtained from a plastic-consistency 1:3 mortar showed the possibility of obtaining cement paste with a strength limit of 200 kg/cm^2 and higher [19].

Based on investigations and factory practice, there has been established the following approximate dependence of the quality of sulfate-slag cement on the properties of the initial slag (table 5) [20].

TABLE 5. *Influence of the properties of the initial slag on the quality of sulfate-slag cement*

Kind of slag	Modulus		MnO	Possible strength class
	Basic	silicate		
			Percent	
Basic	>1	≦3.0	≦1.0	300–400
Basic	>1	3.0–4.0	≦1.5	200–300
Acid	0.90–1.0	≦2.0	≦1.0	400–500
Acid	.75–0.90	≦2.0	≦3.0	250–300
Acid	.70– .75	≦2.0	≦3.0	150–200

Sulfate-slag cement from granulated blast furnace slags with an elevated index with an MnO content of the order of 4 percent and higher has a lowered strength.

One of the causes of the decrease of strength of slag cements in the case of an increased MnO content in granulated blast furnace slags is obviously the formation in acid slags of manganous anorthite, $MnO{\cdot}Al_2O_3{\cdot}2SiO_2$, manganous cordierite $2MnO{\cdot}2Al_2O_3{\cdot}5SiO_2$. and also the formation of a solid solution $2CaO{\cdot}SiO_2$–$2MnO{\cdot}SiO_2$ which is characteristic of basic slags.

On the other hand, the negative part played by MnO in blast furnace slags from manganous cast iron, from the point of view of their hydraulicity, is limited to an increase of waterproofness of vitreous slag matter.

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[5] Chemical composition of acid slags (in %): SiO_2, 28.60; Al_2O_3, 24.93; CaO, 41.25; MgO, 2.19; MnO, 0.60; FeO, 1.54; SO_3, 1.03.

Manganese has a further negative influence because the compound MnS present in granulated blast furnace slags, increasing in volume when interacting with water, creates inner stresses in the hardening cement and in this way lowers its strength.

Sulfate-slag cement is characterized by a high resistance to the destructive action of sweet, sea, and mineralized waters, considerably exceeding in this respect portland cement, pozzolanic portland cement, and slag-portland cement, and stands near to aluminous cement. This valuable peculiarity of sulfate-slag cement (clinkerless cement) is provided by the chemical composition of the cement and by the peculiar nature of the processes and products of its hardening.

The evolution of heat on account of the exothermal processes taking place during the setting and at the beginning of the hardening of sulfate-slag cement is considerably lower than in the case of aluminous, portland, and slag-portland cements. After 7 days of hardening of a normal mortar of a stiff consistency, the heat evolved is 15–26 cal/g, allowing this cement to be used successfully in massive concrete.

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Paper IV–S2. The Mineralogical Examination of Set Portland Cement*

H. G. Midgley

Synopsis

The methods used for the mineralogical examination of set portland cement at the Building Research Station are microscopy, differential thermal analysis, X-ray diffraction, infrared absorption spectrometry, and electron microscopy and diffraction. By a combination of the methods it is possible to get a semiquantitative estimate of the various constituents of the cement paste of neat cements, mortars, and concretes. Differential thermal analysis appears to be the most sensitive and most likely to give quantitative results for the calcium silicate hydrate. The results so obtained are indicative that the main calcium silicate hydrate formed is a gel-like phase related to tobermorite, probably with a CaO:SiO$_2$ ratio greater than 1.5. The calcium aluminates formed are C_4AH_x with varying water content, ettringite solid solutions, and low-sulfate sulfoaluminate. There seems some evidence that all these crystalline aluminates can be formed at any age and that kinetic conditions such as CaO and SO$_3$ concentrations at the C$_3$A crystal face may govern the phase produced.

Résumé

Les méthodes dont dispose la *Building Research Station* pour l'examen minéralogique de la prise du ciment Portland sont la microscopie, l'analyse différentielle thermique, la diffraction des rayons X, la spectrométrie d'absorption infra-rouge, et la diffraction et la microscopie électronique. En combinant ces méthodes il est possible de faire une évaluation semi-quantitative des constituants variés de la pâte de ciment des ciments purs, des mortiers et bétons. Il semble que ATD est la méthode la plus sensible et la plus susceptible de donner des résultats quantitatifs pour l'hydrate de silicate de calcium. Les résultats obtenus jusqu'à présent indiquent que le principal hydrate de silicate de calcium formé est une phase comparable à un gel semblable au tobermorite, avec un rapport de CaO:SiO$_2$ probablement plus grand que 1.5. Les aluminates de calcium formés sont C_4AH_x avec une teneur en eau variable, ettringite, et le sulfo-aluminate avec une teneur plus basse en sulfate. Certains faits semblent prouver que tous ces aluminates cristallins peuvent être formés à tout âge et que les conditions cinétiques telles que les concentrations en CaO et SO$_3$ à la facette du cristal peuvent régir la phase produite.

Zusammenfassung

Die Methoden für die mineralogische Analyse des erstarrten Portlandzements, die in der *Building Research Station* angewandt werden können, sind die Mikroskopie, die differentielle Thermalanalyse, die Röntgenbeugungsbestimmungen, die Ultrarotabsorptionsspektrometrie, die Elektronenmikroskopie und die Elektronenbeugung. Durch eine Kombination der Methoden ist man in der Lage, eine halbquantitative Abschätzung der Bestandteile der Zementpaste des Purzements, des Mörtels und des Betons vorzunehmen. Die differentielle Thermalanalyse scheint die größte Empfindlichkeit zu haben, sie gibt wahrscheinlich die besten quantitativen Ergebnisse für Hydrate des Kalziumsilikats. Die Ergebnisse, wie sie bis jetzt erhalten worden sind, besagen, daß das Haupthydrat des Kalziumsilikat, welches sich formt, eine gelähnliche Phase ist, die mit Tobermorit verwandt ist, und in der das Verhältnis CaO:SiO$_2$ vermutlich größer als 1.5 ist. Die gebildeten Kalziumaluminate sind C_4AH_x mit verschiedenen Wassergehalten, Ettringit und der gering sulfatige Sulfoaluminat. Vermutlich können sich alle diese kristallinen Aluminate in jedem Alter bilden; die kinetischen Bedingungen, wie die CaO- und SO$_3$-Konzentrationen an der Kristalloberfläche des C$_3$A beeinflussen vermutlicherweise die gebildete Phase.

Introduction

The mineralogical method of examining set portland cement has a long and important history. The use of the thin section and the petrographic microscope was described by Parker and Hirst [1][1], who also extended the work of dye absorption to help differentiate the cementitious phase, called by them gel. About the same time Brown and Carlson [2] carried out a very comprehensive petrographic study of set portland cement pastes. These two papers probably represent all the data that may be obtained by such methods.

Alternative methods were now needed to advance the knowledge of the mineralogy of set portland cement. Ordinary powder X-ray diffraction analysis had not proved very successful. Firstly, the cameras in normal use did not record low angles, and secondly, the diffraction patterns of any possible cement hydrate minerals were swamped by the patterns of the still remaining unhydrated cement minerals.

The next big step forward in technique for mineralogical examination of set cements came

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Building Research Station, Department of Scientific and Industrial Research, Watford, England.

[1] Figures in brackets indicate the literature references at the end of this paper.

from Kalousek, who with Davis and Schmertz [3] in 1949 used the method of differential thermal analysis (DTA) for the first time. By this method these workers were able to identify in setting portland cement pastes the minerals ettringite, $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$, and $Ca(OH)_2$. Although in the same paper they investigated the thermograms given by synthetic calcium silicate hydrates, they were unable to use the DTA method to identify the calcium silicate hydrate in set portland cement.

Although a considerable amount of data was known [4–6] on the phase chemistry of the systems $CaO–SiO–H_2O$, $CaO–Al_2O_3–H_2O$, and $CaO–Al_2O_3–SO_3–H_2O$, it was not until 1947 that the team under Bernal began its work on the crystallography of the minerals of the system $CaO–SiO_2–H_2O$. This work, summarized by Bernal, Jeffery, and Taylor [7] and Taylor and Heller [8], led to an attempt to identify the calcium silicate hydrate in set portland cement. Nurse and Taylor [9] reported X-ray diffraction data on a number of set cements, indicating that the calcium silicate hydrate present was of the tobermorite type. The method of separation used was very involved and tedious, involving elutriation and continuous centrifuging in very large quantities of anhydrous alcohol. Taylor [10] later made a separation using only limited quantities of material and centrifuging in bromoform-benzene mixtures. By this method Taylor identified the calcium silicate hydrate as CSH I or II.

Another important method of investigation available is electron microscopy and diffraction, and although a large amount of work has been done on calcium silicate hydrates it is only recently that attention has been paid to set portland cement pastes or mortars. Gille, et al. [11] have investigated set portland cement pastes by replica methods and have identified the plates of calcium hydroxide. Grudemo [12], one of the most important workers in this field, has recently published pictures of calcium aluminate hydrate and calcium silicate hydrate from set portland cement pastes.

The other methods available for mineralogical examination—infrared absorption analysis, nuclear-magnetic-resonance spectrometry and microprobe technique—so far have not been used extensively to determine the mineralogy of set portland cements. Hunt [13] has given infrared absorption spectra of some of the cement minerals, and the author of this paper has used the method extensively and reports the results here for the first time.

Using the techniques described before, together with a much more refined X-ray diffraction method involving X-ray diffractometers instead of film cameras, Turriziani [14] and Copeland, Kantro, and Verbeck [15] have recently described the mineralogy of set portland cements.

This paper sets out the methods and results obtained in similar studies at the Building Research Station.

Methods of Investigation

Microscopy

Reflection microscopy is not yet of great value in investigating the mineralogy of set portland cements, although the method is of some value in determining the microhardness of the minerals. The technique for preparing polished surfaces of set portland cements is under investigation, and a method of preparing good surfaces has been evolved. The method is simple—the section is cut on a high speed, resin-bonded diamond wheel, and the surface is then lapped on a similar diamond high speed plate.

For thin-section work, the required section should be as thin as possible; by the usual techniques sections of about 30μ are possible, but by a technique evolved by Smith [16] at the Building Research Station sections of about 10μ thickness have been prepared. Farran [18] has used microscopy in his investigations into the binding of cement paste and aggregate, but he was not able to deduce anything of the mineralogy of set portland cement from the microscope.

X-ray Diffraction

X-ray diffraction methods have been used extensively in the study of set portland cement pastes, mortars, and concretes. Most of the work has been done using cylindrical Debye-Scherrer cameras of varying radii, but all capable of recording at least 20A with copper K-alpha radiation. More recently some work has been done using a recording diffractometer. This latter method gives greater resolution and gives a better idea of quantities of identifiable minerals, but is not as good as photographic techniques in differentiating weak reflections from background.

An adjunct to X-ray diffraction identification is the possibility of concentrating the cementitious minerals. The method found most effective with concretes and mortars is to crush the sample with an iron pestle and mortar and sieve the fragments first through a 14-mesh sieve; further crushing and passing through a 100-mesh sieve removes a considerable quantity of the aggregate. This method of course precludes the quantitative determination of the cementitious minerals.

A further concentration of the cementitious phases has also been attempted using the technique described by Taylor [10]. This involves centrifuging of a benzene-ground sample in appropriate bromoform-benzene mixtures to produce a light fraction in which the cementitious hydrates are concentrated.

Differential Thermal Analysis

The differential thermal analysis (DTA) of set portland cements has been carried out in an apparatus especially designed for the purpose. The furnaces are of nichrome winding capable of reaching 1,000 °C; they are programed to give better than 10/min ±1 °C accuracy, the temperature of the sample and the amplified difference temperature between the sample and the inert body are recorded on a 0–50 mv, potentiometric recorder. The crucible and thermocouple setup received special attention (figure 1). The crucibles used were ceramic (fired alpha alumina), which were found to give better resolution than metal crucibles. By using two thermocouples, one in the sample and one in the inert body, a high degree of symmetry was obtained. The thermocouples found to be best for this work were chromel-alumel. Care was also taken to match the heat properties of the sample and the inert body. For most of the work about 0.7 g of sample was used. By these methods it has been possible to resolve the low-temperature endotherm around 120 °C into three peaks (figure 2). This resolution is repeatable, and full reliance can be given to the resolution.

Infrared Absorption Spectrophotometry

For these investigations a commercial spectrometer, recording between 2.5- and 15-μ wavelength, was used.

Three methods of sample preparation were used. In the first, about 10 mg of sample was pressed with about 1 g of anhydrous KBr into a disc of 13-mm diameter by means of a vacuum press[17] This method was successful for anhydrous minerals, but there appeared to be interfering chemical reactions when hydrates were tried.

The second method was to mill the sample with an inert oil and make a thin film of the suspension between sodium chloride plates. This method gave good resolution but strong absorptions at 3.6, 7.0, and 7.4 μ due to the oil interference with the pattern.

The third method was to mill the sample with isopropyl alcohol. A sample was pipetted onto a NaCl disk and the alcohol allowed to evaporate. This method gave very good resolution at wavelengths greater than 5 μ, but owing to the specular reflection due to the difference in retractive index between the sample and air, there was a considerable absorption at less than 5 μ. This reflection, however, did not interfere with that part of the spectrum (around 10 μ) of most value in differentiating between the different minerals.

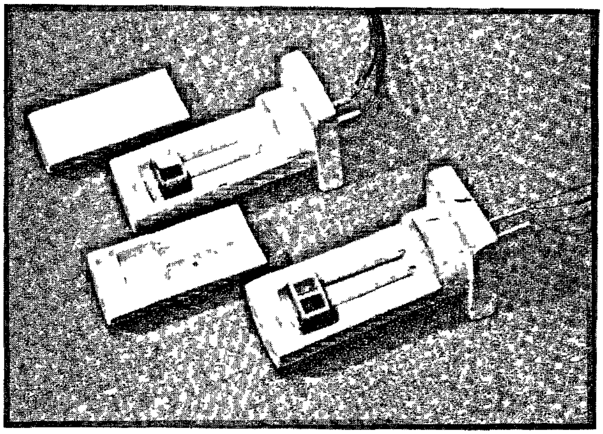

FIGURE 1. *DTA ceramic crucibles and holders showing two symmetrically disposed thermocouples.*

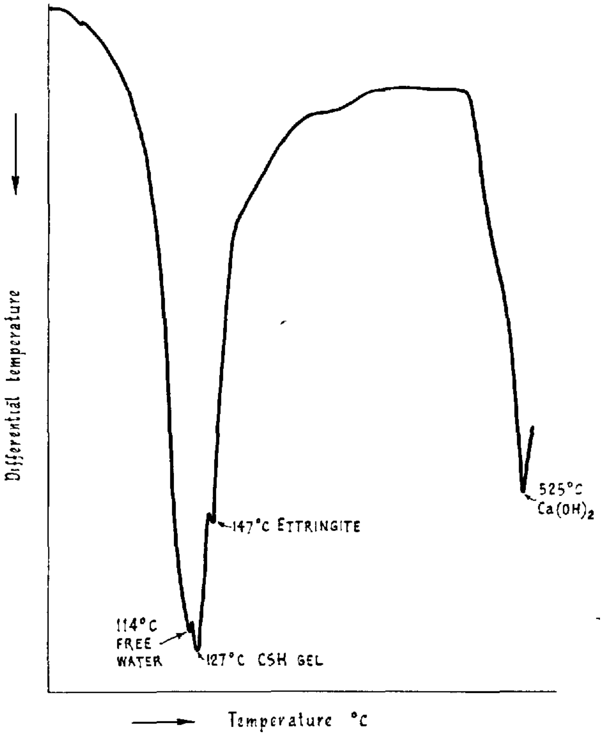

FIGURE 2. *Differential thermogram of set portland cement.*

Experimental Results

Microscopy

With the advent of very thin sections prepared by the Smith method, a new interest has been aroused in thin-section microscopy. Sheaths of isotropic gel have been seen around $3CaO{\cdot}SiO_2$ and $2CaO{\cdot}SiO_2$ grains, as is shown in figure 3. These are taken to be reaction rims of what is probably the calcium silicate hydrate gel phase.

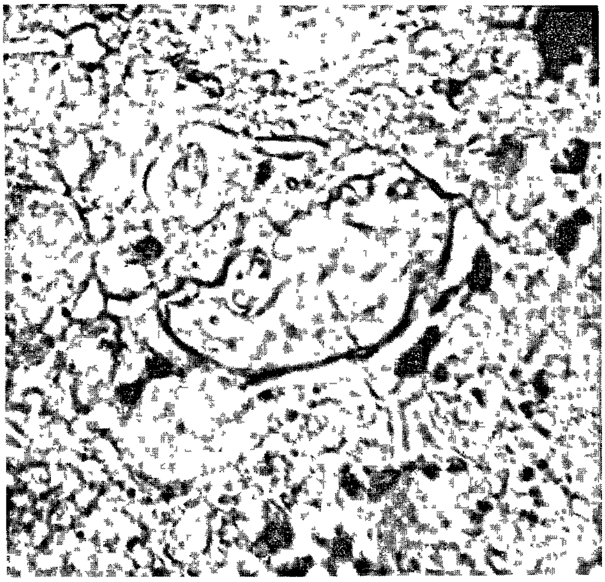

FIGURE 3. *Photomicrograph of thin section of set portland cement paste (normal water-cement ratio) showing rim of calcium silicate hydrate gel around silicate grains.*

X-Ray Diffraction

By film techniques it is possible to detect the presence or absence of the unhydrated minerals; the data used are those of Midgley [19]. Of the hydrate minerals, ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}aq.$–$3CaO{\cdot}Al_2O_3{\cdot}3Ca(OH)_2{\cdot}aq.$) can be detected by its reflection at 9.8A, and the solid-solution composition can be detected by a change in the value of this reflection [20], although DTA would be more accurate. The low-sulfate sulfoaluminate $3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$ is detected by its reflection at 8.92A, and the carbonate-aluminate $3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}12H_2O$ can be detected by the change in value of the reflection to 7.59A. The $4CaO{\cdot}Al_2O_3$·aq. series [21] can be detected by their reflection in the region of 8.05A. Calcium hydroxide and calcium carbonate are easily recognized from their patterms.

Calcium silicate hydrates have not been identified by this method so far. The only strong reflection for CSH I or II at 3.06A is very close to the strong reflections of alite and calcite, so that, if there is more than a trace of either of these minerals, any possible CSH reflection is masked.

In counterdiffractometry the aluminate and aluminate salt hydrates are detectable using the same reflections as by film camera technique, but it is also possible to make quantitative estimates of the amounts.

Figure 4 is the trace given by a neat cement paste 7 days old. The ettringite peak at 9.1 °2θ (d=9.7A) and the C_4AH_{13} peak at 10.84 °2θ (d=8.13A) are clearly seen. Similarly, figure 5 is for a neat cement paste 3 years old. Here the ettringite peak is seen again at 9.1 °2θ and the aluminate peak is spread between 10.4° and 11.0 °2θ, suggesting that more than one hydration state is present.

In both these samples no aggregate was used, and great care was taken to keep CO_2 away so that the amount of calcium carbonate present is very small. So in the case of the cement paste 3 yr old, which is fully hydrated, calcium silicate

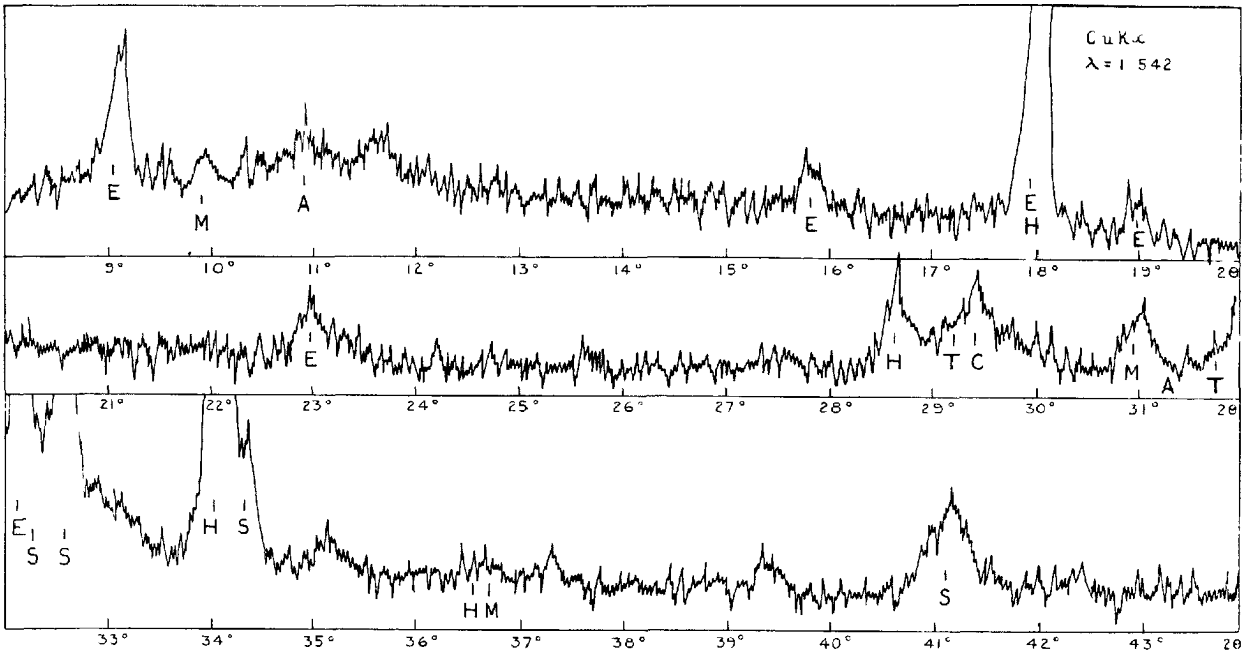

FIGURE 4. *X-ray diffractometer trace of set portland cement, neat; w/c 0.45.*
Made 2/6/60; examined 8/6/60 (see figure 5 for key).

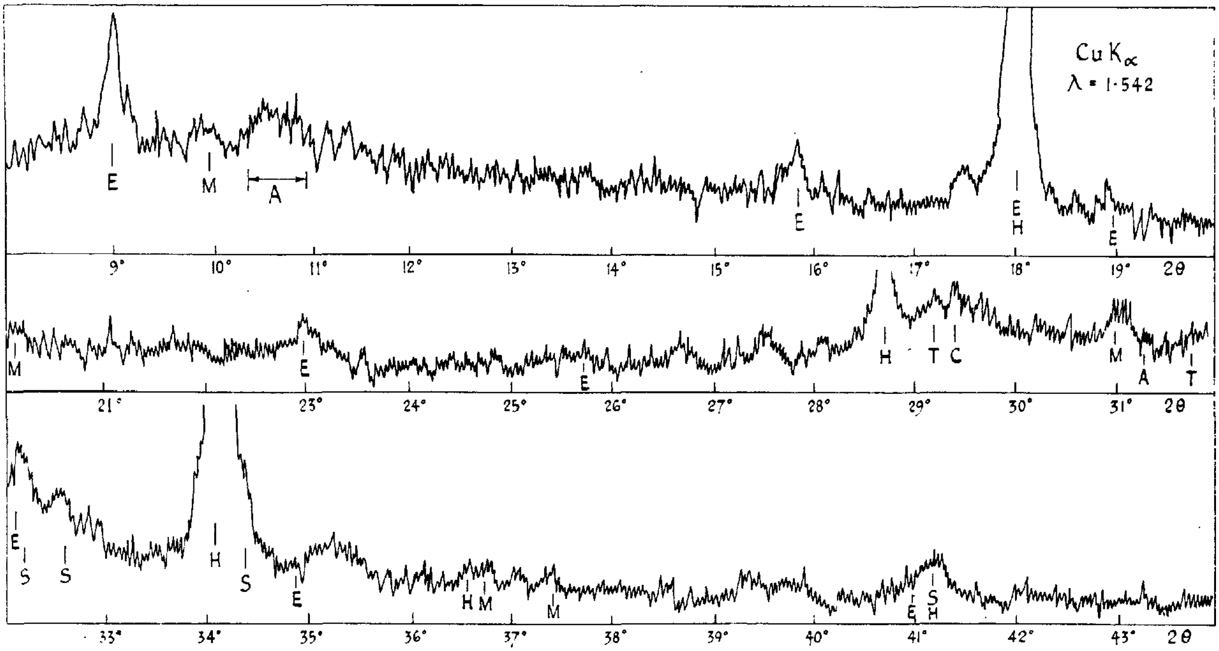

FIGURE 5. *X-ray diffractometer trace of set portland cement, neat; w/c 0.45.*

Made 10/4/57; examined 4/6/60. Key: E=Ettringite, $M=C_3A \cdot CaSO_4 \cdot 13H_2O$, $H=Ca(OH)_2$, T=CSH, $C=CaCO_3$, $A=C_4AH_x$, $S=\beta C_2S$, L=Alite, Q=Quartz.

hydrate is detected by the 3.06A reflection at 29.2 °2θ (fig. 5). Even in this sample where only a very small quantity of anhydrous silicate β-2CaO·SiO$_2$, is detected the peak size for the CSH phase is disappointingly small.

The diffraction trace of the sample 7 days old shows that the CSH phase is undetectable owing to the presence of beta dicalcium silicate.

As the samples referred to above were stored in CO$_2$-free atmospheres, there is no calcite interference. In normal mortars and concretes CO$_2$ will not be absent, and figure 6 shows what happens when a 1:3 mortar is stored without precautions. After 3 and 6 days water storage the possible detection of CSH at 29.2 °2θ (d= 3.06A) is masked by the alite peak (L) at 29.55 °2θ (d=3.03A). Prolonged storage in conditions which would allow carbonation gives patterns such as shown at 3 and 6 months. Here any possible detection of CSH is masked by the very strong calcite peak at 29.4 °2θ (d=3.04A).

Similar results are obtained from the cement fraction extracted from a concrete, figure 7. The concrete was from a roadway and was about 4 yr old. The diffraction pattern shows that ettringite, Ca(OH)$_2$, and calcite, together with quartz from the aggregate, may be detected.

Taylor [10] has shown that a concentration of the hydrate minerals is possible, but repeated attempts by the author and some of his colleagues have failed to repeat Taylor's results.

Recently, Fletcher [22] has modified the method and made an extraction. The method is similar to Taylor's but after grinding the cement in benzene the suspension is put into a centrifuge

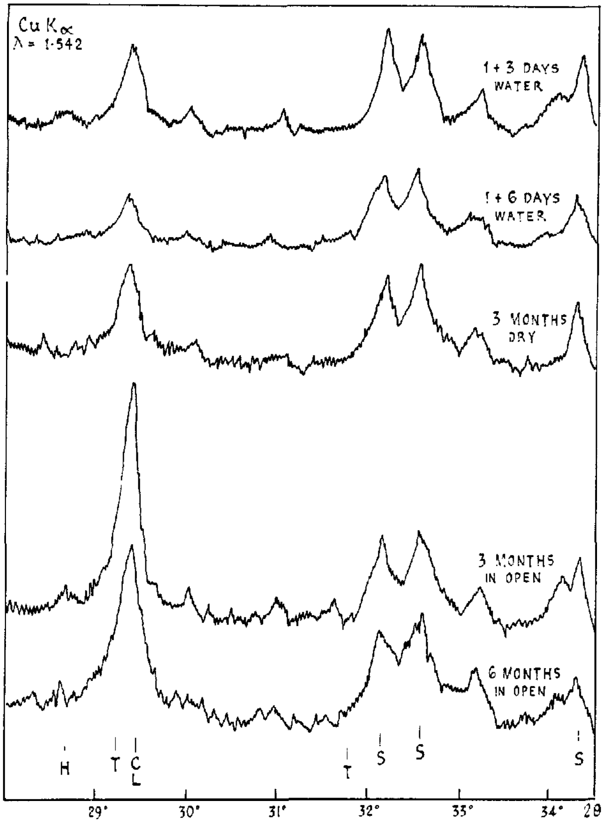

FIGURE 6. *X-ray diffractometer trace of cement fraction from portland cement mortars.*

1:3 standard sand; w/c 0.52 (see figure 5 for key).

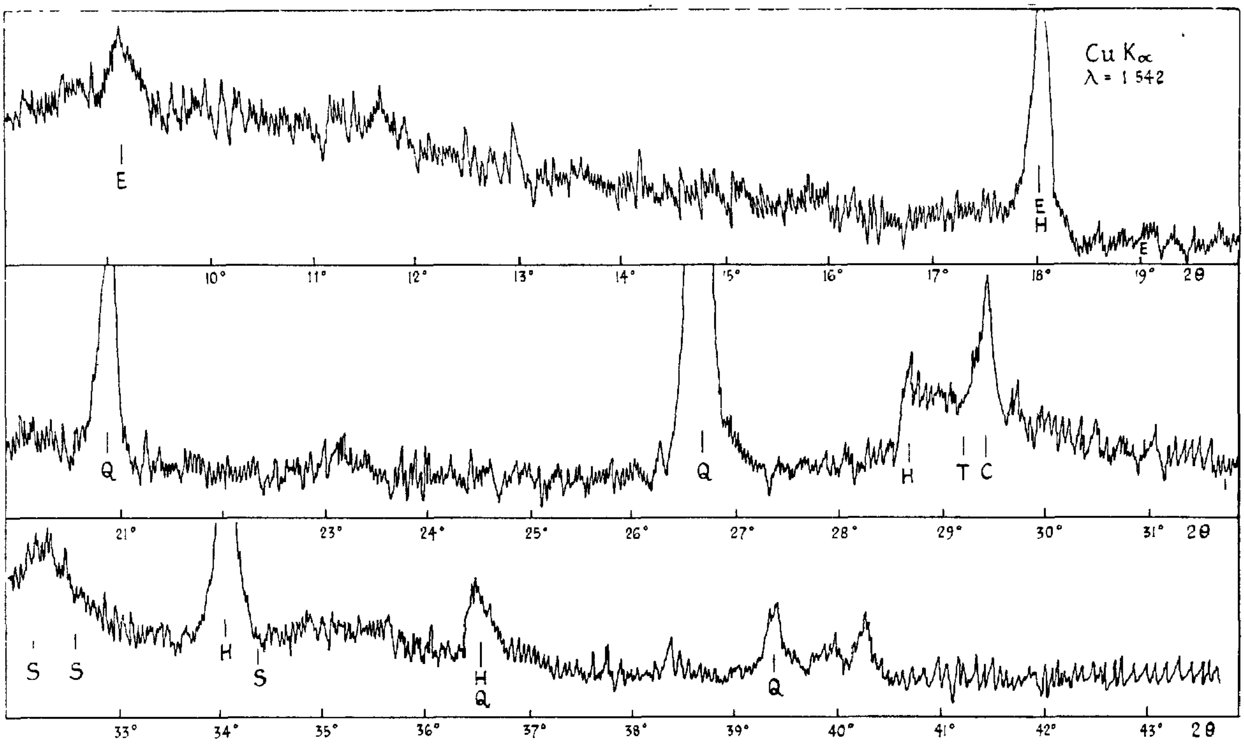

FIGURE 7. *X-ray diffractometer trace of cement fraction from concrete.*
(See figure 5 for key.)

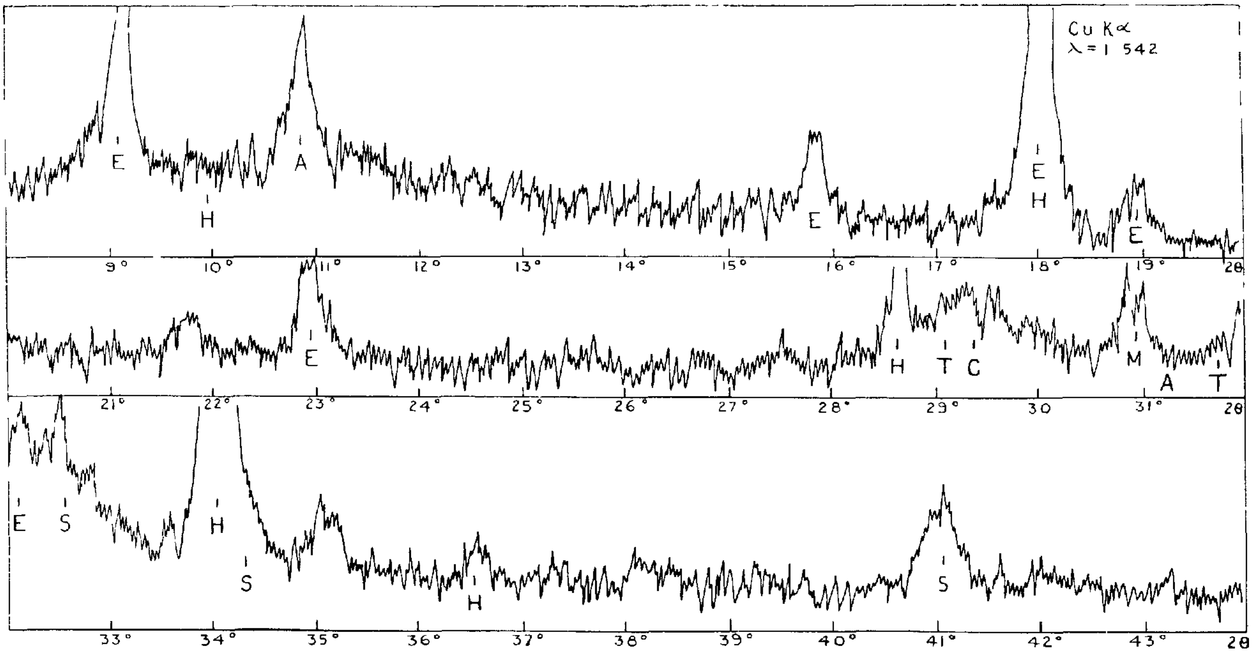

FIGURE 8. *X-ray diffractometer trace of set portland cement, neat; w/c 0.45.*
Made 2/6/60; examined 8/6/60. Light fraction from bromoform-benzene S.G. 1-78 (see figure 5 for key).

tube and drops of bromoform added until a separation is effected. The light fraction contains the concentration of hydrates. In the experiments reported here the specific gravity of the liquid used was 1.78, much lower than that used by Taylor. These experiments seem to suggest that each separation has to be taken on its own and a suitable liquid density determined by trial and error.

A diffraction pattern obtained from such a separation is given as figure 8. This sample is the light fraction of the same cement as shown in figure 3, a neat portland cement paste 7 days old. The C_4AH_{13} is considerably concentrated, and to a lesser extent the ettringite and the calcium hydroxide, but there does not appear to be any concentration of the CSH phase. The beta dicalcium silicate is reduced.

By X-ray methods it is therefore possible to detect the calcium aluminate and aluminate salt hydrates, $Ca(OH)_2$, and $CaCO_3$, and in favorable circumstances the CSH phase may be just identified.

Differential Thermal Analysis

The problems associated with the DTA of set portland cements are the interpretation of the low-temperature endotherms, for, as can be seen from figure 2, the endotherm is made up of three peaks. The temperatures of the peaks on DTA's are known to vary with quantity of mineral present, and it has been suggested by various authors, Keith and Tuttle [23] for example, that the characteristic temperature of a DTA peak should be the inflection point on the low-temperature side of the peak. This point is found to be consistent irrespective of amount. In the case of multiple peaks such as those given by a set portland cement, the inflections of the second and third peaks are not measurable, and the only easily measured parameter is the peak temperature.

If the peak temperature is plotted against the logarithm of the peak area, for reasonable dilutions, a straight line is obtained. This plotting has been done in figure 9 for the important constituents likely to occur in a set portland cement. The ettringite (pure end member $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot aq.$), C_4AH_{13}, and $C_3A \cdot CaSO_4 \cdot aq.$ were prepared in the normal way. The free water was ordinary distilled water added to alpha alumina in the DTA crucible. (In all cases reported in this paper, alpha alumina was used as diluent.) The phase labeled tobermorite gel caused some difficulty, for although the middle of the three peaks in figure 2 was thought to be due to a calcium silicate hydrate [24, 25], some difficulty was experienced in preparing a synthetic sample.

Calcium silicate hydrate I prepared by double decomposition and by shaking silica sol with $Ca(OH)_2$ produced gels which contained very large quantities of free water, giving peaks on the DTA which agreed with the "free water" line on the graph. All attempts to dehydrate the sample by drying at various humidities caused the sample to crystallize and produce tobermorite which was well crystallized, that is, gave good basal spacings at about 11A on an X-ray diffraction diagram.

The only sample of calcium silicate hydrate which gave an endothermic peak anywhere near the middle of the three endotherms found in set portland cement (fig. 2) was CSH II. The sample was prepared by hydrating pure C_3S for 2 yr in a paste at room temperature. The sample was analyzed for $Ca(OH)_2$ and $CaCO_3$ by DTA and thermogravimetry, and the remainder was assumed to be calcium silicate hydrate of the formula $1.77CaO \cdot SiO_2 \cdot 3.00H_2O$. ($CaO/SiO_2 = 1.77$). The X-ray pattern is of a poorly crystallized tobermorite type, reflections occurring only at 3.06, 2.98, and 1.83A. This mineral is equivalent to the CSH II of Taylor [26] and the tobermorite gel of Midgley and Chopra [24, 25].

Using the results obtained from the pure synthetic minerals and the graph in figure 9, it is possible to interpret the DTA thermograms of set portland cements.

Figure 10 shows the interpretation of the DTA thermogram given by a portland cement paste 14 days old. The scale of the curves given for the pure substances has been adjusted so that the peaks are of about the size of those given by the minerals in set portland cement. From this diagram it may be seen that free water, tobermorite gel (CSH II), ettringite, and $Ca(OH)_2$ may be detected. (In these experiments no attempt has been made to determine the ettringite composition by the method of Midgley and Rosaman [20].)

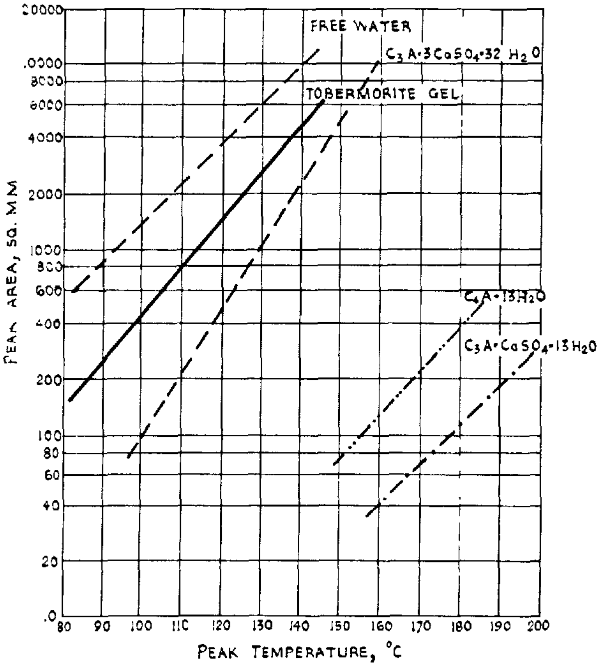

FIGURE 9. *Relation between peak temperature and peak area.*

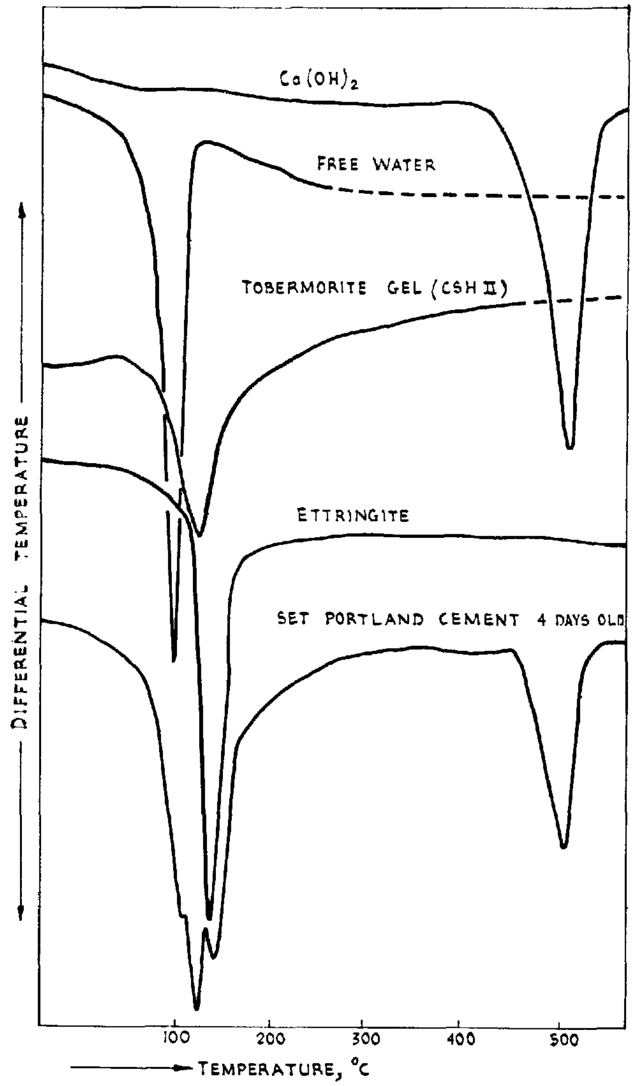

FIGURE 10. *Differential thermograms of set portland cement and constituents.*

A similar interpretation is shown in figure 11 for a portland cement paste 1 yr old, where tobermorite gel, ettringite, and low-sulfate sulfoaluminate are detected.

Now that it is possible to identify the peaks on a DTA, some quantitative estimate of the minerals present can be made by setting up calibration curves for the DTA apparatus, relating peak area to mass of mineral. This calibration has been done for all the important constituents mentioned so far. There is one serious difficulty not wholly overcome; that there is no simple way of determining the constituent parts of a triple peak. The method used in this paper is to construct graphically with reference to standard peaks the two outside peaks (free water and ettringite) giving the remainder as tobermorite gel. This method, although not very precise, is the best available at the moment, and has been employed on a series of setting portland cements stored at 18 °C in water, with the results shown in table 1.

TABLE 1. *Weight percent of cement hydrate minerals in a hydrating 1:3 mortar, w/c 0.52*

Age	Wt percent of		
	tobermorite	ettringite	$Ca(OH)_2$
1 day	1	10	9
3 days	2	35	10
7 days	14	27	10
28 days	18	28	8

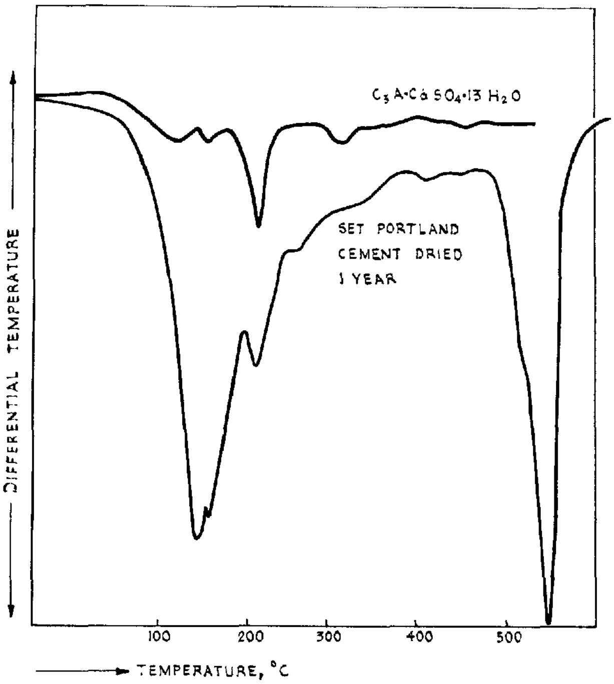

FIGURE 11. *Differential thermogram showing presence of* $C_3A \cdot CaSO_4 \cdot 13H_2O$ *in set portland cement.*

Infrared Absorption Spectroscopy

Absorption curves for all the compounds likely to be met in set portland cement have been prepared. These curves have been obtained for the four main components of portland cement clinker, C_4AF, C_3A, C_2S, and C_3S, shown in figure 12; for gypsum, and hemihydrate, figure 13; and for quartz, MgO, CaO, $Ca(OH)_2$, and calcite, in figure 14. The absorption spectrograms for some of the possible calcium silicate hydrates—Flint's CSH (A), C_2S gamma hydrate, C_2S beta hydrate, and C_2S alpha hydrate—are given in figure 15, C_3SH_2 and tobermorite plus afwillite in figure 16, and crystalline tobermorite and tobermorite gel in figure 17. The spectra for the two important aluminate hydrates are given in figure 18.

The data published here for the first time agree well with the data of Hunt [13] given in his as yet unpublished thesis.

The absorption spectrum of a set portland cement paste is given in figure 19. It is possible to identify the contributions of the various minerals as follows:—unhydrated C_3S by its peak at 10.5 μ; tobermorite gel by its peak at 10.0 μ; (ettringite by its peak at 9 μ, and also possibly calcite from the peak at 11.3 μ. The tobermorite peak is distinguished from the other calcium silicate hydrates by the simplicity of the peak at 10 μ and also by the presence of the double peak at 6.6 and 7.1 μ. Both Hunt [13] and Kalousek and Roy [27] have observed that the ratio of the peak absorption at 7 μ to that at 10 μ is related to the $CaO:SiO_2$ ratio of the tobermorite. Where the 7-μ peak is almost equal to the 10-μ peak, the $CaO:SiO_2$ ratio is highest.

The evidence from the absorption curve of set portland cement 4 days old is that the tobermorite has a high $CaO:SiO_2$ ratio.

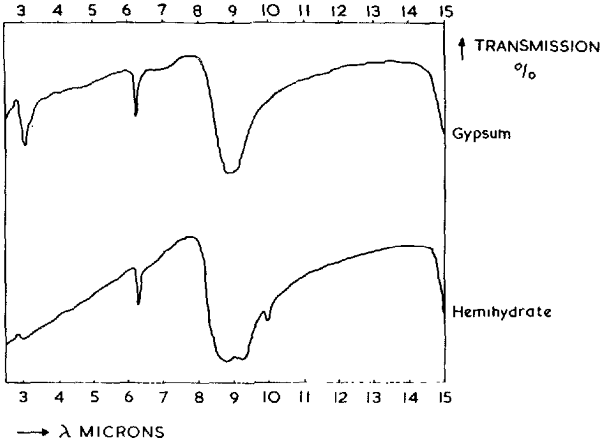

FIGURE 13. *Infrared absorption curves.*

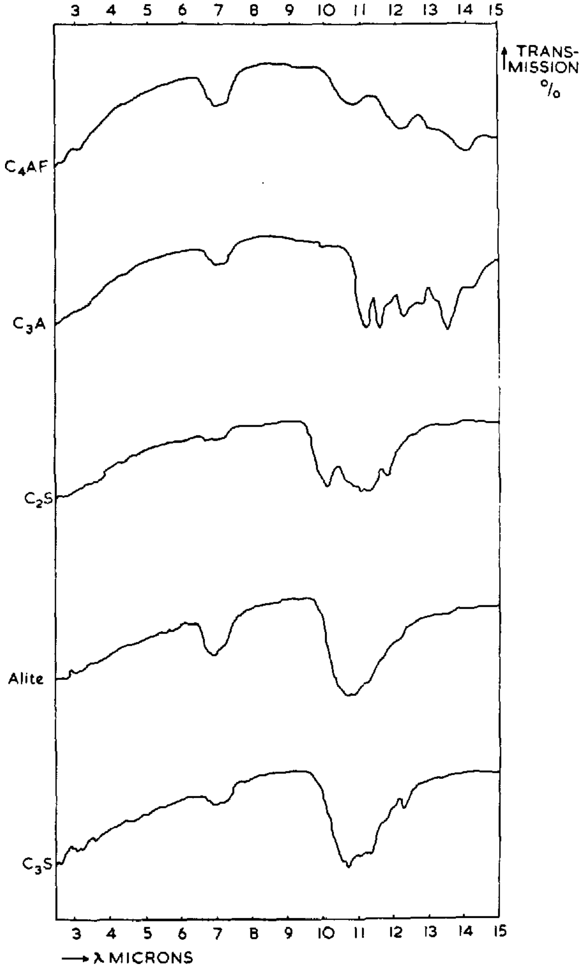

FIGURE 12. *Infrared absorption curves.*

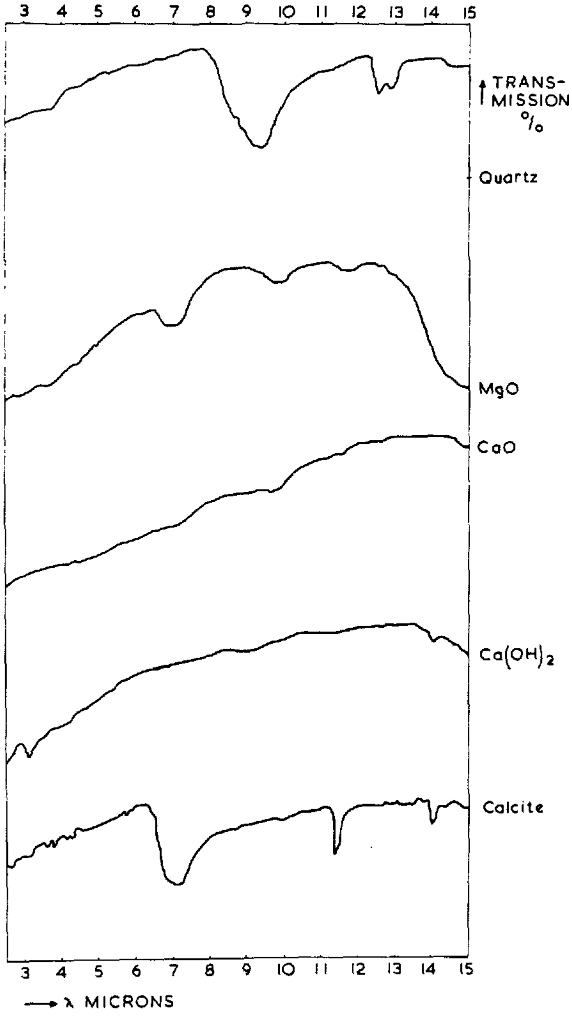

FIGURE 14. *Infrared absorption curves.*

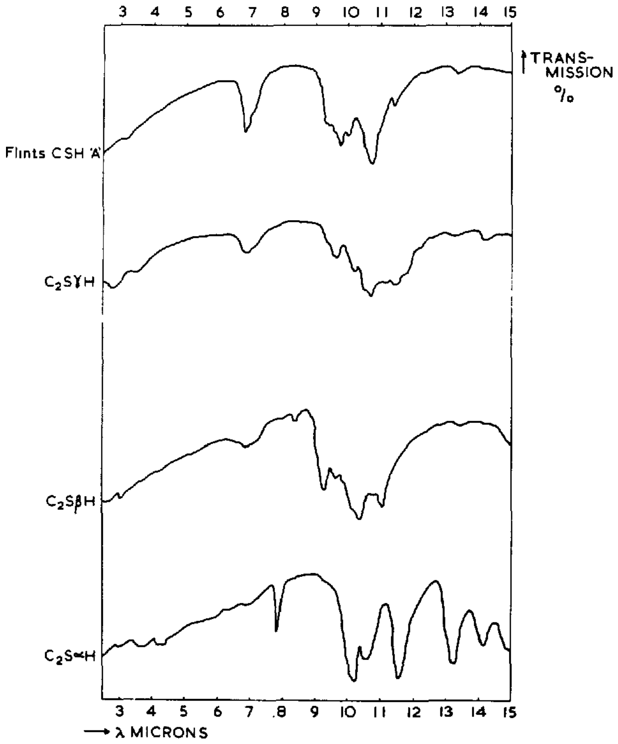

FIGURE 15. *Infrared absorption curves.*

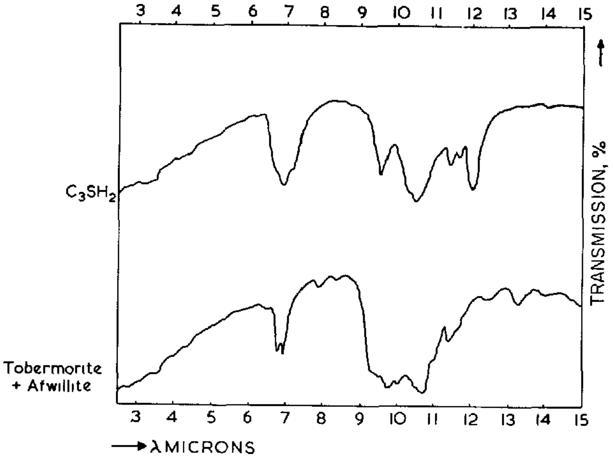

FIGURE 16. *Infrared absorption curves.*

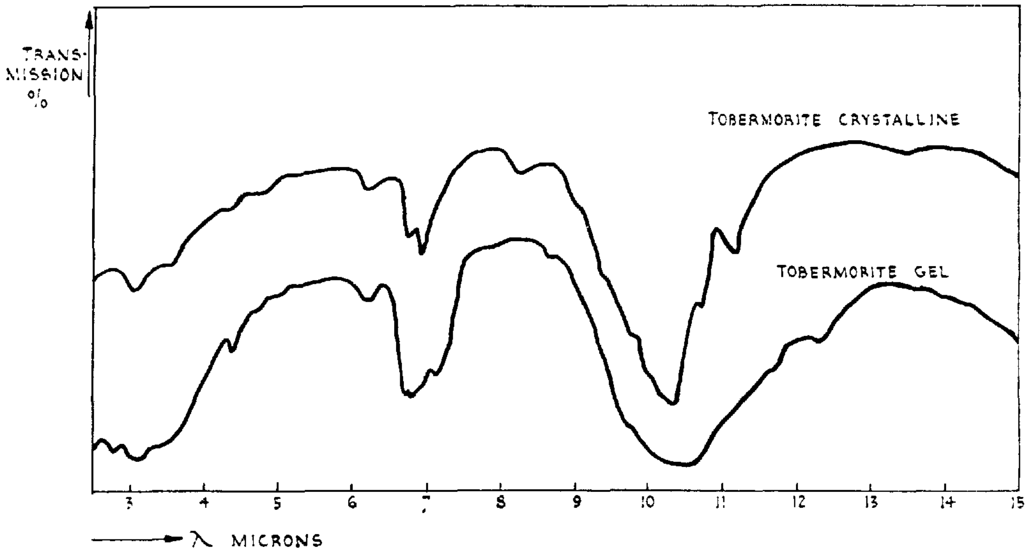

FIGURE 19. *Infrared absorption curve of set portland cement.*

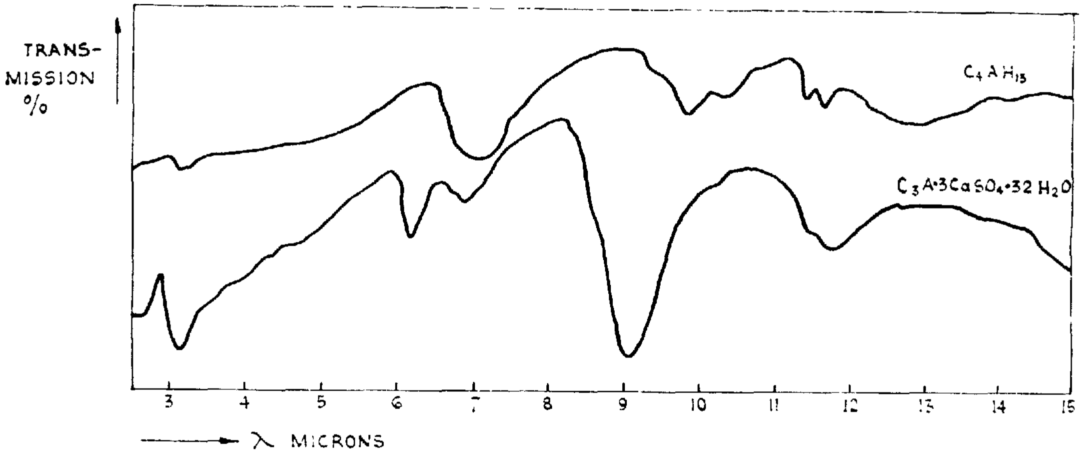

FIGURE 17. *Infrared absorption curves.*

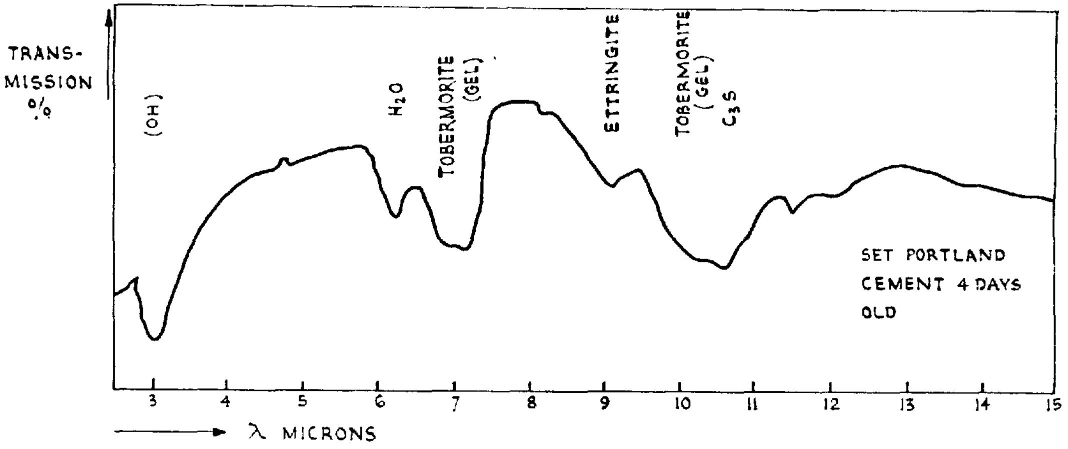

FIGURE 18. *Infrared absorption curves.*

Mineralogy of Set Portland Cements

All the various methods of examining the set portland cement pastes seem to indicate that the main calcium silicate hydrate formed is a gel-like phase related to tobermorite, probably with a $CaO{:}SiO_2$ ratio greater than 1.5; the calcium aluminates formed are C_4AH_x with varying water, ettringite, and low-sulfate sulfoaluminate. There seems some evidence that all these crystalline aluminates can be formed at any age, and that kinetic conditions, such as CaO and SO_3 concentrations at the C_3A crystal surface, may govern the phase formed.

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Discussion

H. Dutz

I will make a brief discussion of the very interesting paper of Midgley.

In the infrared spectrum of calcium hydroxide in figure 14, most of the sample must have consisted of $CaCO_3$. The absorption bands at 7, 11.4, and 14 μ are typical of $CaCO_3$. It is very difficult to get a calcium hydroxide free of carbonate. Therefore, the relation of the absorption bands in figure 19 based on that examination is partly incorrect.

(Editor's note: The comments by Dr.-Ing. Dutz are applicable only to the original version of the paper presented at the Symposium. The author subsequently submitted a corrected copy of figure 14, in which a new absorption spectrum for $Ca(OH)_2$ was substituted.)

Paper IV–S3. Nuclear Magnetic Resonance Study on Hardened Cement Paste*

K. Watanabe and T. Sasaki

Synopsis

To study the hydration of cement and calcium silicate, the nuclear-magnetic-resonance (NMR) absorption method was used. In measurement, samples were cooled from room to liquid nitrogen temperature.

In NMR absorption curves of cement paste cured for 1 day, two peaks were observed during cooling. The inner peak showed the same behavior as that obtained when free water was cooled, and the outer one was similar to that of hydrate water. Further, in this case the peak could be divided into three parts. It seems that these parts correspond to free, adsorbed, and combined water, respectively.

The peak for free water decreased gradually with increase in curing period. In the paste cured for 2 months, two peaks were not observed. This result seems to indicate that the free water has almost disappeared.

The amount of combined water in the paste was determined by integration of the curve. The results obtained were compared with those obtained by the method of Powers. It was found that there are slight differences between these results.

The results obtained by measuring the water-vapor pressure of cement paste showed a similar tendency to those obtained by NMR experiments.

Résumé

Pour étudier l'hydratation du ciment et du silicate de calcium, la méthode d'absorption de la résonnance magnétique nucléaire (RMN) a été utilisée. Dans la mesure, des échantillons furent refroidis de la température de laboratoire à celle de l'azote liquide.

Dans les courbes d'absorption RMN de la pâte de ciment conservée pendant un jour, deux maxima furent observées durant le refroidissement. Le maximum intérieure indiquait le même comportement que celui obtenu dans le cas du refroidissement de l'eau libre, et le maximum extérieure était semblable à celle des hydrates. De plus, dans ce cas-ci on peut diviser le maximum en trois parties. Il semble que ces parties correspondent respectivement à l'eau libre, adsorbée, et combinée.

Le maximum pour l'eau libre diminuait peu à peu avec l'augmentation de la période de conservation. Dans la pâte conservée pendant 2 mois, on ne pouvait pas observer les deux maxima. Il semble que l'on puisse attribuer ceci au fait que l'eau libre est alors presque disparu.

De plus, la quantité d'eau combinée dans la pâte fut déterminée par l'intégration de la courbe. Les résultats obtenus furent comparés à ceux obtenus par la méthode de Powers. On trouva qu'il y a de légères différences entre ces résultats. Les résultats obtenus en mesurant la tension de vapeur de la pâte de ciment indiquaient une tendance semblable à ceux obtenus par l'expérience RMN.

Zusammenfassung

In der Erforschung der Hydratation des Zements und des Kalziumsilikats wurde die kernmagnetische Resonanzabsorptionsmethode benutzt. Während der Messungen wurden die Proben von Zimmertemperatur bis zur Temperatur des flüssigen Stickstoffs gekühlt.

In den Resonanzabsorptionskurven der Zementpasten, die für einen Tag erhärtet worden waren, wurden zwei Extremalwerte während der Abkühlung gefunden. Das innere Maximum war dasselbe wie das, welches erhalten wird, wenn freies Wasser abgekühlt wird; das äußere Maximum war dem des Hydrats sehr ähnlich. In diesem Falle zeigt das Maximum auch eine Feinstruktur; es besteht aus drei Teilen, die scheinbar bzw. dem freien, dem adsorbierten und dem gebundenen Wasser zugeordnet werden können.

Das Maximum für freies Wasser bekam langsam kleiner, wenn die Erhärtungszeit verlängert wurde, und in Pasten, die für 2 Monate erhärtet waren, wurden die beiden Maxima nicht mehr beobachtet, was so erklärt werden muß, daß das freie Wasser dann vollständig verschwunden ist.

Der Betrag des gebundenen Wassers in der Paste wurde auch durch Integration der Kurve bestimmt. Die Ergebnisse, die man auf diese Weise gewann, wurden mit denen verglichen, die Powers veröffentlicht hatte. Ein geringer Unterschied in den beiden Ergebnissen wurde gefunden.

Die Ergebnisse der Dampfdruckmessungen der Zementpasten stimmten im großen Ganzen mit denen der kernmagnetischen Resonanzabsorption überein.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Central Research Institute, Ube Industries, Ltd., Ube-Shi, Yamaguchi-Ken, Japan.

Introduction

Nuclear magnetic resonance (NMR) absorption has recently been considered a useful method for studying the properties of water. Kawachi, Murakami, and Hirahara [1][1] reported that the amount of combined water in set cement can be determined by analyzing the NMR curve, and French and Warder [2] investigated the rate of hydration of cement by measuring the amplitude of the NMR curve. In these experiments, samples were cooled from room to liquid nitrogen temperature. The results obtained were compared with those obtained by the method of Powers [3].

Apparatus and Method

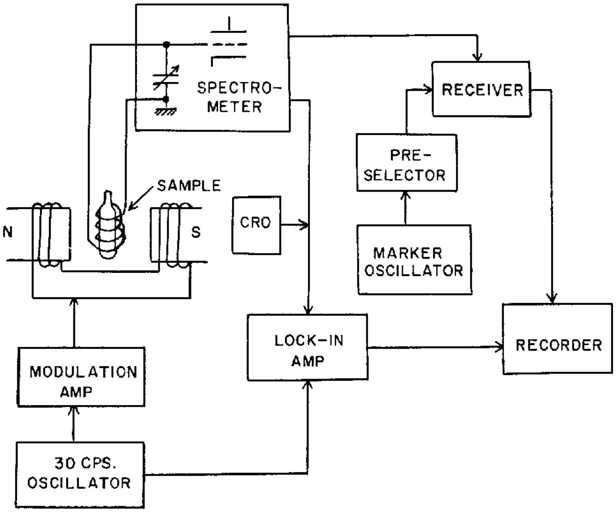

Figure 1. *Schematic diagram of NMR apparatus.*

The apparatus used consists mainly of a permanent magnet and a Pound-Watkins type spectrometer [4]. The magnetic field is about 6,500 gauss, its homogenity is 0.2 gauss/cm, and the frequency at the middle point of measurement is about 28 Mc. The schematic diagram and photograph of the apparatus are shown, figures 1 and 2, respectively.

The experiment was performed by the sweeping method of oscillation frequency. To cool the sample, liquid nitrogen was used. First, the change in the line-width of the absorption curve of water during cooling was examined. Subsequently, similar experiments were also made on cement paste and calcium silicate hydrate. Some of the results obtained have been reported previously [5].

Water

Distilled water containing a small amount of liquid extracted from cement paste was used. The line-width of the absorption curve of the water down to about −80 °C is similar to that at room temperature, but during further cooling, the line-width broadens suddenly, becoming about 11 gauss at the liquid nitrogen temperature.

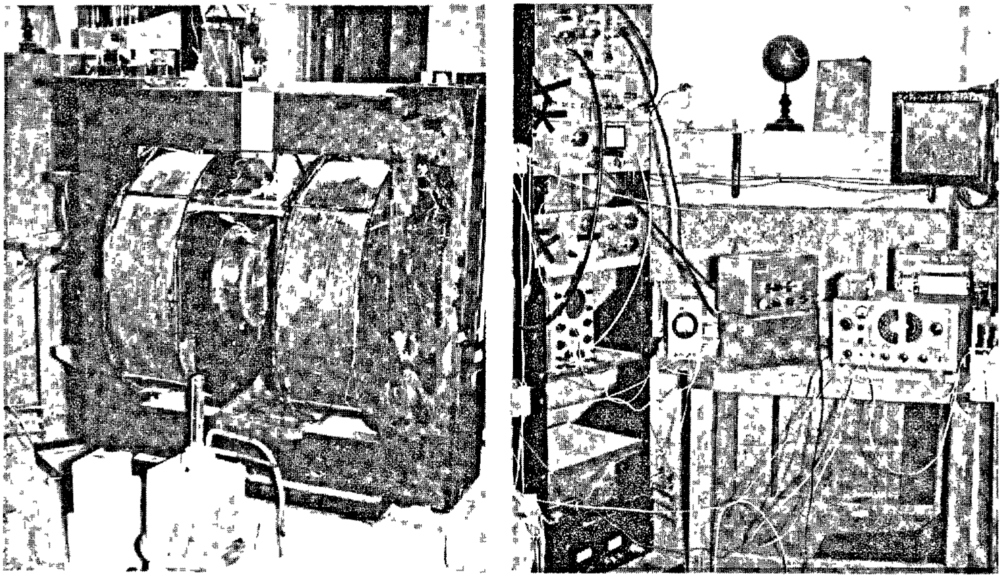

Figure 2. *NMR apparatus.*

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[1] Figures in brackets indicate the literature references at the end of this paper.

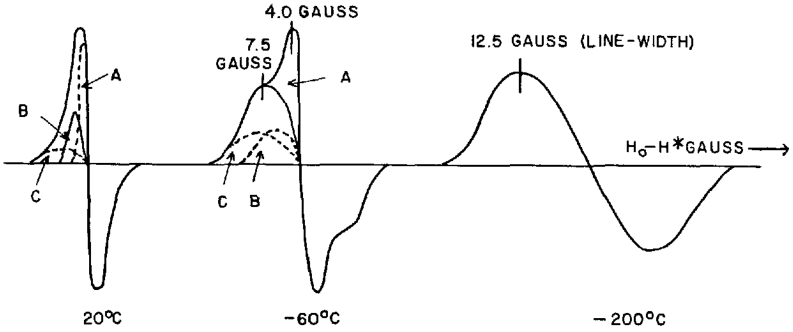

FIGURE 3. *NMR absorption curves of cement paste cured for 1 day.*

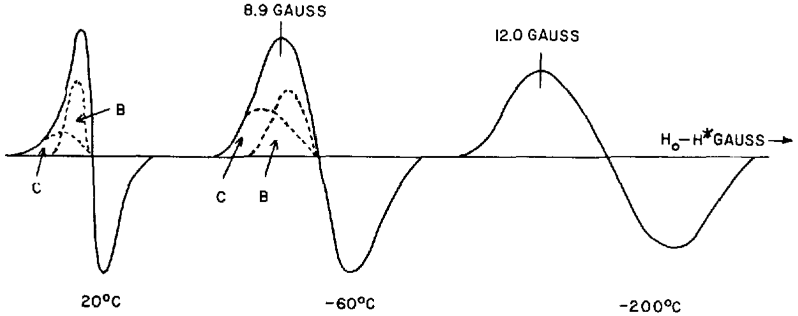

FIGURE 4. *NMR absorption curves of cement paste cured for 3 months.*

Cement

Experiments were made on cement pastes (W/C=0.40) at various curing ages. Some of the results obtained are shown in figures 3 and 4.

As shown in figure 3, the absorption curves of cement paste cured for 1 day showed a sharp curve at room temperature, and two peaks were observed during cooling. These peaks broaden during further cooling. The inner peak showed behavior corresponding to that of free water, and the outer one was similar to that of hydrate water.

In this case, the peak can be divided into three parts (A, B, and C) by the shape and line-width of the NMR curve which indicates the degree of binding of the water. The change in the line-width of each part during cooling is shown in figure 5. Parts A, B, and C of the NMR curve represent free, weakly bound, and strongly bound water, respectively, i.e., these parts correspond to free, adsorbed, and combined water, respectively.

The peak corresponding to free water decreased gradually with the increase in curing period, and in cement paste cured for 1 month only a small peak of free water was observed. In the paste cured for 2 months two peaks were observed at about −20 °C, but not at −60 °C, and this result seems to indicate that the free water has almost disappeared, i.e., the water in paste cured for more than 2 months consists mainly of adsorbed and combined water.

The amount of combined water (part C) in the pastes was determined by the integration of the area of the C part of the curve. It was found that the amount of combined water in cement paste cured for 3 days, 7 days, 1 month, and 6 months was 12.4, 15.2, 18.8, and 23.2 percent, respectively.

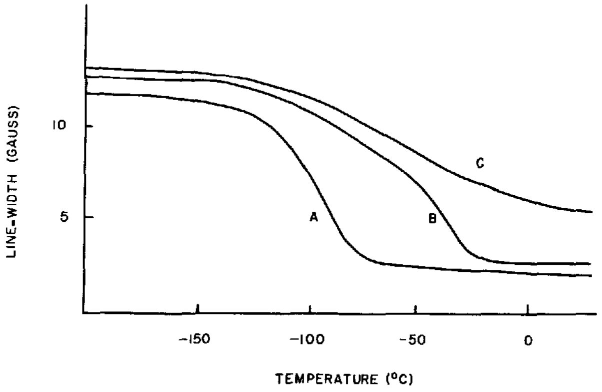

FIGURE 5. *Change in line width of parts A, B, and C of NMR curve.*

On the other hand, the amounts of combined, adsorbed, and free water obtained by the method of Powers [3] are: 3 days 9.2, 7 days 11.4, 1 month 15.9, 3 months 17.1; 3 days 6.0, 7 days 7.9, 1 month 10.2, 3 months 11.1; 3 days 22.7, 7 days 19.3, 1 month 13.2, 3 months 11.3 percent, respectively. In this case, the drying of the sample was done in an oven at 105 °C, and the value of 3 V_m was adopted as that of adsorbed water [6].

C_3S and $Ca(OH)_2$

To C_3S and $Ca(OH)_2$, 40 percent by weight of water was added, and after curing for 1 day, NMR measurements were made on these pastes. The curves obtained were similar to those of cement paste cured for 1 day, but the line width of these pastes was slightly lower than that of cement paste. This seems to be due to the fact that the proton-proton distance in cement paste is narrowed by the effect of the coexistence of other components. Furthermore, no sudden increase in the line-width of C_3S hydrate during cooling was observed. It seems that water is combined in many ways in C_3S hydrate.

Measurement of Vapor Pressure

Measurements of the water-vapor pressure of cement paste (W/C=0.40) were made. It was found that the results obtained showed a similar tendency to those obtained by NMR.

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Paper IV–S4. Rate of Hydration of Cement Compounds and Portland Cement Estimated by X-Ray Diffraction Analysis*

G. Yamaguchi, K. Takemoto, H. Uchikawa, and S. Takagi

Synopsis

The influence of gypsum on the rates of hydration of cement compounds and cement was investigated by X-ray diffraction quantitative analysis. Calibration curves were prepared from mixtures of standard $Mg(OH)_2$, cement compounds or cement, and its completely hydrated material. The probable total error for the rate of hydration was considered to be smaller than 2 percent.

From the rates of hydration of C_3S, β-C_2S, C_3A, C_4AF, and the individuals in their mixtures, determined on the pastes for the test of setting time, it was shown that the vigorous hydration of C_3A after mixing with water was depressed remarkably in the presence of gypsum and $Ca(OH)_2$ or $Ca(OH)_2$ dissolved from C_3S. The rates of hydration after 1 day decreased in the order C_3S, C_3A, C_4AF, and β-C_2S in the case of pastes mixed with 40 percent of water. The hydration of C_3S was accelerated at early ages by the addition of gypsum, but was not accelerated at later ages by its addition in large quantity.

Vigorous hydration of the tricalcium aluminate phase in cement after mixing with water was largely depressed by the addition of gypsum. The degree of hydration of the minerals in cement after 1 day decreased in the order alite, tricalcium aluminate, ferrite solid solution, and belite in the case of pastes mixed with 50 percent of water. The hydration of alite in cement after 1 day was accelerated by the addition of an optimum quantity of gypsum.

Résumé

Par analyse quantitative de la diffraction des rayons X on étudia l'influence du gypse sur les vitesses d'hydratation du ciment et des composés du ciment. Des courbes d'étalonnage étaient préparées à partir de mélanges de $Mg(OH)_2$ normal, de composés du ciment, ou de ciment, et de ses matériaux complètement hydratés. On considéra que l'erreur totale probable en ce qui concerne la vitesse d'hydratation était inférieure à 2%.

D'après les vitesses d'hydratation de C_3S, β-C_2S, C_3A, C_4AF et des composés dans ses mélanges, déterminées sur les pâtes pour l'expérience sur la durée de la prise, on put voir que la vigoureuse hydratation de C_3A après que le mélange avec l'eau a eu lieu, diminuait de façon remarquable en présence de gypse et de $Ca(OH)_2$ ou de $Ca(OH)_2$ dissous provenant de C_3S. Les vitesses d'hydratation après une journée indiquaient l'ordre de C_3S, C_3A, C_4AF, et β-C_2S dans le cas de pâtes mélangées à 40% d'eau. L'hydratation de C_3S était accélérée par l'addition de gypse, mais n'était pas accélérée plus tard par son addition en grande quantité.

L'addition de gypse diminuait grandement la vigoureuse hydratation de la phase d'aluminate tricalcique dans le ciment après le mélange avec l'eau. Le degré d'hydratation des minéraux du ciment après une journée indiquaient l'ordre suivant: alite, aluminate tricalcique, solution solide de ferrite, et belite dans le cas de pâtes mélangées à 50% d'eau. L'hydratation de l'alite dans le ciment après une journée était accélérée par addition d'une quantité optimum de gypse.

Zusammenfassung

Der Einfluß des Gipses auf die Hydratationsgeschwindigkeiten der Zementverbindungen und des Zements wurde durch quantitative Röntgenbeugungsanalyse bestimmt. Eichkurven wurden für Mischungen aus $Mg(OH)_2$, Zementverbindungen oder Zement, und auch aus vollständig hydratisierten Materialien. Der wahrscheinliche Gesamtfehler für die Hydratationsgeschwindigkeit ist vermutlich kleiner als 2%.

Aus den Hydratationsgeschwindigkeiten des C_3S, des β-C_2S, des C_3A, des C_4AF und der einzelnen Mischungsbestandteile, wie sie in den Pasten für die Abbindezeitprüfungen bestimmt wurden, wurde gefunden, daß die lebhafte Hydratisierung des C_3A nach dem Mischen mit Wasser in der Gegenwart von Gips und $Ca(OH)_2$, oder $Ca(OH)_2$ welches aus C_3S herausgelöst wurde, merklich zurückging. Die Hydratationsgeschwindigkeiten nach einem Tage können der Größe nach als die Reihe C_3S, C_3A, C_4AF, β-C_2S ausgedrückt werden, wenn die Pasten mit 40% Wasser angemacht wurden. Die Hydratation des C_3S wurde durch die Gipsbeimischung beschleunigt, aber in älteren Mischungen konnte das nicht beobachtet werden wenn viel Gips vorhanden war.

Die lebhafte Hydratation der Trikalziumaluminatphase in Zement nach der Wasserzumischung wurde durch eine Gipszugabe sehr heruntergesetzt. In den Mineralien des Zements kann nach einem Tage der Hydratationsgrad durch die Reihe: Alit, Trikalziumaluminat, feste Ferritlösung, Belit ausgedrückt werden, wenn die Pasten mit 50% Wasser angemacht worden sind. Die Alithydratation im Zement wurde nach einem Tag beschleunigt, wenn gerade der richtige Betrag Gips verwendet wurde.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Central Research Laboratory, Onoda Cement Company, Ltd., Tokyo, Japan.

Introduction

X-ray diffraction analysis as the method for measuring the rate of hydration is more effective than other methods, in that the individual unhydrated components in the hydrated sample can be estimated directly, regardless of the reaction of hydration. At the present time, however, the published data are very few, as mentioned by the authors of the principal paper.

The present authors have effectively applied X-ray diffraction analysis to clarify the influence of gypsum on the rates of hydration of cement compounds [1] [1] and the minerals in cement [2] during setting and hardening.

Method of X-ray Diffraction Analysis

The hydrated sample and the standard $Mg(OH)_2$ were carefully mixed and ground in an agate mortar in a decarbonated desiccator until their mean diameter reached 5μ so as to avoid the effects of preferred orientation of crystals and microabsorption of X-rays. The conditions of X-ray diffraction were selected after Klug and Alexander's "Time Width" [3], and the mixing ratios with standard $Mg(OH)_2$ were chosen to obtain nearly equal intensities for the sample and the standard. Calibration curves were prepared from the mixtures of standard $Mg(OH)_2$, cement compounds or cement, and its completely hydrated material which was prepared by Brunauer's method [4].

The lines for X-ray diffraction analysis were the 2.19 (319 etc.) and 1.77A(620)($\bar{6}$20) lines for C_3S [5]; the 1.89(231), 2.19(013), 2.79(1$\bar{3}$0)(1$\bar{1}$2)(200)(112), and 2.88A(102) lines for β-C_2S [6]; the 1.907(800), 2.20(444), and 2.70A(440) lines for C_3A [7]; and the 2.646(141)(200) and 1.930A (202) lines for C_4AF [8]. In the case of the 1.930A line for C_4AF the diagramatic determination was used, because its calibration curve was not linear. The lines used for cement were 1.77A for the alite phase, 2.88A for the belite phase, 2.70A for the tricalcium aluminate phase, and 2.65A for the ferrite solid-solution phase.

The intensities of the lines were counted by the Geiger-Müller tube in the range of $2\theta = 1-2°$, and reduced by the value of background near the lines. The source of X-ray was $CuK\alpha$.

The difference between the values obtained for the rate of hydration using the different lines for the same compound was below the experimental error which was obtained in the reproduction of the specimen for X-ray diffraction. The probable total error for the rate of hydration was considered to be smaller than 2 percent.

Rate of Hydration of Cement Compounds

The compounds C_3S, C_3A, and C_4AF were synthesized pure, and β-C_2S was synthesized with 1 percent of Cr_2O_3 as mineralizer.

Rate of Early Hydration

In order to investigate the relation between the rate of hydration and the setting phenomenon of a cement compound, the setting time was tested with a small specimen, and the rate of hydration of its paste was determined by X-ray diffraction analysis. Some of the results are shown in figures 1, 2, and 3.

The rate of early hydration of C_3S after mixing with water was small, regardless of the addition of gypsum, and the pastes showed normal setting.

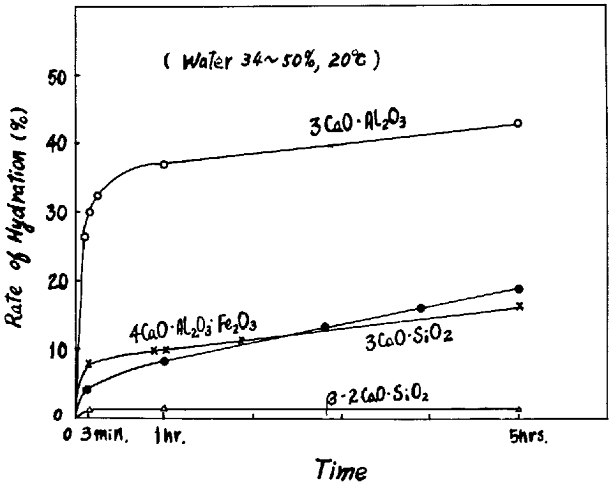

FIGURE 1. *Rate of early hydration of cement compounds.*

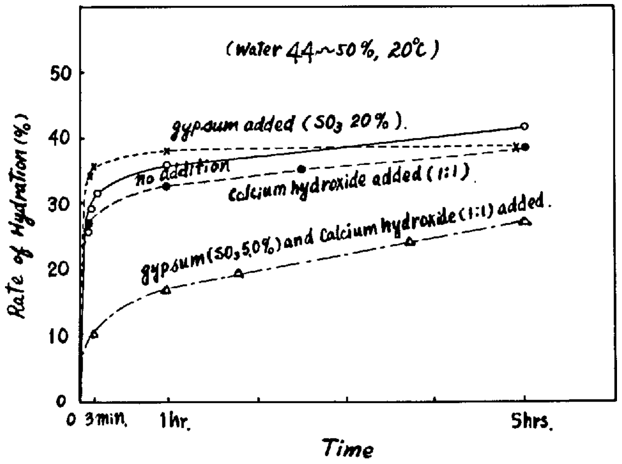

FIGURE 2. *Effects of gypsum and calcium hydroxide on rate of early hydration of C_3A.*

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[1] Figures in brackets indicate the literature references at the end of this paper.

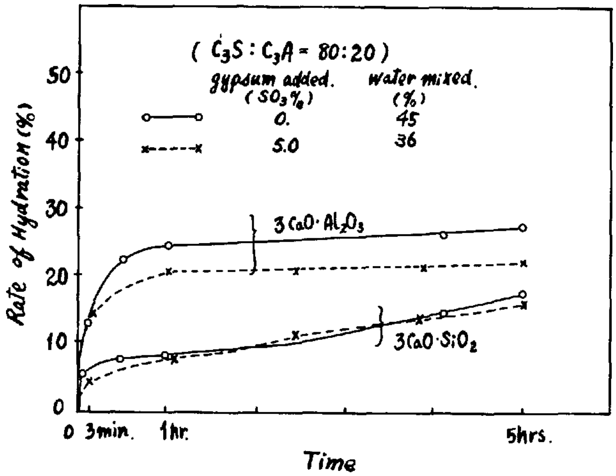

FIGURE 3. *Effects of gypsum on rate of early hydration of C_3S-C_3A mixture.*

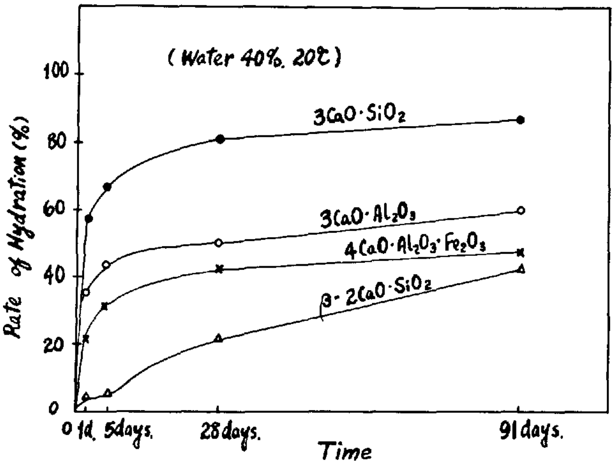

FIGURE 4. *Rate of later hydration of cement compounds.*

The rate of hydration was increased several percent by the addition of gypsum.

The rate of early hydration of C_3A was large at 3 min after mixing with water, regardless of the addition of gypsum (20 percent as SO_3), and the pastes showed flash setting. The difference between the rates of hydration of C_3A with and without gypsum was not great. This result showed that the vigorous hydration of C_3A after mixing with water was not depressed by the addition of gypsum, and that quick setting was caused by the formation not only of calcium hydroaluminate, but also of high-sulfate bacillus.

The rate of early hydration of C_4AF was not as large as that of C_3A, regardless of the addition of gypsum, and the pastes showed normal setting.

The rate of early hydration of C_3A was decreased by the addition of a large quantity of $Ca(OH)_2$, and this retardation was much more marked when both $Ca(OH)_2$ and gypsum were added.

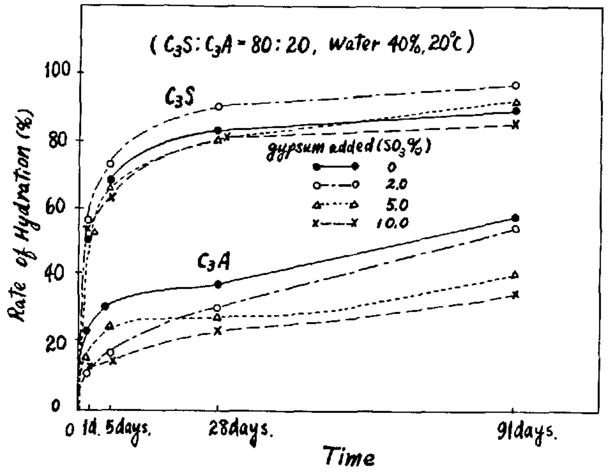

FIGURE 5. *Effect of gypsum on rate of later hydration of* C_3S-C_3A *mixture.*

In the case of the mixture of C_3S and C_3A, the rate of early hydration of C_3S was almost the same as that of C_3S alone, regardless of the addition of gypsum, but that of C_3A was smaller than that of C_3A alone, and was further reduced by the addition of gypsum. The paste without gypsum showed quick setting, and with gypsum showed normal setting.

In the case of the mixture of β-C_2S and C_3A, the rate of early hydration of β-C_2S was very small as was that of β-C_2S alone, and that of C_3A was large, as was that of C_3A alone, regardless of the addition of gypsum. The pastes with and without gypsum both showed flash setting.

In the mixture of C_4AF and C_3S or β-C_2S, the rates of hydration of these compounds were as small as those of the individual components, regardless of the addition of gypsum. The pastes with and without gypsum showed mostly normal setting.

The results above mentioned agreed with those of Forsén [9] who has reported that the rate of hydration of C_3A in a large quantity of water is decreased in saturated $Ca(OH)_2$ solution and further remarkably decreased in saturated $Ca(OH)_2$-$CaSO_4$ solution.

Rate of Later Hydration

The rates of hydration of cement compounds after 1 day were determined by X-ray diffraction analysis on pastes mixed with 40 percent of water. Some of the results are shown in figures 4 and 5.

The rates of hydration after 1 day decreased in the order C_3S, C_3A, C_4AF, and β-C_2S. Those of C_3A and C_4AF were smaller than that of C_3S, and it seemed that the completion of hydration of C_3A and C_4AF needed much more water.

Hydration of C_3S after 1 day was accelerated by the addition of gypsum, especially at the early ages. In the case of the mixture of C_3S (80 parts) and C_3A (20 parts), the addition of gypsum equal to 2 percent of SO_3 accelerated the hydration of C_3S up to 91 days, but the addition of a larger quantity of gypsum did so only at the earlier ages.

Three laboratory and two plant clinkers of various chemical compositions were examined with and without gypsum. In this review, the representative results on a laboratory clinker (G-3) low in CaO and high in Al_2O_3, and a plant clinker (K-2) of the normal composition of Type I are shown in figures 6 and 7. Their mineral compositions are shown in table 1. The values of the mineral compositions determined by X-ray diffraction analysis in table 1 were not always perfectly reliable. Therefore, at the present time, the degrees of hydration of the individual minerals in the clinker, not the rate of hydration of the whole clinker, were to be considered.

TABLE 1. *Mineral compositions of clinkers*

No.	Kind	Potential composition				Determined by X-ray diffraction analysis			
		C_3S	C_2S	C_3A	C_4AF	alite	belite	tricalcium aluminate	ferrite solid solution
		%	%	%	%	%	%	%	%
K-2	Plant clinker	49.5	30.2	8.8	9.4	48.3	31.9	12.2	8.9
G-3	Laboratory clinker	4.8	65.2	14.4	15.7	11.1	59.2	23.2	10.6

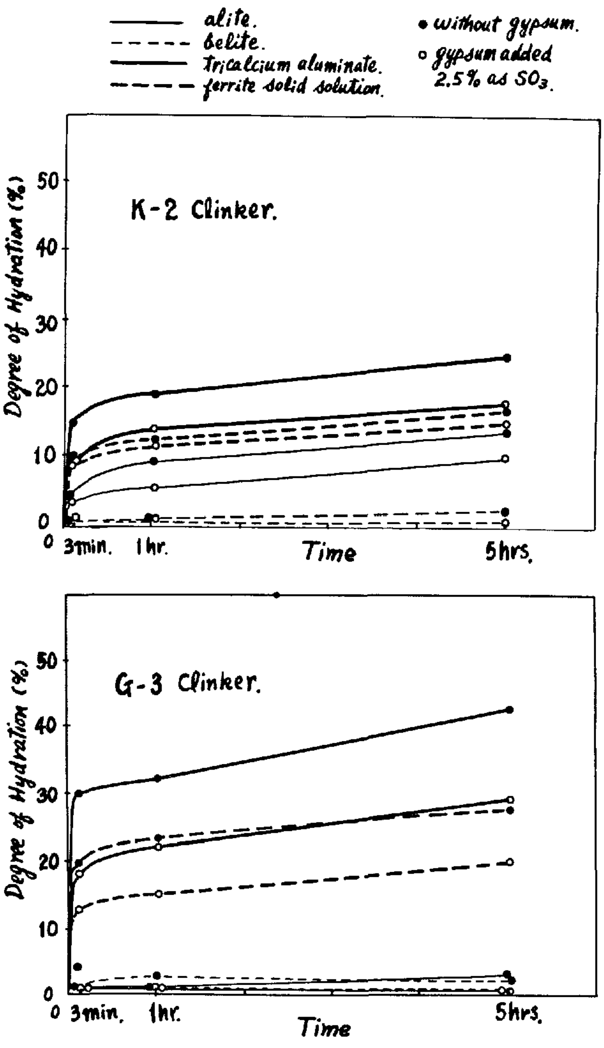

FIGURE 6. *Degree of hydration of minerals in cement during setting.*

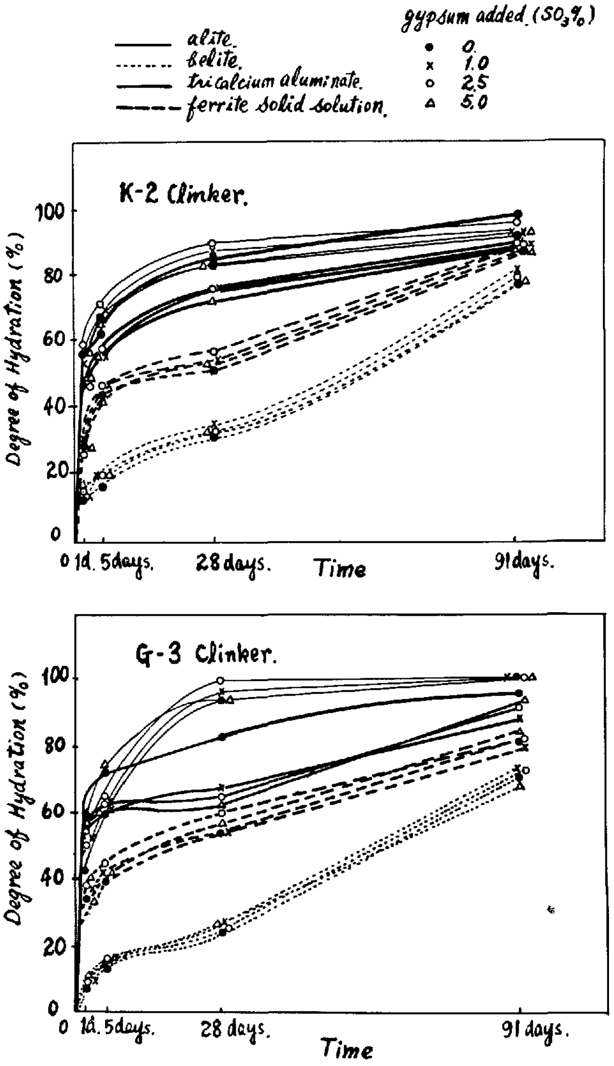

FIGURE 7. *Degree of hydration of minerals in cement during hardening.*

Degree of Hydration During Setting

The pastes for the test of setting time of cement with or without gypsum were examined by X-ray diffraction analysis.

The degree of hydration of the tricalcium aluminate phase was the greatest of the four minerals in clinker, reaching 10 to 30 percent at 3 min. after mixing with water. The largest value was shown in the flash setting of clinker G–3 (low in CaO and high in Al_2O_3) without gypsum. The degree of hydration of the tricalcium aluminate phase was decreased markedly by the addition of gypsum.

The degree of hydration of the ferrite solid-solution phase was 8 to 20 percent at 3 min. after mixing with water, and was decreased a little by the addition of gypsum. The degree of hydration of the alite phase was a few percent at 3 min. after mixing with water, and about 10 percent at 5 hr. The degree of hydration of the belite phase was negligible.

It was concluded from the above results that gypsum depressed the hydration of the tricalcium aluminate phase in cement, and that this action of gypsum needed the coexistence of $Ca(OH)_2$ dissolved from the alite phase.

Degree of Hydration During Hardening

The hardened pastes of cement mixed with 50 percent of water, with or without gypsum, were examined by X-ray diffraction analysis. The strength of the cements was tested on 1:3 cement-sand mortars; w/c=50 percent.

The degree of hydration of the alite phase was the greatest of the four minerals in clinker; it reached 40 to 70 percent in 1 day, 80 to 100 percent in 28 days. That of the tricalcium aluminate phase was next, 40 to 60 percent at 1 day, 60 to 80 percent at 28 days, and 85 to 95 percent at 91 days. It was shown that the tricalcium aluminate phase hydrated very quickly after mixing with water, but hydrated gradually at the later ages. On the other hand, the alite phase hydrated gradually after mixing with water, but had hydrated almost completely at 28 days. The degree of hydration of the ferrite solid-solution phase was 20 to 40 percent at 1 day, 50 to 70 percent at 28 days, and 80 to 85 percent at 91 days.

The degree of hydration of the tricalcium aluminate phase was much lower in cement with gypsum than in cement without gypsum.

Except for clinker G–3, low in CaO and high in Al_2O_3, i.e., low in the alite phase, cement mixed with gypsum equal to 2.5 percent of SO_3 showed the maximum degree of hydration of the alite phase and the maximum strength in four cements mixed with gypsum equal to 0, 1.0, 2.5, and 5.0 percent of SO_3. This result seemed to show that the optimum content of gypsum was preferable to develop the maximum strength by accelerating the hydration of the alite phase, although the strength development of the cement was considered to depend not only on the degree of hydration of the alite phase but also on many other factors.

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Paper IV–S5. Proton Magnetic Resonance in Hydrated Portland Cements*

R. L. Blaine

Synopsis

Exploratory studies are reported of the proton magnetic resonance line widths and peak signal amplitudes for a number of variously hydrated cements and cement compounds. The results confirm the utility of the NMR techniques in the study of such materials. They suggest that the water in the hydration products may not be present as water of crystallization, but as adsorbed water. The peak signal amplitude of cements decreased with increasing time of hydration and with removal of evaporable water. Different cements exhibited different line widths in the fresh pastes. Hydrated cements frozen in liquid nitrogen indicated greatly increased proton mobility with rising temperature.

Résumé

On présente des études exploratoires des largeurs de la ligne de résonnance magnétique du proton et des amplitudes de signal maximales pour plusieurs ciments hydratés et pour plusieurs composés de ciment hydratés tous en manières diverses. Les résultats confirment l'utilité des techniques de la résonnance magnétique nucléaire (RMN) pour l'étude de tels matériaux. Les résultats indiquent la possibilité que l'eau dans les produits d'hydratation puisse exister non pas sous forme d'eau de cristallisation, mais sous forme d'eau adsorbée. L'amplitude de signal maximale des ciments diminuait avec l'accroissement du temps d'hydratation et avec l'enlèvement d'eau évaporable. Les différents ciments présentaient dans les pâtes fraiches différents largeurs de la ligne. Les ciments hydratés congelés dans l'azote liquide indiquaient avec la croissance de la température une forte augmentation de la mobilité du proton.

Zusammenfassung

Forschungsstudien über die Linienbreiten der Energieabsorption und die Signalschwingungsweiten bei Protonresonanzfrequenz für eine Anzahl hydratisierte Zemente und Zementverbindungen sind berichtet. Die Ergebnisse bestätigen die Nützlichkeit der Technik der Protonresonanzfrequenz beim Studien solcher Materialien. Sie mögen andeuten, dass das Wasser in diesen hydratisierten Produkten nicht als Kristallwasser, aber als adsorbiertes Wasser vorhanden ist. Die Signalschwingungsweite der Zemente verminderte mit der Zunahme der Hydratationszeit und mit der Abnahme des verdampfbaren Wassers. Verschiedene Zemente haben in frischen Pasten verschiedene Linienbreiten aufgewiesen. Hydratisierte Zemente, die im flüssigen Stickstoff gefroren wurden, zeigten zunehmende Protonbeweglichkeit mit steigender Temperatur.

Introduction

The principal compounds formed in the hydration of portland and other hydraulic cements are recognized to be, in addition to calcium hydroxide, the hydrates of the calcium silicates and aluminates. These hydrates are generally assumed to be compounds formed with water of crystallization in more or less stoichiometric ratios. In addition, water in excess of that required for hydration remains within the structure as free or adsorbed water. The colloidal nature of the hydration products as well as the effect of minor constituents have made it difficult to assess the true nature of the compounds formed, and the determination of the role of water in the hydration products has been especially difficult.

Studies of adsorption of water vapor, nitrogen, and other gases have indicated to some extent the nature of the gel in the hydrated cement, and electron microscopy has indicated that plate or layerlike and lathlike hydration products are formed. Electron diffraction has indicated that these materials are crystalline although of very small size.

Powers and Brownyard [1, 2][1] have distinguished between evaporable and nonevaporable water. Drying experiments on hydrated cements have indicated that although some of the water is readily removed, some is apparently more closely bound and can only be removed after weeks of evacuation at room temperature [3]. The apparent surface area of hydrated cement as measured by water vapor increases as water is removed, whereas the surface area, as measured by nitrogen adsorbed at liquid nitrogen temperature, has a much lower value than that obtained by water vapor adsorption determination [3]. This behavior has also been found with certain other materials as diverse as montmorillonite [4] and textile fibers [5].

Many techniques have been used in the study of the nature of water in inorganic materials,

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the National Bureau of Standards, Washington, D.C.,

[1] Figures in brackets indicate the literature references at the end of this paper.

among the most recent being the use of broad-band nuclear-magnetic-resonance apparatus tuned to the proton frequency (PMR). The technique was originally developed independently by Bloch, Hansen, and Packard [6], and Purcell, Torrey, and Pound [7]. A comprehensive explanation of the principles involved has been presented by Andrews [8], Pake [9], and others.

The techniques of nuclear magnetic resonance (NMR) were applied to studies on cement by Kawachi, Murakami, and Herahara in 1955 [10]. The ratio of bound (crystal) water to free water in the cements was noted by measuring the proton resonance absorption as a function of time. The authors reported that some crystal water occurred even in the original cement powder. Comparisons were made relating quantity of bound water with mechanical properties.

In 1959, French and Warder [11] applied the NMR method to a study of the rates of hydration of cements and calcium silicates. Test of line width as a function of time after start of hydration showed an altered line width expected from hydration in only 3 of 9 cements. Other tests were made with cements and calcium silicate hydrates at liquid oxygen temperatures. It was claimed that, at this temperature, no signal was given by the frozen "free" water and that the amplitude of the signal received was a measure of the quantity of bound water. It was concluded that the hydration of calcium silicates occurred in steps with intervening latent periods. Progress in hydration was dependent on temperature, the range of 17 to 45 °C being studied.

In 1959 Pickett and Lemcoe [12] reported the results of an NMR study on clay-water systems. The value of this investigation to cement studies lay in its demonstration of the utility of radio frequency spectroscopy as an analytical tool in research on silicate-water systems. Complete quantitative data essential to the proper evaluation of such parameters as bond type and bond energy were not obtained. It was concluded, however, that measurements of the viscosity of the liquid phase under various conditions, inferences which could be drawn from the shape of the NMR derivative curve, and plots of line width versus water content should provide worthwhile contributions to an understanding of the systems under study.

Scope

The above investigations suggest the feasibility of NMR techniques for the study of cements and cement hydration products. The experience of specialists in the field of radiofrequency spectroscopy has shown, however, that results of dependable precision can be expected only from intensive investigations embodying the most exacting refinements in technique and equipment. It seems advisable, therefore, that exploratory studies be made to cover parts of the field with a qualitative rather than quantitative objective. The present investigation was initiated to contribute to that objective.

Measurements of the energy absorption at or near the proton resonance were made at room temperature of hydrated cement compounds, of cements hydrated both at normal temperature and at 38 °C, as well as of cement pastes autoclaved at 295 psi. The measurements were made after various periods of hydration of the moist samples and after drying by evacuation and after carbonation. A limited study was made of the thawing of water in a frozen sample of hydrated cement. Typical derivative absorption curves are presented as well as observed absorption line widths and peak signal amplitudes.

Apparatus

In this work a Model 104 Schlumberger Nuclear Magnetic Resonance Analyzer was used. This apparatus, which has been described by Rubin [13], is of the wide-band type and utilizes a 1720-gauss permanent magnet with a 2 in gap between the 10 in diameter pole faces. A sweep coil on the magnet varies the field by amounts up to 20 gauss. The sample, of approximate volume 1¼ in diam and 2 in height, is held in a glass test tube and inserted in a radiofrequency coil which in turn lies between the pole pieces of the magnet. The radiofrequency circuit has a fixed frequency of 7.3 Mc/s which is the precession frequency of hydrogen nuclei in the particular permanent magnetic field used. As the hydrogen nuclei shift from one of the two possible energy states to the other, under the influence of the radiofrequency energy, some of the latter is absorbed. This energy absorption is measured. If the hydrogen nuclei, or protons, are in a solid, and hence not mobile, the magnetic field experienced by a particular proton will be that of the external field modified by the fields of neighboring protons, whereas if they are in a liquid, the motion of the molecules is so rapid that the local magnetic field is smoothed out to a small average value. Different protons, depending upon the degree of binding of their neighbors, are in resonance at different values of the external magnetic field. Therefore, as the magnetic field strength is continuously varied above and below the value H_0 of the permanent magnet by the sweep coil, an absorption spectrum is obtained. The width of the line produced by protons in a liquid is essentially only that due to inhomogeneity in the permanent magnet. The width of proton resonance lines in nonliquid materials depends, among other things, on the mobility of proton-containing groups or molecules, such as H_2O. Actually, the instrument plots, within certain limitations to be mentioned later, the derivative of the absorption as a function of the external field strength in gauss.

Figure 1 shows the absorption line for a liquid containing protons and also the derivative curve as plotted by the instrument. If the width of the absorption line is defined as the width at maximum slope, the horizontal displacement between the positive and negative peaks of the derivative curve is a measure of the line width. In this paper the term "line width" refers to the distance "ΔH" as measured from the absorption curve.

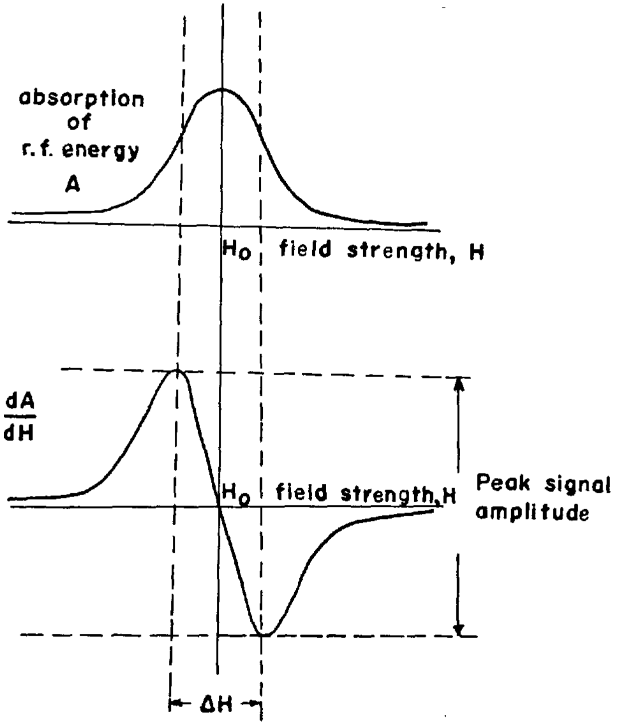

FIGURE 1. *Curves showing NMR absorption and the derivative of the absorption as a function. of external magnetic field strength for a simple material.*

The area under the absorption curve is proportional to the energy absorbed and hence to the number of protons [9]. The peak value of the derivative curve is related to this area and hence is used to furnish a rough estimate of the number of protons involved. In this paper the term "peak signal amplitude" refers to the distance "a" as measured on the absorption curve for free or relatively free water.

Figure 2 shows a possible absorption spectrum and corresponding derivative curve for a sample containing both protons in a solid and protons in a liquid. The use of the derivative curve, which is employed for the improvement of the signal-to-noise ratio, has the additional advantage of showing, through the location of the signal peaks, the approximate widths of the superimposed absorption lines.

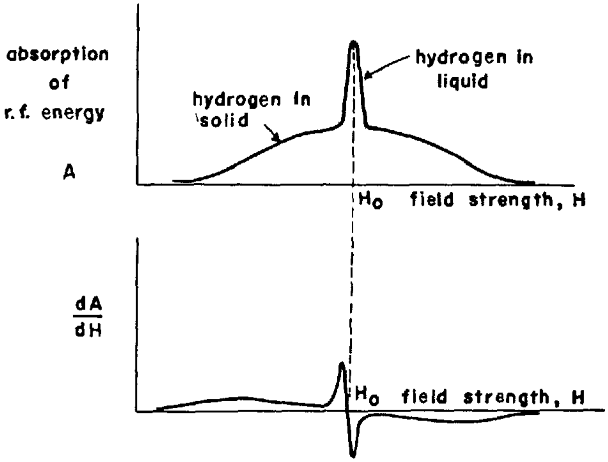

FIGURE 2. *Curves showing NMR absorption and the derivative of the absorption as a function of external magnetic field strength for a material containing hydrogen in both the solid and the liquid state.*

Materials

β-C_2S, C_3S, and C_3A were prepared by procedures similar to those discussed by Bogue [14]. β-C_2S was stabilized by addition of 0.4 percent boric acid to the starting mixture. Powder X-ray patterns were in agreement with ASTM patterns. The samples were pulverized to pass a No. 200 sieve and then allowed to hydrate for 28 days at 38 °C.

The sample of gibbsite was a commercial preparation. The boehmite sample was prepared by autoclave treatment of gibbsite at 200 °C. The hydrated alumina was prepared by heating gibbsite in air at 240 °C, whereby the water content was reduced to about 0.8 mole per mole of Al_2O_3.

The commercial cements used in this investigation were some of those previously studied [15]. These were samples of Types I, II, III, V, and a portland blast furnace slag cement. The average chemical analyses and physical tests are presented in table 1.

TABLE 1. *Chemical analyses and physical properties of cements*

Cement number	2	5	6	7	10
Type	I	II	IS	III	V
SiO_2 ....percent..	21.73	21.24	23.22	20.76	23.48
Al_2O_3 ....percent..	4.95	5.47	8.13	5.60	3.67
Fe_2O_3 ....percent..	2.88	4.76	2.58	2.50	4.44
CaO ....percent..	61.90	61.98	55.35	64.24	64.39
MgO ....percent..	3.81	2.42	3.89	1.97	0.76
SO_3 ....percent..	2.79	1.92	2.43	2.84	1.80
Loss on ignition ....percent..	0.79	1.38	2.63	1.26	0.76
Insol. residue ....percent..	0.23	0.18	0.53	0.21	0.14
Na_2O ....percent..	0.30	0.24	0.10	0.15	0.50
K_2O ....percent..	1.00	0.59	0.25	0.76	0.21
Mn_2O_3 ....percent..	--------	0.09	0.64	--------	--------
Sulfide sulfur ....percent..	--------	0.01	0.59	--------	--------
Initial set (Gillmore) ....hr..	3.45	2.66 [a]	2.97 [a]	2.85	4.76
Final set (Gillmore) ....hr..	5.48	--------	--------	4.81	7.49
Autoclave expansion ...percent..	0.13	0.03	0.04	0.02	0.03
Air entrainment ....percent..	8.5	9.8	11.8	7.0	8.8
Air-permeability fineness cm^2/g..	3442	3573	4564	4588	2949
Compressive strength 3*d*...psi..	2848	1889	2208	2675 [b]	2285
Compressive strength 7*d*...psi..	3675	2674	3645	4794 [c]	3389

[a] Vicat method. [b] 1 day. [c] 3 day.

The hydrated C_2S, C_3S, and C_3A were pulverized to pass a No. 20 sieve prior to making the measurements. The neat hydraulic-cement pastes with 0.25 or 0.50 water/cement ratios (w/c) were made into 1 × 1 × 11-in bars, stored at 23 °C, 95 percent RH, for 24 hr, and then ground to pass a No. 20 sieve. Powdered samples were used to facilitate the removal of water by evacuation in later measurements. Portions of those powders were sealed into vials and stored at 23 °C until making the measurement at 1, 3, 7, and 28 days. Other portions were stored over water in sealed containers at 38 °C for 6 weeks. Some 1 × 1 × 11-in bars were autoclaved at 295 psi steam pressure for 3 hr. Some of the autoclaved specimens were ground to pass a No. 20 sieve, whereas measurements on some of the specimens of suitable length were made without grinding.

In another series of measurements, ½ by 2-in cylinders were made of the neat cement pastes of normal consistency, cured for 28 days at 95 percent relative humidity and then stored for 3 months in closed glass containers having relative humidities of 93, 75, 53, and 33 percent maintained by concentrated salt solutions. Samples of the cylinders were also evacuated for several weeks at room temperature using a dry-ice trap in the vacuum system.

Measurement Procedures

Approximately 50-g samples of the powdered hydrates were weighed to the nearest milligram, placed in 1.35-in o.d. glass vials and compacted to a depth of about 2 in. The vials were placed in the rf coil between the magnets and a plot made of the energy absorption, traversing in 4 min a field strength 10 gauss above and below that normally required for proton resonance of uncombined water. Measurements were made of the line width and of the peak signal amplitude.

To insure a closely approximate derivative curve, the modulation amplitude employed was less than one-fifth the line width in gauss in all reported values for ΔH. However, to improve the signal-to-noise ratio a higher modulation amplitude was employed in determining the peak signal amplitude even though this entailed some sacrifice in the validity of the peak signal amplitude as a linear measure of the total absorption. Normally 3 to 5 determinations were made of the total absorption curve, the line width values, and the peak signal amplitude values on each of the samples.

In the determination of the overall absorption curve, a 20-gauss field strength was traversed, whereas, in determination of the line width of peaks near the resonance frequency, only 1 or 2 gauss were traversed in 4 min and, in determining the peak signal amplitude, 10 gauss were traversed in 30 sec.

The sensitivity selector was set at various values when peak signal amplitudes were determined, but for comparison purposes each value of peak signal amplitude reported in the paper has been corrected to the same arbitrary sensitivity.

The time constant was maintained at 1/30 of the sweep time or less, a necessary requirement for quantitative measurements with the instrument used.

The derivative absorption curves presented have been smoothed by eye to average out the "noise" effect on the signal. The relative magnitude of the noise varied widely, depending upon the sensitivity required to produce a usable signal. Under the most unfavorable conditions reported it is estimated that the signal-to-noise ratio at the peak of the derivative curve for bound water was of the order of 4 to 1, but in most cases it was larger.

Oscillator crystals with frequencies of 7,300 and 7,325 kc/s were used to determine the sweep field traversed per centimeter of recorder chart. The calibration was further verified by using a precision gaussmeter.

Measurements were made at room temperature of the moist samples both immediately after mixing and after evacuation of the samples for periods of about 2, 4, 8, 20, 40, 80, and 120 hr at room temperature. The powdered samples were spread in thin layers in beakers during evacuation. After each evacuation the samples were replaced in the vials, stoppered, and then weighed to determine moisture loss. A few hours were allowed after each evacuation to permit the samples to approach equilibrium.

The nonevaporable water (W_n) of the hydrated materials was determined by the method described by Copeland and Hayes [16] and the CO_2 content by methods described by Hunt and coworkers [17].

For one series of determinations, the moist hydrated cement powders were spread in thin layers in beakers which were placed in a large, open container. The samples were exposed to concentrated CO_2 gas for 3 weeks during the drying process. They were stirred occasionally in order to expose the powders as uniformly as possible. PMR measurements were made on the carbonated samples both before and after evacuation to remove portions of the water.

Exploratory measurements were made of the changes in energy absorption which occurred when a sample of the pulverized hydrated cement, frozen in liquid nitrogen, was permitted to warm up in a Dewar in the apparatus. At the lower temperatures, the 20-gauss field-strength interval was traversed in 2 min. After the pattern of the curve changed, as the sample became warmer, a 5-gauss field was traversed in 2 min. Alternate measurements were made of the energy absorption and the temperature of the sample which was determined by means of a copper-constantan thermocouple.

It should be pointed out, however, that the procedure employed gives no assurance that the temperature measured is precisely that of the portion of the sample actually responsible for the narrow recorded line.

Results of Measurements

1. Cement Compounds

In figure 3 are presented the derivatives of the absorption curves of C_2S, C_3S, and C_3A after hydrating for 28 days at 38 °C followed by partial drying by evacuation for 24 hr. In figure 3 as in figures 4, 5, 6, 7, and 13, H_0 represents the magnetic field strength at which resonance would occur with protons in free water.

The peak amplitude of the signals is dependent on the number of protons in the sample and the amplification used in each experiment. The curves in figure 3 were obtained using the maximum signal amplification; two of the peaks near H_0 were off scale. Using a lower signal amplification, such that the central peaks were within the range of the chart recorder, resulted in correspondingly smaller signal amplitudes in the other portions of the curves. The predominant peaks in the curves of the C_2S and C_3S hydrates indicate small line-width values. The observed line widths of the central peaks were 0.33 and 0.36 gauss respectively after evacuation for 48 hr, using the required instrument parameters. Similar unpublished absorption curves have been obtained by the author for laminar clay minerals, such as illites and montmorillonite with ΔH values ranging from 0.3 to 0.7 gauss. Samples of tobermorite and xonotlite which were evacuated and oven dried at 110 °C exhibited curves similar to that obtained from the hydrated C_2S with no evidence of any absorption other than that close to the resonance condition for free water. The ΔH values obtained for tobermorite and xonotlite after drying 36 hr at 110 °C were 0.26 and 1.2 gauss respectively. These values are, however, all significantly greater than the value of 0.016 gauss obtained using distilled water. It may be noted also that the curve for the C_3S hydrate has shoulders with a ΔH value somewhat greater than 9 gauss. These shoulders were not evident, however, with the curves obtained for the C_2S hydrate, the tobermorite or the xonotlite, indicating that some additional reaction product is present in the C_3S hydrate.

The curve for evacuated C_3A hydrate indicated a ΔH value of 13.5 gauss with little evidence of free water.

The curves obtained with gibbsite, boehmite, and $Al_2O_3 \cdot (0.8H_2O)$ are presented in figure 4. Whereas ΔH values of about 12 gauss were obtained with the gibbsite and boehmite, the ΔH value for $Al_2O_3 \cdot (0.8H_2O)$ was 6.8 gauss.

2. Hydraulic Cements

The curves obtained on hydraulic cements are much more complex and difficult to interpret. Typical curves, as obtained on cement No. 2, mixed with the amount of water required for normal consistency and hydrated for 1, 3, 7, and 28 days as well as the curve of the autoclaved cement paste, all powdered, and then dried at 110 °C for 19 hr, are presented in figure 5. It may be noted that the peaks near H_0, associated with free or absorbed water, are prominent compared to the shoulders and that the peak signal amplitude increased with length of hydration. When these sample were measured prior to drying using the same amplification the peaks near H_0 were off the scale of the recorder. The same samples, oven dried at 110 °C for 3 days, presented patterns as shown in figure 6. Indicated on this chart by the dotted line is the type of curve which may be expected with a dry hydroxide or a compound with water of crystallization. Some cements exhibited greater peaks near H_0 than others, but with the drier samples it was not possible to determine the line width of the central peaks or of the broad peaks, because of the flatness of the curves.

The effect of carbonation of a hydrated cement on the energy absorption is illustrated in figure 7. The determinations on the two samples were made using the same instrument parameters. The curves illustrated are for the No. 5 cement, w/c 0.50, which had been hydrated at 38 °C for 6

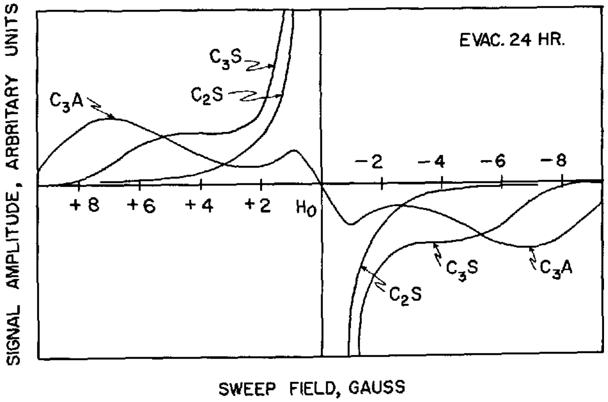

FIGURE 3. *Derivatives of energy-absorption curves obtained with hydrated dicalcium and tricalcium silicates and with tricalcium aluminate after evacuation for 24 hrs.*

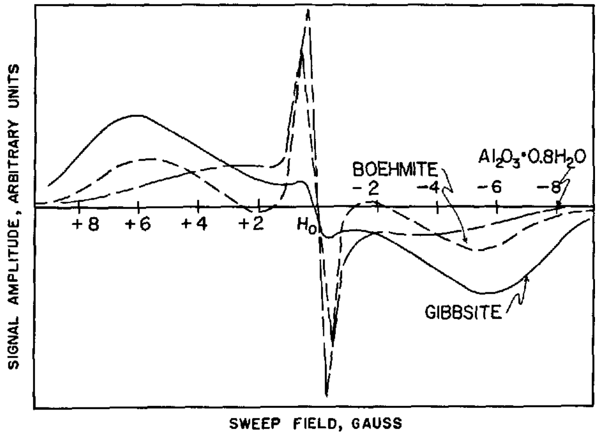

FIGURE 4. *Derivatives of energy-absorption curves obtained with gibbsite* ——, *boehmite* . . ., *and* $Al_2O_3 \cdot 0{\cdot}8H_2O$-------.

weeks. The CO_2 content of the carbonated hydrated cement was 19.7 percent. It may be noted that the energy absorption in the 6- to 16-gauss ΔH range was greatly reduced by carbonation. The decrease in signal amplitude of the shoulders of the curve may indicate the removal of $Ca(OH)_2$ from the hydrated cement. The results obtained with this cement were typical of those obtained with the other cements.

The peak signal amplitude of cement-water pastes in sealed containers decreased with time as indicated in figure 8 and presented in table 2. However, there is no apparent relation between the peak signal amplitude of the different pastes and the strength of mortars made of these cements nor with the chemical composition as presented in table 1. The results obtained on supersulfate cement appeared to correspond fairly well with those obtained on the portland and blast-furnace-slag cements, except that the line widths of the dried samples were somewhat greater than obtained with the other cements. The line width of the high-alumina cement was appreciably greater than those obtained with the portland cements and the curves of the partially dried hydrated cement exhibited very little energy absorption near the resonance condition for free water. The peak signal amplitude of moist pastes made of cements 5 and 7 with two water-cement ratios and different curing conditions (see table 2) were plotted against the nonevaporable

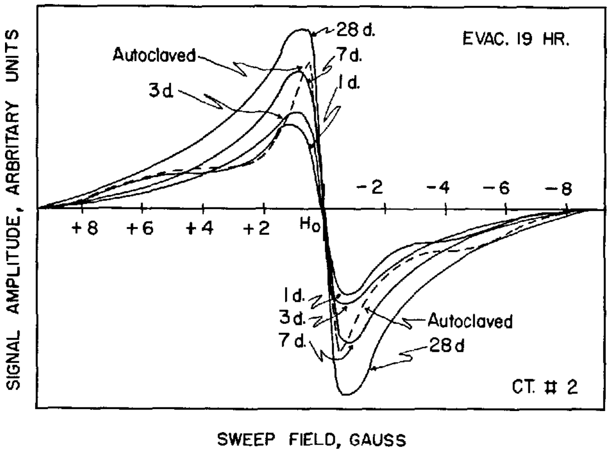

FIGURE 5 *Derivatives of energy-absorption curves of cement No. 2 hydrated for 1, 3, 7, and 28 days, and of this cement autoclaved after one day moist curing.*

All samples were dried for 19 hours at 110 °C before measurements were made.

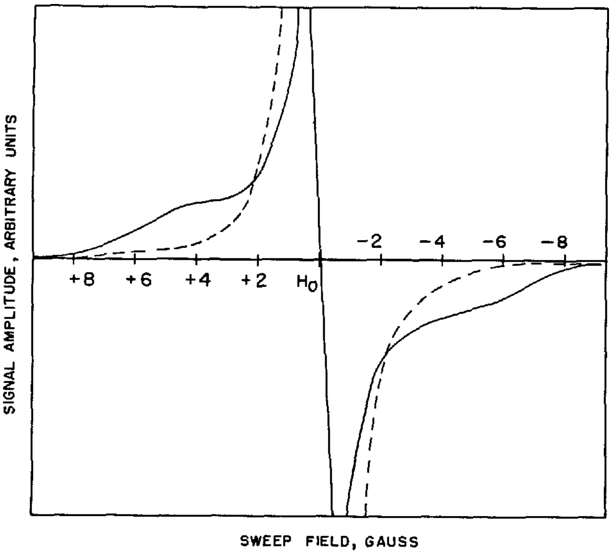

FIGURE 7. *Derivatives of energy-absorption curves of cement No. 5 hydrated at 38° C for 6 weeks and evacuated for 110 hrs at room temperature ——, and for this same hydrated cement after carbonation for 3 weeks ---------.*

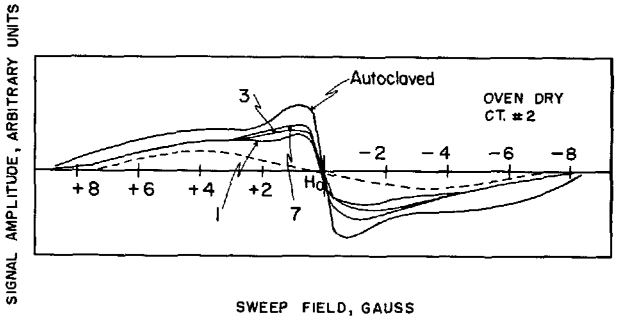

FIGURE 6. *Derivatives of energy-absorption curves of cement No. 2 hydrated for 1, 3, and 7 days, and of this cement autoclaved after one day moist curing.*

All samples were dried for 3 days at 110 °C before measurements were made.

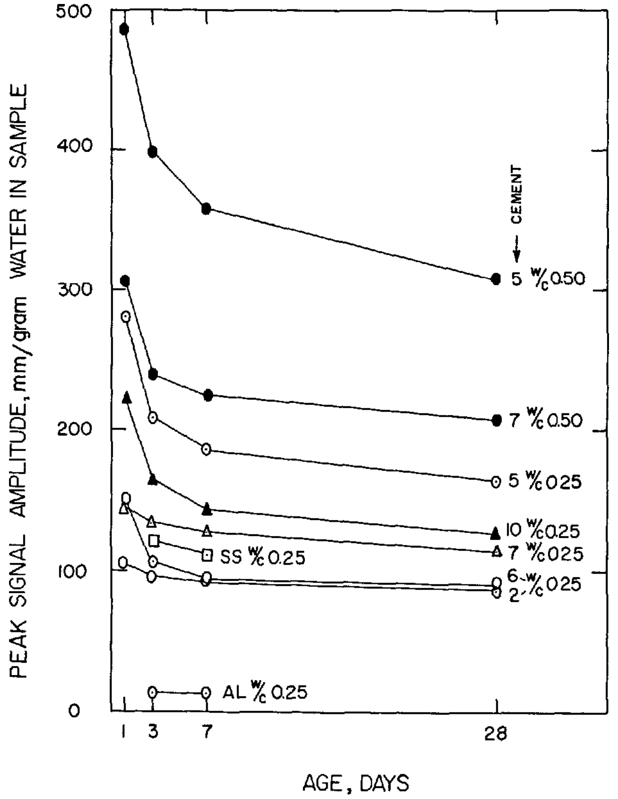

FIGURE 8. *Peak signal amplitudes of moist samples of cements hydrated at room temperature for various ages.*
ss=supersulfate cement; AL=high-alumina cement.

TABLE 2. *Nonevaporable water content, peak signal amplitude per gram of water, and line widths of moist neat cements cured for various periods and at different temperatures*

Also presented are the line widths of these cements after removal of most of the readily evaporable water

Moist samples											Dry samples [c]	
Cement number	w/c	Curing temp.	Age	CO_2	W_n	Sample weight	Cement [b]	Water [b]	Peak signal amplitude per g water	Absorption line width	Absorption line width	
		°C	*days*	%	%	*g*	*g*	*g*	*mm*	*gauss*	*gauss*	
2	0 25	23	1	-------	-------	59 1	47 3	11 8	105	1 0	1 6	8 0
	.25	23	3	-------	-------	58 0	46 4	11 6	96	0 9	1 6	7 3
	.25	23	7	-------	-------	62 6	50 1	12 5	93	1 1	1 6	6 6
	.25	23	28	0 5	9 6	63 0	50 4	12 6	87	1 0	1 6	- -
	.25	38	42	.5	13 3	50 8	39 1	11 7	114	0 85	1 5	
	.50	38	42	.5	16 5	50 0	34 2	15 8	169	.49	1.1	
	.25	(295psi) [a]	-------	-------	-------	57 2	-------	-------	-------	53	0.7	8 3
5	0 25	23	1	0 6	6 1	51 8	41 4	10 4	280	0 25	0 56	
	.25	23	3	.4	8 4	51 8	41 4	10 4	208	.27	.67	
	.25	23	7	.5	9 4	52 2	41 8	10.5	186	.29	.70	
	.25	23	28	3	11 1	52 4	41 9	10 5	164	33	76	
	.25	(295psi) [a]	-------	.4	11 8	52 3	-------	-------	-------	.24	86	4.0
	.25	38	42	.4	12 7	50 3	39 3	11 0	180	31	83	
	.50	38	42	5	16 7	44 3	30 5	13 8	235	24	.86	
	50	23	1	.5	6 8	50 2	33 5	16 7	487	.12	.47	
	50	23	3	.4	9 5	50 0	33 4	16 7	399	.14	.57	
	50	23	7	5	12 2	49 4	33 0	16 5	358	15	.56	
	.50	23	28	5	14 3	49 7	33 2	16 6	308	.19	.72	
6	0 25	23	1	3 1	4 1	51 8	41 4	10 4	150	0 66	1 3	
	25	23	3	3 0	6 4	52 0	41 6	10 4	106	.81	1 6	
	.25	23	7	3 1	7 5	52 3	41 9	10 5	92	93	1.5	
	25	23	28	2 2	9 8	52 1	41 7	10 4	90	86	1 5	
	25	(295psi) [a]	-------	2 5	10 5	51 7	-------	-------	-------	-------	1 3	
	25	38	42	3 2	11 4	50 8	39 0	11 8	99	.79	1.4	
	.50	38	42	4 0	14.1	49 9	34 0	15 9	141	.50	1 4	
7	0 25	23	1	0 6	8 9	52 7	42 2	10 6	145	0 63	1 0	
	.25	23	3	.5	10 0	52 3	41 9	10 5	135	62	1 3	
	.25	23	7	5	10 5	51 8	41 4	10 4	128	65	1 1	
	25	23	28	.4	11 9	52 4	41.9	10 5	114	.63	1 0	
	25	(295psi) [a]	-------	4	9 9	51 8	-------	-------	-------	-------	1 0	
	25	38	42	6	16 5	50 6	38 1	12 6	157	.38	0 90	
	.50	38	42	1 0	20 9	50 2	33 4	16 8	220	30	.81	
	50	23	1	0 6	10 5	49 9	33 3	16 6	305	.24	.67	
	50	23	3	.6	15 4	50 3	33 5	16 8	239	.29	68	
	.50	23	7	4	18 4	49 9	33 3	16 6	224	31	68	
	.50	23	28	.5	19 2	50 7	33 8	16 9	208	33	79	
10	0 25	23	1	0 4	5 7	51 7	41 3	10 3	221	0 42	0 87	
	.25	23	3	3	8 6	51.4	41 2	10 3	164	55	1 14	
	25	23	7	.3	9 8	51 8	41 4	10 4	142	53	1 00	
	.25	23	28	3	11 0	52 3	41 8	10 5	126	.63	0 87	
	25	(295psi) [a]	-------	.3	6 9	51 8	-------	-------	-------	-------	88	
	25	38	42	.7	12 3	50 3	39 6	10 7	159	39	90	
	.50	38	42	6	16 3	50 1	34 5	15 7	236	.24	.76	
Super sulfate	0 25	23	3	-------	5 3	52 1	41 7	10 4	120	1 18	1 95	
	25	23	7	0 5	6 0	53 3	41 9	10 7	112	1 24	2 06	
	.25	(295psi) [a]	-------	-------	8 2	50 6	-------	-------	-------	-------	1 54	
High alumina	0 25	23	3	-------	-------	52 4	41 9	10 5	13	5 8	7 3	
	.25	23	7	-------	-------	52.4	42 0	10 5	13	6 6	7 2	

[a] Autoclave steam pressure

[b] For specimens stored at 38 °C values were computed from ignition loss, others were computed from proportions as mixed

[c] Evacuated at room temperature 80 to 100 hr.

water of those pastes (table 2) after the various periods of hydration and are presented in figure 9. There appears to be a fairly straight-line relation between the peak signal amplitude and the nonevaporable water for each of the cements for each water-cement ratio used for the pastes stored at 23° C. Also it is noted that in the case of both cements the curves for the two water-cement ratios were approximately parallel, but that slopes for the two cements were different. Cement pastes made with a w/c ratio of 0.25 and cured at 38 °C for 6 weeks did not fall on the lines drawn through the corresponding values for the cements cured at 23 °C, but those with water-cement ratio of 0.50 did.

By comparing figures 5 and 6 it may be noted that removal of water from the hydrated pastes resulted in a decrease in the peak signal amplitude.

The decrease in peak signal amplitude with removal of water from the five cements hydrated at 38 °C for 6 weeks is shown in figure 10. The individually determined values are indicated only for cement 7 made with the 0.25 w/c and the 0.50 w/c. With the other cements, the determined values were also close to the straight lines drawn through them. The gram-weight of water in the samples was in each instance based on the ignited weight of the hydrated cement.

The actual amount of cement (ignited basis) in the sample vial for cement no. 7 was 38.06 g for the 0.25 w/c paste and 33.37 g for the 0.50 w/c paste. From the W_n values (nonevaporable water) determined for these pastes it was calculated that the quantities of water in the samples

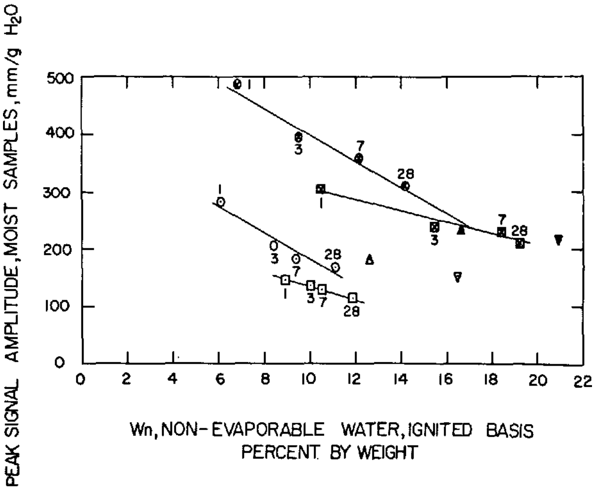

FIGURE 9. *Peak signal amplitude of moist samples of cement Nos. 5 and 7 of different water/cement ratios hydrated for 1, 3, 7, and 28 days at 25 °C and at 38 °C for 6 weeks versus the nonevaporable water content.*

Ct. 7	Ct. 5	w/c	Storage	Age, days
□	○	0.25	23 °C	as indicated
⊠	⊗	0.50	23 °C	as indicated
▽	△	0.25	38 °C	42
▼	▲	0.50	38 °C	42

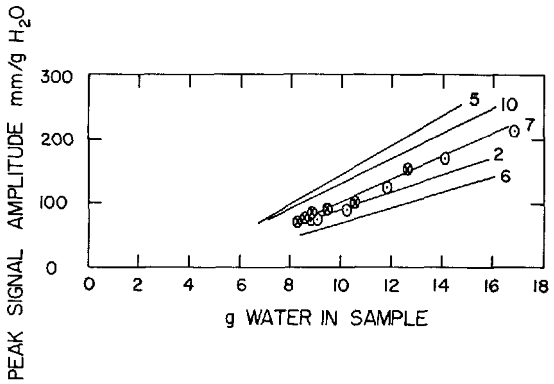

FIGURE 10. *Peak signal amplitudes of different cements hydrated at 38 °C for 6 weeks versus grams of water in sample containers after evacuation for various periods.*

The water content was computed from the ignition loss of the hydrated cements. Plotted points refer to cement No. 7; ⊙, w/c=0.50; ⊗, w/c=0.25.

at that degree of desiccation would be 6.3 and 7.0 g respectively, somewhat less than those for the lowest points on the graph. Similarly, for the other cements, the desiccation was not continued to the moisture content corresponding to the W_n values.

As the free or readily evaporable water is removed from hydrated cement, there is an absorption-line broadening as indicated in figure 11. If extrapolated to the respective W_n values of these cement hydrates the line widths would range from 1 to 2 gauss. It appears from this graph that the values for ΔH are different for different cements and for the same cements made with different water-cement ratios.

Different cements also exhibit different line-width values immediately after mixing with water as the following table indicates:

Cement No.	w/c	Line width
		gauss
2	0.50	0.7
2	.40	.7
2	.33	.8
5	.30	.1
6	.30	.6
7	.30	.3
10	.26	.2
10	.30	.2

It therefore appears that other factors or minor constituents in the solutions present may contribute greatly to the ΔH values obtained for the cement hydrates.

The ½ × 2-in neat cement cylinders cured for 28 days and then stored at different relative humidities for 3 months exhibited lower peak signal amplitude and ignition loss values the lower the relative humidity. This relationship is indicated in table 3 and illustrated in figure 12. There was in most instances no very significant change in either line width or peak signal-amplitude-per-gram-of-water value at relative humidites greater than 33 percent. However, the evacuated samples indicated larger ΔH values in every instance, than those stored at relative humidities of 33 percent or greater. It was noted that specimens stored at the 33 percent relative humidity exhibited very large peaks on the curve near the resonance condition for free water, indicating that a large number of mobile protons can be present in hydrated cement at normal atmospheric humidities. This factor may account for the continued hydration of cement and gain in strength under relatively dry conditions.

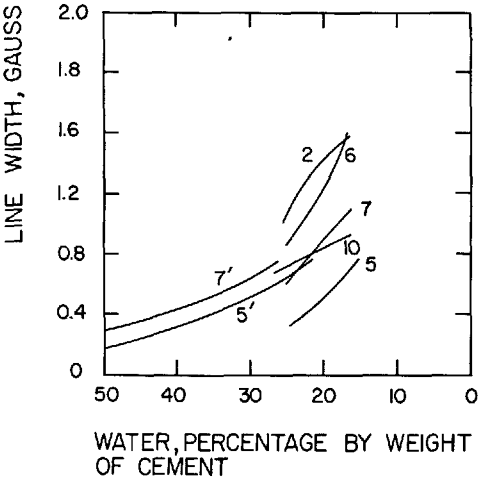

FIGURE 11. *Line widths of different cements hydrated for 28 days at 23 °C and evacuated to different moisture contents versus the water content expressed as percentage by weight of cement.*

Cement pastes were made with a w/c of 0.25 except cements 5′ and 7′ which were made with a w/c of 0.50. The cement numbers are indicated on the chart.

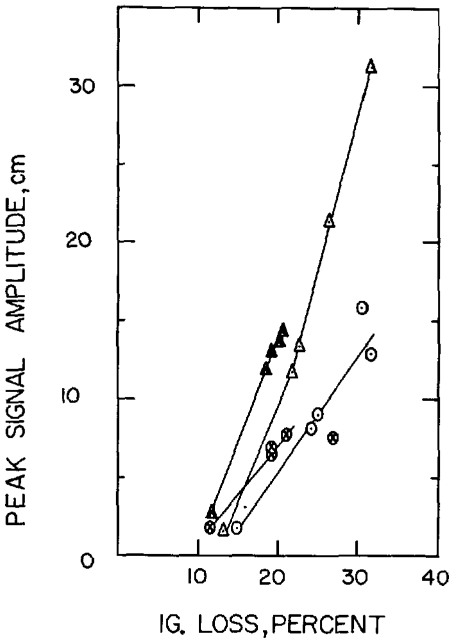

FIGURE 12. *Peak signal amplitude of cements 2 and 5 versus ignition loss of ½ × 2-in cylinders stored at various relative humidities for 3 months.*

○ Cement 2 w/c 0.50; ⊗ Cement 2 w/c 0.25; △ Cement 5 w/c 0.50; ▲ Cement 5 w/c 0.25.

The derivative curves obtained with most of the cements, hydrated in the autoclave at 295 psi steam pressure were similar to those obtained under normal curing conditions as shown in figure 5. Other autoclaved cements, such as No. 5, presented an additional pair of peaks with a line width of about 4 gauss, as shown in figure 13. Differential thermal analysis curves of these oven-dried samples are presented in figure 14. Whereas the endothermic peak at about 550 °C appears normal for most of the hydrated cements studied, the endothermic peak at 470 °C was observed on the DTA curves only on those autoclaved cements which exhibited the 4-gauss line width on PMR curves.

A hydrated cement with 0.25 w/c which was frozen in liquid nitrogen in a Dewar and permitted to thaw in the apparatus indicated a line width of 10.6 gauss up to a temperature of about −70 °C. Between −70 and −50 °C the curve changed, a second peak of approximately 1.4-gauss width appearing. The peak signal amplitude of this narrow peak increased as the temperature rose further. As mentioned earlier the temperature measured may be somewhat different from that of the portion of the sample actually responsible for the narrow line.

TABLE 3. *Peak-signal-amplitude and line-width values of ½ × 2-in neat cement cylinders after storage at different relative humidities*

Cement number	Water/cement ratio	Relative humidity	Weight of sample	Ignition loss	Peak signal amplitude	Peak signal amplitude per gram water	Line width (ΔH)
		percent	*g*	*percent*	*cm*	*cm*	*gauss*
2	0.25	93	43.0	21.2	78	8.5	1.2
	.25	75	42.7	27.6	77	6.5	1.2
	.25	53	42.0	19.4	68	8.3	1.2
	.25	33	42.0	19.4	65	8.0	1.3
	.25	0	38.5	11.5	19	4.4	1.5
5	0.25	93	42.5	20.4	137	15.8	0.40
	.25	75	42.7	20.5	143	16.3	.44
	.25	53	42.5	19.3	130	15.9	.40
	.25	33	41.6	18.6	119	15.4	.40
	.25	0	38.8	11.7	27	5.9	1.1
6	0.27	93	39.9	22.5	65	7.2	1.2
	.27	75	34.4	21.7	68	8.0	1.1
	.27	53	39.1	21.0	62	7.5	1.1
	.27	33	39.6	20.0	62	7.8	1.1
	.27	0	36.3	12.9	19	4.0	1.7
7	0.28	93	41.9	23.6	120	12.2	0.66
	.28	75	41.7	22.6	121	12.8	.62
	.28	53	40.7	21.5	108	12.4	.62
	.28	33	41.3	21.0	100	11.6	.66
	.28	0	37.6	13.6	27	5.4	1.2
2	0.50	93	35.4	30.3	157	14.6	0.75
	.50	75	35.0	31.6	127	11.5	.82
	.50	53	31.9	25.1	91	11.3	.92
	.50	33	30.1	24.3	82	11.2	.85
	.50	0	28.2	14.9	18	4.3	1.5
5	0.50	93	35.1	31.6	313	28.2	0.20
	.50	75	33.0	26.6	214	24.5	.26
	.50	53	30.9	23.0	134	15.2	.31
	.50	33	30.6	22.0	116	17.3	.31
	.50	0	27.8	13.5	20	5.2	1.2
6	0.50	93	34.8	33.6	149	12.8	0.71
	.50	75	31.4	31.6	134	13.5	.71
	.50	53	31.8	28.7	104	11.4	.81
	.50	33	31.6	27.7	98	11.2	.78
	.50	0	26.8	16.2	16	3.5	1.5

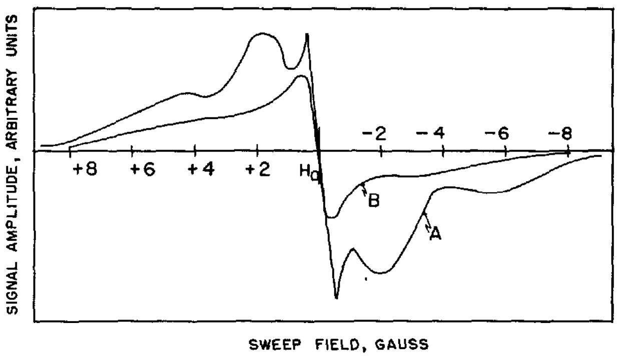

FIGURE 13. *Derivatives of energy-absorption curves of oven-dried samples of cement No. 5.*

Curve A for cement autoclaved at 295 psi for 3 hrs after 24 hrs moist curing and curve B for cement cured at 23 °C for 24 hrs.

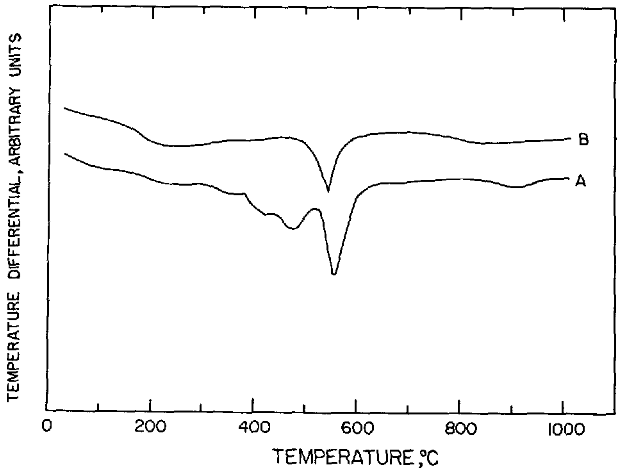

FIGURE 14. *Differential-thermal-analyses curves of oven-dried samples of cement 5, autoclaved "A" and 23 °C-cured "B" oven-dried at 110 °C.*

Summary

Exploratory studies were made at room temperature of the proton magnetic resonance line widths of hydrated cement compounds and of commercial hydraulic cements made with different water-cement ratios and hydrated at different temperatures.

The hydrated dicalcium silicate as well as tobermorite and xonotlite exhibited line widths in the range of 0.33 to 1.2 gauss with no apparent signal in the range of broad widths. Similar values for line widths have previously been obtained for laminar clays such as montmorillonite and illite. These results appear to suggest that the water in the hydration products may not be present as water of crystallization, but as adsorbed water, although further work is needed to confirm this conclusion. The predominant energy absorption of the hydrated tricalcium silicate exhibited a line width of 0.36 gauss with less absorption in the 10-gauss line-width range. The line-width values of hydrated tricalcium aluminate, gibbsite, and boehmite were in the 12- to 13-gauss range, whereas, $Al_2O_3\cdot(0.8H_2O)$ exhibited a line width of less than 7 gauss.

The curves of hydrated cements exhibited strong absorption near the resonance magnetic field associated with adsorbed water together with some absorption in the 10-gauss range. The absorption in the 10-gauss range, normally associated with water of crystallization or hydroxides, was greatly reduced by carbonation of the hydrated cement.

The peak signal amplitude of cements sealed in vials decreased with time of hydration. However, characteristic amplitudes were obtained for each cement indicating either a difference in bonding of the water to the cement particles or the effect of minor constituents. The signal amplitude of any cement mixed with water appeared to be related to the non-evaporable water content of that cement, but different cements and different water-cement ratios resulted in different curves.

The ½×2-in. specimens stored for 3 months at a relative humidity of 33 percent or higher gave curves which suggest the possibility that most of the protons present were highly mobile and were not bonded as water of crystallization.

Some autoclaved neat cement pastes exhibited curves which were different from those obtained with other autoclaved cements or from those hydrated at normal temperatures. The autoclaved cement pastes which exhibited a line width in the 4-gauss range also had an endothermic peak at about 470 °C in differential thermal analysis measurements.

A hydrated cement frozen in liquid nitrogen exhibited a line width of 10.6 gauss up to temperatures, as measured by our procedure, of about -70 °C and a line width of only 1.5 gauss when the sample attained a temperature, as similarly measured, of -50 °C.

It is not intended that the data presented shall be construed as final quantitative evaluation of parameters involving the structure or the hydrogen bonding in hydrated cements or cement compounds. It is concluded that the study confirms the utility of the NMR techniques for better understanding of these materials.

Appreciation is expressed to Dr. George L. Kalousek of Owens-Corning Fiberglass Corporation for samples of tobermorite and xonotlite, and to various members of the National Bureau of Standards including C. M. Hunt and A. Woolf for preparation of C_2S, C_3S, and C_3A hydrates and determining nonevaporable water contents;

to E. T. Carlson for samples of gibbsite, boehmite, and $Al_2O_3 \cdot 0.8H_2O$; to M. R. DeFore and E. Trattner for preparation of cement samples; to E. S. Newman for differential thermal analyses and to others who have assisted in performing the measurements.

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Paper IV–S6. Infrared Spectroscopy Studies on the Hydration of Clinker Minerals and Cements*

H. Lehmann and H. Dutz

Synopsis

The infrared spectra of the dry minerals γ-C_2S, β-C_2S, C_3S, alite, CA, $C_{12}A_7$, C_3A, one portland cement, and one aluminous cement were studied. The spectra can serve as a basis for qualitative and quantitative analysis. The substances were hydrated and examined after 1 hr, 1 day, and 7 days. Progress of hydration, fixation of water, absorption of carbon dioxide, and the nature of the hydration products are discussed.

Résumé

L'exposé étudie les spectres infra-rouges des minéraux secs γ-C_2S, β-C_2S, C_3S, alite, CA, $C_{12}A_7$, C_3A, un ciment portland et un ciment alumineux. Les spectres peuvent servir de base à des analyses qualitatives et quantitatives. Les substances étaient hydratées et examinées après une heure, un jour, et sept jours. Discussion est faite des progrès de l'hydratation, de la fixation de l'eau, de l'absorption du gaz carbonique et de la nature des produits d'hydratation.

Zusammenfassung

Die trockenen Minerale γ-C_2S, β-C_2S, C_3S, Alit, CA, $C_{12}A_7$, C_3A, ein Portlandzement und ein Tonerdeschmelzzement werden ultrarotspektroskopisch untersucht. Die Spektren können als Grundlage für die qualitative und quantitative Analyse dienen. Die Substanzen wurden hydratisiert und nach einer Stunde, einem Tag und sieben Tagen untersucht. Der Hydratationsfortschritt, die Bindung des Wassers, die Aufnahme von Kohlendioxid und die Art der gebildeten Hydratationsprodukte werden diskutiert.

Introduction

Few papers are as yet available on the use of infrared (IR) spectroscopy in cement research, In a doctoral dissertation C. M. Hunt [1][1] reported in investigations of certain silicates, aluminates, and other compounds that are of interest in portland cement chemistry. Unfortunately this work was not available to us. In joint studies, H. Lehmann and H. Dutz [2] established among other things the rate of hydration of some clinker minerals, one portland cement, one aluminous cement, and one blast-furnace slag. D. M. Roy [5] presented spectra of β- and γ-C_2S. G. L. Kalousek and R. Roy [4] studied certain minerals and indicate a possible method of determining interlayer water. H. E. Petch, N. Sheppard, and H. D. Megaw [5] used IR spectroscopy to check the accepted positions of hydrogen in afwillite.

It was the purpose of our studies to follow, in time, the reaction of clinker minerals with water. Relatively small quantities of water were used, and measurements followed within a short time.

Experimental Procedure

The clinker minerals were synthesized in the usual manner and were checked for purity by chemical and roentgenographic methods. The compositions of the cements are given in table 1.

All substances were subjected to sedimentation analysis with isopropyl alcohol, the $<2\mu$ fraction was separated, and the alcohol driven off at 120 °C. Only particles of this size group were used in the investigations, in order to insure that the absorption spectra would not be affected by light scattering. A 40-mg sample of the substance was mixed with water to produce hydration (silicates and portland cement, w/c 0.5; aluminates and aluminous cement, w/c 1.0) and stored in a tightly sealed glass tube at a room temperature of 22 °C.

Before measurement, the substances were freed from adsorbed water by heating for 15 min at 105 °C. The potassium-bromide-pellet method was used. A 0.9 mg portion of the substance (1.8 mg for portland cement) was mixed with 1 g of potassium bromide and pressed in the form of a transparent disk. This method of preparation has the advantage of being quick. For more extensive studies of hydrogen bonds (H-bridging), experiments should be repeated in a suspension medium of lesser polarity than potassium bromide.

The spectra were determined with a Leitz IR spectrograph, working in the 1–15-μ range with a NaCl prism, and in the 15–24-μ range with a KBr prism. The exact position of the bands in the 1.9–3.8-μ range was measured with a LiF prism.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from Institut für Steine und Erden der Bergakademie Clausthal, Clausthal-Zellerfeld, Germany.

[1] Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. *Composition of cements*

	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	Na_2O	K_2O	SO_3	S″	MnO	Mn_2O_3	P_2O_5	Insoluble residue	Loss on ignition
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Portland cement	17.22	8.72	2.63	--------	63.15	4.07	0.22	0.18	1.33	--------	0.35	0.30	0.21	0.54	2.20
Aluminous cement	6.87	45.45	2.45	1.44	39.30	1.04	0.46	0.25	0.30	1.04	--------	--------	--------	1.32	--------

Results and Discussion

Each substance has a characteristic IR spectrum. It can serve as a basis for qualitative and quantitative analysis and for a determination of structure. From our standpoint, the method was of advantage because it permits direct observation of the binding of water, CO_2 absorption, and changes of the structure of silicates and aluminates during hydration.

Before discussing the individual spectra, we will briefly review the fundamental principles of IR spectroscopy.

The frequency of vibration is given in cm^{-1}. The relation to the micron is given by the equation

$$\nu[cm^{-1}]=\frac{10,000}{\lambda[\mu]}$$

The frequency or position of molecular vibration is determined by the number of atoms in the vibrating structure, the mass of the atoms which form the vibrating structure, its symmetry, the bond between the atoms, and the surroundings of the vibrating structure.

In the calcium silicates, the absorption by the SiO_4 tetrahedron appears in the accessible portion of the IR spectrum. The vibrations, in which the O atoms vibrate along the lines connecting them with the central Si atom, are called valency vibrations; they lie at around 11μ. Vibrations in which the bonds undergo flexural stress are called deformation vibrations; they lie at around 19μ.

When the tetrahedra are connected into chains, layers, or lattices, the valency vibrations become displaced toward lower wavelengths, or higher wave numbers, i.e., the structure vibrates more rapidly. Deformation vibrations are displaced only slightly toward shorter wavelengths [2].

Water vapor has a deformation vibration band at 6.27μ and a valency vibration band at 2.66μ. H-bonds affect vibrations according to their strength. For this reason the deformation vibration band of water lies at 6.10μ and the valency vibration band at 2.95μ. From the magnitude of the displacement, the half width and change in intensity of the band one can draw conclusions regarding the strength of H bonds, interatomic spacings, etc.

The carbonate bands lie at 14.16, 11.40, with the strongest at 7.00μ.

γ-C_2S (figure 1)

The absorption bands between 10.0 and 12.5μ are the result of SiO_4 valency vibrations; between 17 and 22μ we find the deformation vibration bands.

Upon completion of hydration no evaporable water or carbonate could be detected in the substance. It has been known for some time that γ-C_2S has no hydraulic properties.

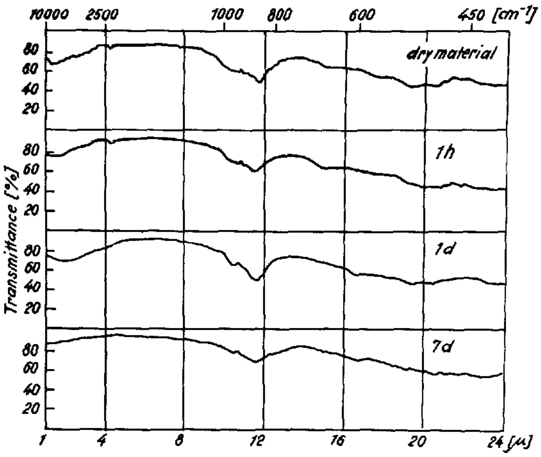

FIGURE 1. *Infrared spectra.*
Hydration of γ-C_2S.

β-C_2S (figure 2)

The spectrum of the β-modification is definitely different from that of the γ-form. Although the valency vibrations still lie in the same range, the β-modification exhibits four maxima, while the γ-form has only two; aside from this difference the band at 11.75μ is weakest in the β-modification and strongest in the γ-form.

The deformation vibrations of the β-modification lie between 18 and 20μ; those of the γ-form between 17 and 21μ.

The progress of hydration can be very satisfactorily followed by the loss of intensity in the SiO_4 valency vibration band. The intensities of the individual maxima of the valency vibration band decrease at different rates; maximum extinction at 11.75μ drops from 0.22 to 0.15; at 11.2μ

from 0.44 to 0.22; at 10.8μ from 0.48 to 0.24 and at 10.05μ from 0.48 to 0.30; on the first and last there become superimposed the absorptions of the newly formed phases, whose spectrum is better revealed in hydrated C_3S and will be discussed in that connection. Half of β-C_2S has reacted at 7 days. Increase of the nonevaporable water, read at 2.95μ, is not very significant. Carbon dioxide absorption can be followed from 6.7 to 7.0μ.

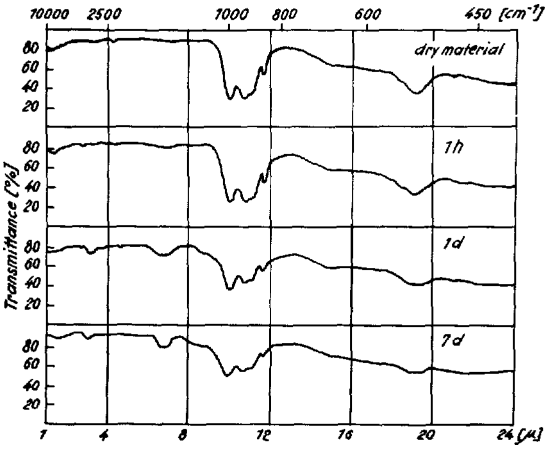

FIGURE 2. *Infrared spectra.*
Hydration of β-C_2S.

C_3S (figure 3)

The valency vibration bands of this mineral are located at lower wave numbers, or higher wavelengths, than for β-C_2S, namely between 10.0 and 12.3μ. Two deformation bands appear at 19.0μ and 22μ. The higher number of calcium ions in C_3S tends to screen the SiO_4 tetrahedra more strongly from each other, the frequencies becoming lower than in β-C_2S.

The reaction with water takes place very rapidly. At the end of 1 day practically all of the C_3S has undergone reaction. The maxima at 10.6μ and 11.2μ disappear and are replaced by a broad maximum at 10.4μ, which migrates to 10.3μ after 7 days. It is produced by the newly formed phase. From the above one may conclude that during hydration of C_3S the SiO_4 tetrahedra combine into larger structures, chains, and layers. The effect can have no other explanation, as water absorption alone during formation of hydrates causes a lowering of frequency and thus a displacement toward greater wavelengths [6]. Numerous other investigations have already shown that calcium silicate hydrates form with continuous molecule growth. The magnitude of the newly formed particles, however, can not yet have attained the order of a few microns in our case, as otherwise light scattering would have been produced at the beginning of the spectrum, i.e., absorption would have become evident. This, however, is not the case.

From the broad and flat shape of the bands of new formations it may be concluded that the molecules are of low crystallinity. This conclusion is also in agreement with the results of other studies.

The water uptake of C_3S is greater than that of β-C_2S. The band shoulder at 2.75μ indicates valency vibrations of free OH-groups, which in all probability belong to calcium hydroxide.

Carbonate formation is more pronounced than for β-C_2S.

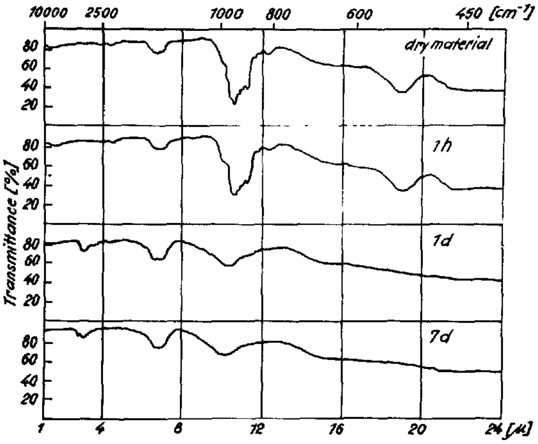

FIGURE 3. *Infrared spectra.*
Hydration of C_3S.

Alite (figure 4)

The alite spectrum is, as expected, very similar to that of C_3S. The valency vibration band is possibly less well defined, and the principal maximum lies at 10.7μ instead of 10.6μ as for C_3S. Aluminum is not present as C_3A, for its typical bands are lacking.

When alite is heated in a glazed porcelain crucible at 800 °C, two double bands appear thereafter, at 8.7–8.9μ and at 16.35–16.8μ (figure 10). These bands are typical for the substances in which an AlO_4 coordination is suspected, e.g., albite, orthoclase, sillimanite, mullite. This is not

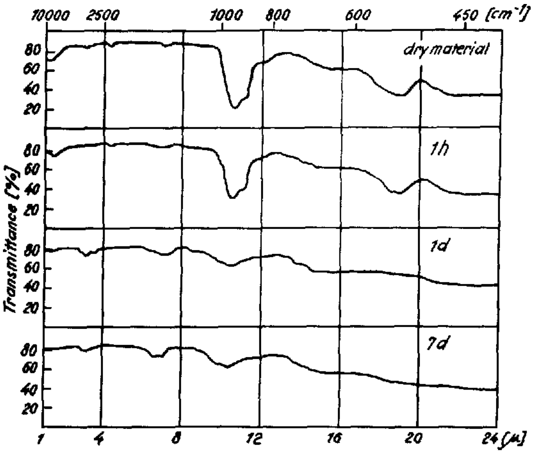

FIGURE 4. *Infrared spectra.*
Hydration of alite.

to say that the above bands actually result from AlO_4 groups. Aluminum can also cause a strengthening of the Si–O bond, which would produce vibrations at higher frequencies. These bands were also observed with portland cement and aluminous cement.

The reaction with water takes place even somewhat more rapidly than for C_3S. Here also the bands of the newly formed mineral phases are broad and flat, and lie at smaller wave lengths than for the dry mineral phase.

Portland Cement (figure 5)

The cement consists essentially of β-C_2S, which can be identified by bands at 10.1 and 11.8μ. Bands at 10.9 and 11.25μ have the same intensity in β-C_2S as that at 10.05μ. In portland cement, however, they are somewhat better revealed, an indication that alite is present, whose bands are superimposed on those of β-C_2S at 10.9 and 11.2μ. All maxima are displaced by 0.05 to 0.1μ in the direction of longer waves as compared with pure minerals. Flat absorption at 13.35 to 14.0μ is attributable to vibration of AlO_6 octahedra.

During hydration the double band at 10.9 and 11.2μ is reduced most rapidly, which points to a rapid reaction of alite. After 1 day the intensities of the three bands at 10.05, 10.85, and 11.25μ are equal; after 7 days the band at 10.05μ is more intense than the two others, as absorption of calcium silicate hydrates adds its effect.

The intensities of nonevaporable water and carbonate are considerably more marked than in hydrated alite or β-C_2S.

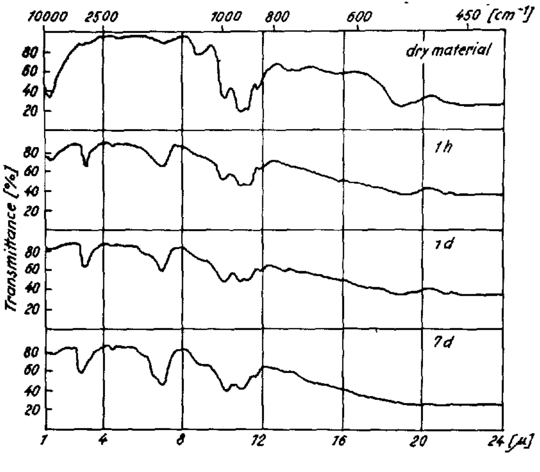

FIGURE 5. *Infrared spectra.*
Hydration of portland cement.

CA (figure 6)

The AlO valency vibrations have lower frequencies than the corresponding SiO vibrations; the deformation vibrations are both lower and higher.

In CA the vibrations have a range from 10.5 to 24.0μ; one could assume that the group from 10.0 to 13.7μ is to be regarded as valency vibrations and the rest as deformation vibrations.

Hydration proceeds quickly, so that at the end of 1 day the greater part of the mineral has undergone reaction. After 7 days one encounters a very broad absorption band, which reaches from 9.0μ to the end of the measurement range and exhibits a larger number of small maxima.

Water absorption is greater than in the silicates; the OH-valency vibration band lies somewhat higher, at 2.90μ. The effect of H bonds is smaller than in silicates; carbonate formation is weaker.

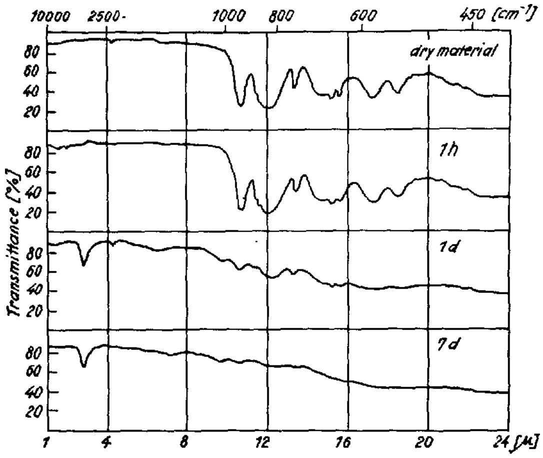

FIGURE 6. *Infrared spectra.*
Hydration of CA

$C_{12}A_7$ (figure 7)

The spectrum of this mineral differs decidedly from the preceding, the number of bands being smaller. The valency vibration band extends from 10.5 to 13.6μ and has a shoulder at 11.1μ, a very intensive maximum at 11.75μ and two smaller maxima at 12.7 and 13.4μ. At 17.25 and

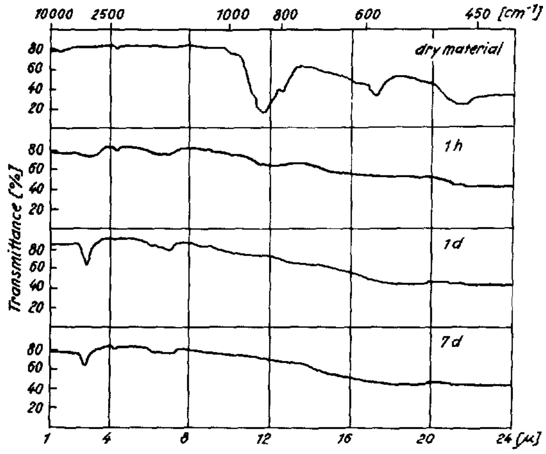

FIGURE 7. *Infrared spectra.*
Hydration of $C_{12}A_7$.

21.6μ we find maxima of two further bands which are probably attributable to deformation vibrations.

Hydration takes place at a rapid rate, so that almost the entire quantity of the mineral has undergone reaction after 1 hr. As in CA a broad absorption band is formed with a maximum at 7 days between 18.3 and 19.9μ.

Water absorption and carbonate formation are about the same as for CA.

C_3A (figure 8)

In the range of valency vibrations from 10.7 to 14.4μ we find four larger and four smaller maxima. The deformation vibration bands are relatively flat and have two maxima at 19.2 and 19.8μ; a further broad maximum begins at 21.4 μ and extends to beyond 24μ.

Hydration is faster than for any of the other minerals; after 1 hr all of the mineral has undergone reaction. A broad band with a maximum at 19.1μ makes its appearance, the peak becoming displaced at 7 days of hydration to 18.8μ, and a second one is added at 12.8μ.

After 1 hr the OH groups vibrate over a wide range. The band extends from 2.75 to 3.0μ; free as well as H-bonded OH groups are present. After 1 day the greater part of the water taken up is present as free OH groups; after 7 days the band maximum has moved to 2.74μ; and two band shoulders appear at 2.77 and 2.79μ. The broad, not very intensive maximum which extends from 2.80 to 2.94μ is attributable to water, whose H bonds are however weaker than is normal for water. Carbonate formation is slight.

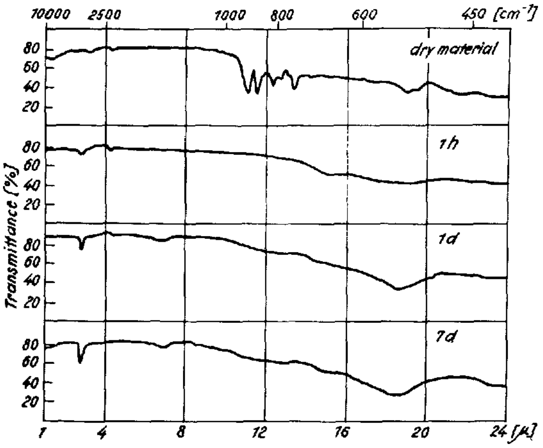

FIGURE 8. *Infrared spectra.*
Hydration of C_3A.

Aluminous Cement (figure 9)

The spectrum is closest to that of CA, although the bands at 10.8, 13.4, 17.3, and 18.5μ are lacking. The double bands at 8.75 and 8.9μ, 9.95 and 10.3μ, and 16.3 and 16.8μ do not appear in pure calcium aluminates. The first and last are typical for substances in which AlO_4 groups are suspected.

Hydration proceeds even faster than in CA, the intense maximum of the dry cement at 12μ disappearing more rapidly than the double bands at $8.75–8.9\mu$ and $9.9–10.3\mu$. Three quite flat maxima in the hydrated material from 11.6 to 12.9μ, from $17.3–19.8\mu$, and from 21.1 to 25μ are rather well covered by the absorptions of calcium aluminate hydrates forming from CA.

The water is taken up primarily as H_2O, identified by a broad band whose maximum extends from 2.84 to 2.97μ. Free OH groups scarcely occur. Carbonate formation is very small.

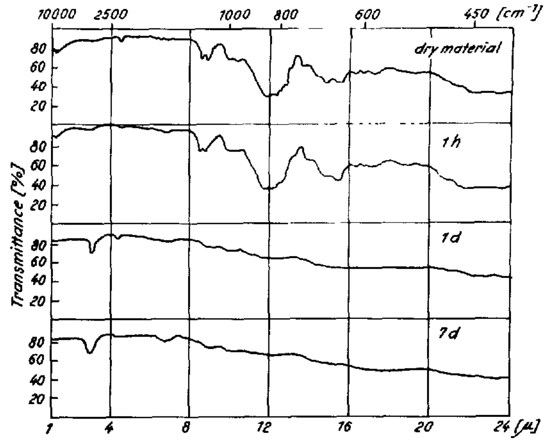

FIGURE 9. *Infrared spectra.*
Hydration of aluminous cement.

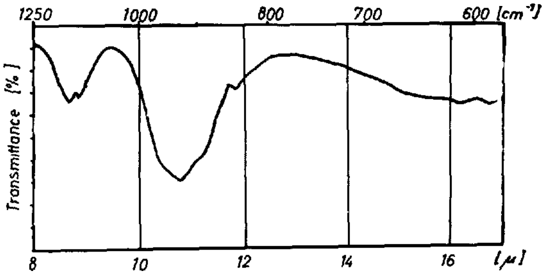

FIGURE 10. *Infrared spectrum.*
Alite, heated for 15 min in a porcelain crucible at 800 °C.

Summary

Clinker mineral phases can be identified and distinguished from one another with the aid of their characteristic IR spectra; β-C_2S can be distinguished from γ-C_2S in this manner. The spectra may be used as a basis for qualitative and quantitative analysis.

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Paper IV–S7. Heat of Hydration of Cement as Affected by Water-Cement Ratio*

Ulf Danielsson

Synopsis

The influence of the water-cement ratio on the heat evolution accompanying the chemical reactions between a portland cement and water has been investigated using a conduction calorimeter. The experiments, which have been carried out at 20 °C and with water-cement ratios ranging from 0.25 to 0.50, show for later ages the well-established direct relation between total heat of hydration per unit weight cement and water-cement ratio. For early ages, up to about 9 hr, the rate of heat of hydration was found to vary inversely with the water-cement ratio. This observed effect can be explained to some extent by temperature differences between the various pastes, both during mixing and while in the calorimeter. The results indicate, however, that in the early stages of hydration the major part of the measured change in rate of hydration with water-cement ratio is of a chemical nature. According to a hypothesis put forward in this paper, this rate dependence is attributable to the presence of alkali in the cement and is explained in terms of the alkali concentration in the fluid phase.

Résumé

L'influence du rapport eau/ciment sur l'évolution thermique concommittante aux réactions chimiques entre un ciment Portland et l'eau est étudiée à l'aide d'un calorimètre à conduction. Les expériences qui ont été effectuées à 20 °C et avec des rapports eau/ciment allant de 0,25 à 0,50 montrent, pour les phases tardives, une relation directe bien établie entre la chaleur d'hydratation totale par unité de poids de ciment et le rapport eau/ciment. Aux phases initiales, jusqu'à environ 9 heures, la rapidité du dégagement de chaleur d'hydratation s'avéra varier en sens inverse du rapport eau/ciment. Ce phénomène ayant été observé peut dans une certaine mesure être expliqué par des différences de température entre les différentes pâtes, aussi bien au cours du mélange que dans le calorimètre. Les résultats indiquent cependant qu'aux premières phases de l'hydratation la majeure partie de la variation mesurée de la rapidité d'hydratation en fonction du rapport eau/ciment est de nature chimique. Selon une hypothèse émise dans le présent compte-rendu, cette subordination de la rapidité peut être attribuée à la présence d'alcali dans le ciment et est expliquée par la concentration d'alcali dans la phase fluide.

Zusammenfassung

Der Einfluss des Wasserzementwertes auf die Wärmeentwicklung, die die chemischen Reaktionen zwischen ein Portlandzement und Wasser begleitet, wurde mittels eines Leitungskalorimeters untersucht. Die Versuche, die bei 20 °C und mit Wasserzementwerten von 0,25 bis 0,50 ausgeführt wurden, weisen ein für spätere Zeitpunkte früher festgestellte direkte Beziehung zwischen der gesamten Hydratationswärme pro Zementgewichteinheit und dem Wasserzementwert auf. Für die ersten Zeitpunkte, bis zu etwa neun Stunden, konnte festgestellt werden, dass sich die Geschwindigkeit der Hydratationswärmeabgabe umgekehrt zum Wasserzementwert ändert. Diese beobachtete Wirkung kann aber gewissermassen durch die Temperaturunterschiede zwischen den verschiedenen Massen, sowohl während der Vermischung als auch im Kalorimeter, erklärt werden. Die Ergebnisse deuten jedoch an, dass bei Beginn der Hydratation der Hauptteil der gemessenen Hydratationsgeschwindigkeitsveränderung bei Variation des Wasserzementwertes von chemischer Art ist. Laut einer in diesem Bericht vorgelegten Hypotese ist diese Geschwindigkeitsabhängigkeit auf das Vorhandensein von Alkali im Zement zurückzuführen, und sie wird durch die Alkalikonzentration der flüssigen Phase erklärt.

Introduction

At the Swedish Cement and Concrete Research Institute, Stockholm, we have carried out an investigation of the kinetics of cement hydration, which is now completed and under publication. Part of this work has been described earlier [1][1]. Another section, concerning the effect of different water-cement ratios on the heat of hydration of an ordinary portland cement, is presented briefly here in advance of publication, because the results supplement the discussion on this point in the paper, "Kinetics of the Hydration of Portland Cement" [2].

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Swedish Cement and Concrete Research Institute, Stockholm, Sweden.

[1] Figures in brackets indicate the literature references at the end of this paper.

Experimental

Materials

The cement used was a normal portland cement with the following oxide composition:

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Ignition loss
Percent	20.9	4.2	2.6	63.7	3.9	2.5	0.4	0.4	1.3

The uncombined CaO was 1.1 percent.

Using the formulae given by Bogue [3], the calculated mineralogical composition was·

Compound	C_3S	C_2S	C_3A	C_4AF	$CaSO_4$
Percent	56.7	17.2	6.7	7.9	4.3

The specific surface of the cement, determined by the Lea and Nurse air-permeability method, was 3,120 cm^2/g. The density, determined with a pycnometer filled with kerosene, was 3.12 g/cm^3.

Distilled water was used for mixing.

Mixing

The investigation comprises four experiments carried out on pure cement paste with the water-cement ratios: 0.25, 0.30, 0.40, and 0.50. The amounts of cement and water required to give each batch a volume of approximately 2.5 liters, were weighed out. Cement and water, both originally at 20 °C, were mixed together in an ordinary household mixer, in a constant-temperature room set for 20 °C. The mixing time was 10 min, and the temperature of the cement paste was taken during the mixing.

Measurements

Test tubes were filled with paste and sealed with rubber stoppers. Twenty min after mixing began, one of these test tubes was placed in a thermos flask containing water at 20 °C. Ten min later, it was transferred to a conduction calorimeter, shown in figures 1 and 2.

Due to the exothermal reactions between cement and water, the temperature of the inner calorimeter tube rose slightly above the temperature of the outer tube. This temperature difference was measured accurately by means of 30 thermocouples arranged in series, connected to a precision potentiometer. The temperature of the outer wall of the calorimeter was constant, and the calorimeter thus worked under almost isothermal conditions. To keep this outer wall at as constant a temperature as possible (for these experiments, 20 °C), which is important if reliable results are to be obtained, the calorimeter was immersed in the oil bath of an elaborate thermostat, specially designed for the purpose. Submerged in the oil bath as a sensing element was a thermistor, coupled to a Wheatstone bridge, the output of which was connected to a servo system turning a Variac. This fed heating elements in the oil bath. In this way continuous, sensitive temperature control was achieved, and the temperature in the oil bath could be kept constant to within ±0.001 °C even for long periods. A view of the whole apparatus is shown in figure 3.

The other test tubes were placed directly in the oil bath, and removed one at a time at predetermined ages, whereupon the total heat of hydration of the paste was measured, using the familiar heat-of-solution method.

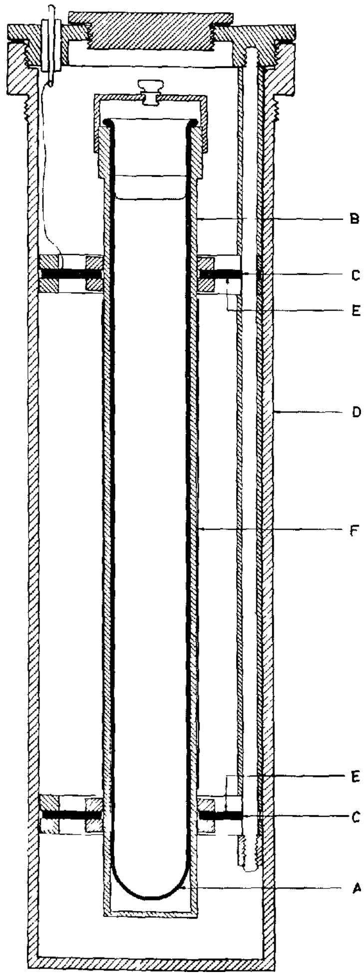

FIGURE 1. *Cross section of the conduction calorimeter.*

A: glass test tube (6 in × 5/8 in) containing cement paste undergoing testing, fitting tightly into inner calorimeter tube (B).
B: inner calorimeter tube of brass, held in central position in calorimeter by means of two rings (C).
C: two rings of bakelized paper.
D: outer calorimeter tube, kept at constant temperature in thermostat.
E: 30 thermocouples in series to measure temperature differences between inner and outer tubes.
F: heating winding for calibration.

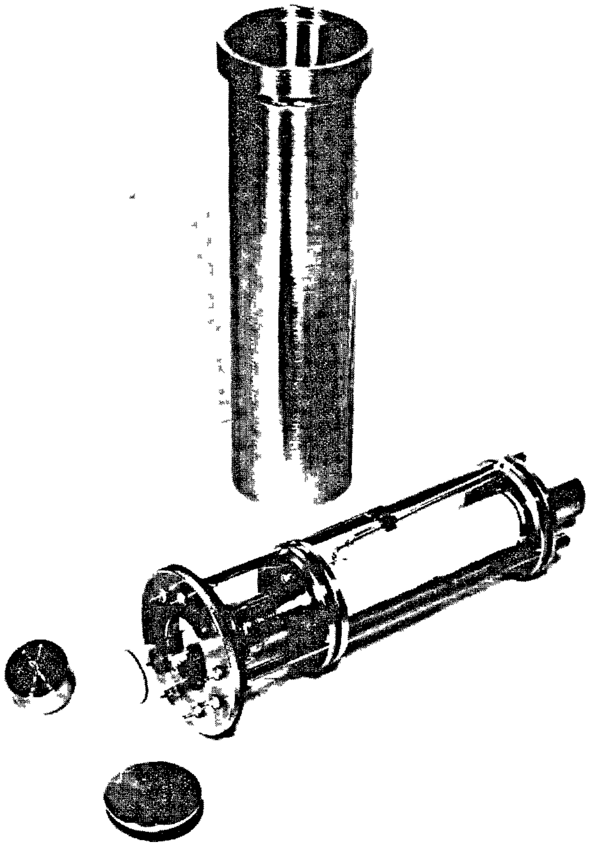

FIGURE 2. *Calorimeter.*

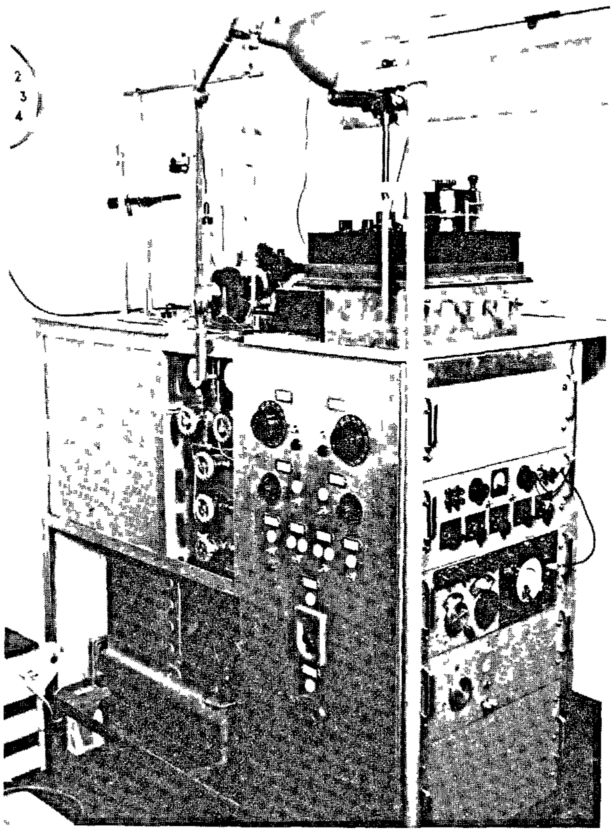

FIGURE 3. *Apparatus for measuring the rate of heat of hydration.*

Results and Discussion

The rate of heat of hydration values obtained with the conduction calorimeter are shown in figure 4, the rate per gram of ignited cement[2] being plotted as a function of time. The estimated errors in the measured rates amount to ±1 percent and ±0.1 cal/g and day, except at the beginning of an experiment, when the errors may be considerably greater due to temperature disturbances in the thermostat as the test tubes are being transferred. These additional measuring errors decrease rapidly and have vanished after 2 hr.

Figure 5 gives the total heat of hydration versus time. The total heat of hydration has been obtained by integration of the measured rates, the constant of integration being established by comparison with the results from the heat-of-solution determinations. It can be seen from this diagram that for later ages the heat of hydration varies directly with the water-cement ratio. Others have found the same, and the usual explanation is that for low water-cement ratios, after some hydration has taken place, there is insufficient water present to keep the reactions going (self-desiccation). Furthermore, when the water-cement ratio is low, the cement paste becomes so dense that the diffusion of water to, and new hydration products from, the reaction zones is difficult. The retardation of the hydration for low water-cement ratios is more clearly shown in figure 6, where the rate of heat of hydration is plotted against the total heat of hydration.

From these diagrams it may also be seen that up to an age of about 2 days, the deviations between the curves are comparatively small. However, taking the accuracy of measurements into account, it is evident from figure 4 that for early ages (that is from 2 hr at the latest, up to about 9 hr), the measured rates of heat of hydration vary inversely with the water-cement ratio. This unexpected finding agrees with the results of Taplin [4], who, in studying the amount of bound water, also found that for the pastes with the lowest water-cement ratios, the rate of hydration during the first hours was higher than for pastes with a high water-cement ratio. Copeland and

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[2] Throughout this paper all values for heat of hydration have been calculated for ignited cement

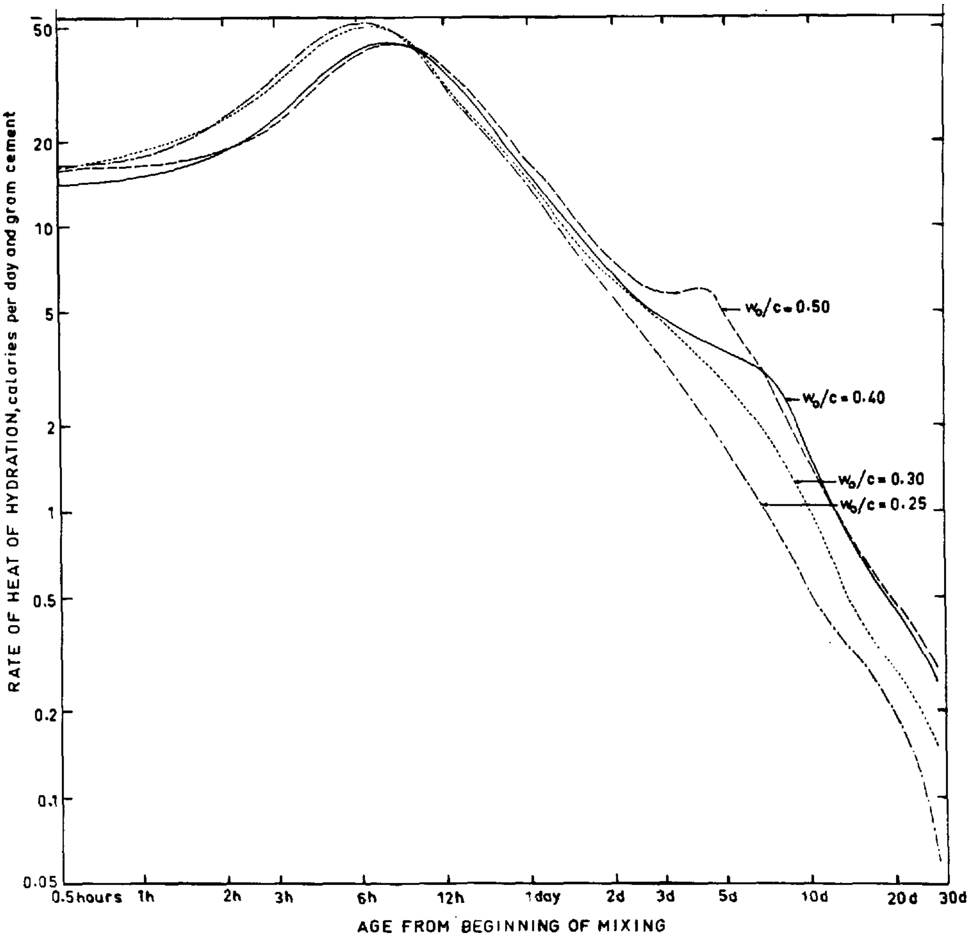

Figure 4. *Effect of water-cement ratio on the rate of heat of hydration.*

Kantro [2], when discussing the results of Taplin, have offered as the probable explanation of this result, the suggestion that the observed differences in the rate of hydration are due to the greater temperature rise above the ambient temperature for paste specimens with low water-cement ratios.

Also in the case of our investigation, there have been dissimilar rises in temperature for the different pastes, as figure 7 shows. Here, to the left in the diagram is recorded the temperature of the paste during mixing, and to the right, the calculated temperature of the inner calorimeter tube. With the X-axis at 20 °C, as in the diagram, the values for the mean temperature of the cement paste while in the calorimeter are correspondingly higher, by a factor of approximately 6 percent, calculated from the thermal conductivities of the various materials. The temperature curves between 10 and 40 min are only schematically drawn to give a rough indication of the temperature course during this interval.

The effect of temperature on the rate of heat of hydration has been studied earlier [1] for the same cement and with a water-cement ratio 0.4. These experiments show that in the early stages of hydration at a temperature of approximately 20 °C the rate increases by about 7 percent per degree centigrade. This figure is not likely to vary much with changes in the water-cement ratio. Because the temperature of the paste specimens deviates from 20 °C while they are in the calorimeter, the measured values for the rate should be corrected before being compared. From figure 7 it can be seen that these corrections reach their greatest values at an age between 7 and 9 hr. The estimated maximum correction is 9 percent for water-cement ratio 0.25, and 5 percent for water-cement ratio 0.50, which should be subtracted from the measured values. But the differences between the measured rates reach considerably higher values, as is demonstrated in figure 8, where the rates of heat of hydration relative to that for a water-cement ratio 0.40 are plotted against time for the early ages considered here. The greatest deviation in rate occurs at an age of approximately 3½ hr and is as much as 40 percent higher for water-cement ratio 0.25 than for 0.40. The correction discussed is thus far from sufficient to explain the observed differences.

When comparing the rates of heat of hydration for pastes of the same age, it is not only the temperature of the cement paste at the moment of

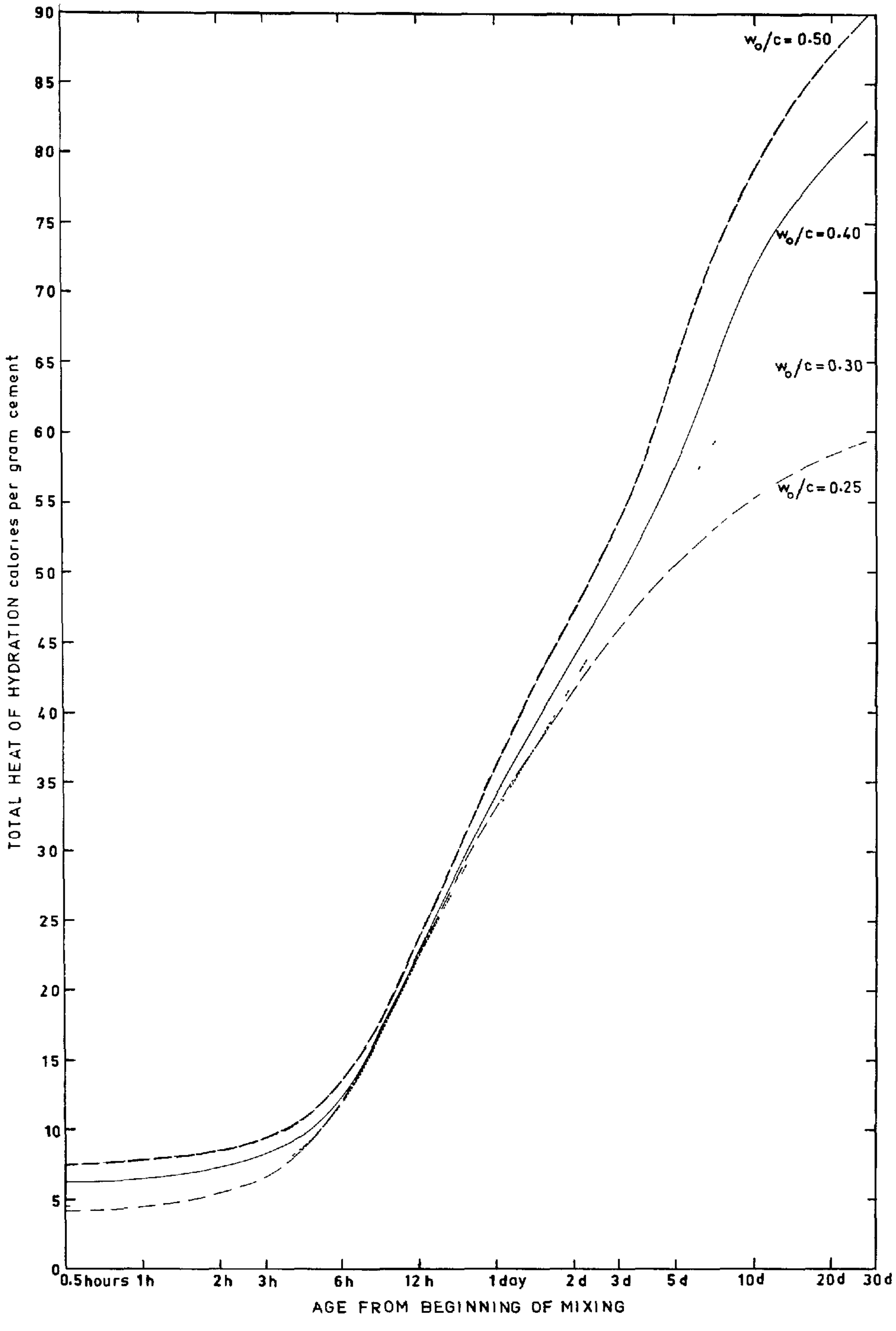

FIGURE 5. *Effect of water-cement ratio on the total heat of hydration.*

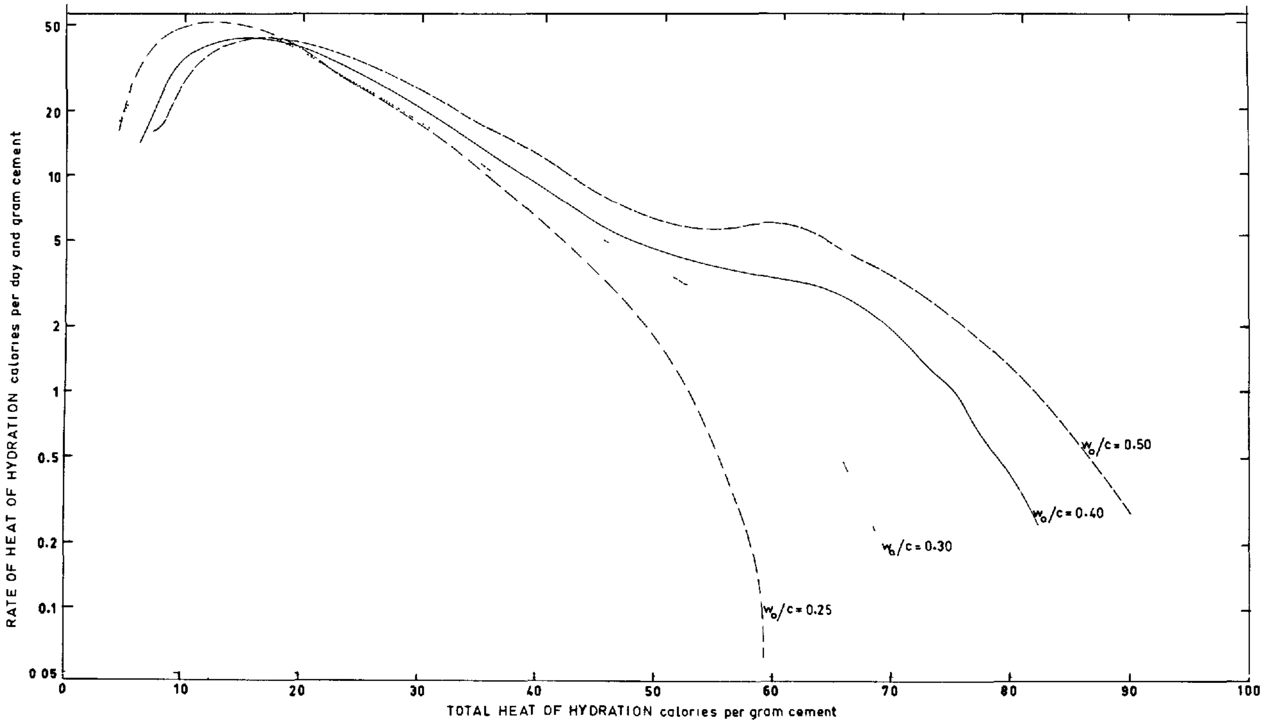

FIGURE 6. *Rate of heat of hydration plotted against the total heat of hydration for different water-cement ratios.*

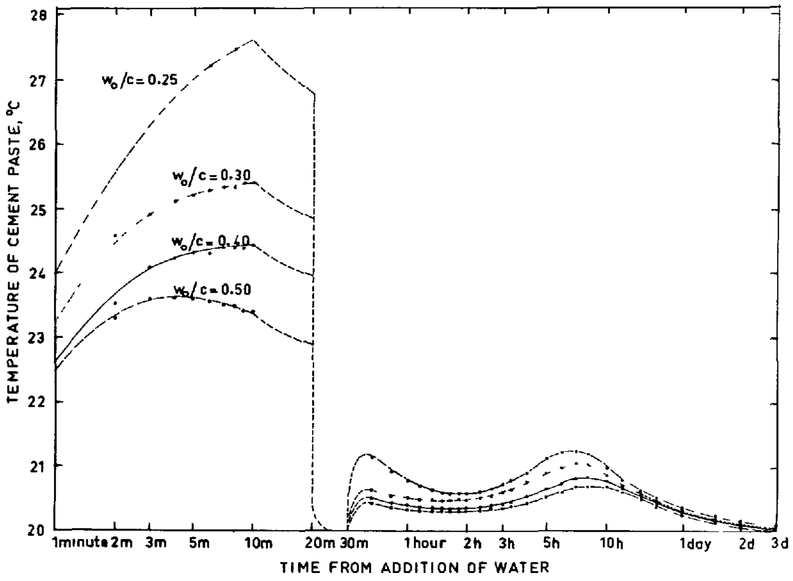

FIGURE 7. *Temperature of the pastes.*

The curves are in the same order, top to bottom, on the right side of the diagram as on the left.

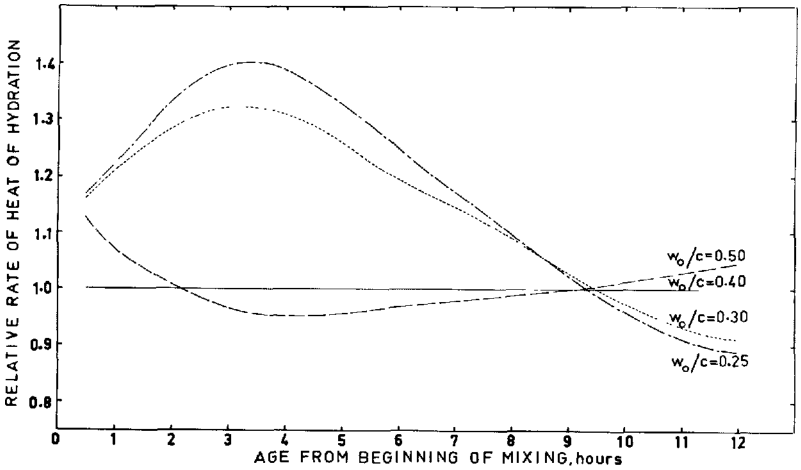

FIGURE 8. *Relative rate of heat of hydration versus time.*

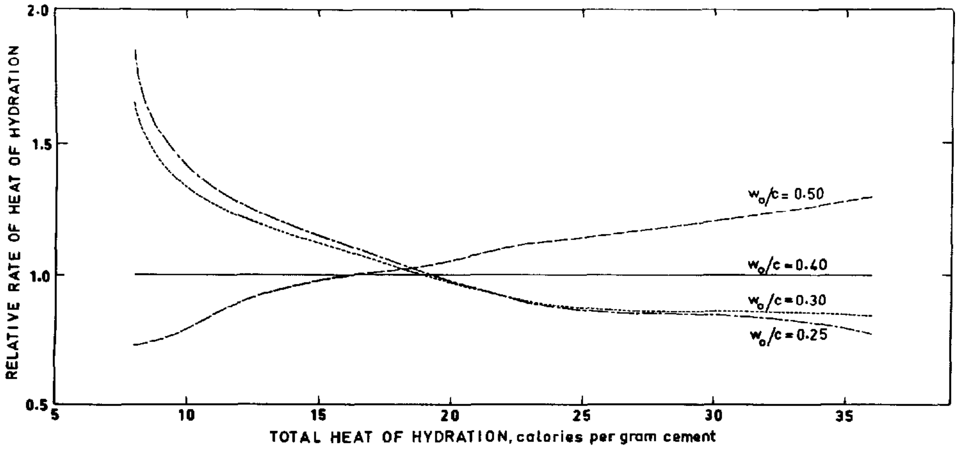

FIGURE 9. *Relative rate of heat of hydration as a function of the total heat of hydration.*

measuring that is important, but the whole temperature history up to the moment of measuring, because the pastes may have reached different degrees of hydration. This difficulty can be avoided by making the comparison when the pastes have developed the same total heat of hydration instead. From the diagram in figure 6 we have determined graphically the rates of heat of hydration for the different water-cement ratios for given values of the total heat of hydration. In figure 9 the rates of heat of hydration relative to that for water-cement ratio 0.40 are plotted against total heat of hydration. When we now compare the rates for the pastes when they have reached the same degree of hydration, the influence on the degree of hydration of the temperature differences during mixing and up to the moment of measuring has been taken care of. We see, however, that when the total heat of hydration has reached for example the value 10 cal/g of cement, which for none of the pastes is earlier than 3 hr, and the measuring errors present at the beginning have disappeared, there still remain differences which amount to more than 40 percent between pastes with water-cement ratios 0.25 and 0.40.

The temperature differences between the pastes, which are comparatively high during mixing, can also cause still other deviations in the measured rates of heat of hydration. We have found earlier [1] that the hydration products formed at different temperatures differ with regard to their influence on further reactivity. If a paste is prehydrated at 20 °C, its rate of heat of hydration measured at 1 °C may be only half that for a paste hydrated to the same degree, but kept at 1 °C all the time. Although the temperature of the paste with a water-cement ratio of 0.25 has exceeded the one for water-cement ratio 0.40 by a full 3 °C during mixing, as seen from figure 7, this can hardly explain the difference in the measured rates, which, even after the previously-mentioned corrections have been taken into account, amount to at least 35 percent.

The results indicate that the rate of heat of hydration would vary inversely with water-cement ratio during the first hours of hydration, even if the measurements could be carried out at constant temperature. Calculations have shown that an explanation based on the assumption that the cement grain boundaries have a higher temperature than the paste as a whole can be ruled out. The reason for this rate dependence must probably be sought in the chemical processes taking place.

When cement and water are brought into contact with each other, the material in the cement grain boundaries passes into solution. Most of the constituents of a portland cement are only slightly soluble in water, and the fluid phase will quickly become saturated. During the process of mixing, the concentrations of the ions these compounds form will have reached fixed values, independent of the water-cement ratio and determined by their solubilities. In the early stages of hydration, the rates of the different reactions must be influenced by the composition and concentration of the fluid phase but not by the solution-cement proportions. However, most portland cements also contain small quantities of sodium and potassium salts. As the solubility of alkalis in water is high, the alkali concentration in the solution will not reach saturation and thus will depend on the water-cement ratio of the paste.

As a hypothesis to explain the observed increase in the rate of heat of hydration with decreasing water-cement ratio during the first hours of hydration, the author suggests that it is due to the alkali salts in the cement accelerating the hydration reactions, and that this acceleration becomes stronger when their concentration in the fluid phase increases with decreasing values for the water-cement ratio.

Many alkali salts have been found to accelerate the hydration when used as admixtures. In cement the alkalis occur mainly in the form of sulfates, but besides these, small amounts of sodium may be present in the calcium aluminates, and potassium in the calcium silicates [5]. In order to verify the hypothesis, we have compared rates of heat of hydration for two prepared pastes, with the same water-cement ratio, the one made with pure water, the other with a sodium sulfate solution. The concentration of this solution was chosen as the difference between the calculated sodium sulfate concentrations one would obtain in two imaginary pastes with water-cement ratios of 0.25 and 0.40, respectively. For these pastes both the amount of potassium oxide converted to the equivalent amount in sodium oxide and of actual sodium oxide, as given in the analysis, have been assumed to exist in the form of sodium sulfate and to dissolve completely.

The experiments showed that the addition of this alkali salt accelerated the reactions during the first hours of hydration to an extent which suggests that the hypothesis can be accepted as the explanation of the dependence, at early ages, of the rate of heat of hydration upon water-cement ratio.

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Discussion

W. C. Hansen

The author suggests that increasing the alkali content of the liquid phase of a cement paste increases the rate of hydration at early ages. This seems logical on the basis that $Ca(OH)_2$ is the compound that retards the rates at which C_3A and aluminoferrites react with water and sulfate. The data by Hansen and Pressler[1] show that, as the alkali content of the liquid phase of a cement increases, the SO_3 content should increase and the CaO content should decrease. If the degree of retardation is a function of the amount of $Ca(OH)_2$ in the solution, then the rate of reaction of the aluminates should increase as the concentration of $Ca(OH)_2$ decreases or as the concentration of alkali increases.

This finding, it seems, is very significant in connection with early reactions. I pointed out in the closure to the paper on false set in portland cement pastes that aeration of a cement may decrease the rate at which the cement minerals release $Ca(OH)_2$ to the liquid phase and that this, in turn, may cause the cement to develop flash-setting tendencies. Heat of hydration studies on cements aerated under controlled conditions might furnish valuable data on the reactions that occur during the handling and storage of cement.

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Paper IV–S8. The Influence of False Setting on Some Properties of Hardening Cement Paste and Mortar*

Jerzy P. Sulikowski

Synopsis

Two normal-setting cements and one false-setting cement were investigated. Both normal-setting cements became false-setting on heating to 200 °C. Samples of the false-setting cements thus obtained were then kept in a moist chamber, whereby they again became normal setting. The third cement, false setting when obtained, became normal setting on storage in a moist atmosphere. A portion of this normal-setting sample was again changed to false setting by heating. Each of the three original samples thus was subjected to a cycle of operations, resulting in nine cement samples, five normal and four false-setting. Each of the nine samples was investigated for bleeding and initial shrinkage.

It was established quantitatively and with good reproducibility that false set, brought about artificially by heating, is connected with appreciable reduction of bleeding and increase in initial shrinkage. A reversibility of the phenomena was also established, as the artificially obtained false-setting cement after storage in moist atmosphere again becomes normal setting, and thereby again expels greater amounts of water and exhibits less initial shrinkage.

Résumé

Deux ciments à prise normale et un ciment présentant le phénomène de fausse prise sont les matériaux utilisés dans cette étude.

Les deux ciments à prise normale furent transformés en ciments à fausse prise sous l'effet de la chaleur. Ces ciments à fausse prise retrouvèrent une prise normale après séjour dans une chambre humide.

Le troisième ciment, qui présentait le phénomène de fausse prise au moment de la livraison, fut soumis à un séjour en atmosphère humide et acquit une prise normale. Une partie de ce ciment à prise normale fut de nouveau transformé en ciment à fausse prise par l'effet de la chaleur.

Ainsi chacun des trois échantillons initiaux fut soumis à un traitement cyclique et en tout ils produisirent neuf échantillons de ciment: cinq présentant une prise normale, et quatre une fausse prise.

Chacun des neuf échantillons fut examiné pour déterminer le ressuage et le retrait du début.

On établit quantitativement, et les résultats se reproduisaient bien, que la fausse prise artificiellement produite par la chaleur est liée à un décroissement visible du ressuage et à un accroissement du retrait du début.

On put également établir que les phénomènes sont réversibles, puisque les ciments à prise artificiellement rendue fausse retrouvaient une prise normale après un séjour en atmosphère humide et de nouveau remontaient de plus grandes quantités d'eau, et indiquaient un retrait du début moins grand.

Zusammenfassung

Als Untersuchungsmaterial wurden zwei normalbindende Zemente und ein falschbindender Zement benutzt.

Beide normalbindende Zemente wurden durch Erwärmen in Falschbinder umgewandelt. Die so entstandene falschbindende Zementproben wurden durch Aufbewahren in feuchtem Raum wieder normalbindend gemacht.

Der dritte, schon im Lieferzustande falschbindender Zement wurde durch Aufbewahren in feuchter Atmosphäre beruhigt, und band normal ab. Ein Teil dieser normalbindender Probe wurde durch Erwärmen wieder in Falschbinder umgewandelt.

Jede der drei Ausgangsproben wurde also einem Bearbeitungszyklus unterworfen, und infolgedessen entstanden 9 Zementproben, und zwar 5 Normalbinder, und 4 Falschbinder.

Jede der 9 Proben wurde auf Bleeding und Anfangsschwindung untersucht.

Es wurde quantitativ und mit guter Wiederholbarkeit der Resultate festgestellt, dass künstlich durch Erwärmen hervorgerufenes falsches Abbinden mit merklicher Verkleinerung der Bleeding und mit Vergrösserung von Anfangsschwindung verbunden ist.

Man hat dabei auch eine Reversibilität der Erscheinungen festgestellt, weil die künstlich erhaltene Falschbinder nach dem Aufbewahren in feuchter Atmosphäre wieder normalbindend werden und stossen dabei wieder grössere Mengen von Wasser ab, und weisen kleinere Anfangsschwindung auf.

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* Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Institute for Mining and Metallurgy, Krakow, Poland.

Introduction

The false setting of cement not only makes more difficult the mixing of concrete, its transport and placing, but probably is also the cause of some defects in buildings and constructions made of concrete. Thus for example during production of large concrete slabs, which are the basic element of highways and runways, often numerous surface cracks appear; they are 300–500 mm long and about 30 mm deep. Such cracks are usually situated parallel to each other and occur in rows over the whole surface of the slab.

It should be pointed out that such cracks appear repeatedly some hours after placing the concrete, therefore before its final setting.

The author is acquainted with a case of the appearance of such cracks on large slabs of a runway some hours after placing the concrete, although it was protected against surface drying by a cover of wet sand and plastic foil.

The cause of this phenomenon has been sought in false setting of cement, although the characteristic premature stiffening of concrete has been, seemingly, ultimately suppressed by means of more vigorous and prolonged mixing of the concrete.

The observations described allow one to assume that the calcium sulfate hemihydrate, present in false-setting cement, affects permanently and specifically the structure of the gels which are the basic constituents of the setting cement paste.

It may be assumed at the same time that the more vigorous mixing of the concrete, although it allows the suppression of the premature stiffening, characteristic of false setting, and makes possible the regaining of the initial consistency of the mixture, does not liquidate the mentioned permanent influence on the structure of the gel.

It is the structure of the gel that undoubtedly determines the properties of hardening and hardened cement, and therefore, any changes in it should in turn cause measurable changes of these properties.

The present work aims at the determination of the influence of false setting on bleeding and on the course and extent of the initial shrinkage of the hardening cement.

Materials

In the investigations three brands of portland cement, delivered by three different cement plants, were used. The characteristics of these cements are presented in table 1. The initial and final setting of these cements were in complete accordance with the standard specifications. Two of them, viz., cements *R* and *S*, do not display false setting, while the third one, cement $W_{(f)}$ is a typical false-setting one.

Cement $W_{(f)}$ contains a scant addition of granulated blast-furnace slag. Because of this in table 1 neither its moduli nor its mineralogical composition are presented.

A portion of the samples of cements *R* and *S* received from the cement plants was subjected to heating to 200 °C during 20 min; thus samples R_f and S_f, with artificially developed false setting were obtained.

Then a part of these false-setting portions of both cements was spread as a layer about 25 mm thick above a water surface in a closed chamber for a period of 24 hr at a temperature about 20 °C.

TABLE 1. *Characteristics of cements*

	Cement *R*	Cement *S*	Cement $W_{(f)}$
Loss on ign.	1.85	2.60	2.74
SiO_2	23.40	21.76	24.20
Fe_2O_3	2.13	3.35	2.50
Al_2O_3	4.33	6.05	6.78
CaO	64.88	62.00	59.20
MgO	1.12	2.02	2.27
SO_3	2.44	1.92	2.26
Insoluble	0.43	0.42	0.38
Hydraulic modulus	2.16	1.96	----------
SiO_2/R_2O_3	3.62	2.31	----------
Al_2O_3/Fe_2O_3	2.03	1.80	----------
C_3S	46.93	35.94	----------
C_2S	31.76	35.34	----------
C_3A	7.87	10.36	----------
C_4AF	6.47	10.18	----------
$CaSO_4$	4.14	3.26	----------

The cements thus treated lost the false setting acquired by heating, and came back to their initial setting behavior without any disturbances. These cements were designated *R′* and *S′*.

TABLE 2. *Origin and preparation of cement samples*

Symbol of sample	Origin or preparation	Setting characteristics
R	Cement plant *R*	Normal setting.
R_f	Heating of cement *R*	False setting.
R′	Humidifying of R_f	Normal setting.
S	Cement plant *S*	Normal setting.
S_f	Heating of cement *S*	False setting.
S′	Humidifying of S_f	Normal setting.
$W_{(f)}$	Cement plant *W*	False setting.
W′	Humidifying of $W_{(f)}$	Normal setting.
W_f	Heating of cement *W′*	False setting.

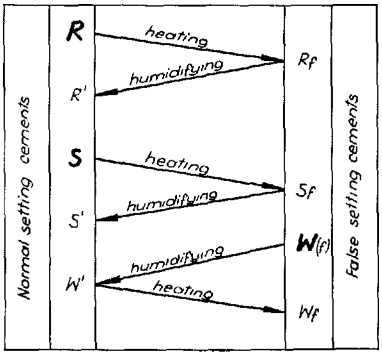

FIGURE 1. *Scheme of sample preparation.*

(Cement samples as received from plants are designated by bold-face letters.)

Cement $W(_f)$ which, as mentioned above, displayed false setting on delivery from the cementworks, was treated in the same manner, though in different order. A part of that cement was subjected for a 24-hr period to the action of atmospheric moisture, thus making it lose its natural property of false setting.

The sample thus obtained was marked as cement W'. A part of it was heated for 20 min at 200 °C, thus acquiring again the property of false setting (cement W_f).

As the result of the above described treatment, from three kinds of cement of different origin, nine samples were obtained. Their symbols, characteristics, and origin or means of preparation are presented in table 2.

In the scheme presented in figure 1 the means of preparation of the samples from the initial three cements, marked by bold-face letters, are given.

Apparatus and Procedure

The cement samples, prepared in the manner described above, were investigated for bleeding. In addition the course and extent of the initial shrinkage of the cement paste were determined.

False Setting

For the detection of false setting a method, the principle of which is based on ASTM C359–56 T, was used. Previous investigations [1][1] have shown the applicability of this method and the good agreement of results obtained by its use.

Bleeding

For the determination of the rate and capacity of bleeding the method and apparatus recommended by ASTM C243–58 T, were used. This method also affords concordant results, as has been found during previous studies.

Initial Shrinkage

The study of the influence of false setting on the shrinkage of cement paste and mortar has been the subject of previous papers [2]. These have dealt, however, with shrinkage after 3, 7, and 28 days, and have shown that the false setting considerably increases the shrinkage of the hardened cement paste and mortar after 28 days.

The investigations described in this paper have been limited to observations of the course of shrinkage during the initial stage of setting, before the final hardening of the cement. Observations have been carried out only during 480 min from the moment of the preparation of the cement paste.

The shrinkage was measured using an ordinary microscope by means of a method proposed by Lefèvre [4]. The cement paste was placed in a mold made of zinc sheet 1 mm thick. The shape and size of the mold are presented in figure 2. The mold rested on a glass plate and the area along which the mold touched the plate was sealed with molten paraffin. The inner walls of the mold and the area of the plate within them were greased with machine oil.

The mold thus prepared was filled with cement paste. On its surface, smoothed with a knife, at a distance of 90 mm from the diagonal, closing wall of the mold, a fragment of steel plate, suitable for microscopic observations, was placed.

The device was put on the stage of the microscope provided with an eyepiece calibrated previously by means of a stage micrometer with a section 1 mm long, divided into 100 parts. Observations were carried out at 80 times magnification and the length of one division of the eyepiece scale corresponded to 10.7μ. The temperature of the surroundings fluctuated from 18 to 20 °C and the relative humidity from 50 to 60 percent.

The sample was placed on the microscope stage so that the metal mark made on the surface of the paste was covered by the first mark of the eyepiece scale. The translocations of the mark in the field of vision were noted each 15 min.

The unpublished preliminary investigations resulted in finding that the measurements of the initial shrinkage made by means of the above-described method are in very good agreement, provided of course that the temperature and humidity of the surroundings are kept constant.

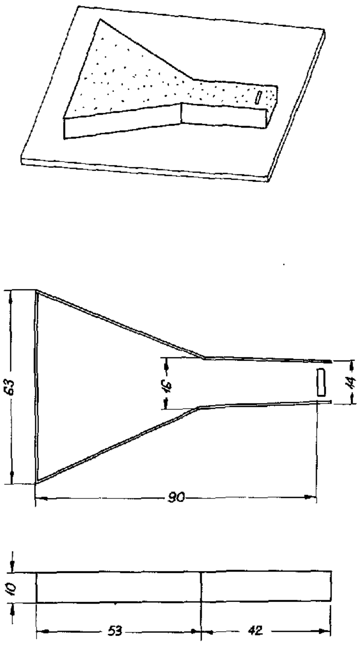

FIGURE 2. *Mold used in preparation of specimens for measurement of shrinkage.*

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[1] Figures in brackets indicate the literature references at the end of this paper.

Results

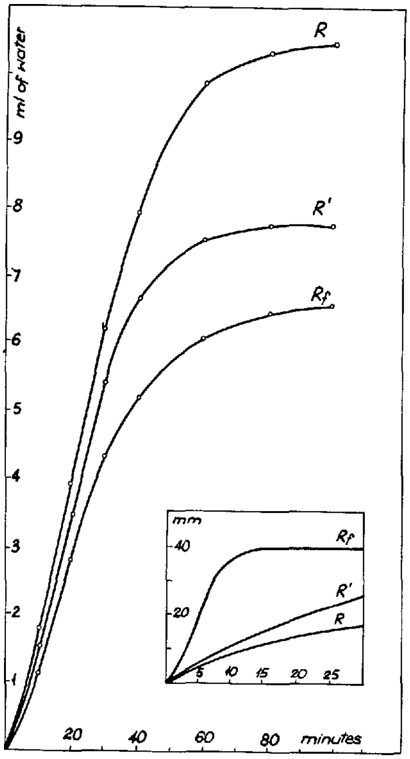

Figure 3. *Amount of bleeding exhibited by samples* R, R_f, *and* R′.
Inset shows penetration in test for false setting.

Since, as had been mentioned in the previous section, the results obtained by means of the methods used are in good agreement, the present paper does not contain tabular representation of numerical values; these are represented graphically only.

The course of bleeding is illustrated by curves in figures 3, 4, and 5. Each of these curves is the mean of six parallel measurements, the results of which differed from the arithmetical mean value by not more than ±7 percent.

In these figures there are auxiliary plots in which each curve is the result of three parallel measurements of false setting.

In table 3 are presented, for each of the nine cements, numerical values of the rate and capacity of bleeding. These values are calculated from the arithmetical mean value of six parallel measurements made for each of the nine cements.

Table 3. *Bleeding rate and capacity*

Cement	Bleeding rate cm³/cm²/sec	Bleeding capacity cm³/cm³
R	0.0000761	0.0228
R_f	.0000524	.0142
R′	.0000658	.0166
S	.0000597	.0176
S_f	.0000546	.0152
S′	.0000628	.0183
$W_{(f)}$	.0000595	.0170
W′	.0000737	.0202
W_f	.0000374	.0115

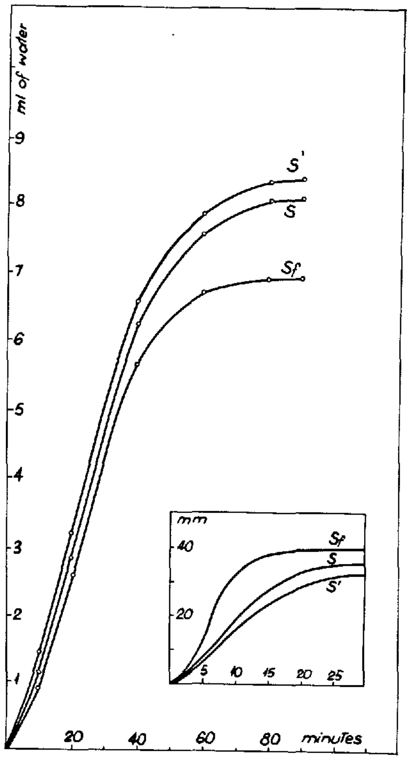

Figure 4. *Amount of bleeding exhibited by samples* S, S_f, *and* S′.
Inset shows penetration in test for false setting.

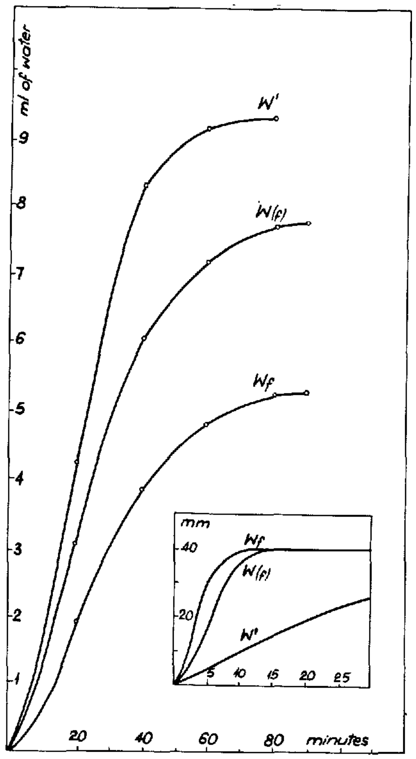

Figure 5. *Amount of bleeding exhibited by samples* $W_{(f)}$, W′, *and* W_f.
Inset shows penetration in test for false setting.

The courses of the initial shrinkage of the setting paste are presented in figures 6, 7, and 8. Each of these curves is the mean of six parallel measurements, the results of which differed from the arithmetical mean value by not more than ±5 percent.

Bleeding

The results presented above confirm the assumption put forward in one of our earlier papers [4] that the occurrence of false set is connected with the decrease of the rate and capacity of bleeding.

The investigations described in this paper have allowed in addition to find a reverse phenomenon, viz, that the loss of the natural or artificially acquired property of false setting of cement is connected with the increase of the rate and capacity of bleeding.

This regularity was found during the study of cements subjected to the closed cycle of operations illustrated graphically in figure 1. The course of bleeding was altered each time according to the order of operations of that cycle.

Initial Shrinkage

The changes of length were observed for 7 to 8 hr from the moment of the preparation of the paste and placing it in the form. After that time the initial shrinkage of the setting paste did not increase any more.

By comparison of the plots in figures 6, 7, and 8 it is found that the three original cements differ considerably from each other. The order of the initial shrinkage of the paste, after 7 to 8 hr, is, for each of these cements, quite different. This is caused undoubtedly by the different chemical and mineralogical compositions of these cements and of their different fineness.

Closer comparison of the course of the curves presented in the above mentioned three plots results in finding that the appearance of the phenomenon of false setting or its disappearance influences very distinctly and always in the same manner the course of the initial shrinkage observed during the first 7 to 8 hr after the mixing of cement with water. In the case of each of the nine studied samples the course of the initial shrinkage of the paste may be divided into several characteristic stages. The pastes made of normal-setting cements shrink in three stages while in the case of false-setting cements four definite stages may be distinguished.

Normal-Setting Cements: *R, R′, S, S′, W′*

The first stage lasts for 3 to 3½ hrs after preparation of the paste, placing it in the mold and

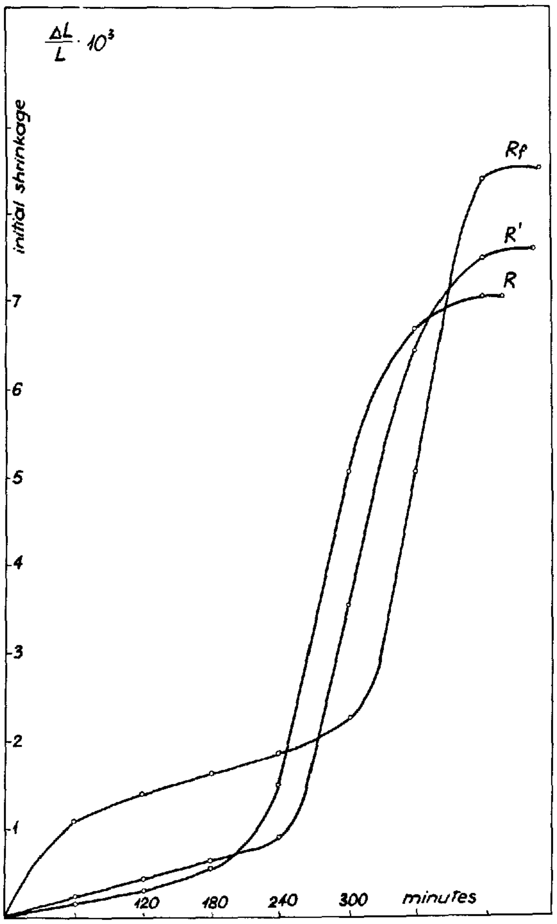

FIGURE 6. *Initial shrinkage of samples* R, R_f, and R′.

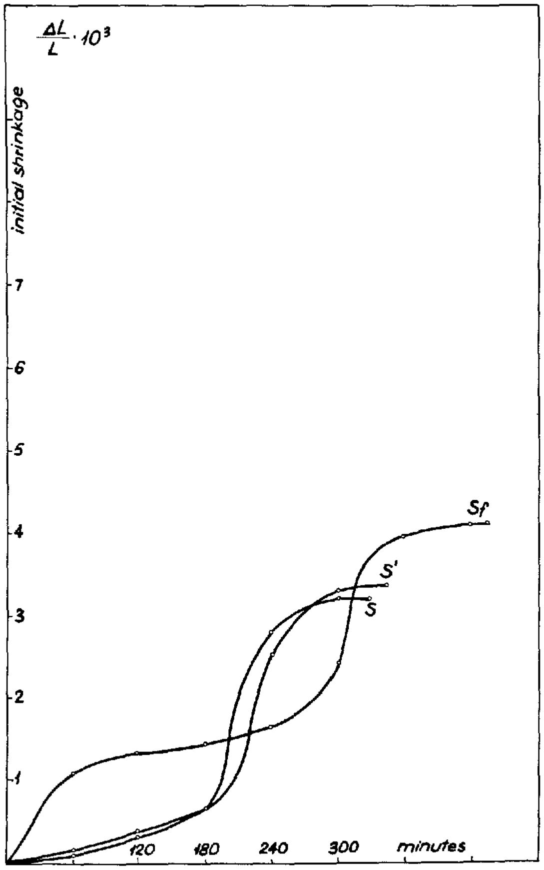

FIGURE 7. *Initial shrinkage of samples* S, S_f, *and* S′.

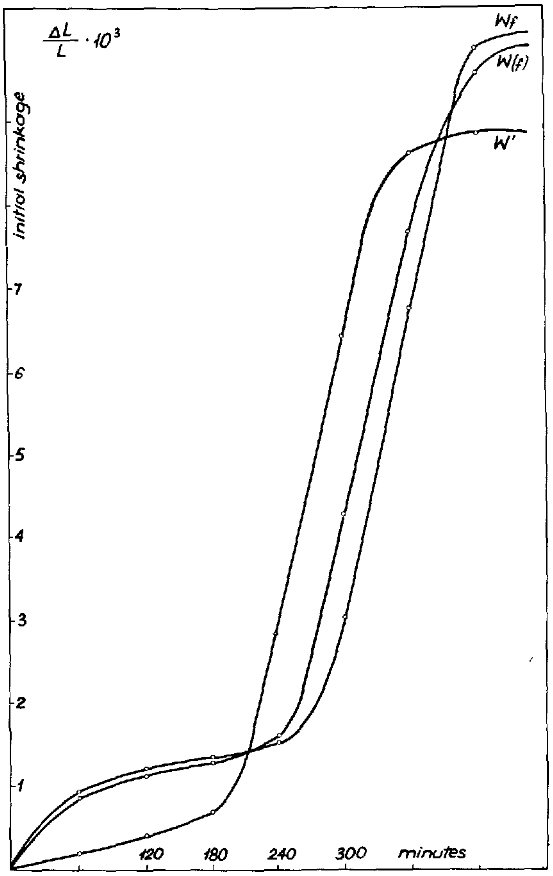

FIGURE 8. *Initial shrinkage of samples* $W_{(f)}$, W', *and* W_f.

starting the observations. This stage is characterized by slow shrinking of the paste which shows, at the end of this stage, a shrinkage of the order of 0.5–0.8 mm/m.

The second stage lasts for 1½ to 2½ hr. In this stage a rapid and very considerable increase of the shrinkage takes place. In the third and last stage the shrinkage comes to a constant value, characteristic for each original cement.

False-Setting Cements: R_f, S_f, W_f, $W_{(f)}$

The first stage comprises the first hour after the preparation of the paste. This short initial stage is typical for false-setting cements and is characterized by a rapid increase of the shrinkage which, after an hour, reaches the value of 1.0–1.2 mm/m, i.e., several times that shown during the same time by normal-setting cements.

In the second stage, lasting 3 to 4 hr, the shrinkage of false-setting cements increases slowly. This increase lasts for about 1 to 1½ hr longer, counting from the moment of the preparation of the paste, than in the case of normal-setting cement of the same origin. At the end of this stage the shrinkage of the false-setting cements reaches the value of 1.8–2.0 mm/m, thus being then more than twice that of normal-setting cements at the end of the first stage.

The third stage is that of a rapid increase of the shrinkage. This stage is late in relation to the analogous (second) stage of the normal-setting cements by about an hour.

In the fourth, final stage there occurs a decrease of the rate of shrinkage. The length of the sample becomes constant, showing, however, a total shrinkage 10 to 20 percent greater than that of the normal-setting cements.

Discussion

The results presented in this paper show that the phenomenon of false setting influences distinctly the process of bleeding of the cement paste as well as the initial shrinkage of the setting paste. This influence is marked in a regular and repeated manner and the quantitative changes of bleeding and initial shrinkage are measurable and considerable.

In addition, the mentioned influence is in a way reversible since it appears when normally setting cement is remade into a false-setting one as well as when falsely setting cement is remade into a normal-setting one.

Both investigated phenomena, i.e., that of bleeding and that of shrinkage of the cement paste, are related to the colloidal structure of the setting paste. Thus, for example, the course of bleeding depends, as is known, on the size and number of capillary canals constituting the fundamental element of the structure of the gels of which the hardening cement paste consists in the major part.

Thus the fact of the influence of false setting on the process of bleeding and shrinkage of cement paste, found in the course of studies being the subject of this paper, proves the decisive and distinct influence of false setting on the structure of the gels which are the main component of the hardening cement paste.

Further studies aiming at learning the influence of false setting on the practical properties of cement are being carried out at the Department of Technology of Binding Materials of the High School of Mining and Metallurgy, Kraków. It is to be expected that these studies will allow the whole-range interpretation of the observed phenomena and regularities, and, first of all, will enable us to know to a greater extent the influence of various forms of calcium sulfate on the structure of hardened cement paste.

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Paper IV–S9. Thermodynamics of the Hardening Processes of Cement*

O. P. Mchedlov-Petrosyan and W. I. Babushkin

Synopsis

To define the energetics of binding properties the authors have used the thermodynamic research method which allowed them to examine theoretically without complex experiments the energetics of hardening processes of binders and on this basis to outline the mechanism of their reactions.

Previously unknown thermic data (ΔH_{298}, ΔF_{298}, S_{298}, and $C_p=f(T)$) for hydrosilicates and hydroaluminates of Ca and silicic acid ions were obtained by approximate methods of calculation, the accuracy of which, as comparison of calculated and experimental data showed, is within the limits of usual experimental errors (±5%).

According to the data obtained there were calculated the equations $\Delta F=f(T)$ of the reactions in the systems: $Ca(OH)_2$–SiO_2–H_2O, β-$2CaO{\cdot}SiO_2$–H_2O, and $3CaO{\cdot}SiO_2$–H_2O under hydrothermal conditions, as well as the hydration reactions of $3CaO{\cdot}Al_2O_3$, $2CaO{\cdot}Al_2O_3$, $12CaO{\cdot}7Al_2O_3$, $CaO{\cdot}Al_2O_3$, $CaSO_4{\cdot}0.5H_2O$, CaO, and MgO at normal temperature.

The results of the thermodynamic calculations enable one to indicate the conditions for synthesis of various hydrosilicates.

Using the values of average bond energies for Ca-O, Si-O, O-H, etc., and taking β-$2CaO{\cdot}SiO_2$ as an example, there is shown the possible mechanism of its hardening process, the first stage of which is the solution of β-$2CaO{\cdot}SiO_2$ in water. This provides conditions for increase of the average bond energy of Ca-O which assures in its turn a considerable supersaturation of the ions of Ca^{++} in the solution and affords the possibility of making them stable. The second stage is the polymerization of the $SiO_3^{=}$ and $HSiO_3^{-}$ ions (depending upon the pH of the medium in the presence of Ca ions) first into chains $[Si_3O_9]^{6-}$ and then into bands $[Si_6O_{17}]^{10-}$, etc. This process is accompanied by the immediate precipitation of submicroscopic poorly soluble calcium hydrosilicates able to join with each other.

Résumé

Pour définir les énergétiques des propriétés liantes les auteurs ont utilisé la méthode de recherche thermo-dynamique qui leur a permis d'examiner théorétiquement sans expériences complexes les énergétiques des procédés de durcissement des liants et sur cette base d'exposer le mécanisme de leurs réactions.

Des données thermiques inconnues jusqu'à présent (ΔH_{298}, ΔF_{298}, S_{298} et $C_p=f(T)$) pour les hydrosilicates et hydroaluminates de calcium et les ions d'acide silicique furent obtenues par des méthodes de calculation approximative, dont l'exactitude, comme l'indique la comparaison avec les données calculées et expérimentales, est dans les limites des erreurs expérimentales habituelles (±5%).

Suivant les données obtenues les équations $\Delta F=f(T)$ des réactions furent calculées dans les systèmes: $Ca(OH)_2$–SiO_2–H_2O, β-$2CaO{\cdot}SiO_2$–H_2O, $3CaO{\cdot}SiO_2$–H_2O sous conditions hydro-thermiques, aussi bien que les réactions d'hydratation de $3CaO{\cdot}Al_2O_3$, $2CaO{\cdot}Al_2O_3$, $12CaO{\cdot}7Al_2O_3$, $CaO{\cdot}Al_2O_3$, $CaSO_4{\cdot}0.5H_2O$, CaO et MgO à température normale.

Les résultats des calculs thermo-dynamiques nous permettent d'indiquer les conditions pour les synthèses de différents hydrosilicates.

Quand on utilise les valeurs des énergies du lien moyennes pour Ca-O,Si-O,O-H etc., et quand on prend β-$2CaO{\cdot}SiO_2$ comme exemple, on voit le mécanisme possible de ce procédé de durcissement dont le premier stade est la solution de β-$2CaO{\cdot}SiO_2$ dans l'eau. Ceci fournit les conditions pour l'augmentation de l'énergie du lien moyenne de Ca-O qui à son tour assure une sursaturation considérable des ions de Ca^{++} dans la solution et offre la possibilité de les rendre stables. Le second stade est la polymérisation des ions de $SiO_3^{=}$ et de $HSiO_3^{-}$ (dépendant du pH du milieu en présence d'ions de calcium) d'abord en chaînes $[Si_3O_9]^{6-}$ et ensuite en bandes $[Si_6O_{17}]^{10-}$ etc. Ce procédé est accompagné par la précipitation immédiate d'hydro-silicates de calcium peu solubles et sous-microscopique capables de se joindre les uns aux autres.

Zusammenfassung

Für Erforschung der Energetik der Bindeeigenschaften benutzten die Verfasser die thermodynamische Forschungsmethode, die es ohne der Durchführung von komplizierten und mühevollen Versuchen erlaubte die Energetik der Erhärtung von Bindemittel zu untersuchen und auf dieser Grundlage den Mechanismus entsprechender Reactionen zu entwerfen.

Die früher unbekannten thermischen Daten [ΔH_{298}, ΔF_{298}, S_{298} und $C_p=f(T)$] für Hydrosilikate und Hydroaluminate des Calciums und der Siliziumsäureionen wurden mittels Näherungsberechnungsmethoden erhalten, die Genauigkeit welcher, wie ein Vergleich berechneter und Versuchswerte zeigte im Bereich gewöhnlicher Experimentalfehler liegen (±5%).

Zufolge den berechneten Daten wurden Gleichungen $\Delta F=f(T)$ der Reaktionen in Systemen: $Ca(OH)_2$–SiO_2–H_2O, β-$2CaO{\cdot}SiO_2$–H_2O, $3CaO{\cdot}SiO_2$–H_2O in hydrothermalen Zuständen, sowie die Reaktionen der Hydratation von $3CaO{\cdot}Al_2O_3$, $2CaO{\cdot}Al_2O_3$, $12CaO{\cdot}7Al_2O_3$, $CaO{\cdot}Al_2O_3$, $CaSO_4{\cdot}0.5H_2O$, CaO und MgO bei normaler Temperatur betrachtet.

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Die Resultate thermodynamischer Berechnungen erlauben es die Bedingungen der Synthese verschiedener Hydrosilikate zu beurteilen.

Mit der Anwendung der mittleren Bindungsenergien von Ca-O, Si-O, O-H, u.s.w., werden am Beispiel von β-$2CaO \cdot SiO_2$ der mögliche Mechanismus seiner Erhärtung gezeigt, deren erster Akt die Lösung von β-$2CaO \cdot SiO_2$ im Wasser ist, was Möglichkeit für die Vergrösserung der mittleren Bindungsenergie Ca-O, eine Bedingung der empfindlichen Übersättigung der Lösung mit Ca^{++} -ionen bildet, und bietet eine Möglichkeit der Erzielung ihres mehr stabilen energetischen Zustandes.

Als zweiter Akt ist die Polymerization von $SiO_3^{=}$ und $HSiO_3^{-}$ ionen anzusehen, in Abhängigkeit vom pH der Mediums in Anwesenheit der Ca^{++}-ionen zuerst in Metasilikat-ketten $[Si_3O_9]^{6-}$ und dann in Bänder $[Si_6O_{17}]^{10-}$ u.s.w. mit sofortigen Ausscheiden aus der Lösung submikroskopischer schwerlöslicher Calciumhydrosilikate, die zur gegenseitigen Verwachsung miteinander veranlagt sind.

In recent years there has been considerable progress in the study of the hardening processes of mineral binders. Formulation of a reliable theory of cement hardening is necessary for rational control of the technology of concrete and other products made with cements, and to assure the fabrication of products of desired quality.

It should be noted that all the numerous aspects of this problem have up to now been divisible either into the crystallochemical study of structural features of binders and their hydration products, represented in the USSR by the works of acad. N. V. Belov's school [1, 2],[1] N. A. Toropov, Yu. M. Butt, and their co-workers [3, 4], and abroad by J. Bernal [5], J. Jeffery [6], R. Nurse [7], F. Ordway [8], Å. Grudemo [9], H. Megaw [10], H. Taylor [11], E. Thilo [12], and others, or the branch of physical-chemical mechanics involving problems of "strength synthesis" of hardened binders, which was developed first in the USSR by acad. P. A. Rehbinder's school [13, 14].

From our point of view, for further fruitful development, a close and extensive application to these problems of the methods of chemical thermodynamics is necessary.

Apparently no one now would have any doubts about the assumption formerly made by us that inorganic compounds with binding properties have differently activated crystalline structures [15].

The crystallochemical aspect of the instability of those compounds was first explained by E. Brandenberger [16], who assumed that the ability to show binding properties is associated with reduced coordination of active cations of the structure. This opinion is, in our point of view, not far from the truth, because any distortion or irregular coordination will inevitably cause a reduction to the next order.

Therefore, without considering M. Bredig [17] incorrect, we assume that for the explanation of binding properties it is not the formal crystallochemical coordination but the quantity of the nearest neighbors that is important. It is just like the zones of different electronic levels in metals [18], or in other words, everything depends upon the yet unknown connection between the limit values of cation-oxygen distances and the energy coefficients of the structure.

Therefore, to explain the energetics of binding properties, the use of thermodynamic research methods becomes of great importance.

Application of thermodynamic research methods to the study of reactions on which the hardening processes of binders are based has up to now been hindered by a number of factors: first, it has not yet been decided to what degree the classical thermodynamic principles might be applied to real irreversible processes such as the processes causing the hardening of cements; second, there have been no initial thermodynamic data for hydrosilicates and hydroaluminates of calcium, because their experimental determination is associated with great difficulties in the synthesis of pure monocrystals and their unique identification [5, 19, 20, 21, 22, 23, 24].

Chemical processes represent combinations of chemical and phase transformations, mass, and heat transfer.

In this connection, thermodynamic potentials as measures of the driving force of the physical-chemical processes must be of decided importance in determination of relative rates and especially in qualitative estimation of the preferred course under given conditions [25].

Ideas on the significance of thermodynamic potentials in the determination of process rate can be found in some works [25–31].

It should be further noted that the assertion that one cannot use the concepts of time, space, and rate in thermodynamics is unsound, for it is correct only within the framework of classical thermodynamics, whose abstract concepts often fail to satisfy today's wants, and especially our desire to interpret in a concrete way the objective contents of thermodynamic laws.

It can be assumed [25] that for each real irreversible chemical process its exact reversible replica can be imagined; a prototype, passing through the same intermediate states. The amounts of work involved in these two processes are equal, but in the second case the work is connected with the covering of external forces influencing the system, while in the first case it is objective work against real internal resistance forces of a nonequilibrium system.

Summarizing all that is said above, we can conclude that for the analysis of hydraulic binders it is quite possible to use classical thermodynamic methods. The simplicity and convenience of their application consist in the fact that the main principles do not depend upon the correctness of our knowledge of the interatomic structure of materials taking part in the reaction and this enables us without complex and laborious experi-

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[1] Figures in brackets indicate the literature references at the end of this paper.

ments to examine theoretically the reactions of interest in order to predict the possibility of obtaining one or another product, or to predict the impossibility of a synthesis under certain conditions.

In connection with the above, the problem of reliable initial thermal data becomes of great importance; such data are heat of formation (ΔH), isobaric-isothermal potential (ΔF), entropies (S), and temperature dependence of heat capacities ($C_p=f(T)$) for the compounds formed through the hardening of binders as well as for their ions in water solution.

In the present work, to obtain the necessary thermal data for hydrosilicates and hydroaluminates of calcium and ions of silicic acid in water solution we used approximate calculation methods for ΔH, ΔF, S, and $C_p=f(T)$ [32, 33, 34, 35, 36]. The use of such approximate methods is justified in this case by the above-mentioned complexity of experiments and nearly complete absence of thermodynamic constants for hydrosilicates of calcium, since their experimental determination would delay this research for many years. The use of approximate methods without pretending to final decision of all questions concerning the hardening of binders allows us to draw important qualitative conclusions in a comparatively short time.

By the authors' methods, ΔH_{298}, S_{298}, and ΔF_{298} of nine hydrosilicates of calcium were calculated: hillebrandite, afwillite, foshagite, xonotlite, riversideite, tobermorite, plombierite, gyrolite, and okenite. The calculations were also made for three hydroaluminates of calcium: C_3AH_6, C_4AH_{12}, C_2AH_5. For the hydrosilicates, $C_p=f(T)$ was calculated by the method of N. A. Landya [37].

ΔF and ΔH for SiO_3 ions in water solution and the average binding energies for Si—O, Al—O, S—O, O—H, Ca—O, and Mg—O were also calculated for the main types of binders and their hydration products. All these calculated data, as well as those previously known, which were generally taken from the reference book by Rossini and associates [38], are given in table 1.

By use of these data, values of $\Delta F=f(T)$ for hydrothermal reactions in the systems $3CaO-SiO_2-H_2O$, β-$2CaO{\cdot}SiO_2-H_2O$, $Ca(OH)_2-SiO_2-H_2O$, and for hydration reactions of $3CaO{\cdot}Al_2O_3$, $2CaO{\cdot}Al_2O_3$, $12CaO{\cdot}7Al_2O_3$, $CaO{\cdot}Al_2O_3$, $CaSO_4{\cdot}0.5H_2O$, CaO, and MgO at room temperature were calculated, and on the basis of the values of average bond energies an energy analysis of binding qualities was made.

TABLE 1

1	2	3	4	5	6
No.	Compound	State	ΔH_{298} *kcal/mole*	ΔF_{298} *kcal/mole*	$C_p=f(T)$
1	CaO	Crystal	−151.90	−144.40	$C_p=11.67+1.08{\cdot}10^{-3}T-1.56{\cdot}10^5T^{-2}$
2	$Ca(OH)_2$	do	−235.80	−214.33	$C_p=19.79+10.45{\cdot}10^{-3}T-2.94{\cdot}10^5T^{-2}$
3	MgO	do	−143.84	−136.13	$C_p=10.18+1.74{\cdot}10^{-3}T-1.48{\cdot}10^5T^{-2}$
4	$Mg(OH)_2$	do	−221.00	−199.27	$C_p=10.4+27.00{\cdot}10^{-3}T$
5	$CaSO_4{\cdot}0.5H_2O(\beta)$	do	−375.97	−342.78	$C_p=18.8+36.3{\cdot}10^{-3}T$
6	$CaSO_4{\cdot}2H_2O$	do	−483.06	−429.19	$C_p=27.03+58.6{\cdot}10^{-3}T$
7	$CaSO_4$ (anhydrite)	do	−342.42	−315.56	$C_p=18.52+21.97{\cdot}10^{-3}T-1.56{\cdot}10^5T^{-2}$
8	β-$CaO{\cdot}SiO_2$	do	−378.20	−358.20	$C_p=26.64+3.6{\cdot}10^{-3}T-6.52{\cdot}10^5T^{-2}$
9	β-$2CaO{\cdot}SiO_2$	do	−538.00	−512.70	$C_p=41.26+5.34{\cdot}10^{-3}T$
10	γ-$2CaO{\cdot}SiO_2$	do	−539.00	−513.7	$C_p=27.16+19.6{\cdot}10^{-3}T$
11	$3CaO{\cdot}SiO_2$	do	−688.10	−653.40	$C_p=49.85+8.621{\cdot}0^{-3}T-10.15{\cdot}10^5T^{-2}$
12	$CaO{\cdot}Al_2O_3$	do	−554.80	−526.80	$C_p=34.62+6.751{\cdot}0^{-3}T-0.76{\cdot}10^5T^{-2}$
13	$3CaO{\cdot}Al_2O_3$	do	−850.00	−809.10	$C_p=52.34+15.81{\cdot}0^{-3}T+0.55{\cdot}10^5T^{-2}$
14	$2CaO{\cdot}Al_2O_3$	do	−704.00		
15	$12CaO{\cdot}7Al_2O_3$	do	−4617.00	−4365.72	$C_p=291.32+50.3{\cdot}10^{-3}T-5.25{\cdot}10^5T^{-2}$
16	$3CaO{\cdot}Al_2O_3{\cdot}6H_2O$	do	−1329.00	−1205.18	
17	$2CaO{\cdot}Al_2O_3{\cdot}5H_2O$	do	−1078.00		
18	$4CaO{\cdot}Al_2O_3{\cdot}12H_2O$	do	−1916.40	−1704.20	
19	$2CaO{\cdot}SiO_2{\cdot}1.17H_2O$ (hillebr.)	do	−624.80	−580.55	$C_p=41.04+22.04{\cdot}10^{-3}T-7.4{\cdot}10^5T^{-2}$
20	$3CaO{\cdot}2SiO_2{\cdot}3H_2O$ (afwill.)	do	−1118.45	−1028.25	$C_p=81.54+45.1{\cdot}10^{-3}T-14.67{\cdot}10^5T^{-2}$
21	$4CaO{\cdot}3SiO_2{\cdot}1.5H_2O$ (foshag.)	do	−1402.85	−1310.85	$C_p=87.95+39.5{\cdot}10^{-3}T-13.48{\cdot}10^5T^{-2}$
22	$6CaO{\cdot}6SiO_2{\cdot}H_2O$ (xonotl.)	do	−2322.82	−2185.32	$C_p=132.25+65{\cdot}20{\cdot}10^{-3}T-18{\cdot}35{\cdot}10^5T^{-2}$
23	$5CaO{\cdot}6SiO_2{\cdot}3H_2O$ (rivers.)	do	−2300.90	−2140.90	$C_p=143.55+74{\cdot}7{\cdot}10^{-3}T-20{\cdot}82{\cdot}10^5T^{-2}$
24	$5CaO{\cdot}6SiO_2{\cdot}5.5H_2O$ (toberm.)	do	−2482.15	−2287.35	$C_p=110.6+189{\cdot}1{\cdot}10^{-3}T$
25	$5CaO{\cdot}6SiO_2{\cdot}10.5H_2O$ (plomb.)	do	−2837.15	−2573.20	$C_p=132.2+270{\cdot}0{\cdot}10^{-3}T$
26	$2CaO{\cdot}3SiO_2{\cdot}2.5H_2O$ (gyrol)	do	−1138.82	−1048.62	$C_p=79.47+36.3{\cdot}10^{-3}T-17.55{\cdot}10^5T^{-2}$
27	$CaO{\cdot}2SiO_2{\cdot}2H_2O$ (oken.)	do	−725.69	−661.70	$C_p=44.81+18.7{\cdot}10^{-3}T-10.35{\cdot}10^5T^{-2}$
28	H_2O	liquid	−68.32	−56.69	$C_p=7.93+16.95{\cdot}10^{-3}T+2.67{\cdot}10^5T^{-2}$
29	SiO_2(β-quartz)	crystal	−205.40	−192.40	$C_p=11.22+8.20{\cdot}10^{-3}T-2.7{\cdot}10^5T^{-3}$
30	Ca	gas	+46.04	+37.98	
31	Si	do	+88.04	+77.41	
32	Al	do	+75.00	+65.30	
33	H	do	+52.089	+48.575	
34	O	do	+59.16	+54.99	
35	S	do	+53.25	+43.57	
36	Mg	do	+35.90	+27.60	
37	SiO_3^{--}	solid	−256.00	−219.20	
38	OH^-	do	−54.66	−37.56	
39	Ca^{++}	do	−129.70	−132.18	
40	α-Al_2O_3	crystal	−399.09	−376.77	
41	$Al_2(SO_4)_3$	do	−820.98	−738.99	

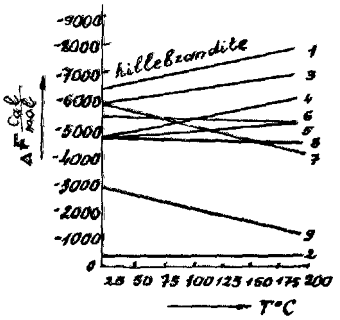

FIGURE 1. *The diagram* ΔF=f(T) *for direct reactions in the system* $Ca(OH)_2$-SiO_2-H_2O; *for compositions* C:S=2:1 *and higher.*

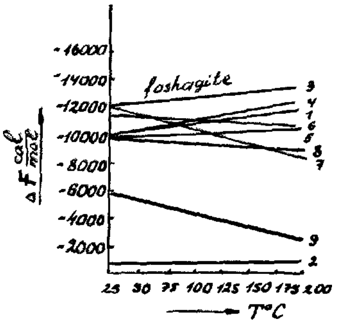

FIGURE 2. *The diagram* ΔF=f(T) *for direct reactions in the system* $Ca(OH)_2$-SiO_2-H_2O; *for composition* C:S=3:2.

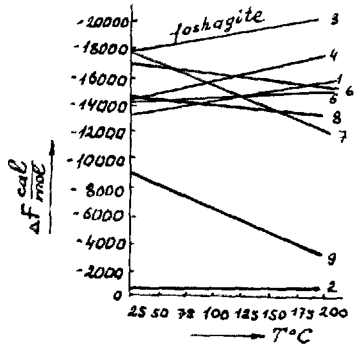

FIGURE 3. *The diagram* ΔF=f(T) *for direct reaction in the system* $Ca(OH)_2$-SiO_2-H_2O; *for composition* C:S=4:3.

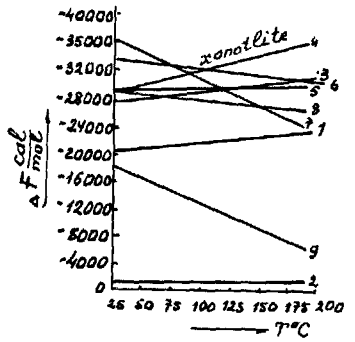

FIGURE 4. *The diagram* ΔF=f(T) *for direct reactions in the system* $Ca(OH)_2$-SiO_2-H_2O; *for composition* C:S=1:1.

Examination of figures 1 to 7,[2] in which ΔF=*f*(*T*) for reactions in the system $Ca(OH)_2$—SiO_2—H_2O is given, allows us to draw the following conclusions:

For compositions C:S=2:1 and more basic, 3:1, 4:1, etc., in the whole range of temperatures, primary formation of hillebrandite is thermodynamically most probable (fig.1).

For compositions C:S=3:2 and 4:3 and intermediate values, primary formation of foshagite is most probable (figs. 2, 3).

For the composition C:S=1:1, the primary products may be tobermorites (plombierite and tobermorite), and above 90 to 100 °C formation of xonotlite becomes thermodynamically most probable (fig. 4).

For the composition C:S=5:6, the primary product at low temperatures is indicated to be plombierite; from 50 to 220 °C tobermorite proper is indicated; and above 220 °C, xonotlite (fig. 5).

For compositions C:S=2:3 and 1:2 and the more acid region 1:3, 1:4, 1:5, etc., up to 230 and 240 °C, primary formation of gyrolite is most probable, and above 240 °C, xonotlite (figs. 6, 7).

In the system β-C_2S–H_2O (fig. 8), primary formation of hillebrandite is thermodynamically most probable up to 65 °C, and from 65 to 170°, afwillite.

In the system C_3S–H_2O (fig. 9), primary formation of hillebrandite is most probable over the whole temperature range, but the absence of data for C_3S–H_2O does not allow us to make at present a full analysis of reactions in this system.

The analysis of side reactions in the system $Ca(OH)_2$–SiO_2–H_2O makes it possible to conclude:

1. Stable hydrosilicates in the absence of excess of SiO_2 and $Ca(OH)_2$ are: hillebrandite (fig. 10), foshagite (though its transformation into xonotlite at high temperatures is not excluded, as is indicated by the inclination of curve 4 in figure 15), and xonotlite (but only at temperatures above 100 °C, for at low temperatures it can be transformed into tobermorite in the presence of water, fig. 18, curve 6).

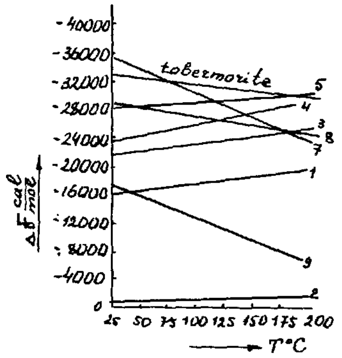

FIGURE 5. *The diagram* ΔF=f(T) *for direct reactions in the system* $Ca(OH)_2$-SiO_2-H_2O; *for composition* C:S=5:6.

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[2] In figures 1 to 27 the following symbols are used: 1—the formation of hillebrandite, 2—of afwillite, 3—of foshagite, 4—of xonotlite, 5—of riversideite, 6—of tobermorite, 7—of plombierite, 8—of gyrolite, 9—of okenite.

2. Tobermorite and gyrolite are thermodynamically stable at low temperatures but tend to transform into xonotlite at temperatures above 170 to 220 °C (figs. 21 and 24).

3. Afwillite and okenite are thermodynamically unstable over all the temperature range. Afwillite tends to transform into foshagite (fig. 12, curve 3), and okenite into gyrolite and tobermorite (fig. 27, curves 6 and 8).

With excess of $Ca(OH)_2$, all hydrosilicates exhibit a tendency to transform into hillebrandite (figs. 13, 16, 19, 22, 25), and with excess of SiO_2, into gyrolite (figs. 11, 14, 17, 20, 23).

A certain peculiarity characterizes afwillite, which in the presence of SiO_2 tends to transform into gyrolite only at temperatures up to 175 °C. At higher temperatures its transformation into foshagite becomes more probable (fig. 14, curve 3).

The results of calculations correspond very well with the experimental data of numerous scientists: P. P. Budnikov and N. V. Petrovykh [39], Yu. M. Butt, L. N. Rashkovich and others [4], H. F. W. Taylor [40], R. B. Peppler [41] and G. L. Kalousek [42, 43], but require the assumption that all the processes of hydrosilicate formation in the system $Ca(OH)_2$–SiO_2–H_2O take place in solution.

For instance, Peppler has stated that the final products are gyrolite and xonotlite when the initial materials are $Ca(OH)_2$ and silicic acid gel at molar $CaO{:}SiO_2$ ratios ranging from 0.26 to 0.63 (at 180 °C from 4 to 15 days). According to our data this can be explained in the following way. At 180 °C the concentration of $Ca(OH)_2$ in the solution is ~1.5 mmole/liter [44], while the concentration of SiO_2 is ~12.9 mmole/liter [45] in the case of amorphous SiO_2. Generally for more accurate analysis it is necessary to take into account the mutual influence of Ca and OH ions upon the solubility of SiO_2, and of silicic acid ions upon the solubility of $Ca(OH)_2$ in water; and instead of concentrations the activities of ions in solution should be used. Taking into consideration the approximate character of the initial thermodynamic data and the expectation of only qualitative estimation of the direction of observed reactions, we have taken as a basis the concentrations of $Ca(OH)_2$ and SiO_2 in solution.

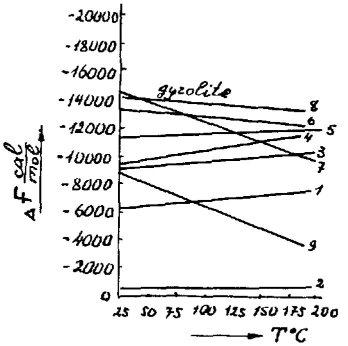

FIGURE 6. *The diagram* ΔF=f(T) *for direct reactions in the system* $Ca(OH)_2$-SiO_2-H_2O; *for composition* C:S=2:3.

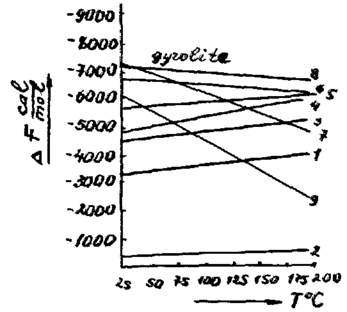

FIGURE 7. *The diagram* ΔF=f(T) *for direct reactions in the system* $Ca(OH)_2$-SiO_2-H_2O; *for composition* C:S=1:2.

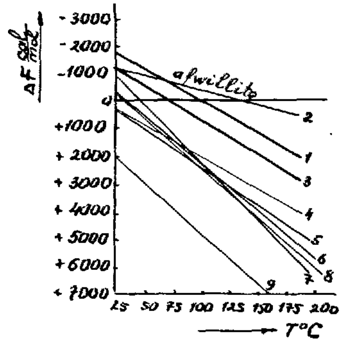

FIGURE 8. *The diagram* ΔF=f(T) *for direct reactions in the system* β-$2CaO{\cdot}SiO_2$-H_2O.

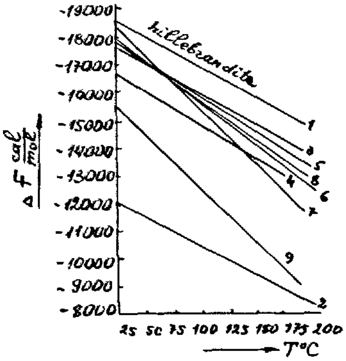

FIGURE 9. *The diagram* ΔF=f(T) *for direct reactions in the system* $3CaO{\cdot}SiO_2$-H_2O.

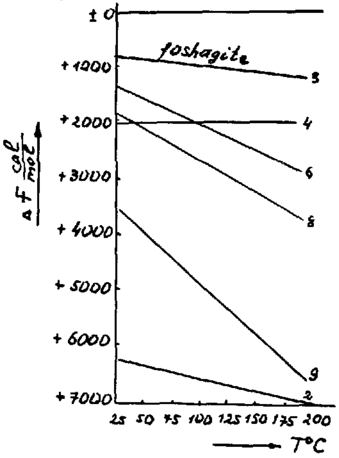

FIGURE 10. *The diagram* ΔF=f(T) *for transformation reactions of hillebrandite.*

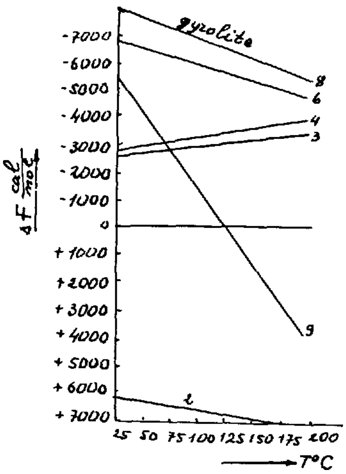

FIGURE 11. *The diagram* ΔF=f(T) *for transformation reactions of hillebrandite with excess* SiO_2.

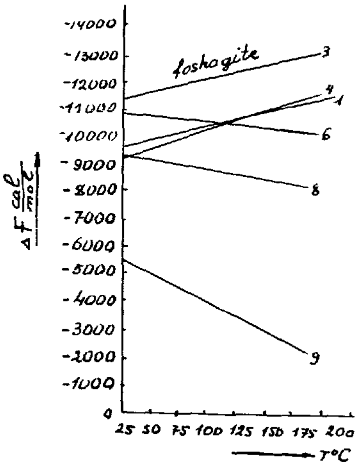

FIGURE 12. *The diagram* ΔF=f(T) *for transformation reactions of afwillite.*

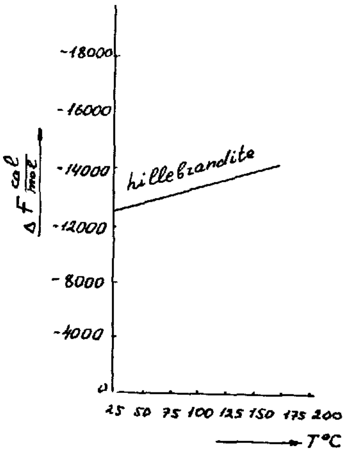

FIGURE 13. *The diagram* ΔF=f(T) *for transformation reactions of afwillite with excess* $Ca(OH)_2$.

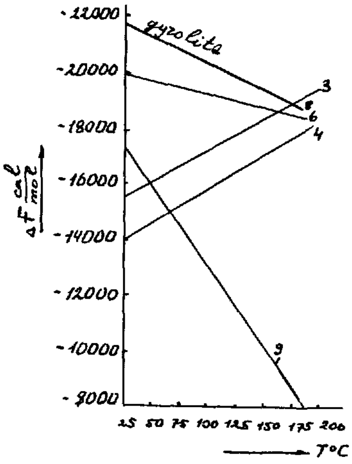

FIGURE 14. *The diagram* ΔF=f(T) *for transformation reactions of afwillite with excess* SiO_2.

Thus, the C:S ratio at 180 °C in this case will be $\frac{1.5}{12.9}=0.12$, or nearly 1:8. For this composition, according to figure 7 (curve 8) the primary product must be gyrolite. But gyrolite at high temperatures is a metastable phase and according to the data of figure 24 (curve 4) is able to transform into xonotlite. The transformation temperature indicated by our data ($\sim$225°) differs from Peppler's data by 45 °C, but for qualitative estimation it is quite acceptable. As the period of 4 to 12 days proved insufficient for the full transformation of gyrolite into xonotlite at 180 °C, Peppler found in this case just a mixture of gyrolite and xonotlite. But for the same composition in a second series of experiments continued for 6 months, Peppler found only xonotlite, which completely confirms the correctness of our conclusions. The results of other researchers correspond with them equally well.

We can draw very important conclusions from the examination of the data of figure 18. As we see in the figure (curve 6), xonotlite is a metastable compound at low temperatures and in the presence of water is able to condense into tobermorite according to the equation:

$$6CaO{\cdot}6SiO_2{\cdot}H_2O+5.5H_2O\rightarrow 5CaO{\cdot}6SiO_2{\cdot}5.5H_2O+Ca(OH)_2$$

This condensation leads to the removal of one molecule of $Ca(OH)_2$ from xonotlite, and this is important for preventing the solution of hydrosilicates in water.

The results of theromodynamic calculations allow us also to analyze the possibility of synthesis of various hydrosilicates.

1. Gyrolite may be obtained only when using active forms of SiO_2 at ratios of CaO and SiO_2 in the solution within limits of 2:3 to 1:∞ (corresponding to certain temperatures and states of initial materials), and when taking into account a

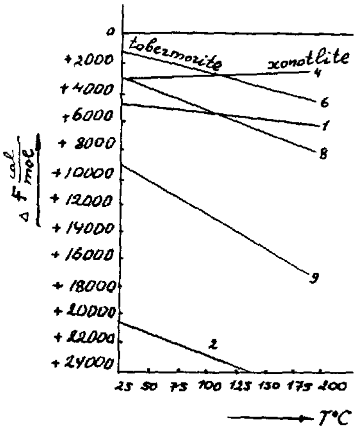

FIGURE 15. *The diagram ΔF=f(T) for transformation reactions of foshagite.*

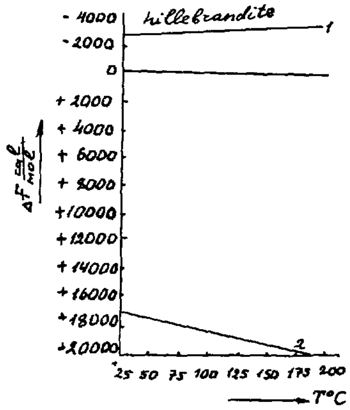

FIGURE 16. *The diagram ΔF=f(T) for transformation reactions of foshagite with excess* $Ca(OH)_2$.

suitable reaction period, because as a metastable phase it can transform fully into xonotlite under long processing.

2. Tobermorites may be synthesized from quartz and lime at such a temperature and with such a physical condition of initial SiO_2 and $Ca(OH)_2$ that the composition of CaO and SiO_2 in solution will be kept near or equal to 5:6 (with initial composition C:S=5:6). If the process is conducted with the initial composition of CaO to SiO_2 differing from C:S=5:6 (that is, with excess of CaO or SiO_2) it will be possible at certain temperatures and particle fineness of materials to obtain tobermorites as primary product, but through long processing they can transform with excess of $Ca(OH)_2$ into hillebrandite, and with excess of SiO_2 into gyrolite. Besides, it should be considered that at high temperatures (>190°) tobermorites are able to transform into xonotlite.

3. Xonotlite is formed when the C:S ratio in solution is nearly 1:1, and the higher the temperature the wider is the composition range near 1:1 for its preferred formation. Besides, xonotlite may be a product of gyrolite and tobermotite transformation at high temperatures.

4. Hillebrandite may be formed in all mixtures of CaO and SiO_2 when the ratios in the solution amount to 2:1 or more. Besides, it should be considered that initial mixtures rich in $Ca(OH)_2$ will consist of hillebrandite as final product after long processing.

5. Foshagite may be obtained as a primary product when the ratio of CaO to SiO_2 in the solution is equal to 3:2 to 4:3. Incidentally, such a composition is difficult to obtain as it lies in a very narrow range of temperatures (~160 to 165 °C for quartz and $Ca(OH)_2$).

6. Afwillite and okenite are not to be expected as products of synthesis from normal SiO_2 and $Ca(OH)_2$.

As to the hydration reactions of aluminates of calcium, gypsum, CaO, and MgO, the values of ΔH_{298} and ΔF_{298} for these reactions are given in

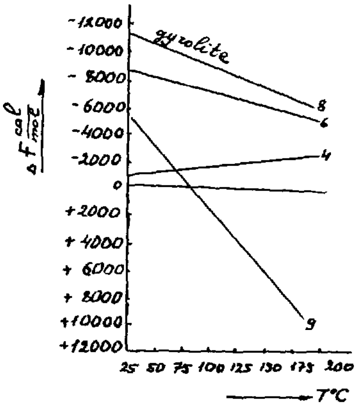

FIGURE 17. *The diagram ΔF=f(T) for transformation reactions of foshagite with excess* SiO_2.

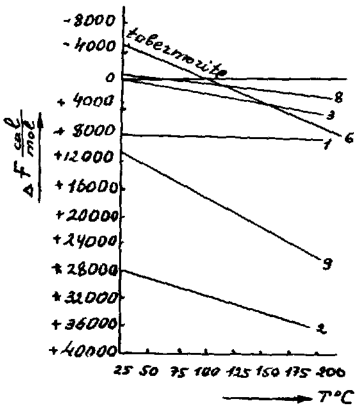

FIGURE 18. *The diagram ΔF=f(T) for transformation reactions of xonotlite.*

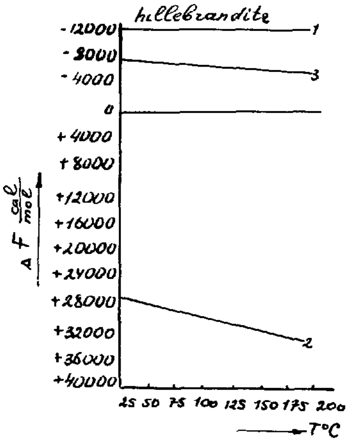

FIGURE 19. *The diagram* ΔF=f(T) *for transformation reactions of xonotlite with excess* $Ca(OH)_2$.

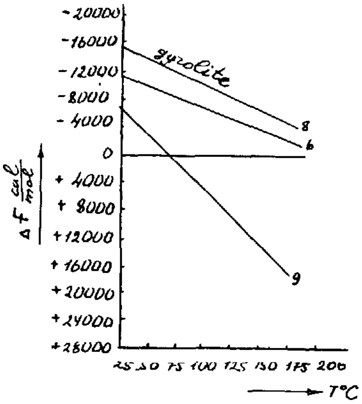

FIGURE 20. *The diagram* ΔF=f(T) *for transformation reactions of xonotlite with excess* SiO_2.

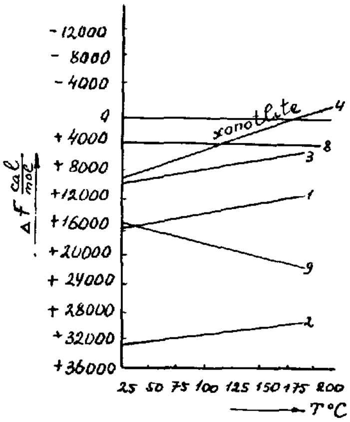

FIGURE 21. *The diagram* ΔF=f(T) *for transformation reactions of tobermorite.*

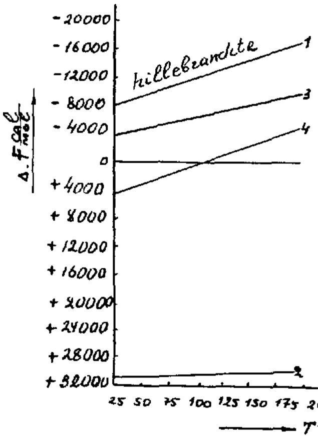

FIGURE 22. *The diagram* ΔF=f(T) *for transformation reactions of tobermorite with excess* $Ca(OH)_2$.

table 2, along with the values of ΔH and ΔF for hydration of CS, C_2S, and C_3S to hillebrandite. Average bond energies of Ca—O and Mg—O for the hydrated and unhydrated forms of these various compounds are given in table 3.

The calculation of the average bond energies of Ca—O and Mg—O, which are the ones that vary the most as functions of the condition and energy state of the oxygen, can be performed only on the assumption that the *average* energies of Si—O, Al—O, S—O, and O—H, which are common to both unhydrated and hydrated (stable) forms, do not change, and if they do, the difference is so insignificant in comparison with the change of

TABLE 2

No.	Hydration reaction	ΔH of the reaction at 298 °K	ΔF of the reaction at 298 °K
		kcal/mole	*kcal/mole*
1	$CaO+H_2O \rightarrow Ca(OH)_2$	−15.60	−13.21
2	$3CaO\ SiO_2+2.17H_2O \rightarrow 2CaO\ SiO_2\ 1.17H_2O + Ca(OH)_2$	−24.50	−18.70
3	β-$2CaO\ SiO_2+1.17H_2O \rightarrow 2CaO\ SiO_2\ 1.17H_2O$	−6.80	−1.72
4	γ-$2CaO\ SiO_2+1.17H_2O \rightarrow 2CaO\ SiO_2\ 1.17H_2O$	−5.80	−0.72
5	β-$CaO\ SiO_2+0.585H_2O \rightarrow \frac{1}{2}(2CaO\ SiO_2\ 1.17H_2O) - \frac{1}{2}SiO_2$	+3.47	+4.89
6	$3CaO\ Al_2O_3+6H_2O \rightarrow 3CaO\ Al_2O_3\ 6H_2O$	−69.08	−56.01
7	$2CaO\ Al_2O_3+5H_2O \rightarrow 2CaO\ Al_2O_3\ 5H_2O$	−32.40	----------
8	$12CaO\ 7Al_2O_3+48H_2O \rightarrow 3(4CaO\ Al_2O_3\ 12H_2O)+8Al(OH)_3$	−307.08	−199.20
9	$CaO \cdot Al_2O_3+4H_2O \rightarrow \frac{1}{2}(2CaO\ Al_2O_3\ 5H_2O) + Al(OH)_3$	−17.77	----------
10	$CaSO_4\ 0.5H_2O+1.5H_2O \rightarrow CaSO_4\ 2H_2O$	−4.61	−1.32
11	$CaSO_4+2H_2O \rightarrow CaSO_4\ 2H_2O$	−4.00	−0.25
12	$MgO+H_2O \rightarrow Mg(OH)_2$	−8.84	−6.45

TABLE 3

No.	Anhydrous compound	Average bond energy of the Ca—O bond	Hydrate	Average bond energy of the Ca—O bond	Energy gain on hydration
		kcal/bond		*kcal/bond*	*kcal/mole*
1	CaO	128.55	$Ca(OH)_2$	141.60	13.05
2	$3CaO\ SiO_2$	133.05	$2CaO\ SiO_2\ 1.17H_2O$	140.60	7.55
3	β-$2CaO\ SiO_2$	135.76	$2CaO\ SiO_2\ 1.17H_2O$	140.60	4.84
4	γ-$2CaO \cdot SiO_2$	136.00	$2CaO\ SiO_2\ 1.17H_2O$	140.60	4.60
5	$\beta\ CaO \cdot SiO_2$	139.21	$2CaO\ SiO_2\ 1.17H_2O$	140.60	1.39
6	$3CaO\ Al_2O_3$	127.75	$3CaO\ Al_2O_3\ 6H_2O$	149.78	22.03
7	$2CaO\ Al_2O_3$	128.82	$2CaO\ Al_2O_3\ 5H_2O$	150.07	21.25
8	$12CaO\ 7Al_2O_3$	128.56	$4CaO\ Al_2O_3\ 12H_2O$	155.56	27.00
9	$CaO\ Al_2O_3$	130.44	$2CaO\ Al_2O_3\ 5H_2O$	150.07	19.63
10	$CaSO_4\ 0.5H_2O$	155.80	$CaSO_4\ 2H_2O$	166.00	10.20
11	$CaSO_4$ (anhydrite)	153.40	$CaSO_4\ 2H_2O$	166.00	12.60
12	MgO	[a] 119.45	$Mg(OH)_2$	129.13	9.68

[a] For MgO and $Mg(OH)_2$ the value of average bond energy is for the Mg—O bond.

average energy of Ca—O and Mg—O that it may be neglected.

This is understandable because the average energies of Si—O, Al—O, S—O, and O—H are the basis of formation of complex oxygen-anions: SiO_4^{4-}, AlO_2^-, SO_4^{2-}, and OH^-, stability of which is large enough, since the radii of Si^{4+} (0.39 A), Al^{3+} (0.57 A) and S^{6+} (0.34 A) ions, compared with the radius of O^{2-} (1.32 A), are very small and will not distort the close packing of oxygen-anions even for considerable energy changes. The influence of these anions on Ca and Mg cations depends in great degree upon the differences of their energy condition, determined mostly by temperature and medium. At high temperatures, the polarization of anions causes decrease of the bond energy of Ca^{2+} with the free bonds of the oxygen of SiO_4^{4-}, SO_4^{2-}, and AlO_2^- anions; at low temperature this bond can return into its normal state.

The bond energy for Si—O was determined from β-quartz, for Al—O from corundum, for S—O from $Al_2(SO_4)_3$, and for O—H from water, in accordance with the methods described by T. Cottrell [46].

As may be seen in table 3, the calculated energy gain for one bond of Ca—O for hydration of CaO is 13.05 kcal. It is quite natural that under

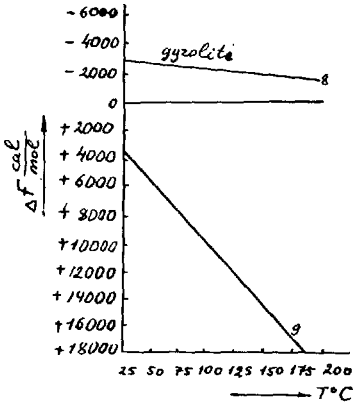

FIGURE 23. *The diagram* ΔF=f(T) *for transformation reactions of tobermorite with excess* SiO_2.

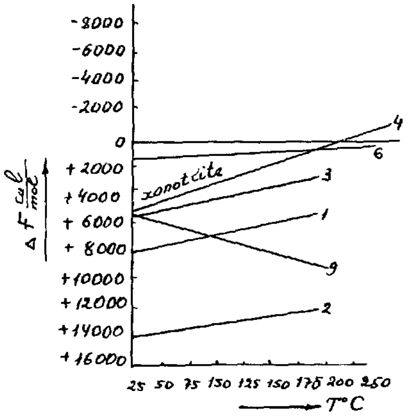

FIGURE 24. *The diagram* ΔF=f(T) *for transformation reactions of gyrolite.*

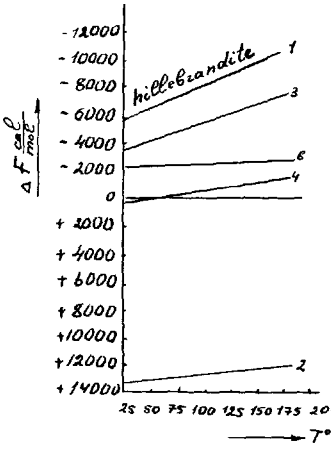

FIGURE 25. *The diagram* ΔF=f(T) *for transformation reactions of gyrolite with excess* $Ca(OH)_2$.

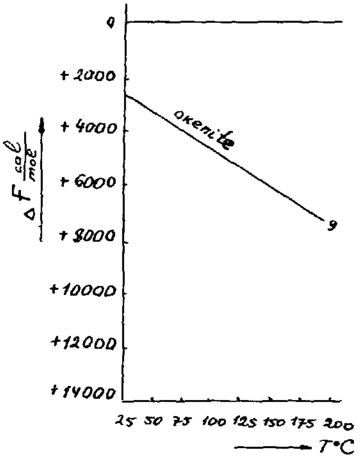

FIGURE 26. *The diagram* ΔF=f(T) *for transformation reactions of gyrolite with excess* SiO_2.

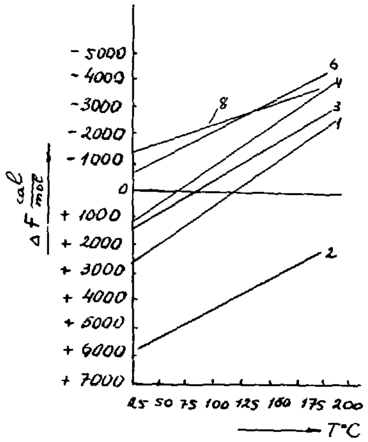

FIGURE 27. *The diagram* ΔF=f(T) *for transformation reactions of okenite.*

certain kinetic conditions, which could make it possible to overcome the activation energy, there would be immediately produced in lime a corresponding rearrangement leading to a lower level of free energy of the system.

The same may be said with respect to C_3S (energy gain 7.5 kcal/Ca—O bond), β-C_2S (energy gain 4.84 kcal/Ca—O bond), C_3A (energy gain 20.15 kcal/Ca—O bond), C_2A (energy gain 21.25 kcal/Ca—O bond), $C_{12}A_7$ (energy gain 27.0 kcal/Ca—O bond), CA (energy gain 19.63 kcal/CaO bond), $CaSO_4 \cdot 0.5H_2O$ (energy gain 10.2 kcal/Ca—O bond) and MgO (energy gain 9.68 kcal/Mg—O bond).

It is interesting to note that ΔF_{298} of these reactions has considerable negative value (table 2), which characterizes the great motive forces of those processes, assuring the spontaneous nature of the transformation.

Such compounds as γ-C_2S, β-CS, and $CaSO_4$ (anhydrite) are in a peculiar position. As table 3 indicates, the average bond energies of Ca—O in them are such that there is a gain of energy during hydration, but ΔF values of these processes (table 2) are found to be either nearly zero (γ-C_2S and $CaSO_4$) or positive (β-CS). Hence the activation energy of hydration processes for them is considerable, and therefore in the presence of water these processes cannot occur spontaneously. Either hydrothermal conditions (for γ-C_2S) or very fine grinding and the use of additions that increase the solubility (for anhydrite) are necessary.

Binders are composed of compounds that are able to harden into stonelike solids. This means not only that the binders must form hydrates stable in water, but a strong concretion of these hydrates must occur as well; therefore supersaturation in water solutions during hardening is necessary for binders [14, 47].

It may also happen that under usual conditions a compound does not give supersaturation, whereas under hydrothermal conditions, or with the help of additions or fine grinding, supersaturation can be secured.

Therefore conditions must be taken into account when defining binders. For most binders these conditions are easily met, as the hardening process is thermodynamically possible for them under normal conditions (t=25 °C, p=1 atm). To this group belong CaO, β-C_2S, C_3S, C_3A, C_2A, $C_{12}A_7$, CA, $CaSO_4 \cdot 0.5H_2O$, and MgO.

Since the main minerals of cement clinker are silicates of calcium, we take them as a model for analysis of the hardening mechanism of binders.

Hardening processes may be divided into the stage of interaction of a binder with water (hydration and supersaturation) and the stage of the formation of crystalline concretion (crystallization, recrystallization, contact formation).

Thermodynamically, the hydration can occur both in the solid phase and through solution [48], since the total energy of the process does not depend upon its path. The formation of hydrates in the solid phase does not provide the attainment of thermodynamically stable hydrate forms, and they, having some supply of free energy, will thus be converted through solution into more stable, well-formed hydrates, but this only over a longer period of time and under conditions of insignificant supersaturation which will not provide a strong concretion.

Hydration of binders through solution presents quite another picture. First of all, solution of the binder will not be hindered by hydrate films. It will be governed by the energy of the crystalline structure of the initial binder and by the properties of the solvent [49].

The activation energy of reactions between saturated molecules amounts to some tens of kcal/mole, and between ions is practically zero. This decides the kinetics of the process.

Therefore, in this case kinetic factors determine that the predominant development of the process is through solution, which was experimentally confirmed by V. B. Ratinov's researches [47].

From the average bond energies calculated by us we can indicate the mechanism of hydration of β-$2CaO \cdot SiO_2$ as follows.

The influence of polar molecules of H_2O weakens the bonds between atoms in C_2S, and heat movement is enough to make the elements of its structure pass into solution. We stated that the average bond energy of O—H in water is 110.57 kcal/bond, Si-O in β-C_2S—102.93 kcal/bond, Ca–O in β-C_2S—139.21 and Ca–O in hillebrandite—140.6 kcal/bond.

As the bond energy of Ca–O in β-C_2S is weaker than in hillebrandite, the Ca ion passing into solution (it will be manifested most probably only by the increase of mobility of Ca^{++} towards oxygen) will try to decrease its free energy, which will be manifested by development of a stronger bond with oxygen. The energy gain will be, as table 3 shows, 4.84 kcal/bond. Though this is not ΔF, it may be used as a measure for qualitative conclusions only.

From the comparison of values of bond energies of Si—O and Ca—O in β-C_2S (102.93 and 135.76 respectively), it is evident that the Ca ion passing into solution does not lose its oxygen, since 135.76 is greater than 102.93. Therefore the Ca ion, occupying a certain thermodynamically most advantageous position in oxygen packing, will assure stability.

In this case far different conditions will arise for silicon. Remaining without surroundings, since all four oxygen ions will pass to Ca^{++}, silicon (Si^{4+}) will immediately try to neutralize its charges. But this is not so easy to do, as oxygen in water is bound with protons by stronger bond (110.57 kcal/bond) than Si with O (102.93 kcal/bond). In this case, silicon can either join with existing OH^- groups, provided ones are in solution, or form double bonds with oxygen (then it will be easy to take oxygen from water, since $2 \times 102.93 \gg 110.57$).

Apparently those processes will depend in great degree upon the pH of the medium. Since pure water is but little dissociated, basic additives will be of great use for stimulating interaction of β-C_2S with water. The initial pH value will influence the primary formation of $Si(OH)_4$ (when all four bonds of silicon are bound with OH^-) or H_2SiO_3 (when two silicon bonds belong to OH while two others belong to oxygen).

Since there are experimental data on dissociation constants of H_2SiO_3 [50], while for $Si(OH)_4$ there are not, it is more reliable in this case to examine formation of metasilicic acid.

In connection with this, it is desirable to know the influence of the pH values upon the form of silicic acid in solution. It is easy to show this by calculations based on known values of the first and second dissociation constants of H_2SiO_3 [50].

$$K_1=\frac{[H^+]\,[HSiO_3{}^-]}{[H_2SiO_3]}\cong 10^{-10}$$

$$K_2=\frac{[H^+]\,[SiO_3{}^{--}]}{[HSiO_3{}^-]}\cong 10^{-12}$$

Denoting by ΣSiO_2 the collective content of all the forms of silicic acid, we can obtain the equations for determination of the percentage contents of H_2SiO_3, $HSiO_3^-$, and SiO_3^{--} in solution corresponding to the hydrogen-ion concentration in solution and K_1 and K_2:

$$\%H_2SiO_3=\Sigma SiO_2\,\frac{[H^+]^2}{[H^+]^2+K_1[H^+]+K_1K_2}$$

$$\%HSiO_3^-=\Sigma SiO_2\,\frac{K_1[H^+]}{[H^+]^2+K_1[H^+]+K_1K_2}$$

$$\%SiO_3^{--}=\Sigma SiO_2\,\frac{K_1K_2}{[H^+]^2+K_1[H^+]+K_1K_2}$$

The results of calculations by means of these equations are given in table 4.

Thus the main form of silicic acid at $pH<8.0$ is the undissociated H_2SiO_3. At $pH>12.0$, H_2SiO_3 is practically absent.

TABLE 4

Form of silicic acid	pH						
	4	6	8	10	12	13	14
H_2SiO_3	~100.0	~100.0	99.00	49.995	0.01	0.001	--------
$HSiO_3^-$	--------	--------	0.995	49.995	49.995	9.099	0.99
SiO_3^{--}	--------	--------	0.005	0.01	49.995	90.90	99.01

The existence of $HSiO_3^-$ ion is limited to the range $pH=8$–13. At $pH>13$ the main form is SiO_3^{--} ion.

SiO_3^{--} ions thus formed will undoubtedly try to be preserved in solution. The only way is by polymerization. The polymerization is aided by the unsaturated character of the double bond. In an acid medium the polymerization process will go with final formation of framework structures of silica which are practically insoluble in water under normal conditions and therefore quite stable.

In a basic medium, SiO_3^{--} ions will form complex radicals of polysilicic acids, the size and form of which will to a certain degree be governed by the character and properties of the cation of the base introduced into solution (Ca, Mg, Na, K, etc.). And, as is stated in the works of acad. N. V. Belov [1, 2], in the presence of Ca^{++} ions in solution, SiO_3^{--} polymerizes with the formation of bands $(Si_6O_{17})^{10-}$, crimps $(Si_{12}O_{31})^{14-}$, and networks $(Si_6O_{15})^{6-}$, at the basis of all of which lie wollastonite chains, Si_3O_9.

With a certain degree of reliability, this scheme may be transferred to the hydration processes of C_3S and the processes of the formation of calcium hydrosilicates from lime and sand under hydrothermal conditions.

Thus, binders are salts and oxides with lowered active coordinations of cations of the second group of D. I. Mendeleev's periodic system: Ca, Mg, etc., capable through this thermodynamic instability, or under conditions promoting the rise of free energy of the system to create supersaturations under the influence of water. The supersaturations permit crystallization through solution of a considerable mass of an initial binder, with the formation of stonelike solid strengthened by its hydrate forms.

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Paper IV–S10. Contribution to the Determination of the Heat of Hydration of Clinker Minerals*

H. E. Schwiete and A. Tan Tik-Ien

Synopsis

The heats of hydration of C_3S and β-C_2S were determined by means of the solution calorimeter as a function of time. The results were compared with those of identified hydration products.

The preparation of the tobermorite-like phase was studied as a function of temperature, pressure and time. The minimum CaO/SiO_2 molar ratio of the clinker hydrates was determined from the measured heats of hydration.

These studies led to the conclusion that hydration in a shaking machine, with a water factor of 50, results in a minimum CaO/SiO_2 molar ratio of 1.6 (C_3S hydrate) and 1.7 (β-C_2S hydrate), respectively.

Also studied was the effect of foreign oxides on the heat of solution of clinker minerals. This effect was particularly marked for incorporation of Al_2O_3 and MgO. Furthermore, when 2.5 weight-percent Al_2O_3 and 1 weight-percent MgO were incorporated in C_3S, thus giving the chemical composition of alite, the heat of solution rose by 14.2 percent. When these quantities of Al_2O_3 and MgO were added to the clinker as impurities a rise of 1.2 percent in the heat of solution was observed.

Incorporation of C_3A, and C_3A and MgO, in C_3S was also investigated. From the totality of the intercalation experiments, there could be determined the variation in the free enthalpy of the system and the quantities which represent maximum inclusion of foreign oxides in the individual clinker minerals. This yields a conclusive proof, that in determining the heat of solution of clinker minerals the nature and quantity of the impurities present should be taken into account.

Résumé

Les chaleurs d'hydratation de C_3S et β-C_2S ont été déterminées au moyen du calorimètre de solution en fonction du temps. Les résultats ont été comparés à ceux des produits d'hydratation identifiés.

La préparation de la phase semblable au tobermorite a été étudiée en fonction de la température, de la pression et du temps. Le rapport moleculaire minimum CaO/SiO_2 des hydrates du clinker a été déterminé à partir des chaleurs d'hydratation mesurées.

Ces études menèrent les auteurs à la conclusion que l'hydratation dans une secoueuse, avec un facteur d'eau de 50, résulte en un rapport moleculaire minimum CaO/SiO_2 de respectivement 1.6 (C_3S-hydrate) et 1.7 (β-C_2S-hydrate).

On a étudié également l'effet des oxydes étrangers sur la chaleur de solution des minéraux du clinker. Cet effet était particulièrement marqué pour l'incorporation de Al_2O_3 et MgO. De plus, quand 2.5 poids-% Al_2O_3 et 1 poids-% MgO étaient incorporés dans C_3S, donnant ainsi la composition chimique de l'alite, la chaleur de solution s'éleva à 14.2%. Lorsque ces quantités de Al_2O_3 et MgO étaient ajoutées au clinker comme des impuretés une élévation de 1.2% fut observée dans la chaleur de solution.

Des recherches furent faites également sur l'incorporation de C_3A, et de C_3A et MgO, dans C_3S. De la totalité des expériences d'intercalation on a pu déterminer la variation dans l'enthalpie libre du système et des quantités qui représentent l'inclusion maximum des oxydes étrangers dans les minéraux individuels du clinker. Ceci donne la preuve concluante que lorsqu'on détermine la chaleur de solution des minéraux du clinker il faut tenir compte de la nature et de la quantité des impuretés présentes.

Zusammenfassung

Die Hydratationswärme von C_3S und β-C_2S wurde unter Verwendung des Lösungskalorimeters in Abhängigkeit von der Zeit bestimmt. Die Ergebnisse wurden verglichen mit denen von definierten Hydratationsprodukten.

Die Herstellung der tobermoritähnlichen Phase wurde in Abhängigkeit von Temperatur, Druck und Zeit untersucht. Das minimale CaO/SiO_2-Molverhältnis der Klinkerhydrate wurde aus den Meßergebneissen der Hydratationswärmen ermittelt.

Bei diesen Untersuchungen konnte festgestellt werden, daß bei der Hydratation in der Schüttelmaschine und bei einem Wasserfaktor von 50 ein minimales CaO/SiO_2-Molverhältnis von 1.6 (C_3S-Hydrat) bzw. 1.7 (β-C_2S-Hydrat) entsteht.

Ferner wurde der Einfluß der Fremdoxide auf die Lösungswärme der Klinkermineralien untersucht. Der Einfluß war besonders stark bei Einlagerung von Al_2O_3 und MgO, weiterhin wurden 2.5 Gewicht-% Al_2O_3 und 1 Gewicht-% MgO in C_3S eingelagert, so daß sich die chemische Zusammensetzung von Alit ergab, dann stieg die Lösungswärme um 14.2%. Diese Mengen Al_2O_3 und MgO wurden als Verunreinigungen dem Klinker beigegeben, hierbei wurde nur ein Anstieg der Lösungswärme von 1.2% beobachtet.

Ausserdem wurde die Einlagerung von C_3A, und von C_3A und MgO, in C_3S untersucht. Aus der Gesamtheit dieser Einlagerungsversuche konnte die Änderung der freien Enthalpie des Systems und die Menge, die maximal an Fremdoxiden in den einzelnen Klinkermineralien eingelagert sind, bestimmt werden. Daraus ergibt sich der eindeutige Beweis, daß bei der Bestimmung der Lösungswärme von Klinkermineralien auf die Art und auf die Menge der vorhandenen Verunreinigungen Rücksicht genommen werden muß.

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Introduction

The determination of the heat of hydration of C_3S and β-C_2S, respectively, was based on the first law of thermodynamics, so that the heats of solution of the substances participating in the reaction could also be determined.

Determinations were also made of the heats of solution of MgO, Al_2O_3, and C_3A, which may become incorporated in the C_3S lattice, as well as the heats of solution of C_3S containing such inclusions of foreign substances. The heats of solution were determined using an acid concentration of 4*N* HF and 11*N* HNO_3 in a ratio of 1:1.

Change in the Heat of Solution of C_3S With Incorporation of Foreign Substances

In accordance with a chemical formula for alite ($C_{54}S_{16}AM$, established by Jeffery [1] [1] and confirmed by Müller-Hesse and Schwiete [2] as well as other authors, the C_3S lattice can contain 0.97 percent (by wt) of MgO and 2.5 percent (by wt) of Al_2O_3. The present part of this investigation concerns the effect of increasing quantities of MgO and Al_2O_3 in the C_3S lattice on the magnitude of the heat of solution of pure C_3S.

The authors' tests have shown that a temperature of 1,350 °C and a temperature duration of 20 hr are needed to incorporate the above mentioned maximum percentages by weight of MgO and Al_2O_3 completely into the C_3S lattice. Figure 1 shows the changes in heat of solution with increasing incorporation of MgO and Al_2O_3 in the C_3S lattice. Curve 1 shows changes in heat of solution with constant admixture of 2.5 percent (by wt) of Al_2O_3 and additions of MgO increasing from 0.2 to 1.0 percent (by wt); curve 2 shows variation with constant admixture of 1.0 percent (by wt) of MgO and additions of Al_2O_3 increasing from 0.27 to 2.5 percent, curve 3 shows variation in heat of solution with an increasing admixture of MgO and Al_2O_3 in equal mole ratio.

A comparision of the three curves shows that, in spite of quantitatively larger additions of foreign oxides in the mixes shown in curves 1 and 2, the heat of solution is lower than that shown in curve 3 for additions of foreign oxides that are gravimetrically smaller but have the mix ratio of 1:1. This means that electron neutrality is not attained with mixing proportions represented by curves 1 and 2, i.e., the added foreign oxides are not completely built into the C_3S lattice.

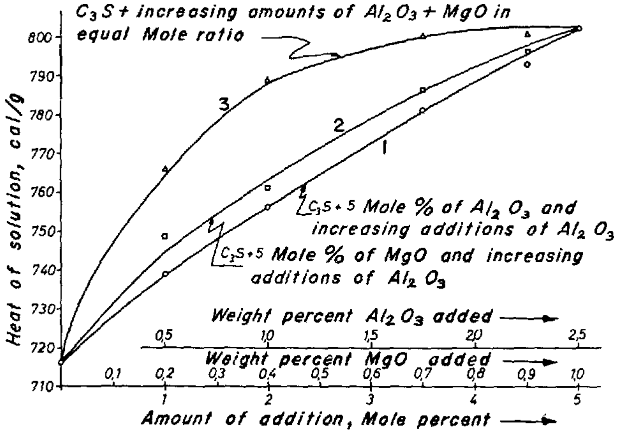

FIGURE 1. *Heat of solution of* C_3S *as affected by increasing additions of* Al_2O_3 *and* MgO.

The values for heat of solution shown in figure 1 can be used in the equation below to compute the heat of formation of alite. This computation gives 83.1 cal/g, and the reaction is endothermic.

$$18\ C_3S + A + M \rightarrow C_{54}S_{16}AM + 2S - \Delta H$$

Incorporation of Al_2O_3 and MgO in the C_3S lattice produces an abrupt increase in the heat of solution:

Heat of solution of	cal/g
C_3S	716.4
Alite	802.4

This change amounts to 14.2 percent. This result shows that the heats of solution of the MgO and Al_2O_3 in the C_3S lattice can not be interpreted as additive. By adding the heats of solution of MgO, Al_2O_3, and C_3S for the percentages present in alite, an increase of only 1.4 percent would be obtained.

This sudden change in the heat of solution can also be negative, as seen in tempering C_3S with C_3A. In tests with mixes of 0.5 to 5 mole percent of C_3A with C_3S a drop in the heat of solution from 7.0 to 6.4 percent was observed after heating at 1,450 °C for 8 hr. With a 1-mole-percent admixture of C_3A in C_3S the heat of solution is lowered from 716.4 to 660.9 cal/g, i.e, there is a drop of 7.7 percent. Figure 2 shows the course of the heat of solution curve as a function of C_3A-admixture in C_3S.

With additions of more than one mole-percent of C_3A a rise in enthalpy of 1.5 cal/g per mole-percent of C_3A was obtained.

Addition of the heats of solution of C_3S (716.4 cal/g) and 1.5 percent of C_3A results in an *increase* in the heat of solution of 1.2 percent. However, the tests (see above) disclosed a drop. The heat of solution of C_3A at the above acid concentration is 813.6 cal/g.

The maximum incorporation of C_3A in C_3S amounts to 1.5 percent. This value was deter-

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[1] Figures in brackets indicate the literature references at the end of this paper.

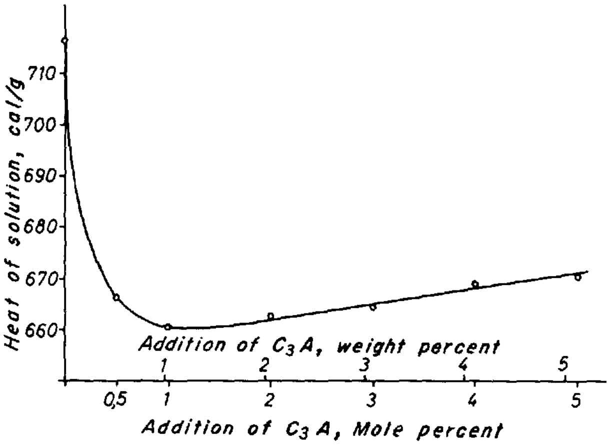

FIGURE 2. *Relation of heat of solution of* C_3S *to incorporated* C_3A *admixture.*

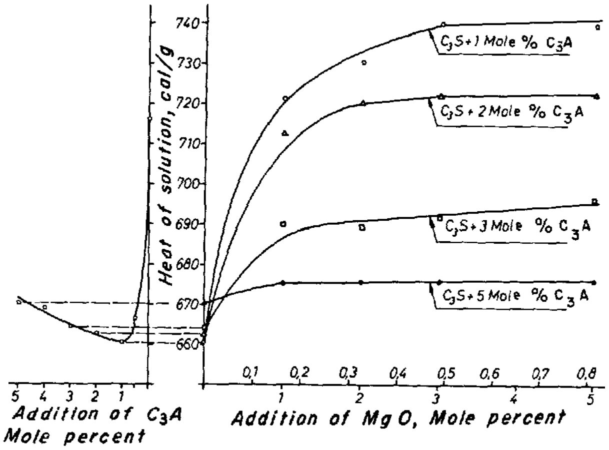

FIGURE 3. *Effect of* C_3A *and* MgO *on the heat of solution* of C_3S.

mined by plotting the algebraic sum of the enthalpies against composition.

Further computations showed that the heat change for incorporation of C_3A in C_3S is exothermic. It amounts to 57.9 cal/g.

The fact that the measured change in enthalpy can be different, as found in the incorporation of Al_2O_3 and MgO or C_3A in C_3S cannot be interpreted for C_3A (in contrast to Al_2O_3 + MgO) on the basis of substitution in the lattice, since in this case the change in enthalpy is negative. From the statistical mole volumes we find that the C_3A lattice must be larger than the C_3S lattice. From this fact we can conclude that C_3A and C_3S combine to form a mixed crystal (solid solution).

The X-ray patterns of alite and C_3S with incorporation of C_3A show no differences. The typical interference of alite at d=1.49 A found by Midgley [3], was also observed when C_3A was incorporated in C_3S.

When MgO was also incorporated in these C_3S–C_3A mixed crystals, the heat of solution began to rise again. The maximum was reached with a mixed crystal of C_3S with 1 mole percent of C_3A and 2.5 mole-percent of MgO. With greater addition of C_3A, the heat of solution again decreases (fig. 3).

This observation led to the conclusion that only small additions produce sudden changes (deviations) in the heat of solution, i.e., form a mixed crystal. Further additions remain present as original components along with the mixed crystal. In this case the heat of solution is additive. From the above reasoning, it can be seen that the solution-calorimeter values used heretofore in computing the percentage composition of clinker minerals are not suitable. In determining the clinker minerals in cements one cannot start with the heats of solution of pure clinker minerals. Rather computation of cement components should be based on such substituted clinker minerals as contain the quantities of foreign substances corresponding to those present in the cement.

Preparation of Calcium Silicate Hydrates

Calcium silicate hydrates can be produced by the following methods: (1) through a reaction of calcium hydroxide on an aero-silica, or calcium hydroxide and soluble silicic acid salts, such as alkali silicates; (2) through the hydration of tricalcium silicate or β-C_2S.

Preparation of Calcium Silicate Hydrates From $Ca(OH)_2$ and an Aero-Silica or Alkali Silica, Respectively

The heretofore known methods of producing calcium silicate hydrates from $Ca(OH)_2$ and an aero-silica or soluble silicic acid salts do not yield crystals without hydrothermal treatment of the specimens. To be sure, a white precipitate forms when $Ca(OH)_2$ solution and an aero-silica solution or sodium silicate solution are combined or come in contact with each other; however, it is not crystalline but X-ray amorphous. Hydrothermal treatment of this precipitate requires 2 months, as reported by McMurdie and co-workers [4] and Taylor [5]. A temperature increase is needed to accelerate crystallization. This temperature increase, however, is limited by the following conditions: (1) the stability of the calcium silicate hydrate products is a function of temperature; (2) at temperatures above 400 °C the calcium silicate hydrate formed is dehydrated into wollastonite. The latter cannot hydrate.

To avoid these difficulties and yet achieve rapid crystallization, the X-ray-amorphous precipitate was subjected to hydrothermal treatment in a nitrogen atmosphere at a constant pressure of 100 atm and for a constant time. This method resulted in the production of tobermorite in 10 days. By simultaneously increasing the temperature systematically, various phases of tobermorite were produced, which finally became converted into xonotlite at 310 °C. The crystalline substances obtained in this manner were studied using solution calorimetry and X-ray methods. As shown in figure 4, a conversion of the X-ray-amorphous substance into the crystalline state is accompanied by a stepwise change in the heat of solution, i.e., each jump corresponds to a new formation, as indicated by the X-ray charts (figure 5). From the fact that no crystalline calcium silicate hydrate can be obtained from a lime solution and sodium silicate, and from the general trend of the hydration of C_3S, one might suspect that hydration of C_3S proceeds topochemically. In further study of the course of hydration, C_3S was hydrated while maintaining a CO_2 pressure of one atm. All of the lime was changed into calcium carbonate in 12 hr. This test leads to the following conclusions:

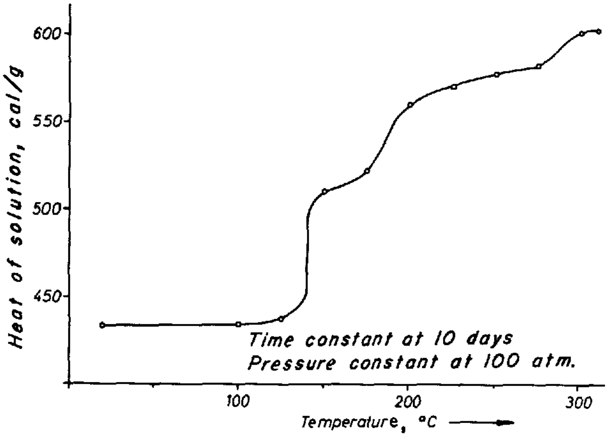

FIGURE 4. *The heat of solution of* CSH *produced hydrothermally at constant pressure (100 atm) and constant time (10 days) as a function of temperature of treatment.*

Had C_3S hydrated topochemically, carbonation should have lasted longer and calcium silicate hydrate should still have been present after 12 hr. However, as no calcium silicate hydrate was found after this time, the test shows that hydration proceeds by ionic reaction, and, in such manner that calcium ions are appropriated by HCO_3 ions, thus preventing the formation of calcium silicate hydrate by the active calcium and silicic acid ions. One must take into consideration that calcium and silicate ions, directly ionized out of C_3S, remain active only for a very short time, during which calcium silicate hydrate is formed if no foreign ions

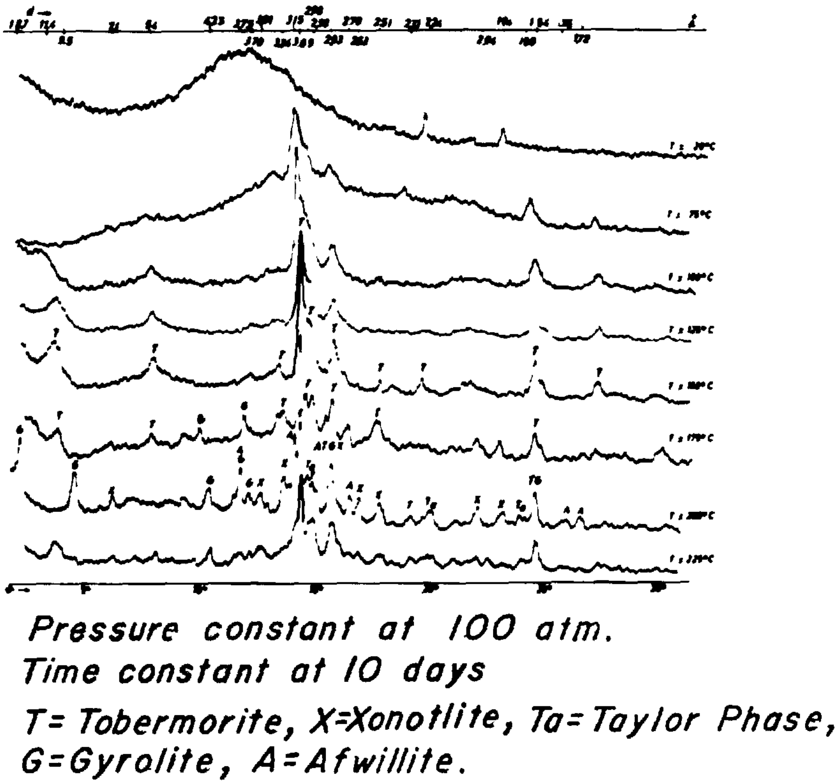

FIGURE 5. *X-ray charts of calcium silicate hydrates produced hydrothermally at constant pressure (100 atm) and constant time (10 days) as a function of temperature of treatment.*

Bottom scale, angle θ, to 30°. Top scale, d-spacing, from 18.7 A to 1.72 A. Top curve, T=20 °C; others, T=75 to 225 °C (bottom curve) by 25° increments.

are present with a greater affinity for calcium ions than the silicate ions.

Also to be noted is the presence of adsorbed water in the calcium silicate hydrate, which causes an endothermic effect on the DDC-curve at 160 °C (dynamic differential calorimeter developed by Schwiete and Ziegler, fig. 6, curve 2).

Curve 1 shows the dehydration curve of moistened $CaCO_3$. This curve indicates that water was not adsorbed in the lattice. This curve was used as a calibration curve in evaluating dehydration results at temperatures of about 100 °C. The water which is driven off at 100 °C is designated as "moisture" water. The double effect at 100 and 160 °C, respectively, is retained when calcium silicate hydrate is dried with acetone and ether prior to test (curve 2). Curve 3 shows the same specimen after 1½ hr of preliminary drying at 75 °C. One recognizes that this drying removed all of the moisture water and part of the adsorptive water. A similar specimen was first completely dehydrated, then wetted, and examined (DDC-curve 4). Curve 5 shows a dehydrated, wetted, dehydrated, and again wetted calcium silicate hydrate. With preliminary drying of calcium silicate hydrate at 110 °C, the adsorptive water appears to be completely driven off; the DDC-curve becomes a straight line.

The above tests indicate that the adsorptive water removed at 160 °C is only loosely bound. The binding forces of the crystal-adsorptive water are greater than the binding forces between adsorptive water and moisture water. It is further revealed that adsorption of water takes place slowly and is endothermic, in contrast to clay minerals. Repeated dehydration renders the surface of calcium silicate hydrates inactive, i.e., it no longer adsorbs water. The heat of adsorption amounted to 4.31 kcal/mole H_2O. After a single dehydration and a single wetting it amounted to 1.39 kcal/mole H_2O.

These dehydration phenomena were observed with hydrothermally produced calcium silicate hydrates as well as with C_3S specimens hydrated in water. In contradiction to this observation is Taylor's [7] experience that this effect occurs only in hydrothermally produced calcium silicate hydrates. One can conclude that the properties of calcium silicate hydrates are dependent on the method used in their preparation.

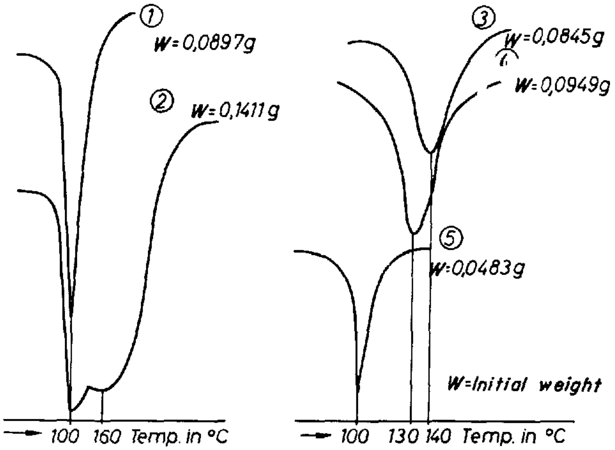

FIGURE 6. *Dynamic-differential-calorimeter curve of water loss in calcium silicate hydrate.*

Preparation of Calcium Silicate Hydrates Through Hydration of C_3S or β-C_2S

In preparing calcium silicate hydrates excess water was used in order to accelerate the reaction. The water-silicate ratio was 50:1. The preparation was energetically shaken during the reaction. Care was taken that no carbonation could take place. To measure the progress of the reaction the hydrated products were analyzed and the liberated $Ca(OH)_2$ determined. In addition, the calcium hydroxide was removed from the solution at constant time intervals to permit completion of the reaction. This removal was necessary because hydration of C_3S with a definite water-silicate ratio results in an equilibrium becoming established after a certain time. Thus, Verbeck and Foster [8] could observe no further rise in the heat of hydration after 1 or 6½ yr.

It was the purpose of these investigations to determine the heat of hydration of C_3S. This determination was to be carried out during progressive hydration, i.e., the liberation of $Ca(OH)_2$ was to progress until a calcium silicate hydrate with lowest CaO/SiO_2 mole ratio was obtained, and finally decomposed into its original components $Ca(OH)_2$ and silica. In this way the heat of hydration of C_3S or β-C_2S was to be determined as a function of the CaO/SiO_2 mole ratio of the calcium silicate hydrates.

Heat of Hydration of Clinker Minerals

The heat of hydration was determined from the results of solution calorimetry. When the heat of hydration is plotted as ordinate and the degree of hydration (course-of-reaction factor) as abscissa, i.e., the CaO/SiO_2 mole ratio, the curve shows a maximum (fig. 7).

The maximum occurs for calcium silicate hydrates at a CaO/SiO_2 mole ratio of 1.6. The heat of hydration amounts to 120 cal/g. If hydration continues, the heat of hydration becomes lower and ends in a decomposition of the components into $Ca(OH)_2$ and silica. The heat of decomposition was established here as 62 cal/g. The maximum indicates that calcium silicate hydrate is most stable, in other words, that free enthalpy is highest, when the entropy of the solid substances is about the same. To confirm this discovery $Ca(OH)_2$ and a silicic acid solution were mixed. The CaO/SiO_2 mole ratio was varied. It was observed that a mix-

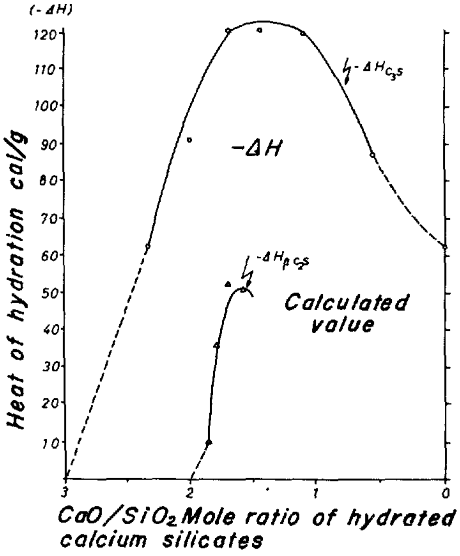

FIGURE 7. *Heat of hydration of* C_3S *and* $\beta-C_2S$, *respectively, as a function of* CaO/SiO_2 *mole ratio of the precipitate (with removal of* $Ca(OH)_2$ *during the reaction, and employment of a water-silicate ratio of 50:1).*

ture with a CaO/SiO_2 mole ratio less than 1.6 forms no calcium carbonate after 2-yr in free air and at room temperature. Above 1.6 the residual calcium was converted by the CO_2 of the air into calcium carbonate. Similar observations were reported by Steinour [9]. This test leads to the conclusion that C_3S cannot hydrate to calcium silicate hydrate when the CaO/SiO_2 mole ratio is below 1.6. In the hydration of β-C_2S this limiting value was reached at a CaO/SiO_2 mole ratio of 1.7. The heat of hydration amounts to 52.7 cal/g.

Our values of the heats of solution agree with those of Verbeck and Foster [8]. No comparison can be made with corresponding test results obtained by Brunauer [10], as he did not hydrate his clinker minerals completely.

The heat of hydration of C_3S with establishment of a CaO/SiO_2 mole ratio of 0.81 amounts to 69.9 cal/g of C_3S for hydrothermally synthesized calcium silicate hydrate, and 115 cal/g of C_3S for normally hydrated C_3S. The corresponding values for β-C_2S are 22.7 cal/g of C_2S. This difference in the values for normally hydrated and hydrothermally produced calcium silicate hydrate is inherent in the greater calcium-ion adsorption in the interlayers of calcium silicate hydrate produced by hydrothermal treatment.

The different heats of hydration of C_3S or β-C_2S show that the magnitude of the heat of hydration depends not only on the degree of hydration, but also on the CaO/SiO_2 mole ratio of the calcium silicate hydrate formed. The results of measurements are also dependent on the hydration method used.

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Chemistry of Cement

Proceedings of the
Fourth International Symposium
Washington 1960

U.S. Department of Commerce
National Bureau of Standards
Monograph 43 — Volume II

UNITED STATES DEPARTMENT OF COMMERCE • Luther H. Hodges, *Secretary*
NATIONAL BUREAU OF STANDARDS • A. V. Astin, *Director*

Chemistry of Cement

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Volume II

Symposium held October 2–7, 1960, at the
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Preface

Symposia on the chemistry of cements have become established through a succession of international assemblies held at irregular intervals. More than a half century ago such meetings among researchers, covering various materials including cements, were sponsored by the International Association for Testing Materials.

The first international congress dealing exclusively with the chemistry of cements and related materials seems to have been a meeting sponsored by the Faraday Society and held in London on January 14, 1918. Because of the priority of that meeting in this special field, it has come to be known as the First International Symposium on the Chemistry of Cement.

The First Symposium was designated as "A General Discussion" on "The Setting of Cements and Plasters." Ten brief papers were presented by 11 scientists from 5 countries. Twelve discussions followed the presentation of the papers. The Proceedings consisted of 69 pages published in the Transactions of the Faraday Society, Volume XIV, 1918–19.

The Second Symposium was sponsored by the Royal Swedish Institute for Engineering Research and the Swedish Cement Association. A 3-day meeting was held in Stockholm in July of 1938 under the designation "Symposium on the Chemistry of Cements." Forty-seven persons from 13 countries participated in the presentation of 13 papers and 52 discussions. The Proceedings, consisting of 578 pages, were published in Stockholm in 1939 by the Royal Swedish Institute for Engineering Research.

The intervention of World War II delayed consideration of the next symposium. Preliminary plans for a general meeting in Washington were abandoned, but eventually arrangements were made for the Third Symposium to be held in London under the sponsorship of the Department of Scientific and Industrial Research and the Cement and Concrete Association. The five-day meeting was held in September of 1952, and was attended by 260 persons, 84 of whom participated with 23 papers and 102 discussions. The Proceedings, consisting of 870 pages, were published in London in 1954 by the Cement and Concrete Association.

Preliminary conversations on the organization of the Fourth Symposium were initiated in April 1956, at which time agreement was reached by the National Bureau of Standards and the Portland Cement Association that the Symposium would be jointly sponsored by those organizations. By the spring of 1959 a tentative program had been set up with the cooperation of leaders in cement research of several foreign countries. Later in that year the organization of the working committees was completed. The sponsors and members of committees are listed below.

Sponsors: National Bureau of Standards, Allen V. Astin, Director; Portland Cement Association, G. Donald Kennedy, President.

Executive Committee: I. C. Schoonover, and A. Allan Bates, Cochairmen; R. H. Bogue, Secretary, Robert E. Pflaumer, Douglas E. Parsons, Myron A. Swayze, W. S. Weaver, C. E. Wuerpel, and Hubert Woods.

Program Committee: T. C. Powers and R. L. Blaine, Cochairmen; H. F. McMurdie, W. C. Hansen, W. J. McCoy, Fred Ordway, Kenneth E. Palmer, and Stephen Brunauer.

Arrangements Committee: J. H. Walker and Bruce Foster, Cochairmen; Clayton Davis and William Lerch.

Editorial Committee: E. T. Carlson and H. H. Steinour, Cochairmen; E. S. Newman and M. D. Catton.

Papers for presentation at the Symposium were received at the Secretary's office, beginning in January 1960, and continuing to September. After review by the Program Committee and some preliminary editing by the Editorial Committee, they were reproduced by a photoduplicating process, and copies were mailed, as they became available, to the Symposium members.

The Fourth Symposium was held at Washington, D.C., October 2–7, 1960. Invitations to membership in the Symposium were accepted by 362 persons, including 169 from the United

States and 193 from 34 other countries. The number actually in attendance was 271. All sessions of the Symposium were held at the National Bureau of Standards.

At the first session, held on Monday morning, October 3, Dr. I. C. Schoonover, Associate Director of the National Bureau of Standards, and Dr. A. Allan Bates, Vice President of the Portland Cement Association, acted as cochairmen. Dr. A. T. McPherson, Associate Director of the National Bureau of Standards, welcomed the guests on behalf of the Bureau, and Mr. G. Donald Kennedy, President of the Portland Cement Association, indicated his pleasure in cosponsoring this important gathering. Dr. Eberhard Spohn, President of the Heidelberg Cement Company, responded on behalf of the members of the Symposium.

The first formal address, given by Dr. Wallace G. Brode, formerly Science Advisor to the Secretary of State, was entitled "Some Problems Associated with the Growth of Science." This was followed by an address, given by Dr. F. M. Lea, Director of the Building Research Station of the United Kingdom, entitled "Cement Research, Retrospect and Prospect."

Succeeding sessions were devoted to technical papers, grouped under seven general topics related to the chemistry of cement.

The titles of the individual papers will not be given here, as they are listed in the table of contents. The program included the following sessions.

Session II—Chemistry of Clinker; Monday afternoon, October 3; Dr. Henri Lafuma and Dr. R. H. Bogue, presiding.

Session III—Chemistry of Hydration of Cement Compounds; Tuesday morning, October 4; Dr. Fritz Keil and Mr. Charles E. Wuerpel, presiding.

Session IV—Chemistry of Hydration of Portland Cement; Tuesday afternoon, October 4; Dr. Niko Stutterheim and Mr. Myron A. Swayze, presiding.

Session V—Properties of Cement Paste and Concrete; Thursday morning, October 6; Dr. Wolfgang Czernin and Mr. Hubert Woods, presiding.

Session VI—Destructive Processes in Concrete; Thursday afternoon, October 6; Dr. Arturo Rio and Mr. Douglas E. Parsons, presiding.

Session VII—Chemical Additions and Admixtures—was combined with Session VIII.

Session VIII—Special Cements; Friday morning, October 7; Prof. B. G. Skramtaev and Dr. A. R. Collins, presiding.

The technical communications were of three categories, as follows:

1. Principal papers by outstanding contributors to the literature of cement and concrete technology, who were invited to present their appraisal of the present state of knowledge in their assigned topics;
2. supplementary papers submitted by members of the Symposium, presenting new and original research dealing with the specific topics of the Symposium, and
3. discussion of principal and supplementary papers, presented by members of the Symposium.

Papers were presented in condensed form, but are given in full in these Proceedings. Some of the discussions were submitted prior to the Symposium, others at the time of the meetings or subsequent thereto.

After the Symposium, authors were invited to submit corrections to their papers, but did not have opportunity to read printers' proof. Readers of the Proceedings are asked to make allowance for this, as well as for the facts that some papers are the joint product of authors and translators, and that translations had sometimes to be edited without access to the original manuscripts.

Following the sessions in Washington, many of the members of the Symposium accepted a general invitation to travel to Skokie, Ill., to visit the laboratories of the Portland Cement Association and to attend a series of seminars there. A two-day expense-paid bus trip from Washington to the vicinity of the laboratories was arranged by the Portland Cement Association for foreign guests to enable them to see the countryside and to observe some typical highway systems, expressways, toll roads, and city streets in the United States.

The program at Skokie, October 10–12, included seminars on cement manufacture and on basic and applied research, as well as laboratory tours and demonstrations.

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Explanatory Notes

Abbreviations. The following symbols, which have been widely adopted by cement chemists for formulating more complex compounds, are used interchangeably with the respective oxide formulas throughout this book: C=CaO, S=SiO_2, A=Al_2O_3, F=Fe_2O_3, M=MgO, N=Na_2O, K=K_2O, H=H_2O. Less common abbreviations of this type are defined as they occur.

Commonly used abbreviations of more general nature include the following:

DTA=differential thermal analysis
FM=fineness modulus
IR=infrared
NMR=nuclear magnetic resonance
psi (or p.s.i.)=pounds per square inch
rh (or r.h.)=relative humidity
w/c (or W/C)=water-cement ratio

Identification Numbers of Papers. Each symposium paper has been assigned an identification number. Examples: Paper II–1 is the first principal paper of session II; paper II–S1 is the first supplementary paper of session II. With few exceptions, the numbers correspond to those assigned to the copies of the papers distributed in advance of the symposium.

Scale of Magnification. In micrographs, the scale of magnification frequently is indicated by a horizontal line. Where not marked, the length represents one micron.

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Proceedings of the Fourth International Symposium on the Chemistry of Cement

SESSION V. PROPERTIES OF CEMENT PASTE AND CONCRETE

Paper V–1. Physical Properties of Cement Paste*

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Synopsis

This paper deals mainly with cement paste in terms of its porosity, internal surface area, interaction between solid substance and evaporable water and related properties. There are 10 sections as follows: (1) introduction; (2) properties of fresh paste; (3) specific volume of hydrated cement and porosity of paste; (4) surface area of hydrated cement, and indicated particle size; (5) minimum porosity of hydrated paste and specific volume of cement gel; (6) concepts of structure of cement gel and cement paste; (7) mechanical effects of adsorption and hydrostatic tension; (8) instability of cement paste; (9) strength; (10) permeability.

Among the subtopics are the following: definition of pore and solid; permeability of paste at all stages of hydration; measurement of surface area; specific volume of cement gel; computation of capillary porosity; physical aspects of hydration products; adsorption and capillary condensation; spontaneous decrease of specific surface area of hydrated cement; irreversible deformations; gel-space ratio vs. strength; theories of permeability; viscosity of water in cement paste; capillary continuity and discontinuity.

A glossary of terms is appended.

Résumé

Cet exposé traite principalement de la pâte de ciment en fonction de sa porosité, de la surface spécifique interne, de l'action réciproque entre la substance solide et l'eau évaporable, et des propriétés qui s'y rapportent. Il y a 10 sections qui sont les suivantes: (1) introduction; (2) propriétés de la pâte fraîche; (3) volume spécifique du ciment hydraté et porosité de la pâte; (4) surface spécifique du ciment hydraté, et indication sur la taille des particules; (5) porosité minimum de la pâte hydratée et volume spécifique du gel de ciment; (6) concepts de structure du gel de ciment et de la pâte de ciment; (7) effets mécaniques de l'adsorption et de la tension hydrostatique; (8) instabilité de la pâte de ciment; (9) résistance; (10) perméabilité.

Parmi les points secondaires, les suivants sont traités: définition de pore et de solide; perméabilité de la pâte à tous les stades de l'hydratation; mesure de la surface spécifique; volume spécifique du gel de ciment; calcul de la porosité capillaire; aspects physiques des produits d'hydratation; adsorption et condensation capillaire; diminution spontanée de la surface spécifique du ciment hydraté; déformations irréversibles; rapport gel-espace versus résistance; théories de perméabilité; viscosité de l'eau dans la pâte de ciment; continuité et discontinuité capillaires.

Un lexique des termes se trouve en appendice.

Zusammenfassung

In dem Vortrag werden hauptsächlich die Porosität, die Größe der inneren Oberfläche, die Reaktion zwischen festem Körper und verdampfbarem Wasser und die damit zusammenhängenden Eigenschaften der Zementpasten beschrieben. Die zehn Kapitel haben die folgenden Überschriften: (1) Einleitung; (2) Eigenschaften der frischen Paste; (3) Das spezifische Volumen des hydratisierten Zementes und die Pastenporositat; (4) Oberfläche des hydratisierten Zementes und wahrscheinliche Teilchengröße; (5) Die Minimumporosität der hydratisierten Paste und das spezifische Volumen des Zementgels; (6) Der Zementgel- und Zementpastenstrukturbegriff; (7) Mechanische Effekte der Adsorption und der hydrostatischen Spannung; (8) Unbeständigkeit der Zementpasten; (9) Festigkeit; (10) Permeabilität.

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Als sekundäre Themen behandelt sind: Definition der Pore und des festen Körpers; Pastenpermeabilität in allen Hydratationsstufen; Oberflächenmessung; Das spezifische Volumen des Zementgels; Berechnung der kapillären Porosität; Physikalische Eigenschaften der Hydratationsprodukte; Adsorption und Kapillarkondensation; Abnahme der spezifischen Oberfläche des hydratisierten Zementes; Nicht umkehrbare Formveränderung; Die Festigkeit als eine Function des Verhältnisses gel/space; Permeabilitätstheorien; Die Viskosität des Wassers in der Zementpaste; Kapilläre Stetigkeit und Unstetigkeit.

Eine Liste der benutzten Worte ist am Ende hinzugefügt.

1. Introduction

The chemical origins of the substance called cement paste, and the physico-chemical processes of its formation, are essential elements of the study of physical properties of cement paste, and the properties of cement paste are reflected in almost every aspect of concrete technology. Thus, the study of cement paste provides a bridge between cement chemistry and concrete technology. A subject of such broad scope involves the whole literature of cement and concrete, and a complete critical review would have required more time than was available. Therefore, a complete review was not attempted.

This review turned out to be an occasion for revision and reassessment of our own work, and this entailed introducing some material not published before. Concepts of structure have been emphasized, and special attention is paid to a few points that have proved to be somewhat controversial. Perhaps the most important of these is the question of internal surface area: Are internal surfaces real, and have we measured them?

Little is said about differences in the chemical compositions of cements because the physical properties of paste are not much influenced by such differences. Any hydrated portland cement is predominantly colloidal and this point of similarity outweighs the points of difference attributable to differences in chemistry.

The words used for describing hydrated cement are those required for describing a chemically unidentified substance. In 1947 it was not possible, and still in 1960 it is not feasible, to use much chemical nomenclature. The ratios $CaO:SiO_2:H_2O$ for substances in cement paste are not definitely established, to say nothing of other components. There is reason to suspect that unique molecular ratios are not characteristic of hydrated cements. So, in this 1960 review it is still necessary to refer to grams of "nonevaporable water", and to "hydrated cement", instead of conventionally designated molecular species. The result is rather unsatisfactory to chemists and nonchemists alike, since a discussion based on arbitrary special definitions often becomes confusing if those definitions are overlooked. (A glossary of terms will be found in appendix 1.) Possibly, after other papers of this symposium have been digested, terminology will be improved.

2. Properties of Fresh Paste

The Dormant Period

During a short period beginning at the time of contact between cement and water, relatively rapid chemical reactions occur. Then follows a longer period of low activity which has been called the dormant period. [1, 2].[1] It is the time during which paste normally remains plastic, and, at room temperature, it normally lasts 40 to 120 min, depending on the characteristics of the cement.

The initial reaction does not seem to alter the size and shape of the cement grains very much. This is indicated, for example, by the following data obtained with a Wagner turbidimeter by Ernsberger and France [3].

Material	Dispersion medium	Specific surface cm²/g
Cement A	Kerosene	1,690
Cement A	Water	1,705
Cement B	Kerosene	2,590
Cement B	Water	2,630

Powers [4] found that the specific surface area calculated from the rate of bleeding of cement pastes by a modified Kozeny-Carman equation, was about the same for a paste made with kerosene as with water. Steinour [5] measured the bleeding rates of one cement in various liquids. The values for specific surface area, calculated from the Kozeny-Carman equation [6] were as follows:

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[1] Figures in brackets indicate the literature references at the end of this paper.

Name of liquid	Surface area, cm²/g
Dioxane	1, 680
Hexyl ether	1, 630
Butyl alcohol	1, 670
Octyl alcohol	1, 680
Diethylphthalate	1, 675
Average	1, 670
Water	1, 710

These figures indicate that reaction with water caused a slight increase in specific surface area.

The constancy of the rate of bleeding during the dormant period shows that the new products formed by reactions occurring during the dormant period do not effectively alter the surface contours of the particles, or change the viscosity of the liquid. Possibly, the layer of hydration products first formed, around which water flows during bleeding, is of loose enough texture to accommodate the small quantity of material produced during the dormant period.

Preparation of Pastes

The physical characteristics of a batch of fresh paste depend on how the paste is prepared. When mixed by gentle stirring, the paste remains stiff relative to the consistency produced by vigorous mechanical stirring [7]. Dry cement, which is normally in a flocculated state, is apparently not uniformly dispersed by wetting alone. To produce a homogeneous paste of lowest possible stiffness, a laboratory mixer able to produce a high rate of shear is necessary.

Length of mixing period is important. If it is of the order 30 sec or less, the paste becomes firm soon after mixing stops [8]. Steinour called this phenomenon "brief-mix-set" and attributed it to the grains becoming stuck together by gel in process of forming on grain surfaces. Even if the mixing period is long enough to prevent brief-mix-set, which is usually the case, it may be too short to eliminate false set. In the laboratory, it is advisable to allow a period of rest between an initial and final mixing period, the length of the rest period having been determined by trial for each cement. Examples of mixing schedules required to eliminate false set are given in table 1.

With the exception of matters pertaining to false set, time effects and mixing procedures are principally laboratory problems. Under normal field conditions, the time of mixing can hardly be so short as to permit brief-mix-set, and the rolling mass of aggregate in a concrete mixer "homogenizes" the paste as effectively as the most vigorous laboratory stirrer.

When a paste is properly prepared, its properties are reproducible, and are amenable to quantitative study. A considerable amount of such study has been done, and it gave information about the structure of fresh paste that is not only essential to an understanding of the properties and behavior of fresh concrete, but also is pertinent to various aspects of mature concrete.

Table 1. *Mixing schedules required by different cements to eliminate false set*

Specific surface: 1,500 cm²/g (Wagner Turbidimeter)

Tests were on 1:2 (by wt.) mortars made with Elgin sand.

w/c is that required for (1±0.05)-inch slump, with 6-in cone, after a 1 min mix

The first number of the mixing schedule is the length of the first period o mixing; the second is the period of rest; the last is the final mixing period.

ASTM type	Lot No.	w/c by wt.	Condition after 1-min mix		Required mixing schedule	Remolding effort, jigs	Slump 6-in. cone
			R.E. [c]	Slump			
					min		*in*
1	15753	0. 36	27	1. 05	2–0–0	25	1. 25
1	15760 [b]	. 35	41	. 85	2–2–2	33	1. 10
2	15755 [a]	. 34	32	1. 10	2–2–2	26	1. 10
3	15757 [a]	. 34	33	. 95	2–3–2	27	1. 05
4	15762 [b]	. 34	42	. 85	2–5–2	22	1. 40

[a] This cement showed evidence of moderate false set.
[b] This cement showed marked false set.
[c] Remolding effort, number of jigs.

The Flocculent State

During the dormant period, properly prepared paste is a thick suspension of particles in a flocculent state. Steinour [9] found that the term "flocculent state" is not to be construed to mean that the paste consists of a collection of more or less separate floccules. Instead, the whole body of paste constitutes a *single floc,* the floc structure being a rather uniform reticulum of cement particles. Because of such structure, fresh paste has some cohesive strength, as shown by its rheological properties.

The flocculent state can be modified or destroyed by means of surface-active agents. Such agents have been studied extensively, particularly in the Soviet Union, but, this being the subject of another paper of the Symposium, it will not be dealt with here.

Studies of sedimentation volume indicate that cement particles in water, though flocculent, are not normally far from the dispersed (nonflocculent) state [10]. The sedimentation volume of cement in dry alcohol, in which the particles are completely dispersed, is only a little smaller than the sedimentation volume of cement particles in water, whereas the sedimentation volume in a nonpolar liquid, benzene, for example, is nearly twice that in dry alcohol. The relatively low intensity of interparticle attraction between cement particles in water is probably due to the hydrophilic nature of cement.

Although the floc structure of cement paste has some strength and rigidity, the cement particles are nevertheless discrete during the dormant period. This was shown by measurements of hydrostatic pressure [11]. The constancy of the rate of bleeding also shows that the particles remain discrete during the dormant period. It appears that where the gel-coated grains are almost in contact, they are separated by a thin layer of water, probably only a few angstrom units thick. The constancy of the bleeding rate signifies in particular that such thin, separating layers of water have no solidity.

This last-mentioned observation seems contrary to what has been reported for some mixtures of clay and water [12], namely, that rigid, ice-like structures develop in the small spaces between solid surfaces. The flocculent state in cement paste seems explicable in terms of classical theory, viz., the gel-coated grains carry a "solvated layer" and they have a positive zeta potential [13]. The combined effect of solvated layer and electrostatic charge is such as to prevent actual contact between adjacent grains. But the grains are concentrated enough to experience interparticle attraction, at least over parts of their boundaries. The effects of repulsion and attraction balance at a certain distance of separation where the potential energy of the particles is at a minimum. The cement grains tend to remain in "potential troughs", which are so located as to require spaces between the particles.

Solvated surfaces and electrostatic charge account in part for the kind of rheological properties exhibited by cement pastes. Other factors are the size, shape, and concentration of particles, and the viscosity of the fluid. In pastes of relatively stiff consistency, effects of interparticle forces dominate, viscosity playing a minor role [14]. At softer consistencies, w/c=0.4 and above, cement paste is, as Reiner puts it, " . . . a first approximation to a Bingham body" [15].

Sedimentation (Bleeding)

Because cement particles remain discrete during the dormant period, and because the suspending medium is viscous, the suspension is not stable under the pull of gravity; cement paste "bleeds". Bleeding has been referred to as an aspect of coacervation [16] but experimental evidence that it is something other than gravitational settlement seems lacking.

The initial rate of bleeding remains constant for a period determined by various factors [1, 2]. Although the largest cement particles are a hundred or more times the size of the smallest, all sizes are forced to fall at the same rate because of the flocculent state. Hence, the fluid appearing above the solids remains clear and free from fine particles. If sedimentation becomes completed within the dormant period, physical factors alone determine the particle concentration in the final sediment. When setting arrests bleeding before the process is physically complete, the final sediment does not have uniform concentration of cement grains. At the bottom there may be a layer of completed "sedimentation zone", but, at the top, w/c remains at the initial value. Thus, the final composition of a specimen of cement paste may differ from the initial composition, and the specimen as a whole may become considerably less homogeneous than it was at the beginning.

The lowest possible water content of the completed sediment is higher, the higher the original water content of the paste [18]. In contrast to this, Steinour found that thick suspensions of emery would always settle to the same final volume, regardless of the initial volume of the suspension, provided the particles were in a nonflocculent state [19]. Presumably, cement particles would do the same were it not for their flocculent state.

The greatest possible amount of water that can be lost from a paste by bleeding under the force of gravity alone has been called the "bleeding capacity" [18]. It is a function of the initial water content, and it appears to follow a regular law. Steinour's studies led to several approximations of it, one of which may be stated as follows:

$$\Delta H' = \frac{K^2 c \rho_c}{V} [w/c - (w/c)_m]^2. \tag{1}$$

Where $\Delta H'$ is the bleeding capacity expressed as settlement per unit of original height; w is the initial weight of water; c the weight of cement; ρ_c is the density of the cement, and V is the initial volume of the paste. The symbols K, and $(w/c)_m$, are empirical constants characteristic of a given cement, and are dependent mostly on the surface area of the cement; $(w/c)_m$ was interpreted as the water cement ratio of a "base" paste in which the particles are so concentrated that bleeding cannot occur. It is evaluated by extrapolation of plotted data, and may be regarded as referring to a hypothetical paste.

The values of the constants in eq (1), for a given cement, can be altered by any means that changes the state of flocculation. Increase of interparticle attraction increases the base water content, and vice versa. Owing, presumably, to the interparticle water films, the base volume is larger the finer the cement.

Permeability of Fresh Paste

Rate of bleeding is related to the coefficient of permeability of the (nonsettled) paste as shown in eq (2).

$$Q = K_1[(\rho_c/\rho_f) - 1](1 - \epsilon). \tag{2}$$

Q is the rate of bleeding in cm/sec, or cc/cm^2 sec; K_1 is the coefficient of permeability to a specific fluid at a specific temperature, in cm/sec; ρ_c and ρ_f are densities of cement and fluid respectively, in g/cc; ϵ is the volume of fluid-filled space per unit volume of paste, i.e., the porosity.

The permeability of paste made with a given cement depends on temperature and water content. There is a limiting water content below which the pastes all maintain continuous floc structure during bleeding, and above which the structure becomes ruptured and "channeled bleeding" occurs [20]. Most of the ensuing discussion pertains to "normal" rather than "channeled" bleeding.

The mean size of pores in fresh paste can be estimated from hydraulic radius, that is, the quotient of water content and wetted surface area. An example is given in table 2. The figures in the final column are based on the assumption that the section of a typical pore resembles a rectangular slit [21]. At a given water content the pore size is smaller the larger the specific surface area of the cement.

TABLE 2. *"Pore" sizes of fresh pastes for cement having a surface area of 6,000 cm²/cc (1,900 cm²/g, Wagner)*

Water cement ratio by wt.	ϵ	Hydraulic radius, microns	Estimated average width of pore, microns
0. 25	0. 44	1. 25	Between 2½ and 5
. 40	. 56	2. 12	Between 4 and 8
. 50	. 61	2. 60	Between 5 and 10
. 60	. 66	3. 23	Between 6½ and 13
. 70	. 69	3. 70	Between 7½ and 15

A theoretical equation for the coefficient of permeability making use of the hydraulic radius, and based on the Kozeny-Carman concept, is

$$K_1=\frac{\rho_f g}{k_0(\rho_c\Sigma)^2(1-w_i)}\cdot\frac{(\epsilon-w_i)^3}{(1-\epsilon)^2}. \tag{3}$$

The corresponding equation for bleeding rate is

$$Q=\frac{(\rho_c-\rho_f)g}{k_0\eta(\rho_c\Sigma)^2(1-w_i)}\cdot\frac{(\epsilon-w_i)^3}{(1-\epsilon)}. \tag{4}$$

Symbols not already used are defined as follows: Σ is the specific surface of the cement grains in cm²/g, as determined by a suitable permeability method; η is the viscosity of the fluid in poises. Theoretically, w_i is related to a fraction of the fluid that remains with the particles during flow. As shown by Steinour's work [22], the term $(1-w_i)$ of eq (4) must be squared when a specific surface value is used that is based on sedimentation analysis and calculated by Stokes' law in the usual way, which does not take account of fluid that accompanies the particles. The w_i seems to be composed of three elements, that is,

$$w_i=\frac{a+b\Sigma}{1+a+b\Sigma}+c \tag{5}$$

where $a(1-\epsilon)$ is a quantity of fluid held stagnant on the irregular grains, and $b\Sigma(1-\epsilon)$ is a volume added to the original cement grains by the initial chemical reaction. The terms a and $b\Sigma$ therefore occur because of an augmentation of the solids, and a diminution of the fluid, so far as flow is concerned. The c in w_i is zero for nonflocculated suspensions, but always appears when a thick suspension becomes flocculated. For spherical particles, $c=0.1$, approximately [23], and a and b are zero. For crushed glass, b is zero and w_i is approximately 0.18. Experiments with pulverized silica in suspensions of lime water with different concentrations of calcium hydroxide showed that as long as the floc structure was strong enough to give normal bleeding, varying the degree of flocculation did not influence c [24]. (The degree of flocculation does, however, strongly influence the bleeding capacity.) Steinour's data on experiments with suspensions of monodisperse emery particles showed that the change from nonflocculated to flocculated state simply increased w_i. Thus c represents the effect of flocculation per se. Perhaps the best explanation of it is that it represents water in isolated pockets excluded from the continuous floc structure, and is therefore not to be considered when computing the hydraulic radius of the floc structure.

The experimentally observed fact that the modified Kozeny-Carman equation represents experimental results accurately indicates that the product $k_0(1-w_i)$ is a constant that can be identified with the Kozeny-Carman constant, k. Thus

$$k=k_0(1-w_i). \tag{6}$$

Steinour's findings, expressed in terms of eq (6), but with $(1-w_i)$ squared since w_i was determined by sedimentation analysis, show that for suspensions of chemically inert spheres, w_i is zero and $k_0=4.06$. Such a value for spheres is in agreement with Carman's statement to the effect that k for fluidized spheres is equal to 4.0 [25]. If the particles are irregular but chemically inert, the a in w_i is finite and b is zero. In this case $k<4.06$. Obviously, if a and b are both finite, k may be still smaller.

Empirically, it was found that the bleeding rates of pastes conformed to eq (7) [26].

$$Q=\frac{(\rho_c-\rho_f)g}{5\eta(\rho_c s)^2}\cdot\frac{(\epsilon-w_i)^3}{(1-\epsilon)}. \tag{7}$$

In this equation s is the specific surface area as determined according to ASTM designation C 115–58. The constant 5 is correct only if this measure of surface area is used. The w_i factor must be evaluated empirically for each different cement by methods that have been described [27]. Steinour showed that variation in w_i among different cements was due principally to differences in specific surface and in the initial chemical reactions with water [28].

Capillary Forces in Cement Paste

The bleeding rate of concrete is of the same order of magnitude as the natural rate of evaporation from an open surface. Sun and wind together often cause the rate of evaporation to exceed the rate of bleeding. When this occurs, the surface loses its sheen, signifying that the plane surface of water has become replaced by myriad curved surfaces, and this signifies that capillary tension has been produced. Carman has shown that the maximum possible capillary tension in a water-filled granular bed occurs just as the water level drops below the upper boundary of the bed, and the meniscuses take on the greatest possible curvature, that being limited by the sizes and shapes of the spaces between particles at the top surface [29]. The approximate value of maximum capillary tension can be calculated from the following relationship adapted from the basic relationships given by Carman.

$$P_C = -\frac{\lambda \sigma \rho_f / \rho_c}{w/c} \tag{8}$$

where λ is the surface tension of water in dynes/cm, σ is the specific surface area of the cement in cm^2/cc, and P_C is capillary pressure, a negative quantity. Substitution of appropriate figures into eq (8) shows that maximum capillary tension will range from about ½ atm upwards depending on the surface area of the cement.

The reaction to capillary tension is, of course, an equal downward force exerted on the particles at the top of the bed. Since the downward force on those particles due to gravitation only is only about 0.001 atm, it is clear that when the rate of evaporation exceeds the normal rate of bleeding the force causing subsidence of the surface may be greatly increased. The effects of such an increase have been measured under controlled conditions by Klieger [30].

When resistance to consolidation becomes high enough to offset capillary tension, the water surfaces retreat to the interior, and lateral consolidation begins. The result is the so-called "plastic shrinkage", often giving rise to "plastic-shrinkage cracking". Swayze has expressed the view that a significant and technically important degree of compaction of fresh concrete can be produced by capillary tensions that may develop throughout a period of several hours, and he proposed a procedure for taking advantage of it [3].

3. The Specific Volume of Hydrated Cement and the Porosity of Hardened Cement Paste

Definition of Pore and Solid

It is undisputed that porosity is a basic property of hardened cement paste, but there may be disagreement as to the definition of pores. In the studies now being reviewed, pores are defined as spaces that can be occupied by water that is evaporable at a constant low external humidity, at a given temperature.[2] A change of either the specified temperature or humidity results in a corresponding change in the apparent ratio of solid to void. Thus, the choice of drying conditions defines the pore space and the solids, and does not assuredly isolate, or precisely establish, the true extent of the solid phases.

Problems of Mensuration

Besides the difficulty of isolating the solid phases, except on an arbitrary basis, the quantitative, accurate measurement of solid volume also presents difficult problems. Hydrated cement is mostly colloidal (see glossary) and of the total number of molecules composing the colloidal part, perhaps one-half to two-thirds of them are exposed at surfaces. Seen on an atomic scale, the surfaces of the particles, i.e., the boundaries of the pores, are transition zones of vibrating atoms, and thus the word surface as applied here does not connote the conventional geometric concept; the boundary is neither sharp, smooth, nor static. In regions of minimum porosity (see sections 5 and 6) the average distance between surfaces is about 5 oxygen-atom diameters, and in these places the rough transition region might constitute a significant fraction of the interparticle space.

The porosity of a given specimen is determined to a small but significant degree by the balance between opposing internal forces. To introduce a fluid into such a system of particles releases energy and alters the balance of forces. The surfaces change their relative positions, and the porosity changes too; swelling occurs. (See section 7). Even the specific gravity of the solid material may change slightly, owing to the change in interfacial free energy. The quantity of fluid that can be accommodated in interstitial spaces thus depends partly on the amount of swelling, accompanying entry of the fluid. It may depend, too, on how the molecules of the fluid "fit" the atomic roughness of the surfaces, and on the size of molecule relative to the size of the smallest interstitial spaces. Swelling produced by water is much greater than that produced by organic liquids or inert gases, water molecules being relatively small and strongly attracted by the surface.

Fluids that affect interparticle forces are themselves affected; they are adsorbed. Possibly, strongly adsorbed water molecules penetrate the transition region of the solid more than weakly absorbed molecules do. It is frequently suggested that some of the space found by sorbed water molecules is inside the crystals, but this seems doubtful, as will be seen further on. Whether or not these phenomena occur, it is probable that the average amount of space required per molecule of water in the adsorbed state is different from that required in the liquid state, which is to say that the average density of water in the adsorbed state may differ from that in the liquid state. Powers and Brownyard [32] estimated the specific volume of gel water, most of which is strongly adsorbed, at 0.90 cc/g. But this estimate was based on density

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[2] This definition is not intended to include entrained air bubbles and the like, which are regarded as cavities rather than integral parts of paste.

of hydrated cement as determined by displacement in helium, and therefore it may not be correct for water, as was acknowledged at the time. Thus, although it is easy to determine the mass of water required to saturate the spaces in cement paste, it is impossible at present to determine a corresponding volume exactly.

Experimental Results

A direct approach to the problem of measuring porosity was based on the following expressions:

$$\epsilon=1-\frac{cv_c}{V}\left[1-m+m(1+w_n^\circ/c)\frac{v_{hc}}{v_c}\right] \tag{9}$$

$$\epsilon=1-\frac{m\left[(1+w_n^\circ/c)\frac{v_{hc}}{v_c}-1\right]+1}{1+\frac{w_0/c}{v_c}}. \tag{10}$$

ϵ is the porosity; m is the maturity factor (fraction of the original cement that has become hydrated); v_{hc} is the specific volume of hydrated cement in cc/g; w_n° is the nonevaporable water content of completely hydrated cement in grams; w_0 is the original water content in grams, corrected for water displaced by bleeding; c is the original cement content in grams, and v_c is the specific volume of the original cement in cc/g.

All the factors in eqs (9) and (10) are subject to direct measurement, but with attendant difficulties, especially for v_{hc}. In attempts to measure v_{hc}, various liquids were used as displacement media with various results [33]. For example, water, acetone, toluene, and helium gave the following values for v_{hc}, based on the normal density of each fluid: 0.395, 0.408, 0.429, and 0.424. These results from preliminary experiments were followed by a considerable amount of work with helium. The displacement in helium of samples prepared by the magnesium perchlorate method was finally reported, from work by Steinour [34], as 0.41±0.01 cc/g for four different cements. Since the four cements were chemically different, and showed similarity in specific volume of hydration products, it was assumed that for any cement the approximate density of hydrated cement might be estimated from the relationship given in eq (11).

$$v_{hc}=\frac{v_c+v_n w_n^\circ/c}{1+w_n^\circ/c} \tag{11}$$

where v_n is the apparent specific volume of the nonevaporable water, cc/g. The values of v_n for the four cements were calculated from their helium displacements by means of eq (12).

$$v_n=\frac{(V_s/c)-v_c}{w_n/c}. \tag{12}$$

V_s is the volume of the dry sample, indicated by its displacement of helium, and c the cement content of the sample, grams. The mean value obtained for four different portland cements was $v_n=0.82$. The individual values ranged from 0.81 to 0.83.

An advantage of eqs (11) and (12) is that they permit evaluation of v_{hc} from gas displacement data on samples of paste that contain unhydrated cement.

Weir, Hunt, and Blaine [35] evaluated v_n from experiments based on eq (13).

$$v_s=v_c+(v_n-v_c)\frac{w_n/c}{1+w_n/c}. \tag{13}$$

In this equation, v_s is the specific volume of the solid material in the sample, cc/g, including unhydrated cement, if any. Small cylinders (½ x 4 in) of cement paste were cured for various periods and then dried by the "dry-ice" method of Copeland and Hayes [36]. Then the specimens were immersed in a light petroleum distillate, and the distillate and the specimen immersed in it were subjected to pressures up to 10,000 atm, the primary purpose of the experiment being to determine the compressibility of the solid phases. After release of pressure, the amount of distillate remaining in the specimen at atmospheric pressure was determined. Also the overall volume of the distillate-saturated specimen was measured by displacement. The resulting values of v_s were plotted against $(w_n/c)/(1+w_n/c)$, producing a straight line having an intercept at $v_s=v_c$. The slope of the line and the corresponding value of v_c gives, for a portland cement, $v_n=0.87$, for an aluminous cement, $v_n=0.75$. Comparing the result for portland cement with that reported by Powers and Brownyard, 0.82, Weir, Hunt, and Blaine mentioned that their higher result might be due to the presence of a little evaporable water in their specimens, because of incomplete drying. However, calculation shows that even if the specific volume of the residue of evaporable water in their specimens was as high as 1.0, the amount would have had to be about 40 percent of w_n, to account for the difference in question. Therefore, the data seem to indicate that helium penetrates regions not accessible to the distillate molecules.

The problem of determining the specific volume of hydrated cement and the specific volume of evaporable water has been approached by considering a saturated paste to be composed of two components: (1) the solid material and (2) the evaporable water [37]. From a normal procedure of physical chemistry, it follows that,

$$v_p'=N_{hc}'\bar{v}_{hc}+N_e'\bar{v}_e \tag{14}$$

in which v_p' is the specific volume of the paste, corrected for any residue of anhydrous cement; N_{hc}' is the weight fraction of hydrated cement; N_e' is the corresponding weight fraction of evaporable water; $\bar{v}_{hc}$ and $\bar{v}_e$ are the "partial specific volumes" of the solid material and evaporable water respectively. For example,

$$\bar{v}_e=\frac{\partial V}{\partial w_e} \tag{15}$$

where V is the volume of the paste and w_e is the weight fraction of evaporable water. As used in the present case, $\bar{v}_e$ pertains to the evaporable water in a saturated specimen.

Among the many test data, the values of N'_e varied widely. When the values of specific volume of the specimen, v'_p cc/g, were plotted against corresponding values of N'_e, the points conformed closely to the straight line represented by the following equation.

$$v'_p=0.398N'_{hc}+0.99N'_e. \tag{16}$$

Equation (16) seems to indicate that 0.398 is the specific volume of hydrated cement, and 0.99 is that of the evaporable water. However, a linear relationship such as eq (16) is characteristic of physical mixtures of two components that do not interact either chemically or physically when they are brought together. In the present case it is known that when dry hydrated cement and water are brought together the energy content of the system decreases, as shown by evolution of heat, the amount of heat released being over 20 cal/g of hydrated cement [38]. In view of this, it does not seem likely that the specific volume of either component would be the same after mixing as it was before. The following considerations seem to reconcile the result indicated by eq (16) and the observations just mentioned.

It is known that at humidities up to about 45 percent, the amount of water held in the adsorbed state is proportional to the amount of hydrated cement in the sample, and is independent of the total capacity for evaporable water. The amount adsorbed at 45 percent humidity is a little less than two molecular layers on the solid surface. This is the strongly adsorbed part of the evaporable water, as shown by its relatively high heat of adsorption. The rest comprises weakly adsorbed water and, if any, water free from the effects of adsorption. The fraction of the total evaporable water in excess of two molecular layers is greater the higher the porosity of the paste, and thus that part does not bear a constant ratio to the amount of hydrated cement.

It follows that if a specimen of saturated cement paste is to be treated as a two-component system, it is not permissible, a priori, to identify hydrated cement as one of the components, and total evaporable water as the other, because the properties of some of the evaporable water are certainly not independent of the other component, hydrated cement, although the properties of the rest of the water might be. It seems therefore that the simplest permissible assumption is that saturated cement paste is made up of three components: hydrated cement, adsorbed water, free water. On this assumption one would write in place of eq (14),

$$v'_p=N'_{hc}\bar{v}_{hc}+N'_a\bar{v}_a+(N'_e-N'_a)v_w \tag{17}$$

where N'_a is the weight fraction of adsorbed water that stands in constant ratio to N'_{hc}, $\bar{v}_a$ is its partial specific volume and v_w is the specific volume of free water. Expressing the proportionality between adsorbed water and the solid material as $N'_a=bN'_{hc}$, and thereby eliminating N'_a from eq (17), we obtain

$$v'_p=N'_{hc}[\bar{v}_{hc}+b(\bar{v}_a-v_w)]+N'_e v_w. \tag{18}$$

On comparing eq (18) with eq (16), we see that $v_w=0.99$ and $v_{hc}+b(\bar{v}_a-v_w)=0.398$. Therefore, the results obtained from this analysis were:

The linearity of the plot signifies either of two conclusions: (A) *All* the evaporable water has a specific volume of 0.99 cc/g (for these particular specimens) whether adsorbed strongly, weakly, or not at all, in which case $v_{hc}=0.398$, or (B) *Some* of the evaporable water in every specimen has a specific volume of 0.99, and the rest, an amount proportional to the amount of hydrated cement, might have a different specific volume, in which case the specific volume of the hydrated cement is not 0.398 cc/g. Conclusion (B) is probably the correct one.

Another analysis [37] was based on the empirical relationship

$$v_t=0.99-0.25\ w_n/w_t \tag{19}$$

where v_t is the apparent specific volume of all the water in saturated specimens, including w_n. It would appear that at $w_n/w_t=1.0$, $v_t=v_n=0.74$, for, if eq (19) is valid over its entire range, the 0.25 is $\bar{v}_e-v_n$. However, on the basis of the same observations and reasoning presented in connection with eqs (16), (17), and (18), $(\bar{v}_e-v_n)w_n$ may be replaced by $(1+B)(v_w-v_d)w_n$, where B is the weight fraction of evaporable water that stands in constant ratio to w_n, and which may have a specific volume different from that of the rest of the evaporable water, and v_d is the mean of the specific volumes of the nonevaporable water and the part of the evaporable water whose density is altered by adsorption. Then

$$v_t=v_w-(1+B)(v_w-v_d)(w_n/w_t). \tag{20}$$

On comparing eqs (19) and (20) it is evident that $(1+B)(0.99-v_d)=0.25$, or, $v_d=0.99-\frac{0.25}{1+B}$.

This result presents the same impasse as eq (18). It cannot be solved unless the fraction, B, of evaporable water having density different from that of the rest is known. Indeed, even if B were known, the apparent volume of the water in the solid phase, v_n, would still be unknown unless the mean density of the adsorbed water were known also. Only if it is arbitrarily assumed that $B=0$

TABLE 3. *Specific volume of hydrated cement*

$$v_{hc}=\frac{v_c+v_n\frac{w_n^\circ}{c}}{1+\frac{w_n^\circ}{c}}$$

v_{hc}=specific volume of hydrated cement
v_c=specific volume of original cement
v_n=apparent specific volume of nonevaporable water
$\frac{w_n^\circ}{c}$ =grams of nonevaporable water per g cement at complete hydration

Cement No.	Computed composition—%					v_c cc/g	$\frac{w_n^\circ}{c}$	v_{hc}, cc/g		
	C_3S	C_2S	C_3A	C_4AF	$CaSO_4$			v_n=0.74	v_n=0.82	v_n=0.87
15754	45.0	27.7	13.4	6.7	4.0	0.319	0.246 [a]	-----	0.418 [b]	-----
15754	45.0	27.7	13.4	6.7	4.0	.319	.227	0.397	.411	0.421
15622	49.2	28.5	4.4	12.8	2.7	.310	.176	.374	.386	.394
15699	33.0	54.2	2.3	5.8	3.1	.311	.174	.374	.386	.394
15497	60.1	11.9	10.3	7.9	3.1	.322	.210	.394	.408	.417

[a] This figure is based on samples prepared by the magnesium perchlorate method. All the rest in this column are for samples prepared by the dry ice method.

[b] This figure is on the magnesium perchlorate basis. All the others in the last three columns are on the dry ice basis, and are subject to limitations mentioned in the text.

and thus that $v_d=v_n$, do we obtain $v_n=0.74$. This is the lowest possible value for v_n.

Table 3 is a summary of the findings in terms of experimental and calculated results for four different cements. Specific volume as given in the first line corresponds to direct determinations by helium displacement of samples prepared by the magnesium perchlorate method. The rest of the values in the last three columns were calculated from the values of v_n at the heads of the columns. Values in the column headed $v_n=0.74$ are based on displacement in water (aqueous solution), and are the smallest possible, entailing the assumption that all parts of evaporable water have a specific volume of 0.99 cc/g. Values reported under $v_n=0.87$ represent displacements in petroleum distillate, applied to different cements on the assumption that v_n is the same for all. Values reported under $v_n=0.82$ represent displacements in helium, and the same value of v_n is assumed to apply to specimens prepared by either of the two methods.

There appears to be little theoretical or experimental support for an assumption that $v_n=0.74$, which is to say that the average density of adsorbed water is the same as that of the aqueous solution in fresh paste. The entropy change on adsorption of the strongly adsorbed part [50] is such as to suggest a considerable change of state from that of free liquid. It seems likely that such a change involves a change of density. If there is a change, an increase seems probable, in view of the openness of the structure of liquid water. The value of v_n obtained from helium measurements, 0.82, indicates either that helium is excluded from some spaces accessible to water, or that when water is used as a displacement medium, it is densified by adsorption, or that both factors are involved. Assuming that the difference is due to densification only, it comes out that the specific volume of gel-water ($w_e=3.0\ V_m$; see section 5) is about 0.90 cc/g.

Although the figures for petroleum distillate probably are valid for that fluid, they do not seem to indicate complete penetration of pores. Calculation on that basis shows that the porosity of cement gel to helium is 7 percent greater than the porosity to the distillate.

On the whole, the state of this subject is unsatisfactory. For general purposes it seems that the helium values give the best estimate of v_{hc}.

4. Surface Area of Hydrated Cement and Indicated Size of Primary Particles

Surface Area From Water-Vapor Adsorption

From work reported in 1946 [40] it was deduced that the specific surface area of the solids in mature cement paste is equivalent to that of a sphere having a diameter of 140 A, which is 430 m²/cc, or about 180 m²/g of dry paste. Subsequent work calls for an upward revision of this figure for surface area.

Determination of surface area of hydrated cement is based on water-vapor adsorption interpreted in terms of the Brunauer-Emmett-Teller theory (BET) [41]. A convenient formula is

$$S_{hc}=3{,}800\,\frac{V_m/c}{m+(w_n/c)} \tag{21}$$

where S_{hc} is the specific surface area of hydrated cement, m^2/g. The numerical coefficient comprises Avogadro's number, the molecular weight of water, and the area covered by a single adsorbed water molecule. Powers and Brownyard [42] used a lower value, 3,570, based on a molecular area of 10 6 A^2/molecule. Recently Brunauer, Kantro, and Copeland [43] concluded that for adsorption of water on tobermorite gel the best value is 11.4. The value 3,800 corresponds to that figure.

Discussion of Eq (21)

BET Surface Factor, V_m

Theoretically V_m is the weight of water required to cover the surface of solid material with a layer 1 molecule thick, and w_n is water that is a component of the solid phase. Actually, there is some uncertainty as to the relations between observed values of V_m and w_n and the theoretically correct values. To obtain the theoretically correct value of V_m the process of adsorption should begin with a "bare" surface. The practice of outgassing with heat to assure this initial condition cannot be followed because the solid tends to decompose when heated. It is necessary to depend on an arbitrarily established drying procedure. Nevertheless, the resulting uncertainty is not such as to destroy the practical value of the data, as is shown especially well by study reported by Tomes, Hunt, and Blaine.

Tomes, Hunt, and Blaine [44] investigated the influence of various degrees of drying of test samples on the experimentally determined values of V_m and w_n. Using the dry ice method described by Copeland and Hayes [36] they tested samples of the same material after seven different periods of drying ranging from 2.6 to 12.1 days, the shortest period giving a value of w_n about 25 percent greater than that given by the longest. Within the range of these data, Tomes, Hunt, and Blaine found that

$$(V_m)_1-(V_m)_2=-0.354[(w_n)_1-(w_n)_2]. \qquad (22)$$

Or, in terms of ratios,

$$\frac{(V_m)_1}{(V_m)_2}=1-0.354\,\frac{(w_n)_2}{(V_m)_2}\left(\frac{(w_n)_1}{(w_n)_2}-1\right). \qquad (23)$$

The graph of these data indicates that experimental data would conform to eqs (22) and (23) even to the ultimate values for the given condition of drying. Thus, if the arbitrary drying procedure is too short to remove all the evaporable water, the difference between the observed value of V_m and the correct value is proportional to the difference between the observed nonevaporable water content and the correct one.

Even if the ultimate values of V_m and w_n for a given procedure of drying are obtained, it may be that the humidity maintained in the desiccator is too high to produce a bare surface at the temperature of the experiment. However, inasmuch as the drying conditions used for the experiments of eq (22) are probably not very far from the theoretically correct one, it may be expected that a change to the correct drying condition would result in a relationship like eq (22) with a slightly different value for the numerical constant. Thus, there is reason to assume that the value of V_m obtained by the arbitrarily chosen drying procedure is not very much different from the correct value.

The proportionality between V_m and surface area depends on two factors: (a) average area covered by an adsorbed water molecule, and (b) the difference between the observed and the theoretically correct V_m. The first factor depends not only on the size of the water molecule but also on the structure and composition of the surface on which it is adsorbed. The second factor depends on drying conditions, as just discussed. It thus seems clear that V_m must be "calibrated" for a given material and drying condition. The calibration involves establishing a value for molecular area. The value now used, 11.4 A^2, is that which gave the same surface area by water-vapor adsorption as was obtained by nitrogen adsorption on a laboratory preparation of afwillite. The first estimate of the area of the water molecule on this basis gave 11.8 A^2 [45]. This was later revised to 11.4 A^2 [43]. This method of establishing the molecular area is not the most rigorous that might be devised. Moreover, there is no way to assess the accuracy of the result, other than by the degree to which the computed areas contribute to the internal consistency of various related data. On this score, the results now appear very good.

The values of w_n formerly obtained were about 8 percent higher than those obtained now by the Copeland and Hayes method. Present values of V_m are correspondingly different from the old values. The relationship between the values of V_m now obtained and those formerly obtained may be shown as follows: Using eq (23), let subscript $_1$ denote values obtained by the magnesium perchlorate method, and $_2$ those obtained by the dry ice method. For a particular cement (No. 15754) experimental values were $(w_n/V_m)_2=3.23$, and $(w_n)_1/(w_n)_2=1.084$. With these figures, eq (23) gives $(V_m)_1=0.904\,(V_m)_2$, and $(V_m/w_n)_1=0.258$. This value, based on the Tomes, Hunt, and Blaine empirical eq (23), is the same as that reported by Powers and Brownyard [46] from direct experiment, 0.258 ± 0.002. The exactness of agreement may be somewhat fortuitous, since the cements were not exactly alike.

Maturity Factor, m

This factor is the weight fraction of cement that has become hydrated, i.e.,

$$m=c_h/c \qquad (24)$$

where c is the original weight of cement and c_h is the weight of that part which has become hydrated.

(This is *not* the weight of the hydrated cement.) For most cements, apparently all but ASTM Type IV, the following relationships may be used for any intermediate stage of hydration after the first few hours;

$$c_h/c=w_n/w_n^\circ=V_m/V_m^\circ=\Delta H/\Delta H^\circ.$$

(The degree mark indicates that the quantity is for completely hydrated cement.) When the above equalities exist it follows that $\Delta H/w_n$ and V_m/w_n remain practically constant throughout the period of hydration at values characteristic of the cement. This means also that the specific surface area of the hydrated cement remains practically constant at a value given by the following equation:

$$S_{hc}=3800\left[\frac{w_n^\circ}{c+w_n^\circ}\right]\frac{V_m}{w_n}. \tag{25}$$

Correction for Calcium Hydroxide

To obtain the surface area of the colloidal part of cement gel (see glossary) it is necessary to make a correction for calcium hydroxide, which has negligible surface area.[3] Eq (26) may be used.

$$S_{\text{col}}=\left[1+\frac{(CH)}{w_n}\cdot\frac{w_n}{c+w_n}\right]S_{hc}. \tag{26}$$

(CH) is the weight of calcium hydroxide, and S_{col} denotes surface area of the colloidal part of cement gel, cm²/g dry weight. (CH) may be determined by X-ray analysis, as described by Copeland and Bragg [47].

Experimental Results

Mature Pastes

Data obtained from four different cements are given in table 4, and the results of applying eqs (25) and (26) are given in the first four lines of table 5. In general, the results are the same as those reported previously [48]: The specific surface of cement gel is not affected very much by differences in chemical composition of cement.

The last two lines of table 5 contain data derived from the data of Brunauer, Kantro, and Copeland on the hydration products of C_3S and C_2S [43]. The values of w_n°/c, $(CH)/w_n$, and V_m/w_n were calculated from the data in their table 3, and from the assumption that in colloidal tobermorite the ratio of CaO to SiO_2 is exactly 3/2. The values for S_{hc} are experimental. From a comparison of these data with those in the upper part of the table it appears that the specific surface of the colloidal part of cement gel is from 10 to 20 percent lower than that of pure colloidal tobermorite. Brunauer, Kantro, and Copeland suggested that the sheets and ribbons of colloidal tobermorite may be two or three unit cells thick.

TABLE 4. *Data used for computing surface area of hydrated cement and cement gel*

Reference No.	w/c	Age, days	Number of values averaged	w_n/c	$\frac{V_m}{w_n}$
Clinker 15367; Cement 15754; $(CH)/w_n=1.18$; $w_n^\circ/c=.227$					
B-8-3	0.40-.70	81-541	10	0.2147	0.304
B-15	.35	511	1	.1900	.317
B-20-1	.45-.65	80-543	70	.2196	.312
290	.23	11 yr	1	.1570	.287
Weighted average					.311
Clinker 15623; Cement 15756; $(CH)/w_n=1.36$; $w_n^\circ/c=0.174$					
B-8-3	0.50-.65	98-224	8	0.1593	0.347
B-15	.35	513	1	.1457	.394
B-20-1	.55	600	6	.1693	.349
290	.23	11 yr	1	.1328	.378
Weighted average					.355
Clinker 15670; Cement 15763; $(CH)/w_n=0.858$; $w_n^\circ/c=0.170$					
B-8-3	0.45-0.65	315-394	4	0.1525	0.409
B-15	.35	505	1	.1337	.452
B-20-1	.55	600	6	.1506	.407
290	.22	11 yr	1	.1210	.424
Weighted average					.413
Clinker 15498; Cement 15758; $(CH)/w_n=1.25$; $w_n^\circ/c=0.210$					
B-8-3	0.50-.65	259-300	4	0.2115	0.276
B-15	.35	513	1	.1870	.335
B-20-1	.55	654	6	.2102	.294
290	.23	11 yr	1	.1711	.286
Weighted average					.292

The calculated specific surface of a sheet two cells thick is 377 m²/g, and for a thickness of three cells, 252 m²/g. On this basis the colloids in cement gel correspond to a three-cell thickness.

Now that more is known about the morphology of gel particles, it is perhaps pointless to express size of particles in terms of spheres. Nevertheless, for comparison with the earlier figures, it may be noted that a specific surface of 210 m²/g, or about 510 m²/cc corresponds to that of a sphere having a diameter of $6/(5.1\times10^6)=118$ A, the

TABLE 5. *Calculated surface areas for cement gels, and for the colloidal part of cement gels*

S_{hc}=surface area of hydrated cement, m²/g

Reference No.	Computed composition, %				$\frac{w_n^\circ}{c}$	$\frac{V_m}{w_n}$	$\frac{(CH)}{w_n}$	S_{hc}, m²/g	S_{col}, m²/g
	C_3S	C_2S	C_3A	C_4AF					
15754	45.0	25.8	13.3	6.7	0.227	0.311	1.18	219	267
15756	48.5	27.9	4.6	12.9	.174	.355	1.36	200	240
15763	28.3	57.5	2.2	6.0	.170	.413	0.858	227	255
15758	60.6	11.6	10.3	7.8	.210	.292	1.25	193	235
Average								210	249
Bulletin 86	100				.200	.277	2.439	210	296
Bulletin 86		100			.160	.458	1.344	279	296

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[3] Possibly there are other noncolloidal components, but if so, we cannot measure them at present.

"specific surface diameter". This figure is to be compared with 140 A given by Powers and Brownyard. The same kind of calculation for the colloidal part only gives a specific-surface diameter of 98 A. The figure for cement 15754, the cement from which a great deal of reported data were obtained, is 92 A.

Intermediate Stages of Hydration

As already indicated, to the degree that c_h/c, the maturity factor $m=w_n/w_n^{\circ}$, and to the degree that V_m/w_n remains constant during hydration of a given cement, S_{hc} is the same at all stages of hydration (eq (25)). The degree of constancy of V_m/w_n has been reported [49]. That early report has been verified by later work, except with respect to Type IV compositions for which the ratio of V_m/w_n changes appreciably during the course of hydration. However, even for those compositions, all the ratios fall within 10 percent of the average. Thus, the specific surface of the hydration products is practically constant so far as this factor is concerned. The validity of the equation $m=w_n/w_n^{\circ}$ is discussed in other terms in another paper of the Symposium [50]. Such variations as there are in the specific surface values of the successive increments of hydration products are probably insignificant in connection with most considerations involving the internal surface area of cement paste.

Effect of Curing Temperature

Ludwig and Pence [51] reported specific surface as measured by water vapor for pastes cured at elevated temperatures. For a Type I cement cured 7 days, the results shown in table 6 were obtained.

TABLE 6. *Effect of curing temperature on surface area of hydrated cement*

(Ludwig and Pence, 1956)

Pressure	Temperature		$(w_n/c)_8$	Surface area, m²/g of dry paste
	°C	°F		
1 atm	27	80	0.142	103
1 atm	66	150	.162	123
300 psi	93	200	.152	75
300 psi	127	260	.139	30
300 psi	160	320	.139	9

Does Water Vapor Adsorption Give Real Surface Area?

From one point of view, the question is not very important, for that part of the evaporable water that is called adsorbed has certain important physical effects on the system as it enters or leaves whether it occupies space in layered crystals or between them. From a less pragmatic view, the question is important, for a considerable edifice of reasoning about this material can rest on the accepted answer.

There are reasons to question the reality of surface area as it has been measured by water vapor adsorption. For example, Kalousek wrote as follows: "The very large 'areas' of cement pastes obtained by water-vapor adsorption are not true areas. Water apparently enters the lattice of some of the hydrous calcium silicates, perhaps as it does in zeolites or certain clays . . . . The areas computed from total amounts [of water uptake] are, therefore, fictitious." [52] On the other hand, McConnell [53], Miss Moore [54] and probably others, while accepting the fact of interlayer penetration in certain types of crystals, seem to question the assumption that cement gel presents a like situation. Also, it has been suggested that gel water may be water of crystallization (e.g., see H. zur Strassen [55]) and thus is naturally present in fixed ratio to the amount of hydrated cement. There is a great deal of experimental data of diverse kinds bearing on these questions, and it is difficult to assess their meaning. One may observe that evaporable water does occupy space in cement gel, and that such space must have a boundary, but it is possible that the boundary indicated by evaporable water does not coincide with the boundaries of the colloidal crystals. However, there appears to be no compelling need to postulate that this possibility is the actual case. The value for mean distance between particle surfaces obtained from the assumption that lattice penetration does not occur is so small, in relation to the reach of interparticle attraction, that effects that might be attributed to lattice penetration are easily accounted for without postulating such penetration. There is a considerable amount of experimental evidence that lattice penetration does not occur, as will be seen below.

The suggestion that gel water might be hydrate water is not easy to reconcile with the results of permeability tests discussed below and in section 10.

Particle Size From Permeability to Water

Powers, Mann, and Copeland [56] studied the flow of water through specimens of saturated paste in terms of an equation based on the Stokes-Navier law, and obtained a figure for the size of the primary particles (exclusive of calcium hydroxide) in terms of a sphericity factor ϕ and a "volume" diameter, δ. The result was

$$\phi^{1/4}\delta=201 \text{ A}.$$

δ is the diameter of a sphere having the same volume as an average particle in the specimen, and ϕ is defined as the ratio of the diameter, d, of a sphere having the same specific surface as a typical particle in the specimen to the diameter δ of a sphere having the same volume as the typical particle. That is, $d=\phi\delta$. The measured specific surface of the hydrated cement, by water vapor adsorption, gave $d=95$ A after correction for volume of calcium hydroxide. Combining these figures gave the value for sphericity factor

$\phi=0.37$ and $\delta=258$ A. In section 10 a discussion culminating in a revision of these figures is given. The revised data give $\phi=0.41$ and $\delta=233$.

The volume per particle indicated by the value of δ is 9.0×10^6 or 6.6×10^6 A^3, for the first and revised data respectively. If the material were tobermorite gel only, for which the molecular volume is approximately 195 A^3, the average number of molecules per particle would be 49,000, or from the revised datum, 34,000.

To illustrate the significance of the value found for sphericity factor, let us consider a hypothetical gel in which the average volume per particle corresponds to $\delta=233$ A, and assume that the particles are thin sheets such as are found in the hydration product of C_3S. If the width is a, the length b, and the thickness c, then, approximately,

$$\text{specific surface}=\frac{2ab}{abc}=\frac{2}{c},$$

as was pointed out by Brunauer, Kantro, and Copeland [43]. If the sheets are 3 cells thick, c is about 30×10^{-8} cm, or if 4 cells thick, c is about 40×10^{-8} cm, and we obtain specific surface=667 m^2/g, or 500 m^2/cc. The corresponding specific-surface diameters are 90 and 120 A. The sphericity factor for the hypothetical sheet is $\phi=90/233=0.39$, for the 3-cell thickness, and $\phi=120/233=0.52$ for the 4-cell thickness. The value $\phi=0.41$, indicated by permeability test and water vapor adsorption, thus could indicate that the hydration products consist principally of thin bodies containing, on the average, about 40,000 molecules and being about 3 molecules thick.

Perhaps the most significant aspect of the results from permeability studies is the evidence of compatibility between the deductions about particle size from two independent methods. Resistance to flow through a saturated specimen of paste seems to be developed by the same particles which, when dry, adsorb water vapor. As shown in section 10, the permeability data seem extraordinarily amenable to analysis, and the necessary assumptions made in the analysis do not seem to offer enough leeway to invalidate the figures for particle volume. The indicated particle thickness and number of molecules per particle seem too large to support a conclusion that lattice penetration occurs.

Specific Surface by X-ray Scattering

According to Copeland [57] a collimated beam of monochromatic X-rays passing through a granular sample is refracted by crystal lattice planes according to the Bragg law, but if the particles composing the sample are of colloidal dimensions, there is also a scattering by refraction at the surfaces of the particles that does not depend on particle shape or crystallinity. This effect is confined to angles less than about 5° from the direction of the primary beam, and it is therefore referred to as low angle scattering. The scattering due to particle surfaces varies in intensity as a function of scatter-angle as shown in eq (27).

$$((4\pi/\lambda)\sin\theta)=\text{constant}/I. \tag{27}$$

I is the intensity, θ is the angle of scatter, and λ is the wavelength of the beam. The specific surface of the particles composing the sample is given by the following relationship:

$$S_{hc}=\epsilon v_{hc}h^4I\int h^2Idh. \tag{28}$$

The left-hand side of eq (27) is represented by h. Copeland applied this method to a sample of the material represented by the first line in table 5. The result was 197 m^2/g. This is to be compared with 219, the figure obtained by water vapor adsorption. This agreement indicates that water vapor gives a real measure, and a fairly accurate one, of surface area. However, there are not enough X-ray data to make this evidence conclusive.

Surface Area by Nitrogen Adsorption

Brunauer, Kantro, and Weise [58] caused C_2S and water to react in a ball mill and found the specific surface area of the product by nitrogen adsorption to be the same as that by water adsorption, provided that the molecular areas of the adsorbates were taken at 16.2 and 11.4 A^2 respectively. The specific surface was about 220 m^2/g. Also, a laboratory preparation of afwillite having a specific surface of about 15 m^2/g showed the same surface area by nitrogen as by water adsorption [45]. But when C_2S and water react in the form of paste, the specific surface area of the product indicated by nitrogen was found to be only 21 percent of that indicated by water vapor adsorption. Surface area indicated by nitrogen adsorption for the colloidal hydration products of C_3S was only about 50 percent of that indicated by water adsorption. In various other experiments made in this laboratory on hydrated portland cement, the surface areas indicated by nitrogen were substantially smaller than those indicated by water vapor adsorption. The same kind of results were reported by Blaine and Valis [59] and by Tomes, Hunt, and Blaine [44]. For example, in the latter report, for neat cement paste, w/c=0.5, cured 1 week, the nitrogen surface area was 22 percent of the water vapor surface area.

Emmett and DeWitt [60] reported that the indicated surface area of anhydrous cement is about 10 m^2/g by nitrogen adsorption, a value much greater than that found by conventional methods. The difference is probably due to the molecular roughness of the surface and possibly due to a very small amount of gel produced by reaction with moisture from the air. Blaine and Valis found the surface area of neat cement, w/c=0.25, to be 10 m^2/g after 1 day of hydration and a little less after 6 months of hydration. In pastes of higher water-cement ratio, the nitrogen specific surface area seems to increase with the progress of hydration up to a certain point, and then ceases to increase. Hunt [61] has observed that, "If one plots water-vapor surface of an initially dried paste against its non-evaporable water content, a straight line is obtained, and the conclusion has been drawn that the gel particles produced at all stages of hydration are the same size. If one makes a similar plot of nitrogen surface areas, using a paste of high water-cement ratio, a curve is obtained which gets steeper with age. It is as if the structural domains measured by nitrogen are getting smaller as hydration proceeds."

All things considered (and there is much more to be considered than is presented here), it is difficult to say what feature of paste structure controls the uptake of nitrogen by a sample. It is clear, however, that the features that govern the uptake of nitrogen vapor are not those that govern the uptake of water vapor.

5. Minimum Porosity of Hydrated Cement Paste, and Specific Volume of Cement Gel

Minimum Porosity

If the cement content of a paste is below a certain limit, and if the paste is kept saturated with water and at normal temperature, all the cement will eventually become hydrated. But, if the cement content is above that limit, the excess will remain unhydrated, apparently for an unlimited period. When the cement content is at the limit for complete hydration, the porosity of a completely hydrated specimen is at a minimum. At any higher cement content, the porosity of the paste is lower only because of the presence of unhydrated cement; the porosity of the hydrated part remains the same.

The first estimate of minimum porosity of the hydration products in cement paste was based on adsorption data, and capacity for evaporable water [62]. The minimum capacity for evaporable water was approximately $w_e/(V_m)_8=4$, w_e being the weight of evaporable water, and $(V_m)_8$ the weight required to form a monomolecular layer on the surface of the solid particles, as determined on samples prepared by the magnesium perchlorate method.[4] Another estimate was based on specific volume measurements, and on this basis the minimum evaporable water content was stated as $w_e/(w_n)_8=0.92$, or, $w_e/(V_m)_8=3.6$, where $(w_n)_8$ is the nonevaporable water content as determined by the magnesium perchlorate method. The computed corresponding figures for specimens prepared by the dry ice method are $w_e/w_n=1.08$, and $w_e/V_m=3.6$, and the helium porosity is about 30 percent.

Although these data were obtained mostly from specimens that had been water cured about 6 months, it was not certain that minimum porosity had been reached [63]. Therefore, additional studies were carried out later by Copeland and Hayes [64]. Using the lowest value found in a group of three dense specimens 11 yr old, they gave $w_e/w_n=0.74$, or $w_e/V_m=2.38$ as minimum evaporable water contents, and the corresponding porosity as 26 percent, these data being on the dry ice basis.

In the course of this review, I considered additional data on minimum porosity as indicated by minimum evaporable water content, with the result given in figure 1. The general relationship it represents is developed from

$$w_t/c=w_0/c+0.254mw_n^\circ/c \qquad (29)$$

where $m=w_n/w_n^\circ$. The second term of the right-hand side is the amount of water that a specimen must obtain from an outside source during the course of hydration in order to remain in the saturated state.

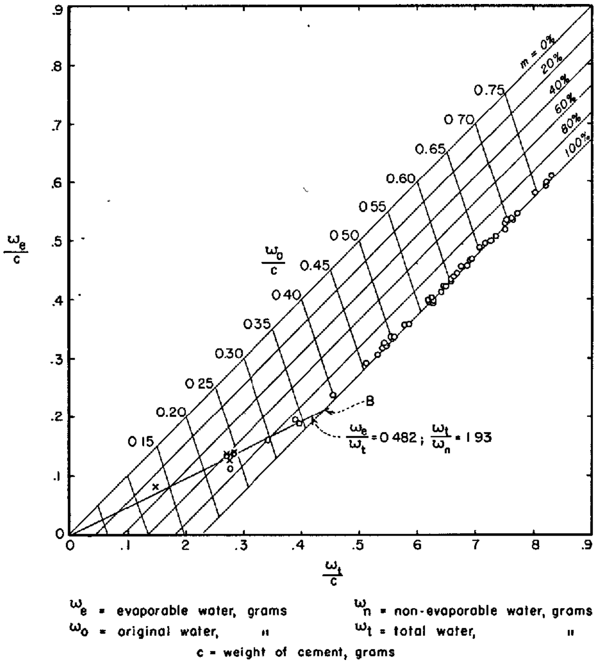

FIGURE 1. *Interrelation of total, evaporable, and original water contents for pastes made with a cement for which $w_n^\circ/c=0.227$.*

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[4] The subscript 8 is used as a convenient means of signifying that the datum is from a sample prepared by the magnesium perchlorate method, which method subjects the samples to an ambient vapor pressure of about 8 μ of mercury. Formerly, a subscript ½ was used to indicate sample preparation by the dry ice method, since that method produces an ambient vapor pressure of about ½ μ of mercury, but in this paper absence of subscript has that significance.

The general expressions for amount of evaporable water are:

$$w_e/c = w_t/c - m w_n^{\circ}/c \tag{30}$$

and

$$w_e/c = w_0/c - 0.746 m w_n^{\circ}/c. \tag{31}$$

For the cement represented in figure 1,

$$w_t/c = w_0/c + 0.058m \tag{32}$$

$$w_e/c = w_t/c - 0.227m \tag{33}$$

$$w_e/w_t = 1 - 0.227 m w_t/c. \tag{34}$$

The plotted points in figure 1 represent fully mature specimens which should conform to eq (33) with $m=1.0$. They do so down to $w_t/c = 0.437$ and $w_0/c = 0.379$. At all lower values of these two ratios, w_e/w_t remains constant at 0.482, or nearly so, as indicated by the points along line O–B. The corresponding value of w_e/V_m is 3.0; that of w_e/w_n is 0.93.

The ratio $w_e/w_t = 0.482$ corresponds to a porosity of 28 percent. This is now considered the best estimate of minimum porosity of dry paste.

When the cement is in excess of that given by $\frac{w_t}{c} = 0.437$, the ultimate value of m is less than 1.0. The value is given by $m = 2.28\ w_t/c$, or, $m = 2.63\ w_0/c$.

Is Stoppage of Hydration Virtual or Real?

Any sample along the line O—B of figure 1 contains both anhydrous cement and chemically free water, i.e., water able to maintain a relative humidity of 100 percent. It is a question, therefore, whether the stoppage of hydration is virtual or real. Czernin [65] carried out two experiments designed to determine whether or not the apparent cessation of hydration in the presence of excess cement is due to the relatively high resistance to diffusion in very dense pastes. If this is the case, the apparent stoppage is not real and is to be explained in terms of relative rates of diffusion. In his first experiment, Czernin used a portland cement paste, "PZ 425", $w/c=0.4$. The paste was water cured 28 days and then ground in a ball mill with added dry cement, reducing w/c to 0.19. After 1 day of grinding, $w_e/w_n = 1.06$; after 50 days, $w_e/w_n = 0.59$, which seemed to be near a limit. In his second experiment, Czernin used a laboratory-made "alite cement" (90 percent C_3S). The cement was milled with 15 percent water without the initial period of paste hydration used in the first experiment. After 11 days of milling, w_e/w_n reached about 0.61, and seemed to remain constant thereafter up to 40 days, the end of the experiment.

Thus, the two experiments gave nearly the same result. Qualitatively, the result agrees with the data cited above; that is, there is a lower limit to the ratio w_e/w_n. Quantitatively, the results disagree, the ball-mill experiment giving a lower value than any of the values indicated by the other data. The value $w_e/w_n = 0.59$ indicated for PZ 425 corresponds to a porosity of about 21 percent.

The meaning of the quantitative difference is not entirely clear. It seems unlikely that the cement represented in figure 1 could differ from PZ 425 enough to account for the difference, since there is no indication that the minimum value of w_e/w_n is influenced much by differences in the composition of cement. Possibly the data mean that a porosity of 21 percent would eventually be reached in pastes, if the curing continued much longer than 11 yr. Another possibility, perhaps more probable, is that the quantity of evaporable water found in the ball-mill experiment is not the same measure of porosity as the quantity found in paste experiments. Dense specimens of paste such as some of those represented in figure 1 are nearly if not quite saturated after continuous water storage for 11 yr. Had they been sealed, without access to curing water, their water content would have been considerably below the saturation point [66, 67]. Perhaps in the ball-mill experiment there was a similar "self-desiccation." If the paste samples had been reduced to the same degree of desiccation before measuring w_e/w_n, the two values of w_e/w_n would have been brought closer together, but neither would have indicated accurately the capacity of the gel for evaporable water. It seems likely that ball-milling would destroy most if not all the structure defined by capillary spaces (see section 6), but it is unlikely that it would destroy the structure of cement gel. Therefore, there is some reason to expect the gel produced in the ball mill to have the same porosity as the gel produced in paste, but there is reason to doubt that evaporable water content is a correct measure of porosity in the ball-mill experiment.

Whether or not hydration in dense pastes actually stops, it is evident that the rate of hydration after several years of curing is so low that it is of no practical interest. If hydration does continue, it does so by an improbable metamorphosis of existing particles, the metamorphosis being such that the interstices among these variously shaped, randomly oriented particles gradually become filled with solid material.

Stoppage of the hydration reactions with both reagents present is not theoretically impossible. The quasi-crystalline hydrates evidently have a naturally restricted growth, possibly due to accumulative misfit of contiguous lattice layers, as suggested by Bernal. After a time when all crystals in a local region have grown as much as they can, further growth requires forming viable nuclei in the presumably supersaturated solution in the gel pores. But in places as small as gel pores, formation of a nucleus of a new crystal would seem a highly improbable event, either from the standpoint of surface energy, or of the size of a unit cell relative to the size of a gel pore. A similar interpretation was advanced recently by Taplin [68].

Specific Volume of Cement Gel

As will be seen in section 6 the massed hydration products in their densest form are called cement gel. The solid matter of the gel together with the characteristic porosity constitutes a solid body having a characteristic specific volume. A general expression for the specific volume of cement paste, on the dry-weight basis, but in the swollen state, is

$$v_p = \frac{v_c + (w_t/c)v_t}{1 + w_n/c}. \tag{35}$$

For cement gel, which is composed only of hydrated cement and gel pores, $w_n/c \equiv w_n^\circ/c$, and $w_t/c \equiv w_t^\circ/c$, the last quantity being the total water content of saturated cement gel, including the nonevaporable water. Each quantity is expressed as a ratio to the original amount of cement. Then, eliminating v_t by means of eq (19), we obtain the following expression for the specific volume of cement gel:

$$v_p = v_g = \frac{v_c + 0.99\dfrac{w_t^\circ}{c} - 0.25\dfrac{w_n^\circ}{c}}{1 + \dfrac{w_n^\circ}{c}}. \tag{36}$$

Complete data for computing the specific volume of cement gel are available for only one cement, PCA lot No. 15754. For this cement, $v_g = 0.567$.

The indications are that corresponding values for other cements are similar. Although the values of w_n°/c vary considerably (see table 5) the value of w_t°/c, the total water, is found to be relatively large where the nonevaporable water is relatively small. For the present, we may use for all cements the value 0.567, with due cognizance of the uncertainty.

Ratio of Volume of Cement Gel to Volume of Cement

The volume of cement gel produced by 1 cc of cement may be called the gel-cement ratio, N. By definition,

$$N = (1 + w_n^\circ/c)v_g/v_c. \tag{37}$$

For the cement represented in figure 1, $N = 2.18$.

Taplin [68] recently advanced a method for obtaining the gel-cement ratio based on the following relationship:

$$N = 1 + \frac{w_{n^\circ}}{c} \cdot \frac{w_o}{v_c(w_n)_u} \tag{38}$$

where w_{n°/c and $w_o/(w_n)_u$ are for tests at different water-cement ratios. The w_{n°/c represents complete hydration at a water-cement ratio high enough to accomplish this. The w_o and $(w_n)_u$ represent, respectively, the initial amount of water and the ultimate value of w_n for a water-cement ratio low enough to assure an excess of cement. Equation (37) should give a more accurate result than eq (38) because it is based on the total water content of a saturated specimen at the time of analysis rather than on the original water content. If the original water content is used it should be corrected for any decrease during the bleeding period, and for increase due to expansion of the specimen during the curing period.

6. Concepts of Structure of Cement Gel and Cement Paste

Evolution of Models

Powers and Brownyard [69] used drawings suggesting that dense masses of gel particles form in and around the sites of cement grains, and that these masses generally do not fill all the space between the original boundaries of cement grains. Later, Powers and Helmuth [70] presented the same idea in greater detail, representing the gel particles as spheres. Originally, this assumption as to shape was adopted for simplicity and convenience, but later [71] some electron micrographs indicated that the particles actually were spherical, and this was mentioned in the paper referred to. In later publications [72, 73] drawings showing the particles to be platy, or ribbonlike fibers, were used, in harmony with electron micrographs by Grudemo from calcium silicate hydrates [74] and from cement paste [75] (see fig. 2). Such drawings give a meager outline of a concept of structure. One may fill in details on the basis of data on the size and shape of particles, the space required by hydrated cement, and the mode of formation of cement gel. It is necessary to deduce various details that are not directly observable. Such deductions are more or less speculative, and it is to be expected that not all will agree on the dividing line between valid deduction and questionable speculation.

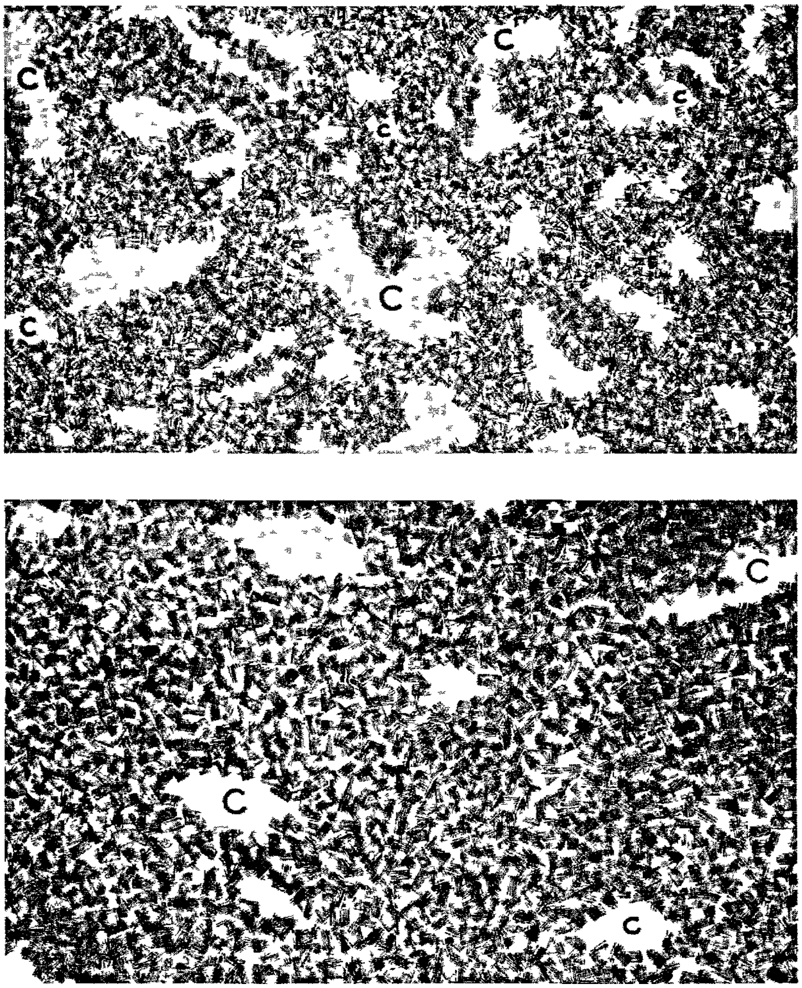

FIGURE 2. *Simplified model of paste structure.*

Masses of randomly oriented groups of black lines represent cement gel. Spaces like those marked C represent capillary cavities. Upper drawing represents mature paste, $w_o/c=0.5$, capillary porosity 20%, lower drawing represents nearly mature paste, $w_o/c=0.3$, capillary porosity 7%.

Space Requirements

As shown in section 5, it is known that cement gel requires about 2.2 cc of space per cc of cement. This means that 1 cc is formed inside the original boundaries of the cement grains, and 1.2 cc is formed outside, in the originally water-filled space. (Taplin's paper [68] indicates that he also made this observation, and developed concepts similar to those described below.)

Mode of Gel Formation [76]

After an initial process peculiar to conditions that can exist only a short time, the main part of the hydration process seems to start at the grain boundaries, and cement gel grows outward and inward simultaneously, each grain residue being continuously encased in gel as long as it exists. Water diffuses inward through the gel pores while the components of hydrated cement, presumably in a state of supersaturated solution, diffuse in the opposite direction to the outer border of the gel layer, where they add on to existing crystals, or start new ones. Approximately 55 percent is transported outward, and 45 percent stays inside.

It is reasoned that since the hydration products in a specimen of paste containing an excess of cement ($w_o/c<0.38$) can eventually produce a gel having a porosity of 28 percent, that same degree of density can be, and is produced locally at various places throughout the paste, even when the cement is not in excess. The part of the gel that is formed by inward growth is produced under the greatest possible concentration of reagents. It seems, therefore, that at least 45 percent of the gel in any specimen has minimum porosity. Also, since every grain of cement in the flocculent, fresh paste (see section 2) is practically in contact at several points on its surface with neighboring grains, the outward-growing gel should reach minimum porosity at these points early in the process. It is not known, of course, whether the minimum porosity reached in the outside material is the same as that of the inside material, but whatever the case may be, it may be assumed that there is a range of pore sizes in the gel as a whole. The smallest size might be of a monomolecular dimension; the largest would seem to be that size just smaller than the smallest in which nucleation is possible. On this basis, it would seem that the overall porosity of any region containing only pores within the size range just described (and consisting of approximately equal portions of the "inside" and "outside" product) is the 28 percent mentioned above. It follows that any region where the porosity exceeds 28 percent is also a region where new crystals could nucleate, or already existing crystals could continue to grow; in other words, it is a region where pores exist that are larger than the largest characteristic of cement gel. During the process of hydration, the components of hydrated cement that are diffusing outward from a grain will be likely to be deposited in the first over-gel-size pore encountered. Thus the "outside gel" tends to achieve characteristic gel porosity as it grows. This idea is expressed in figure 2 by showing the capillary spaces to be orders of magnitude larger than gel pores. However, it is clear that as a given local region approaches minimum porosity, the remaining capillary pores in that region will gradually become indistinguishable from gel pores, and this idea is represented by some areas in the drawing where only slight gaps in the gel appear. One sees the possibility, if not probability, of the gel particles formed by inward growth having a different morphology, and perhaps even a different stoichiometry, from the particles formed by outward growth.

Size of Gel Pores

Powers and Brownyard [77] estimated the width of pores in cement paste from the ratio of pore volume to surface area, i.e., the hydraulic radius. With the data then available, the figure obtained for the hydraulic radius was 10 A. This meant that the average width of pore lay between 20 and 40 A, probably closer to 20 than to 40. From data given in preceding sections we have

$$\text{Hydraulic radius} = \frac{w_e v_e}{38 \times 10^6 V_m} = 2.6 \times 10^{-8} v_e \frac{w_e}{V_m} \text{ cm} = 2.6 v_e \frac{w_e}{V_m} \text{ A}. \quad (39)$$

As shown in section 5, the minimum value of w_e/V_m is about 3.0, and therefore the hydraulic radius of the gel is $7.8v_e$ A. The specific volume of gel water is not known exactly. On the basis of the specific volume of hydrated cement as given by helium displacement, it is 0.9, and this figure gives a hydraulic radius of 7.0 A. The corresponding average distance between solid surfaces in the gel is between 14 and 28 A, 18 A being a reasonable estimate. This distance is about 5 times the diameter of an unbonded oxygen atom, or about 13½ times the diameter of a single-bonded oxygen atom. The unbonded diameter, 3.6 A, is about the same as that of a water molecule.

Size of Capillary Spaces

No systematic attempts to measure the size of capillary spaces have been reported. However, various observations show that they are generally orders of magnitude larger than gel pores. When there are capillary spaces, reflected light is scattered. Such scattering signifies the presence of randomly arrayed structural discontinuities several hundred angstrom units apart. (These are the reasons why mature paste of high quality has a dark, bluish-gray cast, whereas paste of low quality appears much whiter.) Other direct evidence of the relative largeness of capillary spaces will be found in section 10 which deals with permeability to water. When the total porosity of cement paste is increased by reducing the amount of gel and increasing the capillary space, the rate of increase in permeability shows that the capillary spaces are very much larger than gel pores.

Summary Description of Cement Paste

Although the concept illustrated in figure 2 is in several ways oversimplified, it is a useful aid toward understanding the properties and behavior of cement paste and concrete. The main features of paste structure may be summarized as follows: *cement gel* is a rigid substance that occupies about 2.2 times as much space as the cement from which it was derived. Its porosity is about 28 percent, and the average width of its pores is about 18 A, which is about 5 times the diameter of a water molecule. There is evidence that the gel particles are in contact with each other at many points and that some of the points of contact are chemically bonded. The porosity of cement gel is a natural consequence of the growth of irregular particles in random directions from randomly distributed starting points. Cement gel is mostly colloidal matter, but, as defined here, it contains noncolloidal material also, chiefly calcium hydroxide.

Cement gel is one component of cement paste. The other component is the residue of originally water-filled space that has not become filled with gel. These spaces are called *capillaries* or *capillary cavities*. When capillary porosity is relatively high, the capillaries are a continuous interconnected network through the gel, but at normal paste porosities, capillary spaces are interconnected only by gel pores and are accordingly called capillary cavities. The properties of cement gel and the degree to which the gel is "diluted" with capillary spaces, and the effects of water in gel pores and capillaries are factors that determine important characteristics of concrete.

Paste may also contain a residue of anhydrous cement.

Computation of Capillary Porosity of Paste

Since the capillary porosity is a significant factor, fundamental studies of strength, stress-strain-time characteristics, permeability, and durability could be facilitated by dealing with it quantitatively. Convenient means of a computation are indicated in eqs (40) and (41).

$$\epsilon_c=1-\frac{cv_c}{V}\left[1-m+m(1+w_n^\circ/c)\,\frac{v_g}{v_c}\right] \tag{40}$$

$$\epsilon_c=1-\frac{m\left[(1+w_n^\circ/c)\,\frac{v_g}{v_c}-1\right]+1}{1+\frac{w_0/c}{v_c}}. \tag{41}$$

Here ϵ_c is the capillary porosity; v_g is the specific volume of cement gel in cc/g of dry gel. (See section 5.)

7. Mechanical Effects of Adsorption and Hydrostatic Tension

This section may be regarded as an extension of section 6, for a concept of physical structure is sterile unless it is combined with some understanding of the interaction of the solids and evaporable water, which is the present subject. Quantitative data are few, but those given by Powers and Brownyard [78], together with more recent unpublished results, provide a basis for discussion.

Adsorbed Water and Capillary-Condensed Water

At temperatures above the freezing point, chemically free water molecules present in cement paste at any humidity below 100 percent would be gaseous and of negligible amount were it not for forces that hold nearly all of them in a condensed state. All surfaces are usually covered with water molecules, and, except at low humidities, capillary cavities contain water. Powers and Brownyard [79] observed that the amount of water held at any relative humidity below about 40–45 percent (25 °C) was proportional to the internal surface area, i.e., the surface area of the gel particles in the specimen, but at humidities higher than 40–45 percent the amount of water taken up by a dry specimen depended on the porosity of the specimen. It was therefore concluded that at humidities below 40 percent the water was held entirely by adsorption forces, and that most of the water taken up at humidities well above that limit is held by capillary condensation.

The theory of nucleation helps us to understand this observation and deduction [80]. Two different theories of the nucleation of vapor bubbles in pure water under negative pressure at room temperature lead to the result that the "fracture strength" of water is about −1200 atm. This is the negative pressure giving a probability of unity for the spontaneous nucleation within about 1 sec of a vapor bubble by thermal fluctuation of the water molecules in the liquid [81]. The theoretical fracture stress based on nucleation occurring within 1 yr is about −1100 atm [82]. Under such stress, water molecules are unable to cohere, and since a meniscus depends upon molecular cohesion, capillary condensation becomes impossible. It happens that the relationship between the pressure in the liquid phase and the corresponding equilibrium vapor pressure gives, as computed by Barkas [83], −1200 atm at a relative humidity of 40 percent, and −1100 at 45 percent. Thus, the observation that water in cement paste at humidities below about 40 percent is not subject to capillary condensation is in agreement with the theoretical deduction that a meniscus cannot exist below such a humidity. Perhaps that agreement may be regarded as strong support to the theory of nucleation as a means of arriving at the cohesive strength of water, although the fact that water in cement paste is not pure injects some uncertainty as to whether the agreement ought, theoretically, to be as close as indicated. Nevertheless, it seems justifiable to assume that part of the water held in a specimen at humidities above 40–45 percent has the ordinary properties of liquid water. The water held at a humidity of 45 percent is somewhat less than enough to make two complete molecular layers over the surfaces of the solid phases, and such a film does not have the properties of liquid water. Its condensed state is due to the forces of adsorption.

In a specimen saturated with water, and surrounded with water or a water-saturated atmosphere, there is no hydrostatic tension, and as we have seen, some of the water contained in the pores exhibits the normal properties of water. The first question to be considered is how capillary water is lost from the specimen during drying, particularly the first drying.

The Process of Drying

When a small container made of a hydrophilic material contains both air and water, the boundary between the water and air is a meniscus concave toward the air. Water in a glass capillary, bounded at each end by a meniscus, is a familiar example. When water evaporates from such a capillary, it seems that evaporation occurs from the meniscuses, and, from Kelvin's equation, it is understandable that the tendency of water to evaporate is reduced because of the negative pressure in the water induced by the curved surfaces. On the basis of an analogy between a porous solid and a "bundle" of capillaries, it is sometimes assumed that the drying of a specimen of saturated cement paste involves evaporation from the meniscuses in the capillaries within the paste.

We have already seen that the bundle-of-capillaries concept is hardly compatible with evidence concerning the structure of cement paste. It is safe to say that in all cement pastes some of the capillary spaces are in the form of cavities isolated by cement gel, and in some cement pastes, perhaps most, *all* the cavities are so isolated. (See also section 10.) If we are to assume that, during drying, evaporation occurs only from curved surfaces, none of the water in isolated capillary spaces can evaporate until the humidity drops sufficiently low to cause evaporation from the very small gel pores of the surrounding gel. Indeed, a theory of adsorption-desorption hysteresis is based on the notion that such a situation is analogous to an ink bottle: the inside communicates with the outside only through the neck and therefore the contents of the bottle cannot escape by evaporation until the neck has been emptied.

The amount of water lost from cement pastes at relatively high humidities cannot be accounted for on the basis of the theory just mentioned. Water in capillary spaces surrounded by gel evidently does escape at high humidities even though it is not able to present a liquid surface from which evaporation can occur. A different theory that takes into account some consequences of hydrostatic tension is required to account for the observed facts.

When water evaporates from the outside surface of a body of cement gel enclosing one or more water-filled capillary spaces, hydrostatic tension develops, as is shown by the reduction of water-vapor pressure of the water remaining in the body. The magnitude of the tension is limited by the relative humidity of the surroundings. One consequence of hydrostatic tension is that if the water is initially saturated with air, it immediately becomes supersaturated, the degree of supersaturation being a function of the hydrostatic tension. When the degree of supersaturation is sufficiently high, bubbles can develop in the capillary cavities. The degree of supersaturation and hence the magnitude of hydrostatic tension required to produce bubbles depends on several factors, as discussed below. The discussion follows that of Bernath [81].

Let us consider first the conditions necessary for static equilibrium between a bubble and its surroundings, neglecting the force of gravity. The bubble is surrounded by capillary water, and the capillary water is continuous with the gel water that permeates the surrounding structure. The bubble is assumed to be spherical and to contain n molecules of gas, including molecules of water vapor. Let P_b represent the gas pressure in the bubble, and $4\pi r^3/3$ the volume of the bubble, r being the radius. The following "perfect gas" equation gives the free energy content of the bubble, on the left side in terms of the product of pressure and volume, and on the right side in terms of the kinetic energy of the gas molecules.

$$P_b\left(\frac{4}{3}\pi r^3\right)=n_bkT. \tag{42}$$

T is absolute temperature; k is Boltzman's constant (energy per molecule per degree) and n_b is the number of molecules in the bubble. The pressure in the bubble is also equal to the pressure exerted on the gas by its surroundings, that is

$$P_b=P_C+\frac{2\gamma}{r}. \tag{43}$$

P_C is the hydrostatic pressure in the capillary water and γ is the surface tension. The second term on the right-hand side is the capillary pressure due to the spherical meniscus of the bubble. In the present case,

$$P_C=-t \tag{44}$$

where t is hydrostatic tension. Substituting from eqs (43) and (44) into (42), we obtain eq (45):

$$\left(\frac{2\gamma}{r}-t\right)\left(\frac{4}{3}\pi r^3\right)=n_bkT. \tag{45}$$

This equation shows that at a given temperature the free energy content of a bubble is a function of the radius of the bubble. The function is such that the free energy content of the system increases with an increase of r up to a critical value r^*, and for larger values of r, the free-energy content decreases. From this it follows that if a bubble having a radius smaller than r^* should develop, it would probably disappear (dissolve) immediately, but if the radius quickly becomes equal to r^*, the bubble is just as likely to remain as to disappear. Therefore a bubble is likely to be viable if at one instant it can form with a radius greater than r^*. Such a phenomenon can happen only when the water becomes sufficiently supersaturated with dissolved air. When the water is initially saturated with air, bubbles evidently can form with relatively little hydrostatic tension. This is indicated by the fact that relatively large amounts of evaporable water are lost at high humidities. However, it seems clear that bubbles can form only in those capillary spaces large enough to permit a viable nucleus to form, that is, only in those cavities having a radius greater than r^*.

The necessary size of cavity is that which will accommodate a nucleus having a radius slightly larger than r^*, and able to accommodate also a layer of adsorbed water molecules that cannot become a part of the meniscus of the bubble. The thickness of this layer is estimated to be about 5 A.

The value of r^* can be obtained by differentiating eq (45) with respect to r, with T constant, and with $t=t^*$, where t^* is the value of tension at which nucleation is possible. The derivative is then equated to zero, and the equation is solved for r. The result is

$$r=r^*=\frac{4}{3}\frac{\gamma}{t^*}. \tag{46}$$

On comparing eq (46) with eq. (43), with $P_C=-t^*$, we see that eq (46) is not a statement of static equilibrium. In other words, the nucleation radius, r^*, is not the same as the stable radius for static equilibrium at the hydrostatic tension t^*. The expression for equilibrium is

$$r_s=\frac{2\gamma}{t^*+P_b}\approx\frac{2\gamma}{t^*} \text{ when } P_b<<t^*. \tag{47}$$

The value of r_s, the size that would be stable at tension t^*, is not of special interest in the present connection. It only indicates that if t^* is established and kept strictly constant, the bubble would nucleate and the radius would increase about 50 percent to establish equilibrium. Except when r^* is so small that thermal fluctuations might disturb equilibrium, static equilibrium is quite possible. However, the equilibrium is rather unstable in any case, since even the slightest increase over t^* would permit the bubble to expand to the limit fixed by the dimensions of the cavity.

The pores in cement paste range in size from molecular dimensions upwards to perhaps 0.1 μ, the upper limit actually being unknown. Table 7 gives the calculated nucleation radius for different levels of hydrostatic tension and the corresponding values of required cavity size, assuming the cavities to be spherical. If, for example, drying has occurred at a relative humidity of 96 percent, all cavities having radii greater than about 175 A would be able to accommodate the nuclei that could form at that humidity, and all the cavities smaller than that size would remain full of water. When the humidity has dropped to the 50 percent level, all cavities having radii greater than about 15 A should contain bubbles. However, as noted in the table, at humidities below about 45 percent, bubbles cannot exist because the hydrostatic tension exceeds the fracture strength of water, and therefore phenomena arising from molecular cohesion of water disappear. The formation of a meniscus is one such phenomenon.

As shown above, at any given humidity all the capillary cavities below a certain size (table 7) will remain full whereas each of the larger ones will contain a bubble. Nevertheless the hydrostatic tension must be the same in the cavities containing bubbles as in those not containing bubbles. Therefore, beginning with the saturated state, the hydrostatic tension that develops as the specimen is dried to a lower humidity is, after a state of equilibrium has become established, the same throughout the capillary space as if all the capillary space had remained filled with water while the tension developed. Thus shrinkage caused by drying at humidities above about 45 percent is a hydrostatic compression, and the amount of hydrostatic compression depends upon the elastic and inelastic time-dependent deformation characteristics of the paste.

TABLE 7. *Computed inscribed diameters of capillary cavities able to contain spherical bubbles at given humidities (eq (46))*

Relative humidity	Hydrostatic tension	Nucleation radius r^*	Required radius of spherical cavity r^*+5
Percent	*atm*	*A*	*A*
98	28	346	351
96	57	170	175
92	116	84	89
85	226	43	48
70	495	20	25
50	963	10	15
45	1,100	([a])	
40	1,200	([a])	

[a] Bubbles cannot exist at tensions above the fracture strength of water, which is apparently between −1,100 and −1,200 atm.

Only a few data on the shrinkage of mature cement paste samples dried under suitable conditions are now available, but there are some, obtained about 20 yrs ago, from specimens dried in CO_2-free air at four different humidities. An example of the results obtained is shown in figure 3. The changes in volume for drying at humidities of 75, 45, 18, and 1 percent are plotted against the computed tensions for those humidities. These data,

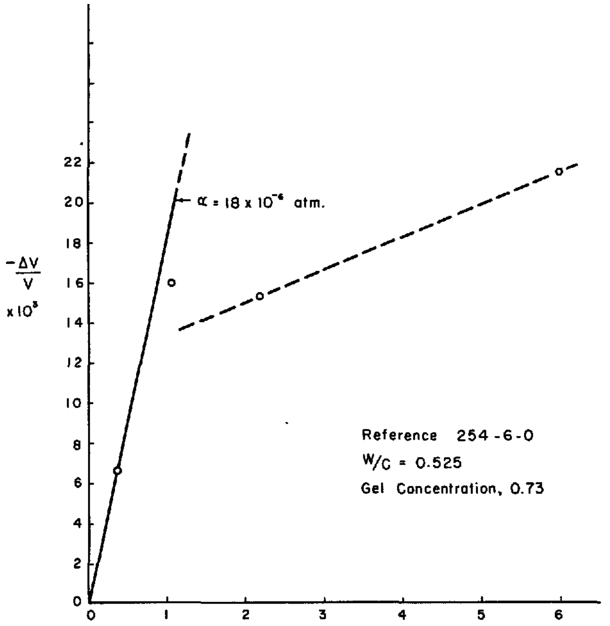

FIGURE 3. *Shrinkage vs. tension.*

considered together with data for various other specimens, indicate that a shrinkage-vs.-stress curve for tensions up to about 1,000 atm resembles one for mechanical loading. Shrinkage is approximately proportional to stress, departure from linearity being greater the higher the capillary porosity of the paste. The slope of a line from the origin to a point representing shrinkage at a given tension gives the coefficient of compressibility [5] for the indicated sustained, isotropic tension. The value indicated in figure 3 is 18 millionths per atm, and that figure appears to apply to all tensions up to about 900 atm, but some curvature would probably be seen if more points were available, since some of the compression is inelastic, and such deformation is not usually exactly proportional to stress. A compressibility of 18 millionths per atm corresponds to a Young's Modulus of about 1.5 × 10^6 psi or 100 kg/cm^2, which is reasonable for the ratio of stress to strain for such a paste under sustained load.

Other data show that when shrinkage stress is released by soaking the specimen in water, the amount of expansion per unit change of stress agrees approximately with the modulus of elasticity of the paste as determined from the resonance-frequency of vibration of a test prism. This is one aspect of the stabilization of paste structure discussed in section 8.

From the above discussion of the fracture strength of water, one might expect some sort of discontinuity in the stress-strain diagram at a tension of about 1,100 atm. A discontinuity does seem to be indicated by these data (fig. 3) but the points are too few to establish the locus exactly. It is not clear whether the transition should be abrupt or gradual, but an abrupt transition seems probable because when the stress in the water reaches the breaking point, which, for 1 yr of sustained stress would be about −1,100 atm, stress due to surface tension in the capillary cavities should disappear. This would reduce the effective area from unity to $1-A_c$, where A_c is the cross-sectional area of capillary spaces that contained bubbles, per unit overall area. If we assume that the break occurred at −1,150 atm, and that expansion is proportional to the reduction of effective area, the indicated value of A_c is about 20 percent, which is not far from the actual capillary porosity of the specimen. After the transition point, further increases in tension are accompanied by progressive emptying of the gel pores and decreasing of the area factor. Thus, for the specimen represented by figure 3, one might suppose that the compressibility coefficient remains about the same while tension increases, but the area factor falls off in such a way as to give the observed diagram.

From this approach, it would seem that as the area factor approaches zero, effective tension approaches zero, and the specimen should expand. This is not the case, however; at the point where all the evaporable water has become lost, and the area factor has become zero, shrinkage is at the maximum possible for the temperature of the experiment. To understand this result, gel structure must be taken into account.

Areas of Obstructed Adsorption

The observed result seems to be due to obstructions that prevent adsorbed water from spreading evenly over the surfaces of the particles. The obstructions are probably in those areas where contiguous particles are bonded to each other, the distance of separation being zero, and in areas (presumably adjacent to those spots) where the surfaces are separated, but not separated enough to accommodate as many water molecules per unit area of surface as could be held in areas of unobstructed adsorption. The evidence of the existence of *areas of obstructed adsorption*, is the same as that indicating the existence of interparticle bonds, and the nature of shrinking and swelling phenomena itself.

Those water molecules that are excluded from areas of obstructed adsorption maintain a pressure—a film pressure—that tends to separate the obstructing surfaces. This film pressure thus causes a slight dilation, or swelling. The amount of swelling produced by film pressure is limited by tensile force corresponding to stress in the bonds that hold the gel particles together. Swelling pressure, and tensile stress in the bonds, is greatest when the specimen is saturated and thus when tension in the evaporable water is nil. When tension in evaporable water appears, swelling pressure is correspondingly diminished and tensile stress and strain in the bonds also. The reduction of swelling pressure is effective in areas of obstructed adsorption only, but, as already shown, when hydrostatic tension is less than the fracture strength of water, hydrostatic tension is effective over the whole area of the paste, and the specimen becomes compressed more than can be accounted for by reduction of swelling pressure only. However, at tensions above the fracture strength of water, further increase of tension serves only to reduce swelling pressure in areas of obstructed adsorption. The effective areas of obstructed adsorption must become smaller as the water content is reduced, reaching zero when all the water has become evaporated. Thus, shrinkage in the high-tension range is primarily caused by cohesive forces between the solid bodies of which the gel is composed.

During the last stages of removal of evaporable water, there is enough increase in interfacial energy at the solid surfaces to cause an increase in specific gravity of the particles and corresponding shrinkage, but this is now believed to be a minor contribution to the total change shown in figure 3.

Effect of External Pressure

Although no direct experimental confirmation can be cited, the foregoing discussion of internal

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[5] As defined here, compressibility is $\frac{\Delta V}{\Delta P}\cdot\frac{1}{V_0}$, where V_0 is the volume in the saturated state.

forces leads directly to conclusions pertaining to the effects of applying pressure externally. If a specimen of hardened paste at equilibrium with the ambient humidity is subjected to an *isotropic* pressure applied to the external surface, the compressive force on the water films in areas of obstructed adsorption maintained by tensile stress in the solid bonds is thereby augmented. Some of the water is displaced immediately from the areas of obstructed adsorption, and since the water lost from the loaded areas must be gained by the rest of the area, the internal humidity rises. A rise of internal humidity produces an increase of swelling pressure, opposing the external pressure and, in effect, the specimen swells. To restore equilibrium with the ambient humidity, some water eventually evaporates, and the swelling pressure falls to its original level, with a further compression (shrinkage) of the specimen.

If the specimen had been subjected to isotropic tension, rather than isotropic compression, the effect would have been as follows: the compressive force on the water films maintained by the cohesive bonds of the gel would have become diminished, and there would have been a concomitant widening of the spaces in the areas of obstructed adsorption, thus creating a deficiency of water molecules in those areas. Molecules from the unobstructed areas would diffuse into the areas of obstructed adsorption, but in so doing, the internal humidity is caused to decrease, the film tension to increase correspondingly and the specimen is caused to shrink. However, to restore equilibrium with the ambient humidity, water molecules from the outside would be received until the original humidity was regained. During the time required for this process, the specimen gradually dilates (swells) under the sustained external tension, finally annulling the shrinkage induced by the application of the external isotropic force.

If external pressure is applied uniaxially, as for example by loading the ends of a cylinder, a combination of effects of isotropic compression and isotropic dilation should be present. Spaces between surfaces oriented principally normal to the axis of the cylinder would be reduced, and those oriented principally parallel to the axis would be increased. The effect is a temporary swelling counter to the direction of compression, and shrinking counter to the lateral extension. Establishing a new state of equilibrium requires transfer of water from the compressed areas to the extended areas, but there may be no appreciable change in an average internal humidity, and hence no change in weight of the specimen.

The foregoing discussion accounts, at least in part, for the time-dependent part of elastic response to an external force which was shown especially well by recent data published by Glucklich [84]. In addition to time-dependent elastic response, there is also a time-dependent inelastic response, apparently related to, if not a direct manifestation of, the instability of cement paste discussed in section 8.

Freezing of Evaporable Water

Following the pioneer work of von Gronow [85], Powers and Brownyard [86] studied the freezing of water in cement paste by means of dilatometry. They showed that at any subfreezing temperature some of the evaporated water remains unfrozen, and for temperatures below −6 °C the amount unfrozen is proportional to the surface area of the gel. At temperatures between 0 and −6°, the amount remaining unfrozen at a given temperature is not proportional to the surface area. Recently, Helmuth [87] found that the departure from proportionality is due to the presence of solutes in the evaporable water, principally sodium hydroxide and potassium hydroxide. In general, the findings have been as would be expected from the characteristics of the sorption isotherms.

Verbeck and Klieger [88] reported the amounts of ice formed in concrete, as measured by the change in heat capacity during cooling. Typical results are given in table 8. The last column of table 8 shows the amount of expansion of water that must be accommodated by space in the concrete during freezing, expressed as a percentage of the total volumn of concrete. It is clear that concrete normally contains more than enough voids to accommodate the expansion of water caused by freezing, and therefore the destructive effect of frost is not due to lack of space in the concrete for expansion of water. Frost action is the subject of another paper of this Symposium [89], and will not be pursued further here.

TABLE 8. *Amount of water frozen at −20 °C (−4° F) in concrete cured 7 days before freezing*

(Verbeck and Klieger, 1958)

w/c	Cement content lbs/yd^3	Amount of ice at −20 °C(−4 °F), percent of concrete vol.	Percent frozen at −7 °C(20 °F)	Water expansion per cent of concrete vol.
0.41	660	3.8	93	0.35
.49	520	4.9	70	.45
.72	380	8.1	57	.75

8. Instability of Paste Structure

Spontaneous Reduction of Specific Surface Area

Because of its high surface area, cement gel is often referred to as a metastable substance on the grounds that if large gel particles were to grow at the expense of small ones, a substantial reduction in specific surface area and in specific free energy content of the gel would take place. Evidence of such a change would be a reduction in the ratio V_m/w_n, which ratio is proportional to the reduction in specific surface area. Over the years during which measurements of V_m and w_n have been carried on, no reduction in the ratio has occurred for any specimen kept continuously moist. This indication of stability may be accounted for in part by the morphology of hydrated cement. If cement gel is made up of thin sheets or ribbonlike fibers, a substantial reduction of surface area and surface energy would require more than mere growth, for if a large sheet became longer and wider while a smaller one changed dimensions oppositely, the resulting reduction in surface energy would be very small. Any substantial reduction in surface area and free energy would require a more profound metamorphosis, particularly a strong tendency toward isometry along with increase in size.

Under conditions other than continuous moist storage, the story is quite different. In an autoclave at temperatures upwards of 100 °C, the kind of metamorphosis mentioned above occurs readily, accompanied by some change in stoichiometry. Powers and Brownyard [90] found the specific surface area of autoclaved hydrated cement to be only 5 percent of that of hydrated cement cured in the ordinary way. Ludwig and Pence [51] obtained a similar result. See table 6 of section 4.

Not so widely known is the discovery by Tomes, Hunt, and Blaine [44] that the very process of determining the surface area of cement gel by water-vapor adsorption causes a reduction of specific surface. After drying samples from the saturated state to a relative humidity of about 0.00002, they carried out eight cycles of adsorption and desorption, the adsorption being in four steps as required by the BET procedure, and the desorption in one step. The range of humidities was from 0.00002 to 0.33. Their data, obtained on granulated samples, are given in table 9.

TABLE 9. *Reduction of specific surface area, caused by cycles of desorption and adsorption*

(Tomes, Hunt, and Blaine, 1957)

Cycle	Specific Surface m²/g of dry sample	Relative surface area
1st adsorption	89.9	100
2d adsorption	75.8	84
3d adsorption	66.5	74
4th adsorption	63.2	70
5th adsorption	58.8	65
6th adsorption	57.5	64
7th adsorption	56.0	67
8th adsorption	56.3	63

Although the change in surface area produced in this way is much less than that produced in the autoclave, it is substantial and significant with regard to various aspects of concrete technology, as well as to laboratory studies. From the trend of the plotted data, it appears that, if the reduction in specific surface occurs during desorption, as seems likely, the original surface area was reduced at least 20 percent before the first adsorption, and thus, by the sixth adsorption only half the original surface remained.

Other experiments were made by the same authors in which the samples were completely saturated between successive BET determinations. The second adsorption gave 97 percent of the area indicated on the first adsorption and the third adsorption gave 89 percent. These figures are to be compared with 84 percent and 74 percent in table 9. Thus, allowing the material to swell as much as possible between surface area determinations seems to undo some of the effect of desorption.

In a recent paper, Hunt, Tomes, and Blaine [91] report additional observations on spontaneous reductions of surface area occurring while samples are in storage in sealed containers. Completely dry samples seemed to be stable, but those containing small amounts of evaporable water, left in the samples deliberately, were unstable. Some of the data are given in table 10. The maximum rate of spontaneous change was found in samples that produced a humidity of about 50 percent in the sealed containers. (The humidity was determined by direct measurement.) The samples that produced humidities below 1 percent and above about 80 percent seemed to be stable.

TABLE 10. *Changes in specific surface area occurring in sealed specimens as a function of amount of residual evaporable water*

(Hunt, Tomes, and Blaine, 1960)
w_e=weight of evaporable water in the sample.
c_t=weight of ignited cement.

$\frac{w_e}{c_t}$	V_m/w_n after storage period indicated		Relative surface area after storage period indicated	
	1 month	21 months	1 month	21 months
0.006	0.300	0.295 [a]	100	98 [a]
.02	.295	.280	98	93
.06	.265	.243	88	81
.10	.262	.230	87	77
.17	.282	.277	94	92
.20	.300	.300 [a]	100	100 [a]

[a] Estimated by extrapolation.

The nature and cause of a reduction in specific surface under the conditions described above remains a matter for speculation. Collapse of a layered structure naturally suggests itself, and Tomes, Hunt, and Blaine offered, tentatively, such an explanation. Other data that appear to be incompatible with such an explanation have already been presented (section 4) and more may now be introduced. Tomes, Hunt, and Blaine found that wetting and drying not only reduced the surface area as measured by water but also reduced the values found by nitrogen. For the specimens that were subjected only to humidity fluctuations between 0 and 33 percent, the nitrogen area was reduced by about the same percentage as the water area. For the specimens represented in table 10, the nitrogen areas were reduced *much more* than the water areas. If water vapor actually penetrated the primary particles, primary with respect to nitrogen adsorption, a reduction of such penetration by water should reduce the indicated water area but not the nitrogen area.

Perhaps the most plausible explanation is that during desorption, gel particles are brought closer together than they have ever been before, and new points of contact are produced under considerable pressure. (See section 7.) If this should create stable chemical bonds between the particles, the irreversibility would be accounted for. If the evidence is construed to indicate such new bond formation, it indicates also that the bonds have various degrees of strength. As shown in table 9 not all possibilities for forming new bonds are exhausted at one time, so that repeated cycles are required to establish stability under a given set of conditions. Also, considering the partial reversal caused by complete swelling between surface-area determinations, one concludes that some of the new bonds that remain intact at low humidities are weak enough to be ruptured by film pressure at high humidity.

The explanation just offered suggests that as the surfaces of adjacent particles are mashed together by shrinkage forces, a partial fusion of the surfaces occurs. If this is so, it indicates that as much as half of the original surface can be eliminated in this way, a fraction so high as to cast doubt on the explanation.

Irreversible Deformations of Cement Paste

Drying Shrinkage

It is a familiar fact that the first isothermal shrinkage caused by drying is only partially reversible and that subsequent cycles of wetting and drying at the same humidity are very nearly reversible. Data published by Pickett [79], are typical. This phenomenon is apparently a manifestation of the same instability that was reported in terms of decrease in specific surface area as discussed above. However, most data on irreversible shrinkage, including Pickett's, are complicated by the effects of carbonation occurring during the period of drying.

Carbonation Shrinkage

Cement gel is unstable in the presence of carbon dioxide and moisture [92]; it reacts chemically, and irreversible shrinkage accompanies the reaction. Rate of carbonation depends on ratio of surface area to volume of the specimen, permeability of the paste, internal relative humidity, and concentration of CO_2. Carbonation shrinkage is greatest when the internal humidity is about 50 percent. Practically no carbonation shrinkage occurs when the internal humidity is 100 or 25 percent. Carbon dioxide is able to react with all components of hydrated cement. The surface area per gram of original anhydrous cement appears to be slightly increased by the reaction. The mechanics of carbonation shrinkage has not yet been explained.

Effect of Externally Applied Force

A specimen of paste when subjected to an externally induced stress, such as, for example, that produced by sustained compressive force, or a bending moment, shows behavior similar to that produced by internal tension (shrinkage). Experiments of this kind are usually carried out to study plastic deformation and creep, and it is common to observe the effect of the applied load at the same time that shrinkage is going on. Experiments done under less complex conditions were reported recently by Glucklich [84]. He used sealed specimens of neat cement subjected to a bending moment. Although a small amount of leakage through the seal, and self-desiccation [66] no doubt resulted in some internal tension, the internal tension was probably moderate and relatively constant throughout the experiment. Repeated loading showed marked permanent set on the first loading, and a little on the second, but further repetitions showed reversible viscoelastic deformation. Thus it appears that the external force produced the same kind of effect as did the internal stresses induced by drying.

9. Strength

Werner and Giertz-Hedström [93] were apparently the first to observe that strength of cement paste and concrete should be a function of the concentration of hydrated cement, although the earlier cement-space ratio of Féret (1897) certainly implied such a relationship. Others who dealt with similar ideas were Work and Lasseter (1931), Woods, Steinour, and Starke (1932), Freyssinet (1933), Eiger (1934), Bogue and Lerch (1934), and Lea and Jones (1935), all mentioned by Giertz-Hedström in his 1938 review [94]. In 1947 Shinohara, [95] and Powers and Brownyard [96] independently published work based on similar ideas, and about the same concepts were used by Taplin [68] in 1959. In a dissertation published in 1953, Dzulynsky published a study of strength in relation to cement hydration in which ideas similar to those reviewed about were developed [97]. Strength was considered to be a function of γ such that

$$\gamma=\frac{C_h}{C_h+W_e+v}. \tag{48}$$

In terms of the notation used in this review,

$$C_h=(c_{hc}v_{hc}/V)\times\text{Constant}.$$

Thus, C_h is the volume of hydrated cement (not volume of gel) per unit volume of sample. W_e is the volume of evaporable water in a unit volume of specimen, whether the specimen is saturated or not, and v is the air-filled space. The indicated constant is inserted because the method of determining fixed (nonevaporable) water used by Dzulynsky was not the same as that on which c_{hc} is based.

From experimental data obtained from tests on pastes and mortars, Dzulynsky concluded that

$$R'_\gamma = R'_0 e^{k\gamma}. \tag{49}$$

Where R'_γ is the observed strength, and R'_0 and k are empirical constants. Adopting this form of empirical equation had the unfortunate consequence that when $\gamma=0$, $R'_\gamma=R'_0$ instead of 0 as it actually is.

Powers and Brownyard [96] adopted the term gel-space ratio analogous in concept to the Feret cement-space ratio. They carried out measurements that gave compressive strength and factors proportional to the amount of gel, and arrived at the following empirical equations that represented the data very well.

$$f_c = M[(V_m/w_0) - B] = M[k(w_n/w_0) - B] \tag{50}$$

where f_c is compressive strength; M, B, and k are constants for a given cement, k being the ratio, V_m/w_n. Since the cement gel produced from a given cement has a characteristic specific surface area proportional to V_m/V_g, where V_g is the volume of cement gel, the quantity of gel in a unit volume of specimen is properly represented by V_m/V_p, where V_p is the volume of the paste. The space initially available to gel is proportional to w_0. However, since the ratio of V_m to w_0 is not literally proportional to the gel-space ratio, Powers later [98] used the function

$$X = \frac{\text{gel volume}}{\text{gel volume} + \text{capillary space}}$$

where X is the gel-space ratio. Another relationship was proposed [72] such that

$$X_F = \frac{\text{gel volume}}{\text{gel volume} + \text{capillary space} + \text{air voids.}}$$

Experimental data conformed closely to an equation of the following form:

$$f_c = f_c^\circ X^n \tag{51}$$

where f_c° and n are empirical constants. Since X is a fraction between 0 and 1, X^n operates as a reduction factor on f_c°. The intrinsic strength of the gel thus seems to be represented by f_c°, although when aggregate is present it probably includes other factors.

Different methods of expressing X have been given [72,98]. The following is perhaps the most convenient expression.

$$X = \frac{N}{1 + \frac{1}{m} \cdot \frac{v_w}{v_c} \cdot \frac{w_0}{c}} \tag{52}$$

As seen in eq (37), N is the volume of gel produced by 1 cc of cement. Constants evaluated from data published by Powers and Brownyard are given in table 11. Calculations for X were based on values of w_n obtained by the magnesium perchlorate method. When X is based on w_n determined by the dry ice method, the values of n come out about 12 percent higher, averaging about 3.0.

Table 11. *Compressive strength functions for mortars made with five different cements*

(Data from reference 17, tables 6-1 to 6-6)

Cement No.	Calculated compound comp., %					N of eq (37)	n of eq (51)	f_c° lb/in²
	C_3S	C_2S	C_3A	C_4AF	$CaSO_4$			
14930J	22.7	55.8	6.1	9.8	2.64	2.15	2.53	18,500
15007J	48 0	29 1	6.8	10.5	2.22	2.18	2.86	17,500
15011J	45.1	29.1	6.7	10.5	2.43	2 18	2.44	16,000
15013J	39.0	29.0	14.0	7.0	3.00	2.18	3.08	13,000
15365	45 0	28.0	13.3	6.7	4.22	2.24	2.68	13,800

The figures in the last column considered in connection with the chemical compositions of the cements indicate that cement gels low in C_3A are stronger than those high in C_3A. Although there is such evidence that the strength of cement gel is a function of its chemical composition, there is no evidence that some of the chemical species present do not contribute to strength. By means of a simple demonstration, Czernin made it clear that the physical state of the solid material may be responsible for strength [99]. He demonstrated (A) that a mixture of 100 g of coarse quartz and 20 g of water was without strength, (B) that when the quartz was pulverized to "cement fineness", the same proportions exhibited some strength and (C) that when the quartz was pulverized so as to have a surface area of 20,000 cm²/g, a cylinder molded with the aid of a press could support more than a 10 kg load. Czernin remarked that in cement paste the surface area is not 20,000 but 2,000,000 cm²/g and thus ". . . the high strength attained by the cement in time is entirely plausible." Such strength is presumably due to the proximity of surfaces and van der Waals forces, as discussed in section 7. Since all the major components of hydrated cement are found in substances having high specific surface area, all contribute to at least the van der Waals source of strength. On the other hand, it seems unlikely that the strength of cement gel is due exclusively to physical forces. For reasons already given, it seems probable that there are many points of chemical bonding between the particles. Whether or not all chemical species contribute to this source of strength cannot be said. As to the relative importance of the two sources of strength, one can only speculate. When a specimen of cement paste is dried in such a way as to avoid excessive stresses during drying, the specimen becomes stronger as its evaporable water is lost; in fact, if some of the chemically combined water is removed, there is gain in strength. In terms of van der Waals forces, this gain of strength could be accounted for in terms of the reduction in average distance between surfaces in the cement gel. There is evidence also that new chemical bonds may be formed during the process of drying (see section 8).

Effect of Temperature of Curing

Ludwig and Pence [51] cured specimens of cement paste at various temperatures, measured the nonevaporable water contents, the surface area of the solids, and compressive strengths, and obtained the results shown in table 12. The relationship between gel-space ratio and compressive strength for curing temperatures 27, 66, and 93 °C conform to eq. (51) with $f_c^\circ=12{,}000$ and $n=3$. At the two highest temperatures, the strength is only 30 percent of that to be expected from the calculated gel-space ratio.

TABLE 12. *Effect of temperature of curing on compressive strength*

(Ludwig and Pence, 1956)
Curing time: 7 days; Nominal w/c=0.46
Cement: ASTM Type I

Temperature of curing		Pressure in autoclave	Surface of solids [a] m²/g	$\left(\frac{w_n}{c}\right)_s$	Gel-space ratio (approx)	Compressive strength, psi
°F	°C					
80	27	1 atm	103	0.142	0.68	3825
150	66	1 atm	123	.162	.79	[b] 6141
200	93	1000 psi	75	.152	.76	5,086
260	127	1000 psi	30	.139	.71	1,281
320	160	1000 psi	9.4	.139	.71	1,330

[a] Including unhydrated cement.
[b] Cured at 140 °F.

10. Permeability of Saturated Paste to Water

Under proper experimental conditions, it can be demonstrated that the flow of water through hardened cement paste complies with d'Arcy's law. To obtain a correct result, the test specimen must be completely saturated, and osmotic pressure developed in the apparatus during the test must be practically constant [100]. This observation of compliance with d'Arcy's law is the beginning point of analytical studies of permeability.

Theories of Permeability

Powers and Brownyard [101] attempted to deal with the flow of water through mature cement pastes in terms of the Kozeny-Carman concepts, as had been done previously for fresh pastes. (See section 2.) According to this approach to the problem

$$K_1=\frac{\rho_f g}{\eta_0(T)k\sigma^2}\,\frac{\epsilon_e^3}{(1-\epsilon_e)^2}\ \text{cm/sec.} \tag{53}$$

The constant k is the Kozeny-Carman constant, embodying a "tortuosity factor" and a shape factor, and σ is specific surface area of the solid particles, cm²/cc. The subscript, e, on porosity, ϵ, indicates that the effective porosity is not necessarily equal to all the space occupied by evaporable water. That is, it was known from Carman's work with clay [102], and from the work on fresh cement paste, that some of the fluid might be "immobile". Powers and Brownyard assumed that the quantity of immobile fluid would be proportional to V_m and obtained the following expression:

$$K_1=(7.85\times 10^{-12})\,\frac{\rho_f g}{\eta_0(T)k}\,\frac{V_m}{V}\left[\frac{w_e}{V_m}-k_1\right]^3\ \text{cm/sec.} \tag{54}$$

The numerical coefficient is the reciprocal of the square of the proportionality between V_m and surface area. k_1 is the amount of "immobile" evaporable water, expressed as a multiple of V_m. As will be seen further on, there is evidence that all the evaporable water is mobile.

Powers and Brownyard assumed that the capillary space in paste is in the form of an interconnected system of capillary channels throughout the gel, and that the hydraulic radius of the principal conduits could therefore not be calculated from the total porosity and total internal surface area. Later, Powers and Copeland nevertheless applied the Kozeny-Carman relationship to mature pastes having capillary porosity, seemingly with some success, but that approach was eventually abandoned in favor of another based principally on Steinour's adaptation of Stokes' law to concentrated suspensions, discussed in section 2. Powers, Mann, and Copeland finally arrived at eq (55) [56].

$$K_1=\frac{B}{\eta_0(T)}\cdot\frac{\epsilon^2}{(1-\epsilon)}\cdot\exp-\left[\left(\frac{\alpha}{T}-\gamma\right)\left(\frac{1-\epsilon}{\epsilon}\right)\right] \tag{55}$$

where

$$B=\frac{\zeta(c)\,\rho_f g d_s^2}{27}. \tag{56}$$

B is a constant comprising the following factors: the density of the fluid in the specimen, ρ_f; the gravitational constant, g; a function of particle shape, the Stokes diameter, d_s; and the number 27 which comprises the numerical constant in Stokes' law for the free fall of spheres, and another function of concentration $\zeta(c)$, introduced by Hawksley [103] which corresponds to the Kozeny-Carman tortuosity factor. The term $\eta_0(T)$ is the normal viscosity of water at temperature T. In the exponential term, $\alpha/T((1-\epsilon)/\epsilon)$ is a correction term applied to normal viscosity, and $\gamma((1-\epsilon)/\epsilon)$ was thought of as a temperature-independent factor of the same kind. The values of the constants in eqs (55) and (56), derived from experimental data, were reported as follows:

$$B=(1.36\pm 0.1)\times 10^{-10}$$
$$\alpha=1{,}242\pm 133$$
$$\gamma=0.7\pm 0.5.$$

The fit seemed good except that γ was not significantly different from zero. Powers, Copeland, and Mann, being at the time mostly interested in *B*, did not pursue the analysis further. Actually, the indication that $\gamma=0.0$ could only mean that the exponential term contains nothing that is independent of temperature. A review of the derivation of eq (55) showed that this might have been anticipated, particularly in the light of Hawksley's treatment. The least-squares analysis was repeated during the present writing, omitting γ, with the following results:

$$B=(1.34\pm 0.099)\times 10^{-10}$$
$$\alpha=1{,}432\pm 22.$$

The values of ϵ used in the above calculations were based on the assumption that the mean specific volume of evaporable water is independent of porosity and equal to 0.99 cc/g. (See section 3.) Based on ϵ_H, the porosity to helium, calculations gave

$$B=(1.18\pm 0.085)\times 10^{-10}$$
$$\alpha=1{,}250\pm 20.$$

The two pairs of values may be regarded as upper and lower limits. Probably the correct values are closer to those based on ϵ_H than to those based on the assumption that the specific volume of adsorbed water is 0.99.

With the success of eq (55) established, it is now clear why a Kozeny-Carman type of expression cannot be applied successfully to the flow of water in hardened cement paste. Steinour [22], experimenting with spherical particles of tapioca suspended in oil at 25 °C, showed that the Kozeny-Carman constant *k* is the following function of ϵ.

$$k=\frac{1}{2}\cdot\frac{\epsilon}{1-\epsilon}\cdot \exp 4.19(1-\epsilon). \qquad (57)$$

For values of ϵ between 0.3 and 0.78, this equation gives $k=4.06$ within ± 0.06. This constancy, together with the limits on ϵ, accounts for the success of the Kozeny-Carman equation, and for its limitations.

For flow through cement pastes, the effects of adsorption produced a function different from eq (57). Thus, from eq (55) (without γ) and from data give above, we have

$$k_1=\frac{1}{2}\cdot\frac{\epsilon}{1-\epsilon}\cdot \exp\left[\frac{1{,}250}{T}\,\frac{(1-\epsilon)}{\epsilon}\right]. \qquad (58)$$

For $T=298°\ K$, $1{,}250/T=4.19$, the same value found by Steinour. With $\epsilon=0.3$, 0.5, and 0.7, eq (57) gives $k=4.02$, 4.05, and 4.07, whereas the corresponding figures for eq (58) are 3,500, 32, and 14. Thus, for flow through pastes, *k* is far from constant, and its magnitude far away from that required for the success of the Kozeny-Carman equation.

The agreement between the numerical coefficients in eqs (57) and (58) is significant, and will be discussed further on.

Viscosity of Water in Saturated Paste

According to the theory of Eyring [104]

$$\eta_0(T)=A_0 \exp E_0/RT \qquad (59)$$

where $\eta_0(T)$ is the viscosity of water flowing under conditions that produce unperturbed patterns of flow, such as between smooth, parallel plates. E_0 is the normal energy of activation for such flow, and A_0 is a temperature-independent constant. Flow of water through hardened paste does not provide the conditions just stipulated, but, according to the same principle, the viscosity for flow through paste should be given by

$$\eta(T,a,m)=A_1 \exp (E_0+E_a+E_m)/RT \qquad (60)$$

where E_a and E_m denote parts of the total activation energy for flow due to adsorption (and solutes) and to mechanical interference of flow patterns, respectively. Thus, relative viscosity η^* in paste is given by

$$\eta^*=\eta(T,a,m)/\eta_0(T)=(A_1/A_0) \exp (E_a+E_m)/RT. \qquad (61)$$

The exponential term in eq (55) is an empirical correction factor for normal viscosity such that

$$\eta^*=\exp (\alpha/T)(1-\epsilon)/\epsilon. \qquad (62)$$

Thus

$$(A_1/A_0) \exp (E_a+E_m)/RT=\exp (\alpha/T)(1-\epsilon)/\epsilon. \qquad (63)$$

The agreement pointed out earlier between the value 4.19 in eq (57), found by Steinour from experiments in which adsorption effects were absent, and $\alpha/T=1{,}250/298=4.19$, found for flow in cement paste indicates that when $E_a=0$,

$$\eta_1^*=\exp E_m/RT=\exp (\alpha/T)(1-\epsilon) \qquad (64)$$

where η_1^* is the relative viscosity when there is no adsorption effect. Thus the effect of adsorption is to require the empirical function of porosity to be $(1-\epsilon)/\epsilon$ instead of $(1-\epsilon)$.

Solutions of eqs (62) and (64) are given in table 13, showing the total effect of mechanical interference and adsorption, and the mechanical effect alone.

TABLE 13. *Computed relative viscosity of fluid in saturated cement pastes, based on eq (63) and (64) with* $A_1 = A_0$, *and* $\alpha/T = 4.19$

w_o/c	ϵ	Hydraulic radius	Factor of viscosity increase	
			Mechanical effect η_1^*, eq 64	Total effect η^*, eq 62
		A		
0.38	0.280	7.8	20.5	[a] 47,600
.45	.346	10	15.5	2,700
.50	.395	12	12.6	600
.60	.461	16	9.6	134
.70	.489	18	8.5	78

[a] This is the value for cement gel.

Magnitude of Activation Energies

Activation energies for flow through different pastes ranged from 8,160 for $\epsilon = 0.414$ to 6,200 for $\epsilon = 0.572$, in calories per mole of water. The mean activation energy for flow of water under normal circumstances is about 4,490 cal/mole. Thus, $E_m + E_a$ ranges from about 3,700 to 1,800 cal/mole for the range of ϵ given.

General View of Factors Determining Permeability of Saturated Paste

Figure 4 is a simplified version of a diagram published by Powers, Copeland, and Mann [105] showing the principal factors controlling permeability to water at constant temperature. Line E represents the permeabilities of fresh pastes over the range of water-cement ratios indicated by the top scale, the permeabilities having been determined from bleeding rates. The resistance to flow depends on the size, shape, and concentration of cement particles, and on the effect on the particles of the initial chemical reactions (see section 2). Since the effect of adsorption on the viscosity of water in fresh paste is negligible, the scale of abscissas should have been in terms of $1 - \epsilon$ instead of $(1 - \epsilon)/\epsilon$. However it was not feasible to combine both functions in the same graph, and the present plotting serves the purpose.

Line A represents the permeabilities of pastes containing completely hydrated cement, and from which all alkali had been leached. The resistance to flow is determined by the size, shape, and concentration of the particles composing hydrated cement, and by the effect of adsorption on viscosity of water in paste. The marked points along line B represent a sample of paste at various stages of hydration from the fresh to the fully mature state, the final point being calculated and the rest experimental. Points along line C are the same for a different water-cement ratio. The dashed lines are estimated curves for other water-cement ratios.

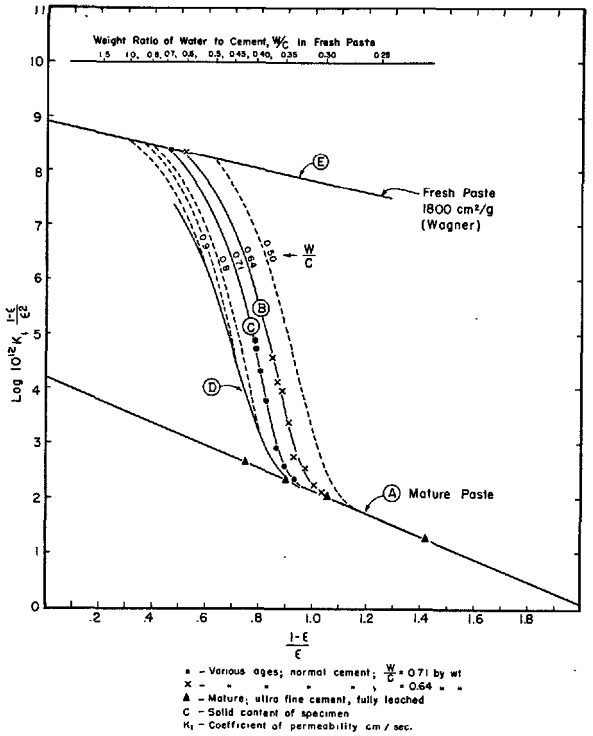

FIGURE 4. *Permeability functions for fresh, hardening, and mature pastes.*

Continuous and Discontinuous Capillaries

The water-filled space in *fresh* paste constitutes a continuous, interconnected system of capillaries. Production of cement gel at first constricts the capillaries without destroying continuity, but finally may divide them into segments that are interconnected only by gel pores. This transition, in terms of changes of permeability, is shown clearly by curves B and C and by dashed lines for other water-cement ratios. Capillary continuity is indicated by any point between E and A. At some stage of hydration of a given paste the point will just fall on line A, and, if there is still a reserve of unhydrated cement, subsequently produced points will follow line A. If the water-cement ratio is too high, complete hydration will not produce enough gel to destroy capillary continuity, and the terminal points fall above line A, along some such curve as D. For the particular cement represented by these points (ASTM Type I, 1800 cm²/g, Wagner), capillary continuity does not disappear at full maturity if w_0/c is greater than 0.7.

Effect of Cement Composition

Differences in chemical composition of cement do not have much effect if the tests are made when the different cements are at comparable stages of hydration [100]. Data given in preceeding sections showing that the quantity and physical characteristics of cement gels produced by different cements are similar would lead one to expect this result. At early ages, pastes made with a slow-hardening cement will of course have relatively high permeability.

Effect of Alkali

Solutes in the evaporable water, particularly NaOH and KOH, reduce the rate of flow through paste by increasing the viscosity of water. Specimens from which alkali has been leached show as much as six times the permeability of companion specimens containing a small amount of alkali. When plotted in figure 4, points representing specimens containing alkali fall below line A, except for specimens having capillary continuity. Verbeck [106] found that a given cement paste, with $w/c=0.55$, was nearly five times as permeable to pure water as to a salt solution containing 12 g/l NaCl. The effect was greater the denser the paste. It seems that the effect here reported is due to the presence of hydrated cations, the effect per ion being greater the greater the degree of hydration of the ion.

Effect of Cement Fineness

The higher the specific surface of the cement, the farther to the left curve D will be, that is, the higher the water-cement ratio at which capillary continuity can be "cured out". This seems to be the only way in which the fineness of portland cement, per se, influences the permeability of mature paste.

Effect of Curing

As is apparent from figure 4, the change in permeability accompanying the transition from fresh to mature states is enormous. For example, at $w_0/c=0.7$, fresh paste is 3 million times as permeable as mature paste, 2×10^{-4} vs. 6×10^{-11} cm/sec.

It is to be expected that if the temperature of curing is high enough to increase the size of the primary particles, permeability to water will thereby be increased. Ludwig and Pence measured the permeabilities of pastes cured under water at elevated temperatures with the result shown in figure 5 [51]. Verbeck reported results of the same kind [92].

Effect of Drying

If a specimen becomes dry at some time before a permeability test, its permeability to water is thereby increased. There are not many data on this point. In one experiment, mature specimens were dried very gradually to equilibrium with 79 percent relative humidity, and then slowly resaturated, first in humid air and then in water. The coefficient of permeability was found to be about 70 times what it would have been had the specimens not been given the drying and wetting treatment. This is probably another aspect of the structural instability of cement paste discussed in section 8.

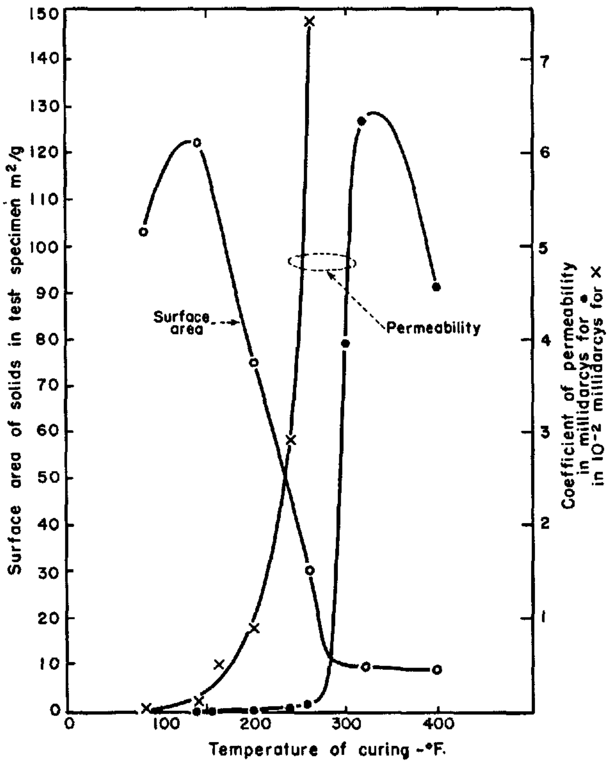

FIGURE 5. *Effect of temperature of curing on permeabilities of water-cured pastes (Ludwig and Pence).*

$w/c=0.46$ (nominal); cement ASTM Type I. All specimens cured under water for 7 days at temperature≥200°F; the pressure was 300 psi.

Permeability of Unsaturated Paste

Not much systematic study of movement of moisture through unsaturated paste has been reported. Powers and Brownyard [101] gave a relationship between the coefficient of permeability of a saturated specimen and a "coefficient of absorptivity" of a dry specimen, but, as the relationship was stated, it is applicable only to specimens containing an interconnected system of capillaries. It has been pointed out [105] that the "water-vapor permeability" is not ordinarily a process of transmitting vapor as such. Once water vapor is in cement paste, practically all of it is adsorbed and the transmission occurs in the adsorbed or capillary-condensed state. The motive force is not the vapor pressure difference, but the gradient in film tension discussed in section 7

Appendix 1

Glossary

To understand some parts of the text, the author's definitions of a few terms must be kept in mind. These terms are given below. (All terms defined in the glossary are italicized.)

Capillaries, or Capillary spaces: in fresh *cement paste*, the space occupied by water; in mature paste, the *pore* space in a specimen of paste in excess of about 28 percent of the volume of the specimen. These spaces are regarded as discontinuities in a mass of *cement gel.*

Capillary cavities: capillary spaces that are isolated by *cement gel.*

Cement: portland cement in the initial, practically anhydrous state.

Cement gel: the cohesive mass of *hydrated cement* in its densest state. It includes *gel pores*, and has a porosity of about 28 percent. The solid material is composed mostly of *colloids*, but noncolloids, particularly calcium hydroxide, are included in this definition. Its overall specific volume is about 0.567 cc/g dry weight; when prepared at room temperature its specific surface area is about 210m^2/g dry weight.

Cement paste: the term is applied at any stage of hydration. As applied to fresh paste, it is the mixture of cement and water, exclusive of air bubbles, if any; as applied to hardened paste, it is the rigid body produced by cement and water, composed of *cement gel, capillary spaces*, if any, and residual cement, if any. When there is neither capillary space nor residual cement, *cement paste* and *cement gel* are identical.

Colloid: a substance in such physical state that its chemical and physical properties are influenced to a significant degree by the surface energy of the substance. A solid colloidal substance may be amorphous or crystalline, but, if crystalline, the crystals are apt to be imperfectly organized. A colloid is characterized by a high specific surface area. In *cement gel* calcium hydroxide, and perhaps some other components are not colloidal.

Dry ice method: the method of isothermal drying of samples of *cement paste* described by Copeland and Hayes [36]; referred to also as the Copeland and Hayes method.

Gel: a cohesive mass of colloidal material. (Compare with *cement gel.*)

Gel pores: the pores in *cement gel.*

Hydrated cement: a collective term for all the chemical species produced by the reactions between *cement* and water, except transient products of initial reactions.

Magnesium perchlorate method: the method of isothermal drying of samples of *cement paste* described by Powers and Brownyard ([17], pp. 249–336) and by Powers [98], now largely supplanted by the *dry ice method.*

Pore (in *cement paste*)*:* space in *cement paste* that is, or can be, occupied by evaporable water. Its definition, quantitatively, involves a standard method of drying the sample.

Appendix 2

List of Repeatedly Used Symbols

$c=$ weight of cement in its original state, grams.

$c_h=$ weight of original cement that has become hydrated.

$c_i=$ weight of cement after being ignited.

$h=$ relative humidity$=p/p_s$ where p is the existing water-vapor pressure and p_s is the water-vapor pressure at saturation and same temperature.

ln= logarithm to the base e.

log= logarithm to the base 10.

$m=$ maturity factor=fraction of cement that has become hydrated.

$N=$ volume of cement gel produced from 1 cc of cement.

$P=$ pressure, either positive or negative.

$P_C=$ pressure in capillary water (usually negative).

$v_c=$ specific volume of cement, cc/g dry weight.

$v_e=$ specific volume of evaporable water, cc/g.

$v_g=$ specific volume of cement gel, cc/g dry weight.

$v_{hc}=$ specific volume of hydrated cement, cc/g dry weight.

$v_n=$ specific volume (apparent) of nonevaporable water, cc/g.

$v_p=$ specific volume of saturated paste, cc/g saturated weight

$v_t=$ specific volume of total water in saturated specimen, cc/g.

$v_w=$ specific volume of water under existing pressure, cc/g.

$v_w^\circ=$ specific volume of water under reference pressure, cc/g.

$V=$ volume of specimen or batch of paste.

$V_m=$ the Brunauer-Emmett-Teller surface-area factor =weight of water required for a monomolecular adsorbed layer on a sample dried by the dry ice method of Copeland and Hayes [36]. (See glossary).

$(V_m)_8=$ ditto for a specimen dried by the magnesium perchlorate method ([17] pp. 249–336).

$w=$ weight of water in fresh paste.

$w_o=$ ditto, corrected for water displaced by bleeding.

$w_i=$ the immobile water factor.

$w_n=$ nonevaporable water=water retained by a specimen prepared by the dry ice method of Copeland and Hayes [36].

$(w_n)_8=$ nonevaporable water=water retained by a specimen of paste prepared by the magnesium perchlorate method, vapor pressure 8μ of mercury. ([17] pp. 249–336).

$\epsilon=$ porosity, ratio of volume of interstices to gross, overall volume of a material.

$\epsilon_C=$ capillary porosity.

$\epsilon_H=$ porosity as calculated from the volume of the saturated specimen and the specific volume of the dried solid as determined by displacement of helium.

$\rho_c=$ density of cement, g/cc.

$\rho_s=$ density of solid, g/cc.

$\rho_f=$ density of fluid, g/cc.

$\sigma=$ specific surface area, cm^2/cc.

$\Sigma=$ specific surface area, cm^2/g.

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Discussion

H. W. W. Pollitt

My remarks concern Mr. Powers' most interesting paper. I should like to say first how much

I agree with him that there is a need for a closer connection between chemical and physical studies of cement and concrete. Particularly welcome from this point of view was the paper in Session II by Welch and Gutt, who discussed the effect of impurities on cement strength. It is by virtue of physical properties such as strength that cement is used in practice so that cement chemistry is chiefly of importance insofar as it can be related to the physical properties of cement.

Returning now to Mr. Powers' paper, I should like to comment on the section dealing with permeability where it is said that the presence of dissolved alkalis in water materially affects its penetrating power and it is remarked that this may be due to viscosity effects.

We, at the Associated Portland Cement Manufacturers Research Department, have some evidence that factors other than viscosity may be important. As everyone present will know, contractors frequently make concrete with insufficient strength which is usually due to too high a water-cement ratio. It is, however, common practice on the part of the contractor to assert that the cement is bad. In self-defense we have developed a method of determining in hardened concrete what was the water-cement ratio at the time of setting.

The procedure is to dry a piece of concrete at 105 °C to constant weight and to place it after cooling in carbon tetrachloride under vacuum. The space left by evaporated water is measured by the amount of carbon tetrachloride absorbed. Normal chemical analysis determines the quantities of cement and of combined water so that the total water and water-cement ratio at the time of setting can be calculated. The method works well, giving usually an accuracy of ±0.02 and often ±0.01.

During the research which led to the development of this test, several liquids were investigated and the effects of entrained air and honeycombing were studied. It was found that carbon tetrachloride would fill the water voids but not enter the air voids, whether these were due to entrained air or to honeycombing, except when large open voids were visible in the surface of the specimen. In that case any carbon tetrachloride taken up by the open voids drained out when the specimen was removed from the carbon tetrachloride. Pure water on the other hand explored a larger volume than did carbon tetrachloride, presumably by penetrating into air voids. When lime water was used the volume of it absorbed by the specimen was intermediate between those for pure water and carbon tetrachloride respectively; the greater the concentration of lime the less the volume absorbed.

Now the viscosity of carbon tetrachloride is very close to that of water. It therefore appears that in dry hardened concrete the water voids are penetrable by fluids having the viscosity of water. This is consistent with the concept of a network of interconnected capillaries. The air voids on the other hand are penetrated by water, rather less by lime water, and not at all by carbon tetrachloride. This suggests that an air void is surrounded by a membrane which is impermeable to an inert fluid having the viscosity of water but permeable to water to an extent depending on its content of dissolved lime. The clear inference is that it is the dissolving power of the fluid with respect to the membrane that governs the degree of penetration into air voids.

It seems possible that chemical reactions may similarly have affected the results reported by Mr. Powers. It is conceivable that precipitation of lime occurs when water containing alkalis passes through capillaries in cement paste and that the precipitate constricts the capillaries and opposes flow.

I should be interested to have Mr. Powers' comments on these facts and opinions.

Discussion

G. E. Bessey

Compared with the complexity of hydraulic cement concrete and cement pastes, the more simple hydrous calcium silicate bonded products, sand-lime bricks, formed by direct reaction of well-compacted mixes of lime and silica in high pressure steam, offer a clearer picture. From all the information now available, as described in various papers presented at the Symposium and from the writer's experience with the industrial products, it seems that the initial reaction in their hardening is normally to form "amorphous" CSH, which slowly converts to a tobermorite phase, and at the higher pressures and still longer times may convert to xonotlite. Determinations of the combined lime and "soluble" silica in a large number of commercial bricks show ranges in lime:silica ratio of only 0.78 to 1.28 with over two-thirds of the analyses between 0.9 and 1.2. Bearing in mind that the calculated ratio involves the combined error in each instance of four separate analytical determinations, the ratio is remarkably constant.

In these materials the water content used in pressing is low, and insufficient to fill the voids in the pressed brick. Consequently strength is independent of water-binder ratio and bears a simple linear relation to the binder (i.e., lime) content over the practical working range.

It is perhaps more interesting in relation to the position with cement products that the drying shrinkage, other things being equal, is similarly related almost linearly to lime content over the practical range.

When the ratio of lime to silica is increased further, beyond the range used in practice, the available surface of silica becomes saturated and a dicalcium silicate hydrate is formed. This is a less effective bonding agent and has also, it seems, lower drying shrinkage, so that the curves of both

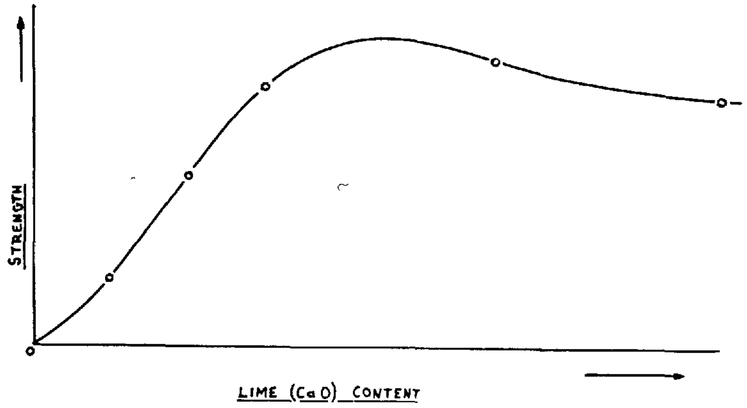

FIGURE 1. *The effect of lime content upon strength of hydrated calcium silicate bonded (sand-lime) bricks*

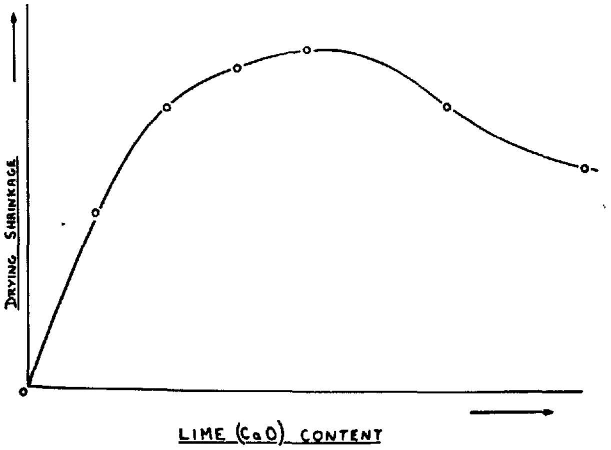

FIGURE 2. *The effect of lime content upon drying shrinkage of hydrated calcium silicate bonded (sand-lime) bricks*

strength and drying shrinkage versus lime first depart from rising linearity and then drop. This is shown in figures 1 and 2, which are reproduced from actual data using a particular sand with the curves passing through all the experimental points. Since the actual values for given lime contents, and the contents at which inflection of the curve takes place, are dependent upon the fineness of the sand, and other factors, the values are not shown on either axis. The form of curve remains the same for all sands.

Closure

T. C. Powers

In his remarks entitled "A Few Unsolved Problems of Cement Hydration", Mr. Czernin raises some questions that deserve careful consideration. One of the questions exemplifies a difficulty confronted by every writer on this subject. The difficulty is that concrete is not a substance that can be described in terms of a few single-valued characteristics—far from it. Several of its important properties may have any one of a wide range of characteristic values, and these various values may appear in one or another of innumerable possible combinations. Furthermore, different parts of a single specimen may show significantly different characteristics. For such reasons, a statement that is true about the characteristics of a particular specimen, or class of specimens, of cement paste or concrete is liable to be untrue if applied generally.

Mr. Czernin cited data showing that cement paste becomes progressively firmer throughout the period we have called dormant. Such behavior is typical of pastes in which the cement grains are initially very close together. Such a paste might have standard, "normal", consistency and a water-cement ratio of about 0.23. It would not bleed, and cementation probably would begin immediately, producing the stiffening reported by Mr. Czernin. On the other hand, if a paste is initially soft enough to bleed, the cement grains are well separated by water, and they remain separated throughout the dormant period, except in the sediment that accumulates on the bottom of the container. The bottom part stiffens, just as does a paste having a high particle concentration at the start, but the upper part of the sample, which bleeds at constant rate, does not undergo cementation, and its consistency does not change very much until the period of set begins.

Thus, Mr. Czernin's argument on this point is right or wrong depending on whether or not one speaks of a paste in which the cement particles are highly concentrated . The point to be emphasized is that setting and cementation depend upon physical factors as well as chemical ones, and what is true about one class of pastes may not be true about another class.

Another question raised by Mr. Czernin pertained to the mechanics of hydration. This bears on the concepts of gel structure and the evolution of that structure dealt with in section 6 of my paper. There is a natural tendency to endow a mental picture of the structure of cement paste with simplicities not required by the basic concept on which the picture is based. It is not necessary to suppose that cement gel grows in such way as merely to translate outward the original contours of each cement grain, thus maintaining a clear demarcation between cement gel and capillary space. Mr. Czernin's excellent pictures as well as many other observations, show that, at least in the early stages, cement gel does not grow that way. At the start, gel substance seems to be deposited on any solid surface that is itself not producing gel. In concrete, such surfaces would be presented by aggregate particles and calcium hydroxide crystals formed early in the process. Since gel substance is insoluble, it cannot remain in solution very long; it seems, therefore, that the development of gel one sees at considerable distances from the source material is the result of surface diffusion, the gel substance being essentially in the adsorbed state until it reaches a place where gel particles can grow.

Regardless of where the gel substance is produced, it cannot achieve a density that averages more than about 0.72 cc of solid per cc of space. When any region becomes filled to this degree, we say that the region is full of cement gel.

I have dealt with this question in considerable detail in a paper prepared for the January 1961 issue of the Journal of the PCA Research and Development Laboratories. The arguments in that paper lead to the conclusion that no single term derived from other contexts, such as solution-and-precipitation, or topochemical reaction is able to designate adequately the complex process by which cement becomes hydrated.

Mr. Czernin's final comment pertains to the matter of gel porosity; he refers to a "theory of constant gel porosity." Actually, I know of no theoretical basis for predicting that the porosity of the heterogeneous mass of hydration products should be always the same when excess cement is present regardless of the amount of excess. Without such a theory, we can only say that this has been observed to be true, within the error of the experimental determinations, as shown in figure 1 of my Symposium paper. Mr. Czernin argues, "If the porosity of the hydrated part remains the same, whatever the amount of unhydrated material distributed in the gel, then the strength should remain at the same level or at least near it when we lower the w/c from 0.4 to the lowest possible ratio." This is a logical argument based on the tacit assumption that the strength of a specimen of cement paste depends only on the porosity of the hydrated part of the paste. However, I do not know of a theoretical basis for such an assumption, and it seems contrary to observation. As Mr. Czernin said, we know that even though the porosity of the hydrated part of specimens is the same when different amounts of excess cement are present, strength is higher, the higher the excess cement content. It seems therefore that we must conclude that gel strength alone does not define strength of a specimen of paste. Also it is probably true that when different cements are compared, gel porosity is not the only factor determining the strength of gel itself. The empirical relationship between strength and gel-space ratio is more general than the relationship between strength and water-cement ratio, but it nevertheless has limitations and uncertainties common to most empirical relationships.

Dr. Bessey's remarks and data bring out a point about empirical strength relationships that is sometimes overlooked. The point is that in concrete, air voids have about the same weakening effect as an equal volume of the much smaller capillary spaces in the hardened paste. This means that void-size does not have much effect on strength. The same seems to be true of pressed, sand-lime brick. Before curing, the spaces between sand grains are filled with three components: air, water, and lime. After curing, some of the water-filled space has become filled with reaction product, and thus the total volume of voids becomes the sum of the volumes of the original air-filled spaces and the residues of originally water-filled spaces. If the water content of the interstitial space is varied while holding the amount of reaction product constant, the effect is to change the ratio between the volumes of the two classes of voids. Dr. Bessey's statement indicates that such a change does not affect the strength, if the properties of the hydration product remain the same.

Mr. Pollitt referred to the remark that alkalis "reduce the rate of flow through paste by increasing the viscosity of water . . . ." This observation pertained to the rate of flow *through* a saturated specimen in a permeability test. The corresponding effect on rate of penetration of a dry specimen was not tested. I should like to suggest that viscosity is not likely to be a factor in the phenomena discussed by Mr. Pollitt. Viscosity affects the rate of flow under a given driving force, but not necessarily the amount of fluid that a given specimen can hold. Water in gel pores seems to have a very high viscosity, perhaps 50,000 times the normal value (table 13) and yet it penetrates dry gel readily. The same forces that affect viscosity also pull the water molecules into dry gel.

Mr. Pollitt's observations pertaining to the penetration of dry concrete by different fluids brings to mind certain experiments we reported in 1947. (Proc. Am. Concrete Inst. **43,** 693, 1947, tables 5–11; Research Lab. Portland Cement Assoc., Bull. 22, p. 693.) These experiments had to do with the determining of the specific volume of dry hydrated cement in the form of small granules obtained by crushing and sieving hardened paste. The granules were free from air bubbles and the like. Being incomplete, the data do not permit direct quantitative comparison between the results obtained in carbon tetrachloride and in water, but it is nevertheless clear that the apparent specific volume of dry hydrated cement is considerably higher in organic liquids than it is in water. The following table illustrates the point.

Apparent Specific Volume of Hydrated Cement (*Cement 20Q*)

Displacement fluid	Molar volume, (temp. 23°)	Relative molar volume	Apparent specific volume of hydrated cement
	cc		*cc/g*
Water	18	1.0	0.395
Acetone	73	4.0	.408
Toluene	106	5.9	.429

The apparent specific volume depends mostly on the degree to which the fluid used in the experiment is able to penetrate the capillary spaces and gel pores in each of the granules of the sample, and to the degree to which the specific volume of the fluid is influenced by adsorption. The subject is discussed briefly in the third paragraph of section 3 of my Symposium paper.

As pointed out in the Symposium paper the mean width of gel pores is estimated to be about 5 times the diameter of a water molecule. Since the carbon tetrachloride molecule is about 5.3 times as large as the water molecule, and since also carbon tetrachloride cannot cause the gel to swell appreciably, it is not surprising that carbon tetrachloride is unable to penetrate cement paste to the same degree as does water.

When a dried specimen of concrete is submerged in water the gel pores and capillary spaces seem to become filled readily, and it is theoretically possible for at least the very small air bubbles to become filled with water. It is our experience, however, that the time required for an appreciable amount of water to enter air bubbles or any voids of that kind is very long as compared with the duration of an ordinary laboratory experiment. Indeed, the effectiveness of entrained air in protecting the cement paste in concrete from frost action out of doors can be considered practical evidence that air voids do not become filled with water under ordinary circumstances. It seems, therefore, that the differences in penetration found by Mr. Pollitt are probably due to differences in size of molecule and degree of swelling, and probably not to a difference of penetration into air voids.

It does seem likely that the solubility of lime and alkali compounds in water should make more space available to water than to a fluid in which these salts are insoluble. Similarly, an aqueous solution of lime should find less space than pure water. However, considering the solubilities and quantities involved, it seems unlikely that this factor could be large. The amount of difference between absorption of pure water and lime water observed by Mr. Pollitt was not stated.

Paper V–2. The Microstructure of Hardened Cement Paste*

Åke Grudemo

Synopsis

The review covers not only the microstructures of hardened paste products but also the formation of lattice structures and the crystal habits of various compounds related to cement hydration in general, and represents a compilation of available data obtained especially in electron-optical studies.

Experimental methods of studying colloidal structures are reviewed briefly, with particular reference to the use of electron microscopy and electron diffraction in the examination of cement hydration products.

Different types of compounds appearing in the hydration of portland cement are reviewed separately with respect to their microstructural properties, starting with various modifications of lime hydrate.

In dealing with the hydrated aluminate and aluminoferrite phases, and the complex salts of the sulfoaluminate hydrate type, various possibilities of arrangement of their lattice structures are suggested. The appearance of hexagonal-plate phases of calcium aluminate hydrates in pastes is described. The problem of ettringite formation is treated in relation to some phenomena observed in cement slurries.

The general principles governing the formation of lattice structures in calcium silicate hydrates are described and illustrated by reviewing a number of crystal structures determined. The crystal habits and the principles of structure formation in tobermorite phases are treated in particular detail, as is also the problem of afwillite formation.

The hydration products of pure calcium silicates are reviewed and considered with special reference to paste-hydration processes. The experimental data from structural studies of paste-hydrated silicates are compared with corresponding observations of the gel phases in portland cement pastes. These are illustrated by a number of electron micrographs from paste samples of various description, selected in order to elucidate the influence of such factors as time of hydration, type of cement used, w/c ratio, fineness of grinding, and curing conditions.

The data obtained in structural studies of pastes are found to disagree with a number of current theories on paste microstructure. The need for a reconsideration of these theories is emphasized, and a few problems of special importance for further research are indicated.

Résumé

Le présent compte-rendu n'embrasse pas seulement les microstructures de produits en pâte durcie mais également la formation de réseaux cristallines et les modes de cristallisation de différents composés se rapportant à l'hydratation du ciment en général; ce compte-rendu est également une compilation des données disponibles obtenues essentiellement par des études optiques électroniques.

Il est brièvement rendu compte des méthodes expérimentales d'étude de structures colloidales, une attention particulière ayant été accordée à l'emploi de la microscopie électronique et de la diffraction électronique pour l'examen des produits d'hydratation du ciment.

Différents types de composés apparaissant lors de l'hydratation du ciment portland sont traités séparément en ce qui concerne leurs propriétés micro-structurales, en commençant par différentes modifications de l'hydrate de chaux.

Au sujet des phases d'aluminate et d'aluminoferrite hydraté ainsi que des sels complexes du type hydrate de sulfo-aluminate, il est proposé différentes possibilités de disposition des elements de structure dans le réseau cristalline. L'apparition des phases de plaques hexagonales des hydrates d'aluminate de calcium dans les pâtes est décrite. Le problème de la formation d'ettringite est traité par rapport à certains phénomènes observés dans les laits de ciment.

Les principes généraux régissant la formation de réseaux moleculaire dans les hydrates de silicate de calcium sont décrits et illustrés par la présentation d'un certain nombre de structures cristallines déterminées. Les modes de cristallisation et les principes de la formation de structure dans les phases de tobermorite fait l'objet d'études détaillées particulières, de même que le problème de la formation d'afwillite.

Les produits d'hydratation de silicates de calcium purs sont étudiés du point de vue spécial des processus d'hydratation de la pâte. Les données expérimentales des études de structure de silicates hydratés en pâte sont comparées aux observations correspondantes des phases de gel dans les pâtes de ciment portland. Ces données sont illustrées par un certain nombre de microphotographies électronique d'échantillons de pâte de descriptions diverses choisies dans le but de mettre en lumière l'influence de facteurs tels que le degré d'hydratation, le type de ciment utilisé, le rapport eau/ciment, la finesse du grain et les conditions de durcissement.

Les données obtenues lors d'études de la structure des pâtes sont en désaccord avec un certain nombre de théories courantes sur la microstructure des pâtes. La nécessité d'une révision de ces théories est soulignée et il est fait mention de quelques problèmes revêtant une importance particulière pour les recherches futures.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Swedish Cement and Concrete Research Institute, Stockholm, Sweden.

Zusammenfassung

Dieser Bericht umfasst nicht nur die Mikrostrukturen von gehärteten Pasten sondern auch die Gitterstrukturbildung und die Kristallformen verschiedener, sich auf die Zementhydratation beziehende Phasen im allgemeinen, und stellt eine Zusammenfassung der, besonders durch elektronoptische Untersuchungen gewonnenen, erhältlichen Angaben dar.

Über Versuchsmethoden für die Untersuchung von Kolloidalstrukturen wird kurz berichtet mit besonderem Hinweis auf die Anwendung der Elektronenmikroskopie und der Elektronenbeugung zur Untersuchung von Zementhydratationsprodukten.

Über die Eigenschaften von verschiedenen in der Hydratation des Portlandzementes erscheinenden Verbindungen wird einzeln berichtet mit besonderer Rücksicht auf deren mikrostrukturellen Eigenheiten, wobei mit den verschiedenen Modifikationen des Kalkyhdrates begonnen wird.

Betreffs der hydratisierten Aluminat- und Aluminoferritphasen sowie der zum Sulfoaluminattype gehörenden Komplexsalze werden verschiedene Möglichkeiten für die Anordnung ihrer strukturellen Elemente in Gitterstrukturen vorgeschlagen. Die Bildung und Eigenschaften der hexagonalen Plattenphasen der Kalziumaluminathydraten in Zementpasten wird beschrieben. Das Problem der Ettringitbildung wird erörtert mit Bezugnahme auf einige in Zement-Wasser-Mischungen beobachteten Erscheinungen.

Die allgemeinen Gesetze, die die Bildung von Gitterstrukturen in Kalziumsilikathydrate regeln, werden beschrieben und durch eine Anzahl von experimentell bestimmten Kristallstrukturen illustriert. Die Kristallformen und die Prinzipien der Strukturbildung in den Tobermoritphasen werden besonders eingehend behandelt, sowie auch das Problem der Afwillitbildung.

Die Hydratationsprodukte von reinen Kalziumsilikate werden mit besonderer Rücksicht auf die Hydratationsvorgänge in Pasten behandelt. Die Ergebnisse, die durch Strukturuntersuchungen von reinen, in Pastenform hydratisierten Silikaten erhalten sind, werden mit entsprechenden Beobachtungen der Gelphasen in Portlandzementpasten verglichen. Diese werden durch eine Anzahl Elektronenmikrophotographien von Pasteproben verschiedener Typen illustriert, die in der Absicht, den Einfluss von solchen Faktoren wie die Hydratationsdauer, der Typ des verwendeten Zementes, das Wasser/Zementverhältnis, die Zermahlungsfeinheit und die Erhärtungsverhältnisse zu erläutern, ausgewählt worden sind.

Es ergibt sich, dass die durch Strukturenuntersuchungen von Pasten erhaltenen Angaben nicht mit einigen, vorläufig gültigen Theorien über die Mikrostruktur von Pasten übereinstimmen. Die Notwendigkeit einer erneuten Prüfung von diesen Theorien wird hervorgehoben, und einige Probleme von besonderer Bedeutung für weitere Untersuchungen werden angegeben.

Introduction

As is generally recognized by all who have anything to do with cement research, hardened cement paste is a complex and highly variable system of particles of a manifold of sizes, shapes, and compositions, of water in different states of fixation, and of pores and voids, the sizes and distribution of which depend on how the particles of solid matter are aggregated and linked to each other. It can of course be stated quite generally that the microstructural properties of this system, as well as of any multicomponent hydrate system, are functionally dependent on a number of primary variables such as, in addition to time and the thermodynamic variables (temperature and water vapor pressure), the initial chemical and mineralogical composition, the initial particle size distribution, the amount of mechanical work applied during mixing, etc. In review of the present-day knowledge of the microstructure it would therefore, strictly speaking, be necessary to consider first the fundamental theories of the processes taking place in the reaction of cement with water, and to refer to a great number of papers dealing with different aspects of the chemistry and crystallography of components within the cement hydration system.

However, since the time of the 3d Symposium on cement chemistry in London, 1952, the literature on cement has been enriched by a number of textbooks, viz. (in order of time of publication) Kühl [1],[1] the Proceedings of the London Symposium [2], Bogue [3], Lea [4], Heller and Taylor [5], and the Proceedings of the Moscow Symposium 1956 [6]. Taken together, these books provide a most exhaustive account of practically everything written on the subject of the chemistry of cement and its constituents up to 1956. In addition, the latest developments in cement research are reviewed in a series of principal papers presented at this Symposium. In the present review, therefore, only papers dealing more specifically with matters pertaining to the microstructural properties of cement-hydration constituents will be referred to and commented on in connection with the discussion of various microstructural problems.

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[1] Figures in brackets indicate the literature references at the end of this paper.

Definitions and Nomenclature

Only materials and paste constituents within the general field of portland cement hydration will be considered in this review, and the term "cement" is used in the meaning of portland cement, if not otherwise stated.

In addition to the accepted abbreviations of chemical symbols (C–S–A–F–H), the oxide symbols $\overline{S}=SO_3$ and $\overline{C}=CO_2$ are introduced for the sake of uniformity. Further abbreviations used are EM = electron microscopy, ED = electron diffraction, and XD = X-ray diffraction.

Compounds of unknown or unspecified composition are generally denoted with dashes instead of subindices, e.g., C–S–H. Some problems of nomenclature concerning compounds within the C–S–H system still remain unsettled. The nomenclature proposed by Bogue [7] some years ago, which aimed at reconciling the various names and notations used, and at introducing a system of uniform symbols, has not been generally accepted. Some writers have preferred to use mineral names even for ill-crystallized and ill-defined products exhibiting certain structural or stoichiometric analogies to some natural mineral previously described in the literature on mineralogy. It does not seem possible, at present, to find a completely unambiguous denomination system. In the present review, Bogue's nomenclature and mineral names will therefore be used alternatively or in combination, as the case may be

Experimental Methods for Studying Microstructure

General Remarks

The subject indicated by the heading is in itself a very large one, and only a few comments will be given here, in order to clarify in some degree the present situation regarding the various possibilities of exploring the microstructures of hydrogels, or in general, systems of colloidal particles.

It should be recognized that the concept of microstructure can be divided into two distinct (although closely related) parts. First, microstructure can be considered from the point of view of crystallography pertaining to the repeat units of crystal structure, and the spatial arrangement of ions and ionic complexes within the unit cells, and studied by means of diffraction methods (XD and ED). Second, there is the morphologic aspect, involving the shape, size, and distortion of more or less well-crystallized particles, and the aggregation of such particles to condensed systems, characterized, among other things, by the nature of the interparticle links and the distribution of pores and voids, and studied in magnified images (light microscopy and EM).

It is evident that the development of ideas concerning the crystallographic aspect of cement hydration constituents is largely dependent on data obtained using analytical methods of study of a more conventional type, and related to the reaction chemistry and the phase diagrams of hydration systems which are less complex than the cement-water system.

The morphologic aspect, on the other hand, may serve to bridge the gap between pure and applied cement research, being closely related to problems concerning the physical properties of cement paste, especially its mechanism of deformation when used as a construction material in cement and concrete technology.

Crystallographic Methods

In the review of the structures of cement hydration compounds given by Bernal [8] at the London Symposium, it was emphasized that although at that time a comparatively large number of crystal structures related to the cement hydration compounds had been at least partly resolved, it would be necessary to develop essentially new XD techniques in order to attack the structures of other compounds of great interest in the field of cement hydration, especially within the C–S–H system. The reason for this, it was stated, was that most of the compounds formed in the reaction of cement with water, including hydrothermal products of autoclaving at elevated temperatures, or occurring as natural minerals, are only available as materials of a very low degree of crystallinity, consisting of small and mostly distorted crystals possessing large unit cells of low symmetry.

It seems that the situation has changed radically in this respect during the last few years. Difficulties which were at one time regarded by many crystallographers as nearly insurmountable, are at present well on their way to being overcome, due to the combined efforts of crystallographers all over the world, using refined methods of XD analysis and applying recently developed crystallochemical theories of structure formation. The most notable contributions in this field have perhaps been given by crystallographers at the University of Aberdeen and the Academies of Science of Moscow and Berlin. Some implications of the results of these studies of crystal structures for the more general problem of structure formation in cement hydration processes will be considered in later sections of this review.

In general, rational applications of standard single-crystal or powder XD techniques have proved to be sufficiently effective. However, great care must be taken to select suitable and well-defined crystal specimens for investigation, and preparation and mounting of crystals must often be executed under the microscope. Structural transformations during dehydration at elevated temperatures have been studied by *in situ* XD techniques. Electron-diffraction single-crystal diagrams have sometimes been useful in the determination of the true unit cells.

Microfocus X-ray tubes in combination with microcameras have in some cases been successfully used to improve the resolution of powder patterns and to decrease the exposure times. However, the X-ray diffractometer with Geiger-Müller tube counter and recorder units seems to have become the standard X-ray crystallographic equipment in most cement research laboratories, chiefly because of the high adaptability of this type of instrumentation for different purposes, for which either high resolution, high recording speed, or high accuracy of intensity measurements is essential. Some typical uses of the recording diffractometer are, e.g., the quantitative analysis of the mineral composition of a mixture of crystalline compounds, and the determination of particle size from small-angle scattering or line-width measurements. Other instruments which have been commonly applied in cement research in recent years, are powder cameras equipped with focusing monochromators, which are capable of resolving even the very closely spaced diffraction lines frequently appearing in powder photograms from a mixture of cement hydration minerals, especially the clinker minerals themselves, or steam-cured C–S–H mixes. The monochromator camera is superior to ordinary diffractometers for the special problem of detecting with certainty the presence of weak reflections which are, in diffractometer records, either masked by strong reflections nearby, or not clearly resolved from the background ripple. On the other hand, it would seem very difficult to avoid selective crystal-orientation effects in the very thin, and strongly compressed, powder layer samples used in monochromator cameras, which make them less suitable for measurements of relative line intensities in general, and, specifically, for a quantitative analysis of mineral composition.

It would seem that whereas different ways of using XD methods to their full capacity in examining crystal structures related to cement hydration have been well demonstrated, this is not nearly true with regard to the application of ED techniques, and major contributions to the advancement of knowledge of cement hydration processes are probably to be expected from investigators using ED methods.

Facilities for recording ED patterns are normally incorporated in different types of three-stage electron microscopes. Because of the strong interaction of electrons with matter, extremely small sample volumes can be singled out and examined by means of the so-called selected-area diffraction technique. In this way even minor constituents of a composite material can be detected and studied with respect to their diffraction characteristics, crystal symmetry, and unit cells. This possibility constitutes the main difference between XD and ED methods. An XD powder pattern of a mixture of crystals gives the superimposed patterns of different constituents with intensities proportional to their relative amounts, whereas the ED patterns vary from one point to another in a suitably prepared sample scanned with the electron beam.

The electron beam in an electron microscope is almost completely absorbed by solid matter of an effective thickness of the order of 1,000 A, which is thus the maximum particle thickness permitting ED diagrams to be obtained. This is also the upper limit rather arbitrarily set for colloidal particle size, and ED methods are therefore particularly suitable for studying structures of colloidal particles

It is an intrinsic property of colloidal particles, if at all crystalline, to have their crystal lattices restricted in one or more directions This restriction is equivalent to a degeneration of the points of the so-called reciprocal lattice into reciprocal density distributions of ellipsoidal symmetry. Since the ED pattern is a practically undistorted image of a section through the reciprocal lattice, the ED reflections from very small and distorted crystal elements are often observed to be diffuse or streaky. Because of the special method of preparing and mounting EM samples, crystal-orientation effects are also, as a rule, strongly pronounced. Owing to these circumstances, the relationships, as measured in XD diagrams, between stronger and weaker intensities of reflections, are often observed to be reversed or strongly changed in ED diagrams of the same sample. It can thus be stated that selected-area ED patterns can hardly be used for a quantitative determination of relative intensities in the same way as diffracted X-ray intensities are employed in electron-density syntheses.

A further consequence of the strong interaction of high-speed electrons with matter is that the sample particles will be heated when hit by the electron beam. It is mostly difficult to estimate the temperatures reached in this way, since too many uncertain factors are involved. However, under normal conditions, and when care is taken not to increase the electron beam intensity to a higher level than is strictly necessary for observing and recording the images visible on the fluorescent screen, the temperature of at least the thinner particles or particle aggregates in a sample is probably well below 100 °C.

Even these comparatively low temperatures, especially in combination with the vacuum maintained in an electron microscope or ED instrument, are still sufficient to cause dehydration and destruction of delicate or ill-crystallized hydrate structures. Crystal-structure transformations and changes in morphology are frequently observed in EM studies, and can sometimes be expected to have occurred even before the electron beam is switched on. Although in most cases the effects of heating can be considered negligible, one can never be quite certain that some unobservable change has not occurred. This circumstance is obviously a disadvantage of EM and ED techniques applied to the study of metastable and easily decomposing cement hydration constituents, since it may lead to serious misinterpretations of various observations made.

On the other hand, valuable conclusions on compounds of unknown identification can sometimes be drawn by using the technique of deliberately increasing the intensity of the electron beam successively, until a transformation of crystal structure or habit takes place and can be observed as a radical change in the ED diagram given by the substance studied.

Temperatures amounting to several hundred degrees C can be reached in this way, which is in many cases sufficient to remove all volatile oxide components from the specimen and transform it to some anhydride compound, the ED pattern of which can be used for identification and further analysis of the hydrate originally present.

The fact that the temperatures of the sample particles heated by the electron beam cannot be easily controlled or measured is evidently a disadvantage inherent in this technique, although in many cases of minor importance. In special electron-microscope constructions, the specimen stage is equipped with electric heating, or alternatively, liquid-air cooling, and a device for temperature measurement and control. It is possible that such devices will be of great use in future research on the microstructural properties of thermally unstable colloidal materials.

The commonly used XD technique of bringing out the whole spectrum of crystal reflections by rotating a specially selected crystal about one or more of its principal crystal axes cannot be employed in ED, on account of obvious difficulties of design caused by the extreme minuteness of the single crystal specimens. Disregarding the use of devices for tilting the specimen through a limited angular range [9], a single-crystal ED pattern represents a section of the reciprocal lattice, recorded for one particular, and mostly arbitrary, setting of a stationary crystal in a stationary. and very nearly monochromatic, electron beam.

Because of these circumstances, and because of the above-mentioned effect of various types of lattice restrictions and distortions, single-crystal patterns given by different crystals within a homogeneous sample frequently exhibit a wide range of variation, and each pattern must be interpreted separately in order to determine the symmetry elements common to all the patterns observed. A systematic approach to the analysis of crystal structure by means of single-crystal ED data would therefore necessitate the employment of statistical methods of synthesizing data obtained from a sufficiently large number of single-crystal patterns.

Morphology Examination Methods

The ordinary light microscope is undoubtedly still an indispensable tool in the examination of microcrystalline mixtures and hydrated paste structures. However, whereas it can be used to advantage for such purposes as the surveying of cement paste specimens, mineralogic and petrographic examinations of coarsely crystalline structures, and studies of residual unhydrated constituents of the course and rate of hydration, and of the distribution of larger pores and voids in cement paste, it is clearly incapable of revealing the finer details of paste structures, owing to the limited resolving power of visible light. According to Lea [10], "in a powdered set cement calcium hydroxide crystals can be detected and, occasionally, calcium sulphoaluminate, but the remainder cannot be differentiated". To provide a representative example of the information obtainable in microscope examinations of cement hydration, Lea can further be quoted on some interesting observations made by Brownmiller [11], "who noted that many of the cement particles were composite and that hydration proceeded by a gradual penetration into the particle from the surface. Except at, or near, the surface, therefore, the hydration of the coarser particles may not be very selective even though the hydration rates of the various cement compounds differ. Some of the interstitial material in the cement grains seemed to hydrate more slowly than the silicate crystals. A content of 10–15 percent of $Ca(OH)_2$ crystals was observed after 28 days".

The use of electron microscopy in cement hydration studies dates back about 20 yr, but it seems that different constructions of electron microscopes have only during the last decade reached such a high degree of reliability and versatility that they can be used for analytical work of a more systematic character. It has also been necessary to develop special methods of sample preparation and EM analysis, in order to avoid contaminations and artifacts, and, in the case of hardened pastes, to leave the original microstructure intact and undisturbed by various treatments.

The particle aggregates in hydrated cement materials are mostly so large and dense that the electron beam is completely absorbed in them, only the edge structures being observable. In order to facilitate the EM examination of cement-water reaction products, many investigators have selected to study the looser and more well-dispersed structures obtained in mixes containing a large excess of water, as compared with the w/c ratio normally used in pastes, and have thereby tacitly assumed that as long as saturation is maintained in the solution phase, the constitution and morphologic properties of the solid hydration product formed cannot differ very much from those of products formed in a paste. However, whereas the examination of more-or-less dilute suspensions can give a great deal of information on the microstructural properties of cement hydration constituents in their most well-developed states, the assumption of equality of phases is obviously, judging from various observations, justified only to a rather limited extent. The application of results obtained by using methods of preparation involving high water-to-solids ratios for drawing conclusions on the microstructure of setting and hardening pastes has also been criticized in the literature [1, 12, 13].

A method of letting extremely thin layers of cement paste of normal w/c ratios hydrate directly on the specimen screens for various times before introducing the specimen into the electron microscope has been devised by Bernard [14], and also adopted by Stork and Bystricky [15]. It is preferentially the contour structures in pore surfaces, and at the edges of cracks, that can be examined by this method, whereas the internal texture of aggregates of the colloidal particles is largely hidden from inspection.

For obvious reasons, it is necessary to break down hardened paste into a finely subdivided powder before it can be examined by EM methods. Clearly, any procedure used is likely to cause disturbances of the original paste structure in the form of fractures of crystalline materials, distortion of delicately built particles, etc. However, in the experience of some investigators, including the present author, ordinary methods of grinding and milling apparently leave most of the microstructural details relatively unaffected. The dry powder can simply be dusted on to the specimen support film, preferably by placing this film in the dust cloud formed in an elutriation column, or alternatively, it can be spread out in a thin and evenly distributed layer by means of electrostatic methods [16]. In order to improve the dispersion of EM specimens, the powder can also be suspended in a suitable organic liquid, and a drop of the suspension spread over the specimen support screen. Care must be taken, however, to make certain that the suspension medium does not produce any undesirable effects of interaction with the suspended solid particles. Ordinary laboratory ethyl alcohol has been found suitable in this respect, and also affords an excellent protection against carbon dioxide attack.

The application of more powerful techniques for achieving a high degree of dispersion of paste specimens, such as prolonged ball-milling or high-power ultrasonoration, will almost inevitably lead to serious disturbances, and eventually to complete disintegration of hydrated structures.

A technique involving replication of fresh cleavage surfaces of cement paste by evaporation of a thin film of highly resistant, and chemically inert, amorphous material, such as carbon, on to the surface, has been used by some investigators in later years. This method is supposed to give a true reproduction of the internal structures of the paste, and is likely to cause very little damage to the structure. Dehydration phenomena such as crumbling and cracking of the fractured paste surface may occur, owing to the unavoidable exposure of the paste specimen to the high vacuum necessary for a successful evaporation of the replica material. Difficulties in interpreting various observations must largely be overcome by comparing the replica structures with those observed in dispersed specimens using ordinary EM methods.

Microstructures of Lime Hydrate Modifications

Immediately upon mixing cement with water, Ca ions are dissolved from the surfaces of the calcium silicate crystals, and other Ca ions come from the dissolution of gypsum admixtures. In the highly supersaturated lime solution thus formed, CH crystals are precipitated out at an early stage of cement hydration. The XD diagram from portland cement paste also contains a strong and easily recognizable CH pattern, developed already in the first few hours after mixing, whereas patterns originating from other hydrated constituents are mostly weak and can be identified with certainty only by means of special methods [17]. As stated previously, CH is also the only crystalline hydrate readily detectable in the microscope, a content of 10 to 15 percent of CH crystals being observed after 28 days of paste hydration. A few percent more may be detected in fully hydrated paste, depending on the clinker mineral composition.

Macrocrystalline CH takes the form of hexagonal plates or prisms, and it is therefore rather surprising to find that in all the earlier studies of precipitates from lime solutions, whether formed by precipitation from pure solutions or by the decomposition of cement constituents, solid CH was identified as having the appearance of rounded platelets or spherulites which were found to grow into each other at the points of contact, forming long chains [18, 19, 20, 21, 22, 23, 24] (fig. 1).

The amorphous character of these formations is revealed by ED diagrams which show only a strong but very diffuse reflection at about 2.8 to 3.0 A.

The reason why CH precipitates in amorphous structures rather than in its natural crystalline habit was not given by the various observers. It was probably believed that in highly supersaturated lime solutions formed by rapid evaporation of water or in the first stages of cement hydration involving rapid dissolution of lime, especially from C_3S, a high concentration of small nuclei of CH crystals was momentarily attained, and that this unstable colloidal solution coagulated into spherulitic aggregates of an amorphous, frozen-in structure.

A simple, and apparently correct, description of the true nature of the spherulites, at least those formed from pure lime solutions, was given rather recently by Schimmel [25]. He observed that when spherulitic lime aggregates were moderately heated in the electron beam, they suddenly changed appearance, and simultaneously the easily recognizable pattern of calcite, $C\bar{C}$, appeared in the ED diagrams. Further heating in a beam of strong intensity caused the $C\bar{C}$ pattern to disappear gradually, being replaced by a ring pattern of calcium oxide, C, of cubic symmetry. Similar observations were reported earlier by Eitel [19], but were obviously overlooked by later observers, or considered to be of an occasional nature.

If rigorous precautions are taken to avoid carbon dioxide contamination, the precipitates forming in a supersaturated lime solution are observed to consist of well-crystallized particles, predominantly plates or slabs of a more or less regular, hexagonal shape.

These observations which have been confirmed by the present author, show that atmospheric carbon dioxide readily taken up by lime solutions may act as an inhibitor of the formation of the CH crystal lattice of regular hexagonal symmetry. Ordinarily, the microstructure of the $\bar{C}$-contaminated precipitates is that of chains of rounded platelets, but other formations of a similar nature and behavior have also been observed, such as networks of fibrous particles, or thin slabs with two parallel edges, exhibiting internal striations or cracks parallel to these edges [26]. These latter formations are obviously very easily decomposed in the electron microscope, the ED diagrams showing modified single-crystal spot patterns from oriented aggregates of calcium oxide.

Similar phenomena have been observed by Andrievskii, Tikhonov Shepinova, and Nabitovich [27], who also described the hardening process of lime mortar as being caused by bond formation in the superposition of growing hexagonal-plate crystals. These authors also explain the effect of sulfate in the mixing water as an increase in the rate of hydration and formation of the hexagonal-plate phase, combined with an inhibition of carbon dioxide attack. On the other hand, the introduction of a small amount of a surface-active agent, sulfite alcohol waste, with the mixing water is observed to prevent the growth of larger crystals, and the hardening mass remains for some time in a state of very fine subdivision.

In specimens containing lime solutions which have been exposed to the attack of atmospheric carbon dioxide for a longer time, $C\bar{C}$ has been observed to take the form of regular crystals of calcite, mostly appearing as rhombic slabs, with the crystalline angles of calcite, superimposed in aggregates with sawtooth-shaped edges [20, 21, 22, 23].

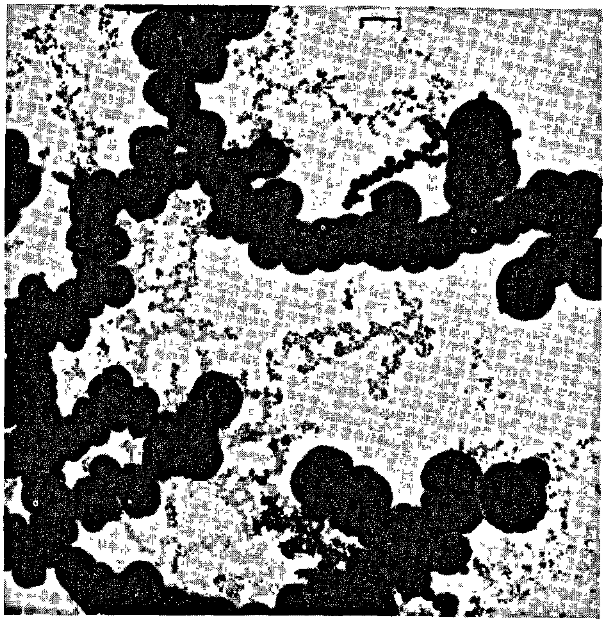

FIGURE 1. *Calcium hydroxide chains precipitated from solution in the presence of carbon dioxide contamination.*

It can be expected that the process of regular crystallization of CH will be disturbed by the presence in the lime solution even of certain ionic groups other than $\bar{C}$ anion. Brunauer, Kantro, and Copeland [28], in studying the stoichiometry of C_3S and β-C_2S hydration products, found that certain quantities of CH which, for stoichiometric reasons, were expected to be precipitated in the samples, could not be accounted for by the data obtained in XD quantitative mineral analyses. The most probable explanation for the apparent absence of this quantity of lime was found to be that a minor part of the amount of solid CH resulting from the hydrolysis of the anhydrous silicates was present in an amorphous, or at least very poorly crystallized, state, owing to lattice disturbances caused by inclusions of silica groups. Electron-microscopical observations on paste-hydrated materials from these studies confirmed the presence of considerable quantities of more or less amorphous-looking matter, part of which could well be imagined to be composed of disordered aggretates of extremely small CH crystal nuclei.

The normal appearance of CH crystallized in cement pastes and in suspensions protected from the attack of carbon dioxide is that of plates. These are sometimes of comparatively large dimensions, more than 1 μ across, but mostly so thin that they are transparent to electrons.

Examples of electron micrographs and ED patterns of CH plates in cement pastes and similar preparations have been given in various reports [29, 30, 31, 32, 33, 34]. One such plate is shown in figure 2 a, b. The identification of CH crystals is readily made by means of their characteristic and mostly well-developed ED patterns which, due to the effect of orientation, contain in general only the hexagonal (hk.0) (prism) reflections corresponding to the unit cell $a_H = 3.59$ A.

In cement slurries of higher w/c ratios than is normal in paste hydration, numerous CH crystals, of comparatively small dimensions and mostly very thin, are observed to precipitate out at an early stage of reaction. Owing to conditions of crystallization which are less cramped than in ordinary paste hydration, these CH plates often assume the habit of almost regular hexagons. An example is given in figure 3 a, b, where some plates are observed to stand more or less on edge, resulting in the appearance in the ED diagram of reflections from oblique (hk.1) lattice planes. In other diagrams even the basal (0001) reflection at 4.91A lattice planes is occasionally observed.

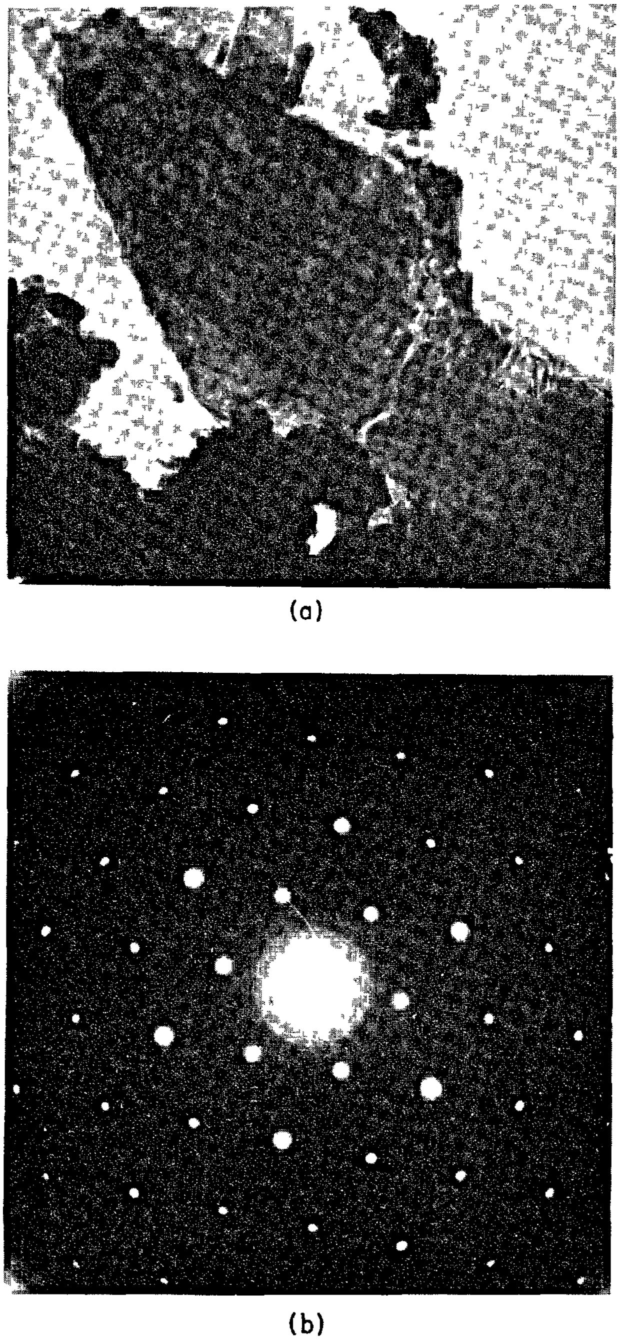

FIGURE 2. *(a) Calcium hydroxide plate as formed in cement pastes and similar preparations. (b) Electron diffraction pattern of calcium hydroxide plate shown in figure 2a.*

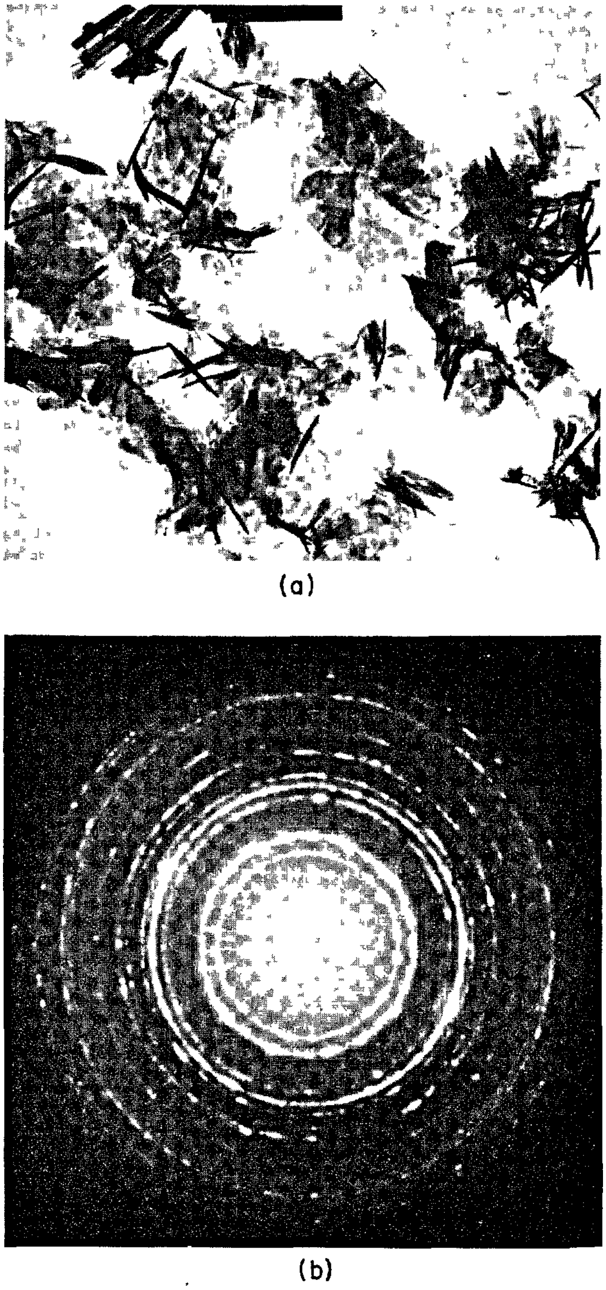

FIGURE 3. *(a) Calcium hydroxide plates formed in a cement slurry of high w/c ratio. (b) Electron diffraction pattern of calcium hydroxide plate shown in figure 3a.*

Microstructures of Phases Related to Calcium Aluminate Hydrate

General Character of Compounds in the C–A–F–H System, and of Complex Salts

The subject indicated by the heading has been treated in detail in another review article at the Symposium, and will be reviewed here only in very broad outline.

The only compound stable in the low-temperature region of the system C–A–H, except AH_3 and CH, seems to be the hydrate end member of the hydrogarnet series, C_3AH_6 [35]. The characteristic isometric crystal shapes of this compound well known from a number of microscope observations, have also been observed in EM studies to form in large amounts in e.g. rapidly mixed suspensions of pure C_3A in water, and with crystal sizes of the order of 1 μ [26].

Metastable hexagonal-plate phases are very frequently observed to be the products first formed in the hydration of the aluminate components of cement, and to persist over long periods. The crystalline compounds which are of greatest interest in connection with cement hydration, are generally assumed to have the composition C_4AH_{13} or C_4AH_{19}, depending on the state of hydration, and C_2AH_8, together with forms intermediate between these, of the character of mixed-layer compounds. Analogous compounds are formed in the C–F–H system, and in the C–A–F–H system various types of solid-solution compounds are possible. The stability of the hexagonal phases seems to increase with the content of F, and it is even reported that a stable C_3FH_6 hydrogarnet compound does not exist [36].

The hexagonal-plate phases have been observed in several optical and EM studies on products of hydration of C_3A and $C_2(A, F)$. A typical electron micrograph and ED pattern combination is shown by Buttler, Dent Glasser, and Taylor [37]. The ED patterns of the pure compounds are strictly hexagonal, giving a unit cell of about $a_H = 5.7$ A. Isomorphous substitutions of different cations for protons, e.g., $\bar{C}$ for 2 H in the natural mineral hydrocalumite, lead to deviations from exactly hexagonal symmetry. The first transformation occurring upon heating consists in the formation of oriented layers, of the CH type and unit cell (about 3.6 A), within the matrix of the original structure. The common occurrence of this type of transformation, as described by Buttler, Dent Glasser, and Taylor, has been observed also by the present author. Thus, upon heating in unsaturated conditions to temperatures of 100° C or somewhat higher, the hexagonal phases seem to convert more easily to another hexagonal layer lattice hydrate phase than to the isometric hydrogarnet structure, supposedly stable in this temperature range.

In reconsidering the crystal structure originally suggested [38], Buttler, Dent Glasser, and Taylor proposed a model for $C_4A \cdot aq.$ consisting essentially of an octahedral layer of the type occurring in CH however with Ca ions in ⅓ of the octahedral positions replaced by Al ions and with hydroxyl and water groups accommodated outside this layer. The Al ions are arranged in an ordered pattern with a unit cell a_H of about 5.7 A, a distance intermediate between the orthohexagonal cell distances of CH and AH_3 (gibbsite) which are about 6.2 and 5.0 A, respectively.

The compound $C_4A \cdot aq.$ has a number of comparatively well defined states of hydration, judging from the dehydration curves of Buttler, Dent Glasser, and Taylor, and including the most saturated state C_4AH_{19}, according to Jones and Roberts (ref. [7] of review paper by Jones, this Symposium). The sequence of layers within the molecular units is illustrated diagrammatically at the foot of the page, with the contents of each layer given per orthohexagonal unit cell ($a_H \times a_H \sqrt{3}$).

As suggested by Jones, the $C_2A \cdot aq.$ structure can be derived from that of C_4AH_{19} by substituting Al ions for protons in the intermediate double layer of water, according to the following model.

	——2 Al——
	$3\ H_2O + 4\ OH$
	6 OH
$2\ C_2AH_8$ $c_o = 10.7$ A	4 Ca+2 Al
	6 OH
	$3\ H_2O + 4\ OH$
	——2 Al——

An alternative principle of arrangement of these structures presents itself on noting the great sim-

C_4AH_{19} $\longrightarrow$	C_4AH_{13} $\longrightarrow$	C_4AH_{11} $\longrightarrow$	C_4AH_7
$c_o = 10.7$ A	8.2 A	7.9 A	5.8 to 6.5 A
$6\ H_2O + OH$——	——$6\ H_2O + 2OH$——	——$4\ H_2O + 2OH$——	——2OH——
6 OH	6 OH	6 OH	6 OH
4 Ca+2 Al	4 Ca + 2 Al	4 Ca+2 Al	4 Ca+2 Al
6 OH	6 OH	6 OH	6 OH
$6\ H_2O + OH$——	——$6\ H_2O + 2OH$——	——$4\ H_2O + 2OH$——	——2OH——

ilarity of the C–A–F–H phases to clay minerals. As is well known, the molecular unit layers of clay minerals consist of $(M(6)O_2)_n$ layers, with M(6) denoting cations in octahedral positions (in clays usually Al or Mg ions), unilaterally or bilaterally polymerized with $(M(4)_2O_5)_n$ layers, with M(4) denoting cations in tetrahedral positions (in clays usually Si ions). Separate $(M(6)O_2)_n$ layers occur in some types of clay minerals. Excessive negative charge is balanced by introducing a suitable number of protons. In the isolated state, the layer units possess hexagonal symmetry, but polymerization and stacking lead to lower crystal symmetry, monoclinic or triclinic.

It is generally assumed that octahedral CH (or $(CaO_2)_n$) layers and tetrahedral S_2H (or $(Si_2O_5)_n$) layers cannot polymerize, because of a too-large misfit of the hexagonal unit cell sizes. This is considered to be the reason why no C–S–H minerals of the clay-type structure have been found. On the other hand, Al ions can occur in tetrahedral AlO_4 coordination, and a hypothetical $(Al_2O_5)_n$ layer would have a calculated cell size a_H of about 6.2 A, approximately equal to the orthohexagonal cell size in the CH layer.

Such a unit, with all the tetrahedral sites filled, would probably be highly unstable, but it is conceivable that partly filled $(Al_{2q}O_5)_n$ layers can combine with partly filled $(Ca_pO_2)_n$ layers (q and p denoting degrees of filling) to form a structural element in which the two components stabilize each other, and in which the positive charge deficiency is compensated for by protons. The C_4A·aq. and C_2A·aq. structures originally suggested by Tilley, Megaw, and Hey [38] are essentially of the type now described. It seems natural to modify these proposed structures in such a way that the structure models related to C_4A·aq. would be isomorphs of the 1:1 kaolinite-type clay structure, those related to C_2A·aq. isomorphs of the 2:1 montmorillonite-type clay structure.

It can be further noted that extra water molecules can be accommodated in the "holes" of $(M_2O_5)_n$ layers, one molecule per hexagonal unit cell and sheet, without any essential increase of the basal spacing. The formation of CH-type layers upon dehydration can be interpreted as a collapse of the tetrahedral layers, the Al ions being accommodated in the empty octahedral positions, or segregating in the form of amorphous alumina hydrate.

In similarity to clays, mixed-layer compounds may form, with layer sequences of, e.g., C_4A·aq.-C_2A·aq.-C_4A·aq., etc., possibly accounting for the observations of formation of C_3A·aq. reported in the literature.

Possible layer sequences for various C–A–H compounds are indicated in the following diagrams, in which the compatibility with known data for the composition and cell sizes have been taken into consideration. Partial or complete replacement of Al ions by Fe ions can occur, but is not indicated.

C_4AH_{19}	→	C_4AH_{13}	→	C_4AH_{11}	→	C_4AH_7
—6 H_2O—						
6 OH+2 H_2O		6 OH+2 H_2O		6 OH		6 OH
2 Al		2 Al		2 Al		3 Ca+2 Al
2 OH+4 H_2O		2 OH+4 H_2O		2 OH+4 H_2O		6 OH
4 Ca		4 Ca		4 Ca		
6 OH		6 OH		6 OH		+
—6 H_2O—						
						OH
						Ca
						OH

C_2AH_{9-7} $c_o=10.7$ to 10.4 A (Roberts [100])	$C_3A_3H_{28}$ ("CAH_{10}") $c_o=14.3$ to 14.6 A
6 OH(+2 H_2O)	6 OH+2 H_2O
2 Al	2 Al
4 OH+2 H_2O	3 OH+3 H_2O
4 Ca	3 Ca
4 OH+2 H_2O	3 OH+3 H_2O
2 Al	2 Al
6 OH(+2 H_2O)	6 OH+2 H_2O
	3 OH+3 H_2O
	2 Al
	3 OH+3 H_2O

Under the conditions prevailing in the reaction of portland cement with water, the formation of hydrated C—A—F—H compounds is likely to be influenced by the presence of varying amounts of admixtures, specifically sulfate ions from gypsum, which are incorporated in the C—A—F—H compound structures, forming complex salts of widely varying types and compositions [36, 39, 40].

It is generally postulated that two series of such complex salts exist, the generalized oxide formulas of which are usually written $C_3A{\cdot}CY{\cdot}H_m$ and $C_3A{\cdot}(CY)_3{\cdot}H_n$, with Y denoting a structurally equivalent unit amount of a large number of oxides. For the cement hydration system, substitutions of H, $\bar{S}$, $\bar{C}$, and even S for Y are of greatest interest.

The clay-type structure model containing voids in tetrahedral and octahedral cation positions can be applied in conceiving hypothetical crystal structures even for these compounds. Some examples are given below.

It can be added that the hexagonal unit cells of all the compounds for which structure diagrams have been given above have been observed to be either in the vicinity of $a_H=5.7$ A, or simply related to this distance ($a_H\sqrt{3}$, $2a_H$) in the case of compounds with larger true unit cells. A possible exception is the "gehlenite hydrate", for which Fratini and Turriziani [102] give a hexagonal unit cell of 8.85 A. However, the cell size 9.96 A ($5.75\sqrt{3}$) given recently for this compound by Schmitt (see discussion of paper by Jones, this Symposium) seems to be based on more reliable XD data. A similar hexagonal cell unit, 8.8 A, was found for C_4A·aq. and C_2A·aq. in an earlier work by Wells, Clarke, and McMurdie [103], but more recent studies have given values related to 5.7 A [37].

In the diagram for "gehlenite hydrate" below, two alternatives are given, of which the latter one represents an attempt to explain the comparatively large spacing of 12.4 to 12.7 A, as found by different observers. This model contains Si—OH apices of tetrahedra directed outwards from the molecular layer, and is thus a hypothetical analog of the much-debated Edelman-Favejee model for the structure of certain clay minerals [104].

The structure indicated for ettringite is an alternative to the zeolitic structure suggested by Bannister [41], the details of which have not been confirmed by a complete structure analysis. Obviously, further work is needed for the establishment of the details of this structure, as well as of all the structures in the group of compounds now described.

Isomorphous substitution of Fe ions for Al ions leads in general to a somewhat larger unit cell, due to the slightly larger equivalent ionic radius of the Fe ion. In the case of phases in the hydro-

$C_4A\bar{S}H_{16}$(?)	→	$C_4A\bar{S}H_{14}$	→	$C_4A\bar{S}H_{12}$	→	$C_4A\bar{S}H_{10(\to 8)}$(?)
"low sulfate sulfoaluminate" [100, 101]						
c_o=10.4 A	→	9.5 A	→	8.9 to 9.0 A	→	8.2 A→8.0 A.
——6 H_2O——		——4 H_2O——		——2 H_2O——		
6 OH+2 H_2O		6 OH+2 H_2O		6 OH+2 H_2O		6 OH (+2 H_2O)
2 Al+S_2		2 Al+S		2 Al+S		2 Al+S
2 O+4 OH		2 O+4 OH		2 O+4 OH		2 O+4 OH
4 Ca		4 Ca		4 Ca		4 Ca
6 OH		6 OH		6 OH		6 OH
——6 H_2O——		——4 H_2O——		——2 H_2O——		

C_2ASH_7		C_2ASH_8
"gehlenite hydrate"		
c_o=12.4 to 12.7 A		
	or	OH
		Si
6 OH+2 H_2O		6 OH+2 H_2O
2 Al+Si		2 Al
2 O+4 OH		O+5 OH
4 Ca		4 Ca
2 O+4 OH		O+5 OH
2 Al+Si		2 Al
6 OH+2 H_2O		6 OH+2 H_2O
		Si
		OH

$C_6A\bar{S}_3H_{30-34}$	$C_4A\bar{C}H_{11}$ *
ettringite	hydrocalumite
c_o=10.8 A (41)	c_o=7.86 A
——6 H_2O——	
6 OH(+2 H_2O)	6 OH+2 H_2O
Al+1.5 S	2 Al+C
6 OH	6 OH
3 Ca	4 Ca
6 OH	6 OH
——6 H_2O——	

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* The hydrocalumite studied by Buttler, Dent Glasser, and Taylor held much less $\bar{C}$, approximate formula unit $C_4A\bar{C}_{\frac{1}{4}}H_{12}$.

garnet series, $C_3(A,F)(S,H_2)_3$, it has been suggested by Jones that the expanding and labilizing effect of the introduction of increasing amounts of Fe ions into the lattice is counteracted by the simultaneous uptake of Si ions in tetrahedral sites, the SiO_4 group requiring less space than the $(OH)_4$ tetrahedral group. It is probable that similar substitutions influence also the formation of phases within the hexagonal structure group under various conditions when silicon ions are present, as for example in a cement-water mixture. The sulfur and carbon ions, with six and four positive charges, respectively, have very small equivalent ionic radii and are easily accommodated in oxygen tetrahedra. They can therefore be expected to have a similar, stabilizing effect on the formation of the C–A–F–H solid-solution phases.

The size of the hexagonal unit cells may obviously be influenced also by the degree of occupation of octahedral cation positions. According to available data, most of the compounds now discussed possess hexagonal, or pseudohexagonal, unit cells relatable to a distance between 5.6 and 5.8 A. The exceptions are CAH_{10} (5.46 A) and ettringite (5.55 A). It is perhaps significant that in the hypothetical structures indicated above, the octahedral sites are only half-filled in these compounds, but two-thirds filled in all the others.

C—A—H and Related Phases in Hardened Portland Cement Paste

Of C–A–F–$\bar{S}$–H compounds possibly present in hardened pastes, only the hexagonal-plate phase has been observed by the author [26, 32, 33, 34]. In crushed or ground paste samples the hexagonal shape is of course less evident than in the C–A–H plates formed in suspensions. Figure 4 a, b shows the characteristic appearance of such a plate from a nearly 10-yr-old paste sample, together with amorphous-looking or fibrous C–S–H material. The ED single-crystal pattern corresponds to a nearly hexagonal unit cell, $a_H=5.70$ to 5.62 A, as measured in different directions of the pattern with strong spots. Weaker spots halfway between the stronger ones indicate that the true unit-cell length is twice that given above, and prove the existence of a superstructure in this crystal, as well as in the majority of crystal plates of this type found in pastes. This doubling of the 5.7-A unit cell seems in most cases to be connected with deviations from exact hexagonal symmetry, whereas in ED patterns from hexagonal-plate crystals obtained by the hydration of C_3A, in water or in lime solutions, superstructure spots and measurable deviations from perfect hexagonal symmetry cannot be detected. These facts are indicative of a lattice with isomorphous ionic substitutions of F or $\bar{S}$ for A, or alternatively, with $\bar{S}$ replacing void tetrahedral groups. The composition can probably be approximated by the formula $C_4(A,F,\bar{S})\bar{S}H_{10}$. The substitutions are believed to be of the ordered type, but the evidence is inconclusive on this point.

Plate crystals of the C–A–H type occur in small quantities in nearly all paste samples examined, but the ED patterns are not always as easily interpreted as in the example now given. The superstructure spots may be very weak, the pattern of strong spots may have an irregular intensity distribution, and the reflections may be

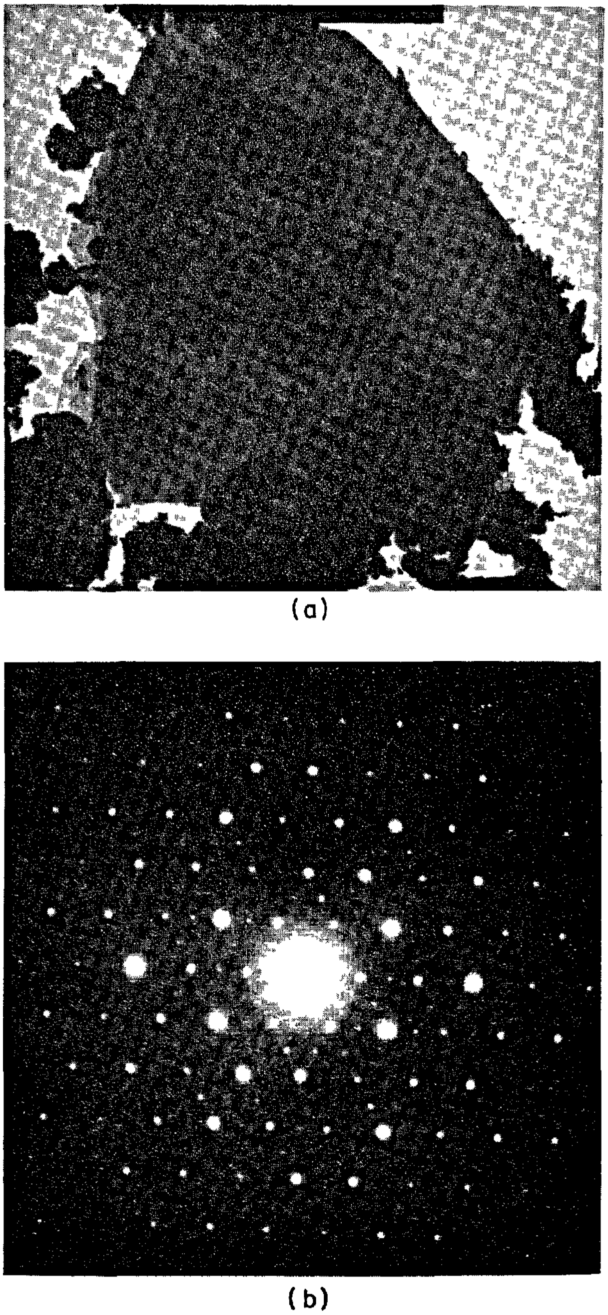


FIGURE 4. (*a*) *Calcium aluminate hydrate plate from a 10-yr-old hardened paste.* (*b*) *Electron diffraction pattern of calcium aluminate hydrate plate shown in figure 4a.*

Weak spots indicating a true unit-cell length of 11.24 to 11.40 A are shown.

diffuse or streaky. All these effects indicate the presence of various types of disorder in the corresponding lattices.

A commonly observed phenomenon is that the C–S–H gel particles tend to develop fibrous structures in the vicinity of the C–A–H plates, and that fibers of tobermorite are adsorbed on their surfaces. An extreme case is shown in figure 5 a, b, taken from a highly porous paste. The spot pattern, corresponding to $a_H=2\times5.70$ A, is superimposed by a spot-ring diagram from the CSH(B) tobermorite fibers. The implication of this observation would be that the hexagonal C–A–H phases take an active part in the formation of paste structures, first, by acting as a kind of template for other structures crystallizing in the vicinity of its surfaces, and second, by forming bridges between gel structures adhering to different parts of the plate surfaces.

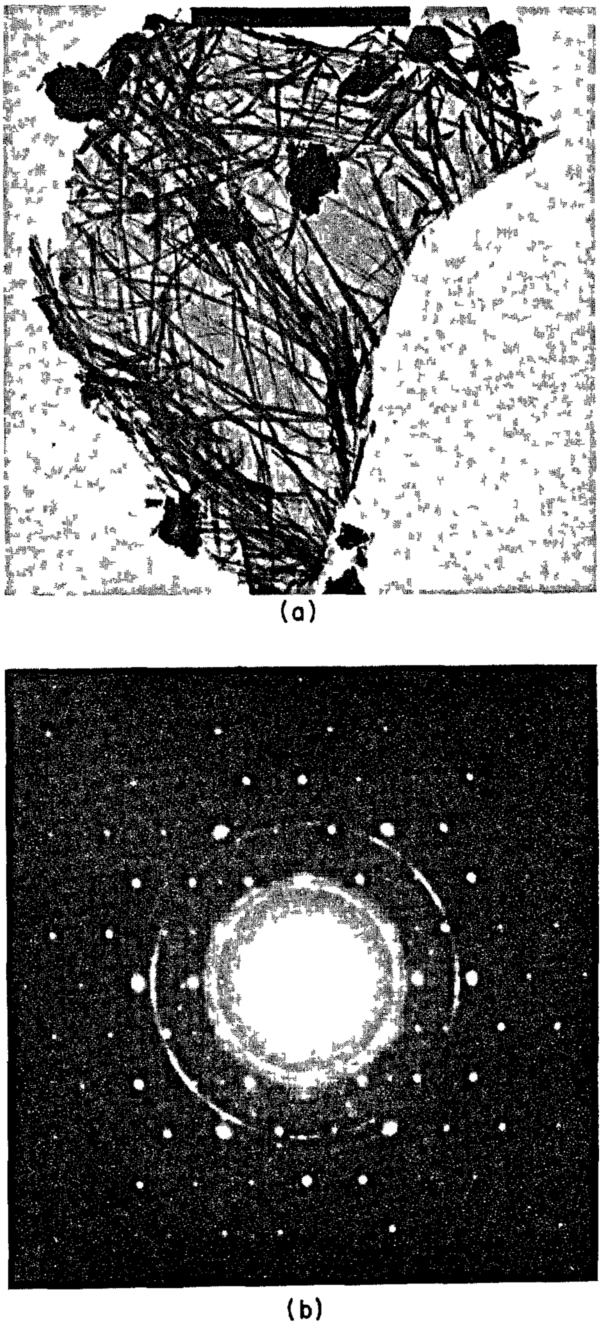
On the other hand, the plates are rarely observed to form coherent structures linked together by the coalescence of partially overlapping plates. A similar mechanism is regarded by Rehbinder [42] and his associates to be responsible for the process of setting of cement pastes of the quick-setting type, i.e , without gypsum or surface-active-agent admixtures. However, in normal portland cement pastes, the structures causing the initial set are probably of a different type, due to the formation of sulfoaluminate hydrate and so-called adsorptive modifications of hydroaluminate caused by surface-active agents [43]. The C–A–H crystal plates in old pastes may be secondary formations, resulting from a process of recrystallization following the breakdown of structures developed during the period of setting.

Judging from the common occurrence of particles of the hexagonal C–A–H phase even in old pastes, the expected transformation to the isometric $C_3(A,F)H_6$ compound does not take place As mentioned previously, the isomorphous replacements and possibly the introduction of additional cation complexes seem to stabilize the hexagonal structure.

Ettringite and Related Phases

The characteristic crystal habit of ettringite, as reported from microscopic examinations, is that of long rods or needles or, in well-crystallized specimens, that of hexagonal prisms with sharply cut off end faces. EM studies by Iwai and Watanabe [44] show this compound in the form of heavy rods or splines.

Particles of the described habit have not been observed in cement pastes examined by the present author. It is very unlikely that ettringite can be kept from decomposing in the electron microscope without taking special precautions of cooling the specimen. However, if present in a paste, it may be expected to form pseudomorphs upon rapid dehydration.


(a)

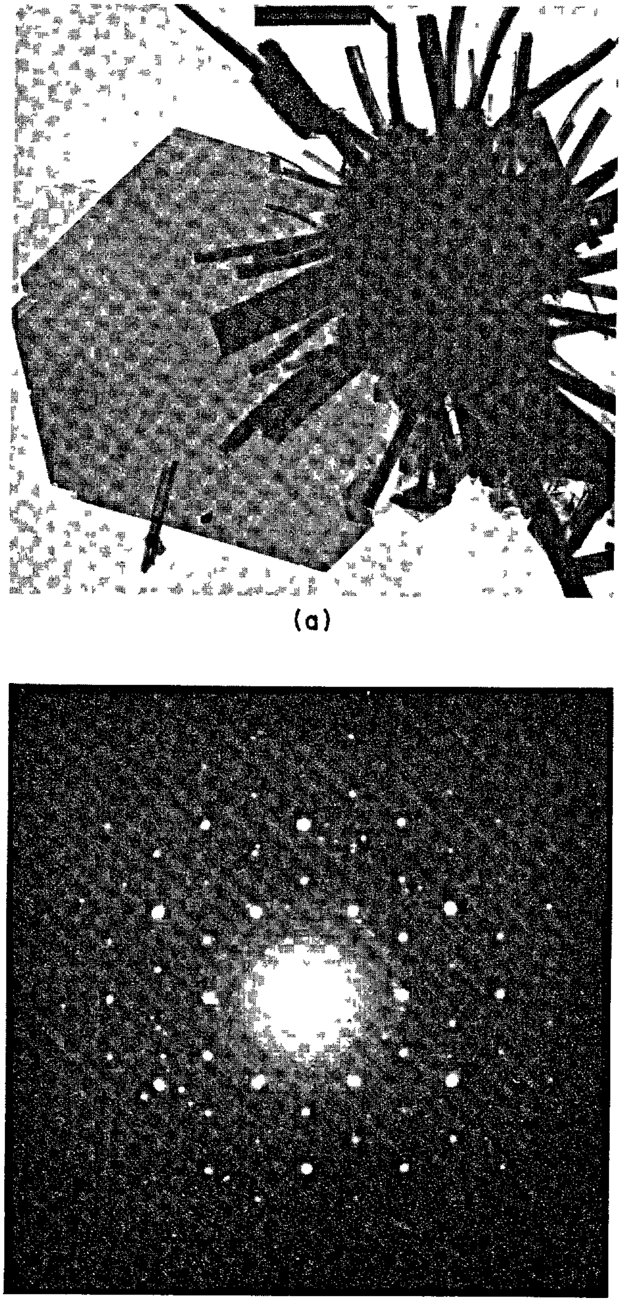
(b)

FIGURE 5. (a) *Tobermorite fibers, CSH(B), formed in vicinity of calcium aluminate hydrate plates in a highly porous paste.* (b) *Electron diffraction pattern of material shown in figure 5a.*

w/c=1 5

The spot pattern corresponding to $a_H=2x5$ 70 A is superimposed by a spot ring pattern from the tobermorite fibers

At the London Symposium, Nurse and Taylor [17] presented XD evidence for the presence of ettringite in a sample of old paste. Unpublished XD data for hardened cement paste, obtained by the author, also showed a number of reflections considered to be characteristic of ettringite. The intensities of the ettringite reflections were about equally strong from 2 days to 1 yr of age of the paste samples. On the other hand, Taylor [45] observed, in another series of paste samples, that the ettringite reflections disappeared after a couple of weeks, and were replaced by reflections belonging to a compound isomorphous with C_4AH_{13}. Other workers have reported the decomposition of ettringite upon storing in air or upon heating at 40 to 80 °C, yielding gel-like products. A detailed account of XD data obtained recently on the appearance of ettringite and other sulfoaluminate phases in cement pastes is given by Copeland and Kantro (this Symposium).


(a)

(b)

FIGURE 6. *(a) Hydration products formed by 24-hr shaking of a slurry of Type I portland cement. (b) Electron diffraction pattern of material shown in figure 6a.*

w/c=4.
A hexagonal plate of C_4AH_{13} is shown together with a cement covered with splines pseudomorphic possibly of a C–A–$\bar{S}$–H compound

It may be of interest in this connection to describe some observations made by the present author [26, 34] of the hydration products of a Type I portland cement after 24 hr of shaking in a slurry with w/c=4. The character of the slurry constituents is shown in figure 6 a, b. Disregarding the hexagonal plate of C_4AH_{13} structure which gives the ED spot pattern of figure 6b (corresponding to a hexagonal cell a_H=5.68 A), it is seen that the original cement grains are covered with thick, radiating splines or rods, of a habit associated with ettringite. It is likely that these formations are only pseudomorphs of an easily dehydrated structure originally present, since the ED patterns contain no trace of crystalline diffractions, except sometimes a very diffuse ring at about 2.7 to 3.2 A. Judging from the abundance of these structures, in comparison with the normal content of $\bar{S}$, amounting to about 2 to 3 percent, in commercial portland cements, and taking into account the fact that the splines appear to form from the material in the surface of the C–S anhydride particles, it seems unlikely that silica groups do not take part in building up these structures. It is very tentatively suggested that they are composed of a C–A–S–$\bar{S}$–H compound of the ettringite variety, $C_6(A,F)(S,\bar{S})_3H_n$, in which, upon the structural collapse following dehydration, a fibrous internal structure is still retained, due to the formation of polymerized silica chain elements.

However, even various forms of pure calcium sulfoaluminate hydrates can be partly deprived of their water of crystallization, without apparent change in outer form, as shown by EM data given by Astreeva and Lopatnikova [46].

After a few days of standing in paste form, the rod-like elements became covered with a felt-like mass of crinkly foils of CSH(B) tobermorite developing from the surfaces of the cement grains, and simultaneously the rod elements seemed to loosen up and unfold (fig. 7). This change may indicate that some structural elements are being replaced by others, e.g., A and $\bar{S}$ by S, leading to structural rearrangements.

It is evident that the suggestions now made are of a very uncertain nature, and there are probably alternative ways of interpreting the phenomena observed. However, it seems worthwhile to include these observations here, in order to indicate an important problem for future research. It may well turn out that the effect of admixtures of sulfate and similar ions on structure formation is more complicated than is generally assumed.

Although a coherent picture of these processes has yet to be attained, at least some of the available data seem to indicate that the first stages of structure development in setting cement paste are

Figure 7. *Tobermorite, CSH(B), foils formed in a cement slurry on standing.*

governed by a delicate balance in the composition of the minor anhydrous phases and admixtures, and by the formation of complex C–A–F–S–$\bar{S}$–H phases which, although of a transient nature and later decomposing, still leave their imprint on the structures developing in the subsequent processes of hardening.

Structures similar to those described by the author as heavy splines, have been observed in cement hydration studies by Sliepcevich, Gildart, and Katz [20], by Smolnikov [22], who identified them as ettringite, and by Boutet [21], who observed them in such abundance that he considered them to be C–S–H compounds which, due to their densification and interlocking in fibrous networks, gave a major contribution to the development of strength in cement paste. The structures formed in C_3A suspensions with small admixtures of lignosulfonate [24, 42] may be of a related type.

The so-called "stressing cement" developed by Mikhailov [105] (cf. also his paper in this Symposium) represents an interesting application of the principles of crystal chemistry and microstructural development in the sulfate-cement field. This cement is a specially proportioned mixture of portland cement, high-alumina cement, and gypsum, and its reaction with water is characterized by the formation of a paste structure consisting of an expanding framework of high-sulfate sulfoaluminate crystals, and C–S–H gel material accommodated in the meshes of this framework. Under certain rigorously specified conditions of curing, this composite system of particles integrates and hardens to a mass of high strength. Similar principles of structure formation are employed in other types of expanding cements, such as the well-known Lossier cement, developed in France.

Microstructures of Calcium Silicate Hydrates

General Remarks

Schematic phase diagrams of the C–S–H system were presented at the London Symposium [8, 47]. Although a great number of studies of various compounds and phase relationships within the C–S–H system have since been executed, no major changes in the general outlines of these schematic diagrams have been introduced.

In the products of normal cement hydration, the phases occurring in the low-temperature region of the C–S–H phase diagram, viz. the CSH(B) and C_2SH_2 tobermorite phases, seem to predominate. However, some investigators have presented evidence for the appearance of other compounds, such as $C_3S_2H_3$ afwillite, $C_2SH(B)$ hillebrandite, and $C_2SH(A)$ in various preparations obtained in the hydration of portland cement or its pure silicate constituents. These and other compounds are also likely to be present in cement paste products autoclaved at elevated temperatures, and have in fact been identified and studied in various hydrated cement samples. For this reason, it seems worthwhile to review separately the most essential microstructural properties of various C–S–H materials.

Arrangements of Lattice Elements in C–S–H Structures

The formation of lattice structures from the structural elements of the C–S–H system, i.e., $Si(OH)_4$ tetrahedra, Ca ions, and O ions with or without attached protons, is commonly recognized to be governed by a few simple principles.

A factor of primary importance is the tendency of free silica groups to polymerize into larger complexes, such as rings, chains, layers, and networks [48, 49], each condensation of pairs of tetrahedra being accompanied by the expulsion of a water molecule. A second factor is that the Ca ion has a great capacity of accommodating itself in oxygen or hydroxyl coordination polyhedra of widely varying type and coordination number. A natural consequence of these circumstances is that the groups involved may combine into crystalline structures in a great number of different ways.

Further, the difference in lattice energies of two alternative compound compositions is often small, and the rate of transformation low, causing certain compounds which are in reality unstable under the prevailing thermodynamic conditions to persist over long periods without changing observably.

In a few C–S–H compounds, the silica constituent of the lattice is present in the form of unpolymerized, isolated SiO_4 tetrahedra. The two most well-known of these compounds are $C_3S_2H_3$ (afwillite) and $C_2SH(A)$, both containing discrete $SiO_3(OH)$ ions as lattice constituents. It is natural that such compounds are found among those having a comparatively high C/S ratio, where the tendency of polymerization of silica groups is counteracted by the presence of relatively large amounts of Ca, O, and OH ions that tend to screen the SiO_4 groups from each other.

The three-dimensional character of such lattices promotes the growth of crystals of macroscopic size, and this is perhaps the reason why of all C–S–H structures those of afwillite and $C_2SH(A)$ were the first ones to be determined [50, 51]. Another hydrate compound of similar type which has been described recently with respect to its crystallographic properties, is C_5S_2H, calcio-chondrodite [52], which has a structure closely related to that of γ-C_2S, with discrete SiO_4 groups. The high-lime end member of the C–S–H system, $C_3SH_{1.5}$, is believed to contain isolated Si_2O_7 groups as structural elements [53]. However, judging from the observed fibrous habit of $C_3SH_{1.5}$ particles, the presence of chains of silica would seem to be a more likely alternative.

The C–S–H compounds possessing a more or less clearly pronounced fibrous particle habit have attracted special attention because of the relationships probably existing between one or more of these phases and the fibrous constituents of cement paste. The repeat unit distance of about 7.3 A along the fibers has been observed to be common to all fibrous C–S–H compounds. The true nature of the structural elements causing this repeat unit to appear was first established in studies of the structure of the anhydrous mineral CS, wollastonite [54, 55, 56], for which the previously suggested structure containing Si_3O_9 rings was found to be essentially incorrect and was replaced by a structure containing metasilicate chains of ideal composition SH and a repeat unit of Si_3O_9 ($Si_3O_3(OH)_6$ if written formally as a silicic acid).

A characteristic feature of this 3-metasilicate chain is that on one side of the chain the free OH—OH tetrahedral edges perpendicular to the chain axis are spaced at intervals of about 3.65 A along the axis, whereas on the opposite side the repeat distance is 7.3 A. It can be observed that the minimum need of space across the chain is equivalent to the space occupied by an OH—OH group, or about 5.6 A.

In the wollastonite structure, the chains are arranged in layers of parallel-oriented separate chains, with Ca ions accommodated in the oxygen polyhedra formed by superimposed layers of chains. The various forms of wollastonite can be described as polymorphic modifications corresponding to different alternatives for the arrangement of 3-metasilicate chains in layers.

The simplest possible silica group formed by condensation of 3-metasilicate chains is of course the double chain, of composition Si_6O_{17}. Mamedov [57] showed that in the structure of xonotlite, of ideal composition C_6S_6H, layers of such double chains alternate with layers of Ca ions. Liebau [48] gives a list of minerals, among them several C–S–H compounds, in which the silica groups are likely to occur as such double 3-metasilicate chains.

The double chain in xonotlite contains 8-membered rings of SiO_4 tetrahedra. By further edge-to-edge condensation of Si_6O_{17} chains, in which process 5-membered rings of tetrahedra are formed, a polymerized sheet of composition Si_6O_{15} may be built up. It has been suggested by Mamedov and Belov [58] that such layers, stacked in various ways together with Ca and OH ions, occur as the structural elements common to a number of C–S–H minerals of low C/S ratio, the okenite-nekoite group with fibrous crystals [59], and the truscottite-gyrolite group with tabular crystals and hexagonal or trigonal symmetry [60, 61]. Although nothing is known with certainty about the details of these structures, it seems possible that in the first group the Si_6O_{15} sheets are stacked with the fiber axes of different sheets parallel-oriented, whereas in the second group more or less orderly trigonal rotations of the sheets take place in the process of superposition.

An alternative structure of the silica sheet, analogous to the $(Si_2O_5)_n$ sheet occurring in clay minerals, was considered in the analysis of gyrolite by Mackay and Taylor [61] but was rejected by them, since the distortion of the sheet necessary to fit it in the observed unit cell would be unduly large. It may be worth pointing out that just as in the case of the hexagonal C–A–H phases described in the previous section, it would be possible to obtain a fit with observed data on composition, unit cell, etc., by assuming the existence of tetrahedral and octahedral voids and proton substitutions in the structure of minerals of the truscottite-gyrolite group. However, some difficulties would be raised because of the relatively low content of water of crystallization of these minerals, leading to a low degree of proton substitution computed for hypothetical lattices of this type. Further, a conversion into chain structures (wollastonite), observed to occur upon heating, would seem unnatural, if no chain elements were present in the unheated minerals.

None of these compounds is likely to occur in cement paste cured under ordinary conditions. Gyrolite, or similar phases not described here, could possibly form in autoclaved cement-silica paste products.

The structure of the mineral tobermorite, of approximate composition $C_4S_5H_5$, as worked out by Megaw and Kelsey [62], contains discrete 3-metasilicate chains arranged in a structural unit consisting of two sheets of parallel chains superimposed in such a way that the free OH–OH edges of 7.3-A spacing are pointing outwards and are parallel to the plane of the layer thus formed. Calcium ions are accommodated in internal positions in the planes of the free OH—OH edges of 3.65-A spacing, replacing all the protons. This arrangement corresponds to a C/S ratio of 2/3, or somewhat smaller than the ratio observed in natural tobermorite minerals. The positions of additional Ca and OH ions, and water molecules, were left undetermined, but the authors state that the inclusion of these groups in the calculations is not very likely to destroy the established agreement between observed and calculated X-ray intensities. These groups can well be accommodated in lattice positions between the protruding OH—OH edges, which form a very open layer surface network of approximately hexagonal symmetry.

Another, and completely different structure model for tobermorite has been suggested by Mamedov and Belov [63]. The essential element of this structure is a silica layer formed by polymerization of two sheets of Si_6O_{17} xonotlite chains, each double chain in one sheet sharing tetrahedral corners with two chains in the other sheet. The resulting corrugated silica layer has a unit cell of about 11.3 by 7.2 A, and the composition $Si_{12}O_{31}$. Ten Ca ions per cell are accommodated within and between layers, the C/S ratio thus being 5/6. This structure is believed to expand in a direction perpendicular to the layers in the presence of excess water, by means of a process of diffusion of sheets of water molecules entering interlayer positions.

Even in the case of the fibrous C–S–H compounds C_4S_3H, foshagite, and $C_2SH(B)$, hillebrandite, two different structure models have been proposed. Gard and Taylor [64, 65] postulate a general formula $C_{3+n}S_3H_n$, with n between 0 and 3, for the series wollastonite-foshagite-hillebrandite. The structures of the hydrated compounds are derived from the wollastonite structure by splitting up the layers of single chains into bands and replacing missing valencies by OH ions. Mamedov and Belov [66, 67], on the other hand, are of the opinion that the structures of these compounds can be described in their essential features as association complexes of xonotlite chains and CH columns (foshagite) or CH layers (hillebrandite). However, results obtained recently in an analysis of the foshagite structure, quoted by Taylor (see review paper of this Symposium) are definitely in favor of the structure containing single 3-metasilicate chains, at least in the case of foshagite.

Tobermorite Phases

At the London Symposium, tobermorite was hardly recognized as more than the name of a mineral among many others within the C–S–H system, of rare occurrence in nature and of unknown significance in relation to cement hydration.

It was soon recognized, however, that the naturally occurring mineral was in certain features strikingly similar to the synthetic materials observed in the low-temperature region of the C–S–H system. The existence of a *C*-face-centered, pseudo-unit cell of probably orthorhombis symmetry and of approximate dimensions 5.6 by 3.6 A is the most obvious property common to different tobermorite phases of widely varying C/S ratios. Further, both natural and synthetic tobermorites are composed of layer-lattice structures in which fibrous elements can also be discerned, and the basal spacings of which have been found to vary with the content of water within a certain range of spacings, about 9 to 14 A. Specifically, the value 11.4 A has been used to characterize well-crystallized tobermorite of low C/S ratio. The basal spacings may be constant, or may increase or decrease with the ambient water vapor pressure, depending on the type of tobermorite. The latter properties place the tobermorite phases in a class by themselves among the C–S–H compounds. The similarities to certain types of clay minerals have also been emphasized [68, 69].

Observations on the microstructural properties and particle habits of tobermorite phases have been reported in numerous papers. Owing to large variations in the conditions of formation of the materials studied, such as differences in temperature, composition of raw materials in synthesis mixtures, time of processing, water-to-solid ratio., etc., any attempt to summarize the hitherto observed data in a few simple statements will necessarily leave many observations unexplained.

In general, and especially regarding the colloidal compounds formed at temperatures below about 100 °C, a distinction is made between tobermorite products obtained in two ranges of C/S ratio, viz. the CSH(B) type in the range 0.8 to 1.33 C/S, and the C_2SH_2 type in the range 1.5 to 2.0 C/S [70, 30]. Alternatively, other limits for these C/S ranges have been assumed, e.g., 0.8 to 1.5 and 1.7 to 2.0, respectively [71]. It seems probable that in batches of average C/S ratio about 1.5 both phases are present, or that transitional phases exist. On the whole, the common phase rules of reaction chemistry are hardly applicable to these ill-crystallized and inhomogeneous nonequilibrium solids. The scarcity and diffuse character of XD and ED reflections observed for some CSH(B) and C_2SH_2 phases are indicative of a comparatively low degree of order in the arrangement of parallel-oriented $(SH)_3$ chains and CH complexes, and regions of regularly crystalline lattice formation may extend over only a few unit cells in some directions. Observed variations in particle habits for different C/S ratios may imply that the $(SH)_3$ chains are longer and more isolated from each other in fibrous particles, shorter and more aggregated in coherent sheets in layerlike particles. There is even a remote possibility that the established agreement between the unit-cell dimensions of CSH(B) and well-crystallized tobermorite is fortuitous. An example of two radically different ways of arranging a given number of ionic groups within the same frame is afforded by the structures suggested by Megaw and Kelsey, and by Mamedov and Belov, described in the preceding paragraph.

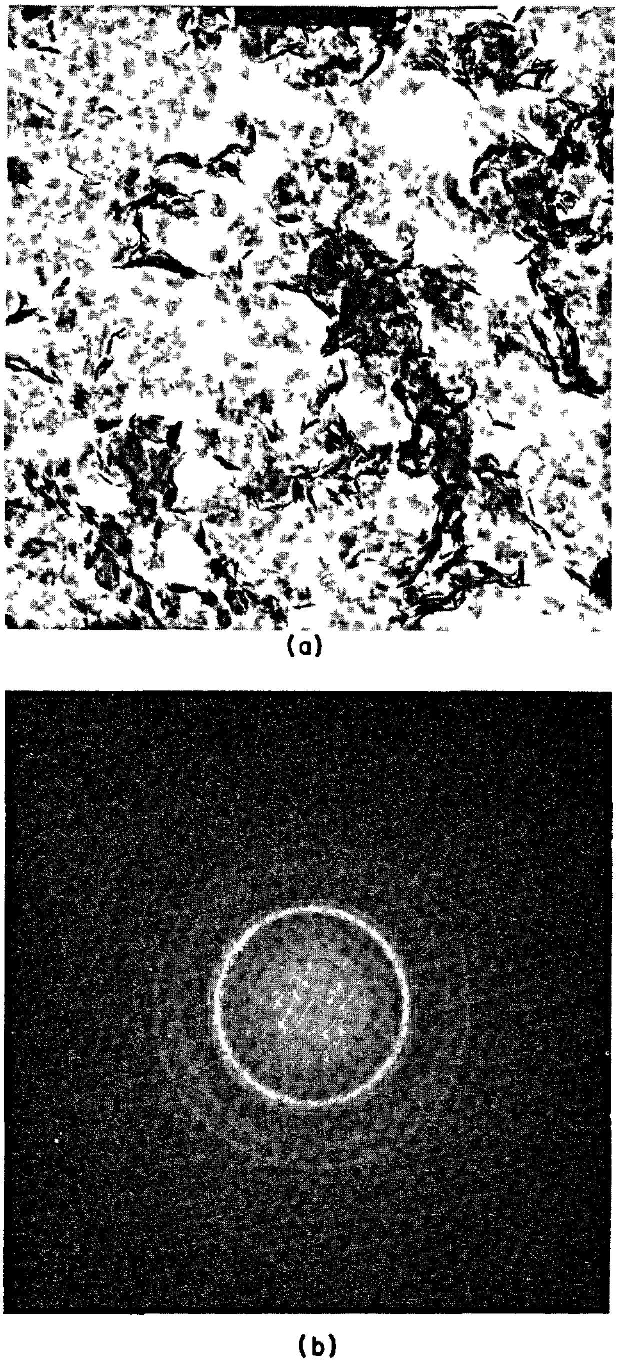


FIGURE 8 *(a) CSH(B) foils and plates, C/S ratio about 1.1, precipitated from a* Ca(OH) *solution containing about 3.8 mM/liter. (b) Electron diffraction pattern of material shown in figure 8a.*

Finally, the high-temperature exothermic peak in DTA diagrams, the variation in temperature and height of which has been used to distinguish in a reproducible way between compounds of different C/S ratios [70], is of dubitable significance when it comes to recognizing these compounds as crystallographically distinct species.

Similar ideas on the CSH(B) and C_2SH_2 structures have been expressed by Taylor [72], and by Assarsson [73] in a discussion on what he calls "phase B", the cryptocrystalline substance formed as a metastable phase prior to the crystallization of distinct compounds in hydrothermal reactions of lime and silica at 120 to 160 °C.

The most commonly observed particle habit of CSH(B), tobermorite, is that of thin sheets or foils, estimated to be only one or two molecular units thick in extreme cases. These particles are also easily deformed, and appear mostly as large conglomerates of crinkly foils. The first EM observation of such crinkly foils was made by Eitel [19] in a product formed in the reaction of a CH solution with an SH hydrosol. Different varieties have later been observed in several EM studies [70, 30, 23, 26, 74, 75]. Gaze and Robertson [76] report the extensive formation of crinkly foils of tobermorite in mixed portland cement-asbestos pastes produced by low-temperature foaming. It seems probable that silica dissolved from the asbestos component and reacting with the lime solution can have contributed to the formation of a product having a C/S ratio in the CSH(B) range. Similar compounds were also observed [77] in lime-quartz paste mixtures of low overall C/S ratios, cured at temperatures of 100 °C and above, but in some products of very low C/S ratio (about 0.4) and cured at 165 °C the paste aggregates consisted of decidedly fibrous or lathlike elements. The crinkly-foil type of CSH(B) appears to be predominant in the pore surfaces of the cement-paste specimens prepared by Bernard [14], using a special technique of preparation. These formations, termed monocalcium silicate hydrate by Bernard, were frequently observed to occur together with acicular particles, and thickened in the course of hydration, forming dense, opaque aggregates.

One form of CSH(B) is shown in figure 8 a, b. It consists of small, and comparatively flat, platy particles, together with crinkly foils, and gives a well-developed ED ring pattern of CSH(B)(hk) reflections. The C/S ratio is about 1.1, reached in a CH solution of about 3.8 mM/liter.

The appearance of foils persists almost throughout the whole range of concentration of CH solution phase, except in the immediate vicinity of saturation where a finely fibrous or needlelike growth is promoted [23]. It is questionable if a transformation from CSH(B) to the C_2SH_2 phase can be achieved in temporarily supersaturated solutions. However, Kalousek and Prebus [30] report the formation of a mixture of 1.33 C/S CSH(B) foils and a high-lime solid in the form of coarse, bundled fibers, in a 1.5 C/S batch processed at 60 °C. Fascicular aggregates of fibers, considered to be the characteristic habit of C_2SH_2, have been observed in the products of hydration of C_3S and β-C_2S [78, 23, 71, 79] (cf. also review paper by Brunauer and Greenberg, this Symposium). Similar formations are also common in some varieties of hardened cement pastes, where they can be expected to contribute to the formation of a rigid gel structure (cf. below).

The tobermorite compounds formed at elevated temperatures (approximate range 110 to 170 °C) generally exhibit more characteristic crystalline habits. The low-lime phase, of C/S 0.8 to about 1.2, forms large, flat plates, estimated to be of the order of 10 to 20 unimolecular layers in thickness [80, 81, 82, 70, 77]. A consequence of the more or less regular superposition of layers is that (hkl) reflections and strong basal reflections occur in the XD powder diagrams, which agree well with those obtained from certain natural tobermorites. ED single-crystal diagrams fully confirm the symmetry and dimensions of the postulated unit cell, but are sometimes indicative of polymorphic stacking disorder of the same type as is observed in clay minerals. The transformation from CSH(B) foils, estimated from specific-surface-area measurements and from their transparency to electrons to be only two or three molecular units thick [28, 77], to tobermorite plates is accompanied by a large decrease in specific surface [70].

With increasing C/S ratio the high-temperature tobermorite phases tend to become increasingly fibrous. An electron micrograph from a 1.25 C/S tobermorite prepared at 150 °C shows long, straight rods together with thin plates splitting up into lathlike particles, and the corresponding 1.5 C/S phase consists entirely of long, straight, lathlike or tubular crystals [30]. Ribbonlike crystals of similar appearance are shown by Akaiwa and Sudoh [82], and have also been observed to form slowly during prolonged boiling of afwillite–CH slurry mixtures resulting from ball-milling of C_3S in water [28, 26] (fig. 9 a,b). ED single-crystal diagrams indicate the existence of a simple (not face-centered) base unit cell of dimensions 5.2 to 5.4 by 3.6 A, although reflections with h+k odd are generally weaker. A possible way of interpreting these data in terms of structure would be to suggest the presence of a layer lattice element of the unsymmetric SH—CH type, instead of SH—C—SH, as in the tobermorite structure model proposed by Megaw and Kelsey. Of special interest is the decrease in unit distance across the chains, which leads to a displacement of, e.g., the strong hk=11 reflection from about 3.07 A, normally observed in tobermorites, to about 2.96 A. The formation of mixed-layer compounds may account for the general blurring of the strong ED reflections in the 2.8- to 3.1-A range, observed in different constituents of hardened cement pastes, as is further exemplified in later sections of this review.

Of considerable interest in this connection is the study made by Kalousek [83] of tobermorite prepared with varying amounts of alumina present in the reaction mixture. He found that it was possible to replace a limited amount of Si ions by Al ions in tetrahedral positions, 4 to 5 percent A per $C_{4-5}S_5H_5$ tobermorite. Increasing the amount of alumina in the mixture above about 5 percent

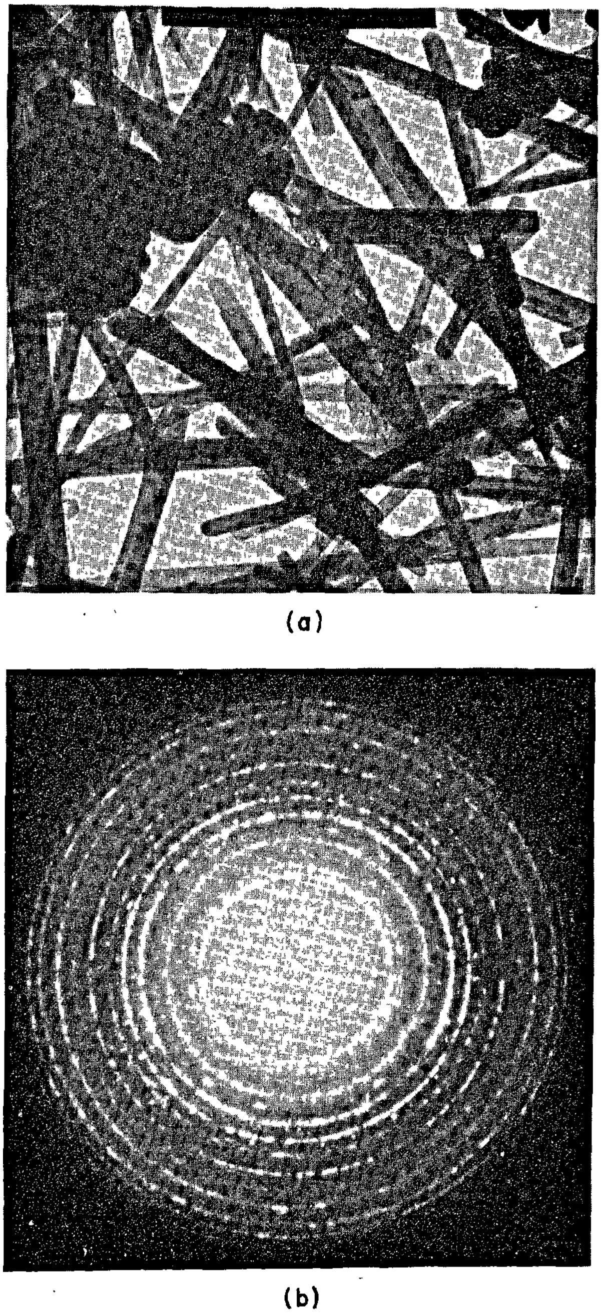


FIGURE 9. *(a) High-temperature tobermorite phase formed by boiling of an afwillite-*Ca(OH) *slurry prepared by ball-milling* C_3S *in water. (b) Electron diffraction pattern of material shown in figure 9a.*

resulted in the formation of increasing amounts of the hydrogarnet compound C_3ASH_4 (or possibly $C_3AS_2H_2$) as a second phase. The crystals of the Al-substituted phase showed a marked decrease in size but were still of a platy habit, and the XD powder patterns exhibited slight changes from those of tobermorite without substitutions. If observations of a corresponding limit of substitution of Al ions could be made also in the case of the low-temperature compounds, CSH(B) and C_2SH_2, a method would be afforded of testing the postulate of relative independency of reaction with water of the C–S and C–A–F clinker constituents. This postulate, once advanced by the cement chemists as a kind of working hypothesis for lack of evidence to the contrary, seems to have acquired a degree of general validity which may not be altogether justified.

Some considerations and evidence on the probable incorporation of silica groups in the hydration products of the C–A–F and C–S constitutents of cement were presented in the previous section. Concerning the question of alumina in the C–S–H gel phases, it can be shown by a simple calculation that in a cement containing alite of a composition approximating the well-known Jeffery formula, $C_{54}S_{16}AM$, the alumina held by the alite itself would correspond almost exactly to a 5 percent substitution limit in the tobermorite phase formed from this alite, thus no alumina would be exchanged with the other clinker constituents. On the other hand, some alumina in solution may enter into the C–S–H gel phase formed from belite, which is assumed to contain no alumina initially. In view of the low rate of hydration of β-C_2S, it would seem that only a very small amount of alumina is involved in this process, at least in the early stages of setting and hardening. It is conceivable, however, that the presence of aluminate ions in the liquid phase may accelerate the hydration of belite considerably.

Structure Elements in Colloidal Tobermorite Phases

It is a matter of some interest to speculate on the possible relationships between the CSH(B) and C_2SH_2 structures and the structure models proposed for tobermorite, as described earlier. As has been shown, sheetlike habits predominate in CSH(B) particles, in spite of the probable existence of one-dimensionally coherent lattice elements in them. It would appear, therefore, that the Mamedov-Belov structure model, containing polymerized silica layers, is the most likely alternative. However, this structure has a comparatively rigid, self-contained character, and it seems difficult to imagine an incorporation of extra lime to take place without increasing the unit layer distance to impossible values. This lattice may well apply to certain types of well-crystallized tobermorite, but silica layers of a correspondingly high degree of complexity and polymerization are unlikely to be present in the ill-formed structures of CSH(B) and C_2SH_2. The Megaw-Kelsey structure model is, on the whole, more flexible, and can be modified theoretically in various ways in order to fit observed data without violating the principles of arrangement of structural elements inherent in this model. One such hypothetical modification, the unsymmetric SH—CH layer, has already been described. This layer has a C/S ratio of 4/3. It is perhaps fortuitous that Kalousek and Prebus set a limit in the range of existence of CSH(B) at 1.33 C/S, or that Pressler, Brunauer, and Kantro [84], in extracting lime from a mixture of lime and 1.5 C/S tobermoritic material obtained in a hydrated C_3S paste, found an abrupt break in the rate-of-extraction vs. time curve, occurring at 1.34 C/S in the tobermorite phase. Certain observations of basal spacings decreasing with C/S ratios increasing in the 1.0 to 1.5 range [23] are, however, more easily explained by a mechanism of structural change involving the removal of SH elements from the layers, rather than by an addition of CH elements to a layer core of constant composition. The accommodation of additional C—H complexes in the two structural "holes" (per 11.2 by 7.2 A unit cell) between the ridges of the silica sheet would bring the C/S ratio up to the maximum value of 2.0, assumed for C_2SH_2.

The electron-optical evidence presented in a recent paper by Gard, Howison, and Taylor [85] fully confirms the description given above of the various morphologic habits and other properties of the synthetic tobermorite phases, and in addition furnishes data on the modes of transition between different particle habits and on transformations to dehydrated C–S compounds on heating. Two observations seem to be of special interest. One of these is the suggestion of the existence in C_2SH_2 of unsymmetrical SH—CH layers coupled together by C—H layers, in analogy to halloysite among the clay minerals and agreeing with the considerations put forth in this review. The other observation is that of the common occurrence in well-crystallized tobermorite plates of aggregates stacked with the *b* axes of separate layers rotated through approximately hexagonal angles. According to the authors, this suggests that the surfaces of tobermorite crystal elements consist of CH layers rather than SH chains. However, it seems that also the open, nearly hexagonal structure of the layer of SH chains of the Megaw-Kelsey lattice model would equally well permit a fit between adjacent units with mutually rotated directions of chains. However this may be, it can be assumed that such modes of rotational superpositions would occur frequently for subcrystalline tobermorite unit layers crystallizing in the very narrow gel spaces of a cement paste. An aggregation of the type suggested is likely to cause restrictions in particle size and to favor the development of small particles tending to assume the habit of flakes rather than fibers. Further, it would be almost impossible to detect any crystalline properties in such formations by means of diffraction methods. We have here a possible explanation of the fact, exemplified in later sections of this review, that in some cement pastes of normal data the expected formation of fibrous structures of C_2SH_2 tobermorite largely fails to occur.

It must be emphasized that the ideas put forth in the last paragraph are of a highly speculative nature, representing only one of a few alternative ways of reviewing the object matter. Buckle and Taylor [29] regard the problem of structure formation in ill-crystallized tobermorite from a somewhat different angle. They assume a structure composed of a mosaic of crystal elements of extremely small size, with a short-range undulation of structure type between pure CH and pure tobermorite. It seems that this is merely an alternative way of describing the molecular texture of an ill-crystallized composite gel material, not a fundamentally different conception of the structure.

Another theory of the relationship between structure and C/S ratio of tobermorite gel phases is advanced by Taylor and Howison [68], supported and further developed by Brunauer and Greenberg (this Symposium). According to this theory, the degree of polymerization of the metasilicate chains decreases with increasing C/S ratio. It is assumed that, at certain intervals of the chain, the ionic bond connection is interrupted, due to the absence of $Si(OH)_2$ groups described earlier in this paper as protruding OH—OH edges of the Megaw-Kelsey model structure for tobermorite. Instead of a missing $Si(OH)_2$ group, one Ca ion and possibly one water molecule are assumed to enter nearby sites in the lattice. Complete replacement would correspond to a C/S ratio of 1.75.

This theory, if developed in further detail, seems to afford interesting possibilities for a revision of current ideas on the C–S–H gel structure, as reviewed earlier in this paragraph. However, conclusive evidence is still largely missing, and it is obvious that further experimental work, with the purpose of obtaining a confirmation of structural theories or a better resolution of the tobermorite gel structure, will meet with great difficulties. Because of the apparent importance of some form of the tobermorite phases for the formation of an integrated gel structure in hardening cement paste, it seems urgent to make some attempts at forming a conception of the various arrangements of ionic groups in the structures of these compounds, specifically the crystal patterns in the outer surfaces.

Afwillite

Although afwillite is not very likely to develop hydraulic properties, owing to the essentially noncolloidal character of its crystals, it has nevertheless been mentioned in the literature as a possible constituent of cement hydration products.

Judging from evidence obtained in microscope studies, Nacken [86] suggested that in the successively proceeding hydrolysis of C_3S crystals, first $C_2SH(B)$, hillebrandite, then $C_3S_2H_3$, afwillite, and possibly CSH_2, plombierite, are formed as surface layers on the anhydride crystals. Other observations, made in EM studies by Zhuravlev (unidentified reference given by Schwiete and Müller-Hesse [31]), indicated the formation of needlelike crystals, probably of afwillite, in the early stages of hydration of calcium silicates. However, too much importance should probably not be attached to these observations which are difficult to reconcile with later findings.

In reports by Swerdlow, McMurdie, and Heckman [87, 88], dealing in particular with products obtained by ball-milling of C_3S slurries, the suggestion is made that afwillite could be a hydraulically active constituent of hardening portland cement pastes, probably constituting, together with crystalline CH, the product of ultimate equilibrium in fully hydrated C_3S paste. The active ingredients of the observed gel structures were considered to be extremely small, discrete gel globules conglomerated in spherical clusters, and a theory was advanced explaining tentatively the mechanism of hydraulic hardening as being a process of coalescence and intergrowth of the spherical clusters. The XD patterns given by extracted fractions of the small, discrete particles agree with that of afwillite, whereas the ED patterns from the surfaces of the large agglomerates are said to resemble the diffraction patterns given by tobermorite and possibly hillebrandite.[2]

In order to verify these observations, which lead to a conception of structure formation in cement paste differing considerably from those of other commentators [8], the present author examined the hydration products in C_3S slurries, ball-mill-hydrated in a similar way but omitting the subsequent dispersion by ultrasonic treatment [26].

The fully hydrated product was composed of about equal amounts of CH crystal plates, sometimes aggregated in large, flaky structures, and aggregates of rather large and thick afwillite crystals, of the appearance of rhombic slabs with somewhat rounded corners (fig. 10). Owing to the intimate mixture of CH and afwillite, the ED diagrams consist of mainly CH spot-ring reflections, whereas the afwillite crystals are generally too thick and well-crystallized to give ED effects. However, in many diagrams diffraction spots not belonging to the CH pattern are observed, especially at about 6.48, 5.04, 4.12, 3.20, 2.82, and 2.14 A, coinciding approximately with some strong, or medium strong, reflections of afwillite. A few other strong XD reflections

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[2] In the opinion of the present author, the distribution of intensities and the relative spacings of the ED patterns shown are in good agreement with those of ED patterns of C, calcium oxide. For lack of numerical data, no absolute comparison can be made. However, it can be pointed out here that C patterns frequently appear, even at low levels of electron irradiation intensity, in EM studies of freshly precipitated hydration products which have not yet had time to stabilize.

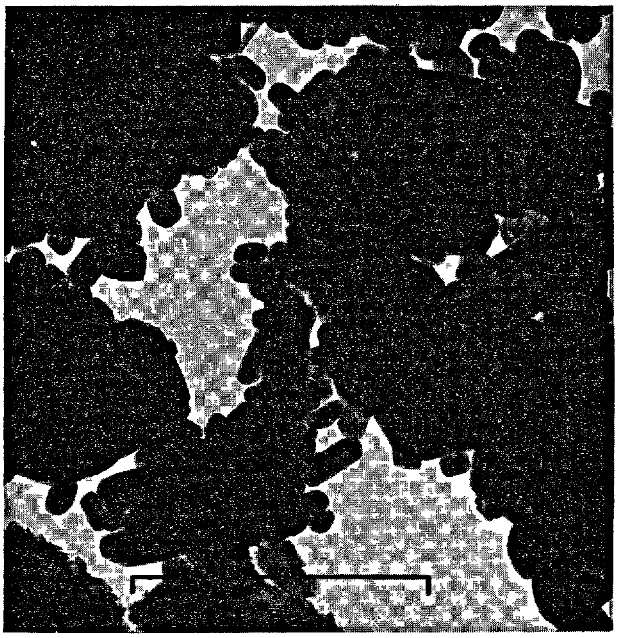


FIGURE 10. *Calcium hydroxide plates and aggregates of afwillite crystals formed by ball-milling* C_3S *slurry without subsequent ultrasonic dispersion.*

of afwillite are not observed in ED patterns, but it should be pointed out that one can never expect a complete agreement in weak spot patterns of this erratic character. The XD diagram contains the spectra of both CH and afwillite.

These results indicate that the nature of the crystallization processes taking place in the course of hydration of cement can be changed radically by applying a procedure of mixing involving prolonged and intensive mechanical treatment. Since both C_3S and afwillite contain isolated SiO_4 tetrahedra in their lattices, it seems natural to explain the effect of ball-milling by assuming that it prevents the SiO_4 groups from polymerizing into chains, or breaks up any chain structures incidentally formed. It can be noted that β-C_2S slurries, similarly treated, yield tobermorite materials in the hydration products [28]. This result indicates that the presence of a sufficiently large excess of Ca ions in the mixture is also required, in order to keep silica groups from combining.

It can be further supposed that the application of high-power ultrasonoration may lead to complete peptization and destruction of crystalline structures, as is indicated by the observations just described.

Xonotlite, Hillebrandite, and Tricalcium Silicate Hydrate

The morphologic habit of xonotlite, of composition CSH_n, with n variably reported to be 1/3, 1/5, or 1/6, has been observed by Kalousek [80] and by Akaiwa and Sudoh [82]. This mineral consists of long, slender, fibrous or lathlike crystals.

Similar habits are exhibited by $C_2SH(B)$, synthetic hillebrandite, which also forms aggregates of broom-shaped or fascicular character, resembling C_2SH_2 [82]. An electron micrograph of the natural mineral shows aggregates of particles of fusiform shape, giving ED spot patterns indicative of three-dimensional crystallization [23].

Tricalcium silicate hydrate, $C_3SH_{1.5}$, is of considerable interest because of its occurrence in C_3S pastes cured at different temperatures after long periods of curing even at temperatures as low as 50 °C, as observed by Buckle and Taylor [29]. These authors state that "although persistent, $C_3SH_{1.5}$ is probably not a thermodynamically stable product below at least 170 °C. The restrictions on atomic transport and rearrangement in pastes cured at these relatively low temperatures possibly favour formation of compounds with the same Ca/Si ratio as the starting material. After the $Ca(OH)_2$ has had time to segregate into relatively large crystals, tricalcium silicate hydrate does not form below about 200 °C".

No sign of the presence of $C_3SH_{1.5}$ could be detected in electron micrographs of C_3S pastes cured for long periods at room temperature. Crystals of $C_3SH_{1.5}$ produced at high temperatures showed characteristic habits of long needles or rods, often with foil-like or tubular extensions at the ends [53]. Single-crystal ED patterns can be indexed on the basis of a unit cell of hexagonal symmetry, with the *c* axis of length about 7.5 A (i.e., slightly larger than the unit distance in the 3-metasilicate chain) parallel to the fiber axis. It remains to find a lattice structure compatible with this rather peculiar relationship between morphologic properties and crystal symmetry.

C_3S and β-C_2S Suspensions and Pastes

General Considerations on Hydration Reactions

The extensive literature on the reaction chemistry of the hydration of C_3S and β-C_2S, the two main ingredients in portland cement, will not be reviewed here. It may suffice to state that these compounds give mainly the same hydration products at temperatures up to at least 100 °C, viz., colloidal or microcystalline tobermorite phases, C_3S producing one extra mole of CH per formula at complete hydration [28]. It is observed that C_3S hydrates much more rapidly than β-C_2S. In matters pertaining to the development of microstructures in the hydrated phase, the ideas put forth by van Bemst [71, 89] can serve as a basis for further discussion.

In general agreement with the theories on cement hydration once developed in the classical works of Le Chatelier, van Bemst observes that the silicate constituents are dissolved superficially, and that CSH (B) is precipitated in the outer solution phase thus formed. This reaction is rapid at first but slows down considerably as the effective Ca ion concentration increases. At a certain concentration of Ca ions in solution, assumed by van Bemst to be normal saturation point (about 20 mM C per liter), but probably in reality far exceeding this value, conditions are favorable for the formation of C_2SH_2. This phase forms directly on the surfaces of residual anhydride cyrstals. The precipitation of the C_2SH_2 phase proceeds at a comparatively high rate, and the decomposition of the anhydride compounds is again accelerated.

A consequence hereof, according to van Bemst, is that paste hydration of the silicates proceeds more rapidly than hydration at higher water-to-solid ratios. In the case of paste and slurry hydration of β-C_2S at 100 °C, a similar observation is made by Funk [79], who noticed that complete hydration of β-C_2S at $w/c = 0.5$ could be reached in about 10 days, whereas at $w/c = 3$ the product was only about 50 percent hydrated after the same time. In addition, further reaction seemed to proceed at an exceedingly slow rate.

A possible explanation of these phenomena would be that the CSH (B) foils, if formed in larger amounts with excess water, adhere to the anhydride silicate surfaces, covering them with a more or less impermeable coating. On the other hand, the fibrous particles of C_2SH_2 type, if once formed, radiate outwards from the surfaces, furnishing paths of easy diffusion of the ionic groups participating in the process of hydration and hydrolysis.

It should be noted, however, that other investigators have arrived at quite different results, indicating that in general the rate (or degree) of hydration tends to increase with increasing w/c ratio. The relative amount of water in a mix is only one among several factors that determine the rate of reaction at various stages of the process of hydration, as is elucidated in further detail by Brunauer and Greenberg (this Symposium).

Observations made by the present author on hydration products formed in C_3S suspensions in water and in lime solutions are mainly in agreement with the conceptions of structure development now described. The solid phase produced by long-time shaking of C_3S-water mixtures of such proportions that a C/S ratio of about 1.7 was reached in a nearly saturated solution (small but undetermined amounts of solid CH modifications were present) consisted of large flocs of foil-like material of a rather open texture, giving ED ring patterns indicating ill-crystallized CSH(B) (3.0- and 1.8-A reflections).

Corresponding hydration products of C_3S suspended in a saturated CH solution were still largely foil-like, but with some foils rolled up to form long and rather thick fibers. This product gave an ED pattern consisting of only one diffuse ring at about 2.8 to 3.1 A. Another phase, observed to be present in small quantity, appeared as fusiform particles consisting of bundles of parallel fibers. The ED patterns were those of calcite, and these particles are therefore pseudomorphs caused by carbonation of the original structure.

Finally, with C_3S suspended in a highly supersaturated CH solution (about 31 mM C per liter), large flocs showing at the edges a feltlike texture of finely fibrous particles were predominant, but considerable quantities of the fusiform particles were also observed. Also present, of course, were large amounts of CH precipitates, of the $\overline{C}$-contaminated type.

The introduction of certain types of surface-active agents in solution can change the rate of hydration and modify the hydration products. This has been shown by Adamovich [24], reporting data from EM studies of C_3S and β-C_2S hydration in suspensions, with or without admixture of small amounts of lignosulfonate (sulfite liquor). He states that the hydration process is considerably accelerated in the presence of the surface-active agent, which also acts as an inhibitor of hydrolysis, especially of C_3S. The hydration products are characterized as fascicular fiber aggregates with splintered ends, strongly resembling C_2SH_2 tobermorite particles.

C_3S Pastes

The products of hydration in C_3S pastes cured for long periods up to more than 5 yr at room temperature, were examined in the electron microscope by Buckle and Taylor [29]. All pastes showed the same structure, that of irregular masses possibly composed of small plates. These aggregates gave no ED pattern, but occasional larger crystalline fragments were identified by means of their ED patterns as CH crystals. The irregular masses are almost certainly very ill-crystallized tobermoritic material. The structure of this material is tentatively described as intermediate between those of CH and tobermorite, with metasilicate anions partially and disorderly replacing OH ions in the CH structure.

No electron-optical data are given by Buckle and Taylor on the C_3S pastes cured for prolonged periods at higher temperatures, but their optical and X-ray evidence seems to indicate that the phase composition, and most probably also the morphologic character, is changing rapidly with increasing temperatures of curing. Some support for this statement is given by observations of structure formations in a C_3S-water suspension boiled for a few minutes [26]. This treatment resulted in the appearance of a mixture of hydrated solid phases of particle habits quite different from those observed under similar conditions at room temperature.

Data on phase compositions of the hydration products of C_3S and β-C_2S hydrated under different moisture and temperature conditions and with various additions of asbestos and quartz, have recently been reported by Berkovich, Kheiker,

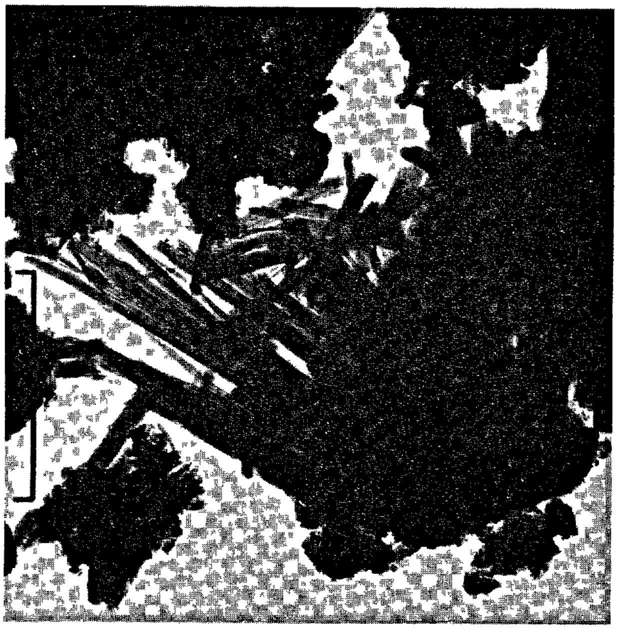


FIGURE 11. *Fibrous tobermorite formed in a fully hardened paste of* C_3S.

Water-to-solids ratio=0.7, age=7 months.

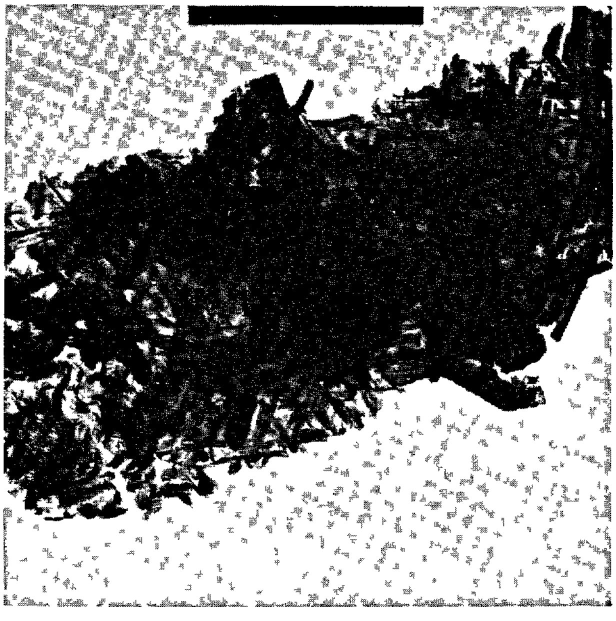


FIGURE 12. *Skeletal framework of elongated particles remaining after brief shaking of dried and powdered fully hydrated* C_3S *paste with water.*

Gracheva, and Kupreeva [90]. With special reference to low-temperature hydrates, it is stated that fibrous C_2SH_2 and CSH(B) can be identified in materials cured at 20 and 60 °C. The mixtures autoclaved at higher temperatures show complex compositions. It can be specially noted that the appearance of $C_2SH(A)$ seems to correspond to a lowering of the mechanical strength of mixed C_3S-asbestos pastes, but the decrease in strength is ascribed to corrosion of the asbestos particles. On the other hand, the formation of CSH(B) in mixed C_3S-quartz powder pastes is connected with an increase in strength.

Some fully hydrated C_3S paste materials (water-to-solid ratio 0.7, age 17 months) produced in the stoichiometric studies made by Brunauer, Kantro, and Copeland [28] were examined by the author [26, 32, 33]. A large part of the material consisted of irregularly shaped agglomerates of small and thin particles, similar to those described by Buckle and Taylor, and showing in ED diagrams at most a very diffuse ring at about 2.8 to 3.1 A. However, a second phase was also observed in about equal amounts. It consisted of long and rather thick needles or rods, obviously composed of bundles of fibers or tubularly rolled sheets, often radiating from a common center (fig. 11). The ED patterns from such aggregates contained a diffuse ring at about 2.9 to 3.0 A, and a mostly weak but sharp reflection at 1.80 to 1.82 A, characterizing these products as fibrous tobermorite. A third phase, that of large and fairly thin plates of CH crystals, easily recognizable by means of their characteristic ED spot patterns, was also found in appreciable amounts.

If the dried and powdered C_3S paste was shaken with water for a very short time prior to the preparation of EM samples, some amount of the irregular masses seemed to dissolve or become rinsed away, revealing in many aggregates a skeletal framework of elongated particles (fig. 12). This observation seems to indicate that the amorphous-looking masses may be aggregated in and around the meshes of a rigid structure which holds them together.

Microstructural elements very similar to those now reported have been observed by Kurczyk [91] in C_3S pastes, hydrated one month at 30 °C. Apart from larger unhydrated particles, the material seems to consist of about equal amounts of finely textured irregular masses, of rather long branched needles, and of thin plates, presumably CH crystals. An addition of small amounts of gypsum to the paste mixture is said to influence the development of hydrated structures in an unfavorable way, but the character of the changes taking place is not clear.

β-C_2S Pastes

The products of paste hydration, at 50 and 100 °C and a water-to-solid ratio of 0.5, of β-C_2S containing additions of small amounts of various stabilizers (to prevent conversion to γ-C_2S), were studied by Funk [79]. These pastes consisted almost entirely of fibrous C_2SH_2-type tobermorite, with minor amounts of CH crystals. The materials prepared at 50 °C were composed of dense aggregates of thin fibers, whereas at 100 °C longer and thicker needles or rods were observed. The C/S ratios in the solid phases varied from 1.7 to nearly 2.0, the materials produced at 100 °C being higher in lime. When β-C_2S was hydrated in water vapor at 100 °C it gave a product composed of loosely aggregated bundles of fine needles. It was observed that the mechanical strength of such products was very low, whereas paste-hydrated β-C_2S materials were quite hard. From this fact Funk concludes that the presence of a solution phase during hydration is essential for the formation of a hardening, integrated structure.

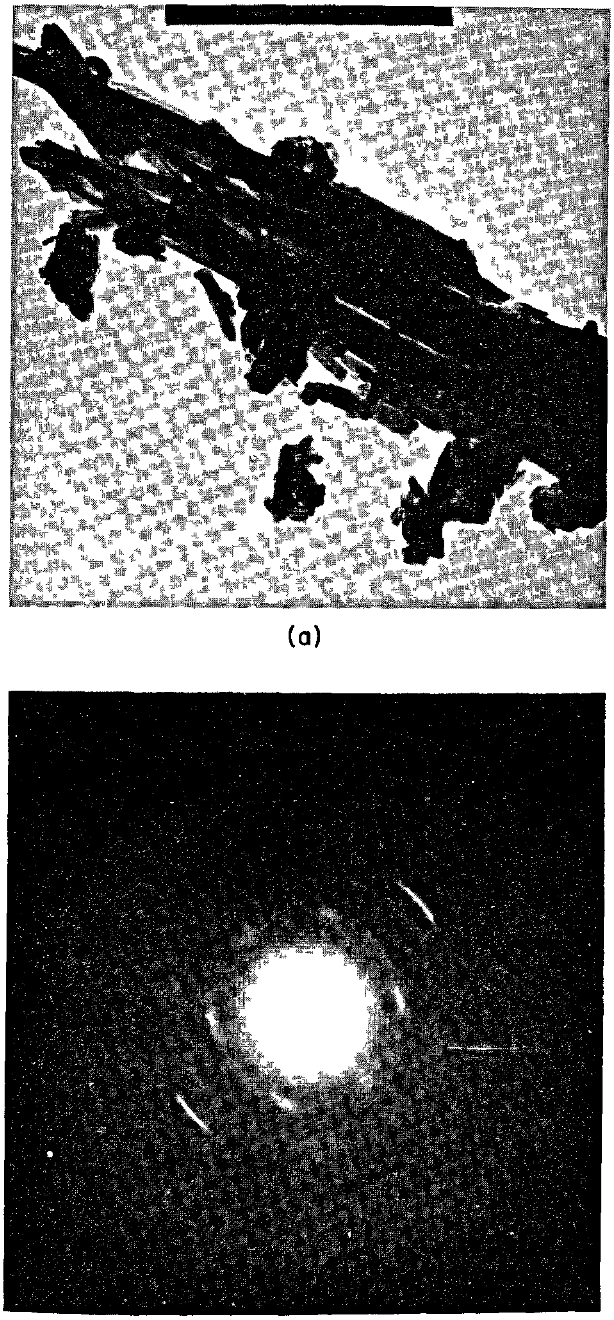


FIGURE 13. (*a*) *Coarsely fibrous particles from hydrated* β-*C S paste.* (*b*) *Electron diffraction pattern of fibers shown in figure 13a.*

Water-to-solids ratio=0 7. Seventy percent hydrated at 17 months

The present author examined dried and ground material from β-C_2S paste (water-to-solid ratio 0.7) hydrated at room temperature for 17 months, after which period it was found to be nearly 70 percent hydrated [28]. The microstructures of this material resembled those observed in correspondingly hydrated C_3S pastes described in the preceding section, with irregular aggregates of small, distorted plates as the predominating phase. However, the coarsely fibrous or tubular particles also occurred in appreciable quantities. A bundle of such fibers is shown in figure 13 a, b, together with some irregularly shaped material. The ED fiber pattern consists of six diffuse, hexagonally arranged spot reflections at about 2.95 A, and a sharp streak at 1.83 A (corresponding to $b=7.32$ A along the fiber axis). Occasional large, thin plates of CH crystals were also observed, indicating that some hydrolysis of β-C_2S had taken place.

Considerations on Differences in Structure Development and Hardening Processes

The evidence available on low-temperature paste-hydrated C_3S and β-C_2S seems to show that the phase composition and particle habits are essentially the same in both materials, with the exception that the amount of crystalline CH is considerably larger in C_3S pastes. It is well known that C_3S pastes harden and develop a high mechanical strength much more rapidly than do β-C_2S pastes. It seems natural to assume that the rapid development of a crystallized CH phase at early ages in C_3S pastes is the main factor responsible for this discrepancy in the rate of hardening. This opinion is held by Ershov [92], who concludes that CH participates in the hardening process, and, in particular, that "the basic factor controlling early strength of portland cements should be viewed as the quantitative content of $Ca(OH)_2$ in the products of hydration", whereas "the basic factor controlling strength gain at later periods of hydration is the delayed hydration of C_2S and the continuous process of densification of gel structure"

These views cannot be directly substantiated by the EM data. On the contrary, the crystal plates of CH seem to be easily broken away from the rest of the gel structure, and practically always appear as detached particles with clean surfaces, with no signs of adsorption or bonding of gel material, or of formation of continuous structures by an intergrowth of partially overlapping plates, as is probably the case in hardening lime mortars.

The alternative explanation of the difference in the rates of hardening, that of the generallv higher reactivity of C_3S in contact with water, leading to a more rapid development of colloidal C–S–H phases, is of course of a very vague nature. The relative rates of development of the amorphous and the coarsely-fibrous phases during the early stages of paste hardening must first be studied, before any opinion can be formed on the true nature of early hardening and subsequent strength gain in calcium silicate pastes.

Gel Phases in Portland Cement Pastes

Introductory Remarks

Hitherto published EM data on the microstructure of cement paste materials [14, 15, 30, 32, 33, 34, 88] have established in broad outline the character of various constituents of the hardened cement gel, and there seems to be reason to hope for major contributions to the systematic solution of important problems relating to this subject to be forthcoming in the near future. For the present review, the author finds it convenient to use mainly his own observations on various paste materials which, however, have not been prepared in a systematic way, but rather selected from available samples of pastes of different description [26].

Observations on Pastes Hardened at Normal Temperatures

Since about 70 to 80 percent of portland cement of normal composition consists of a mixture of alite and belite, the impure clinker modifications of C_3S and β-C_2S, it can be expected that the predominant phases in hardened portland cement pastes would be very similar to the gel phases observed in the pure silicate pastes. This is found to be the case. It can be stated that by far the largest part of the cement pastes examined consists of exceedingly ill-formed, colloidal products, in which it is sometimes difficult to discern any definite morphology. The remainder of the pastes consist of relatively large-sized plates of CH and C–A–H (possibly C_4 (A, F, S)·aq.) crystals, the properties of which have already been described, and which are always present in some quantity, mostly small

The lightly ground paste materials are mostly found to be composed of rounded, irregular aggregates of diameters generally ranging between 0.5 and 2 μ. It is supposed that these aggregates correspond to the initial cement particles, and that grinding or milling operations have the chief effect of splitting the material along zones of contact between hydrated particles.

As in pure C_3S and β-C_2S pastes, the particulate structure in the interior of the aggregates is a mixture of fibrous or acicular elements and elements of the shape of small and thin, rounded flakes, of the order of up to a few hundred A in diameter. The latter phase is predominant, and the fibrous phase has in general a finer and more distorted texture than in pure silicate pastes.

The ED diagrams from representative aggregates are extremely weak and diffuse, mostly showing only a broadened reflection at about 2.7 to 3.1 A. Whenever the fibrous phase is present in noticeable amounts, a weak but sharp fiber reflection at 1.81 to 1.82 A can also be detected. These diffraction effects are, exactly as in XD patterns, the only reflections recorded, except spot reflections from CH and C–A–H plates, in case such particles occur in the image field.

Figure 14 shows a representative aggregate in a Type I (ASTM) cement paste (specific surface 1,800 cm²/g in cement, w/c 0.55, 5 months old). Figure 15 is taken from a similar paste (w/c 0.65, 5½ yr old). Fibrous or bundled structures are visible in both pastes, but the more amorphous masses predominate. In figure 16, from the same paste as figure 15, heavy bundles of long fibers are seen together with finely textured material. Such formations are, however, not very common. In rare cases, similar particles have given ED patterns consisting of six hexagonally arranged, diffuse 3.0-A spots plus a fiber reflection streak at 1.81 A, similar to the pattern in figure 13b.

Pastes made up with other types of cement were in general found to be very similar to the Type-I cement pastes. Figure 17 represents gel-structure elements from a Type-IV (low-heat) cement, higher in β-C_2S and lower in C_3S and C_3A (2300 cm²/g, w/c 0.6, 7½ yr old). Figure 18 shows a type of aggregate consisting of very fine (less than

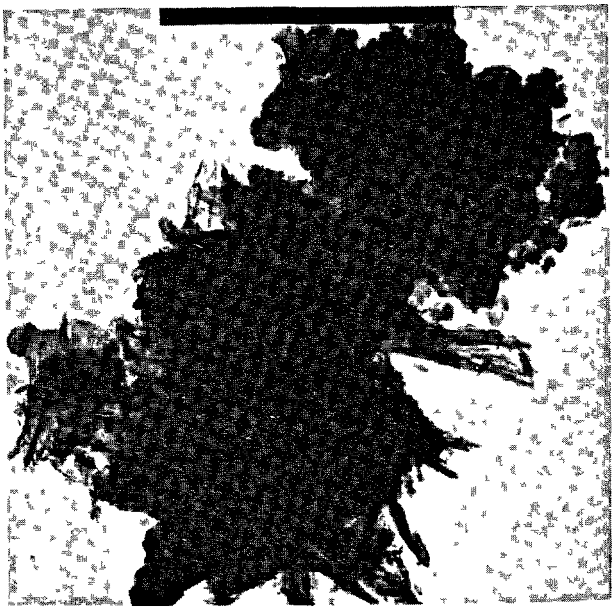


FIGURE 14. *Representative aggregate from lightly ground hydrated Type I cement paste.*

w/c=0 55, age=5 months.

100-A wide) fibers appearing as a common constituent, together with flaky aggregates, in a paste of Type III (rapid-hardening) cement, high in C_3S and ground slightly finer than normal (2,500 cm^2/g, w/c 0 6, 7½ yr old) The ED patterns are indistinct, in spite of the fibrous appearance

An effect of higher degree of fineness of grinding is exemplified in figure 19, originating from a paste prepared from the 8000-cm^2/g fraction of an ordinary Type I cement (w/c 0.7, 2½ yr old). The increase in porosity and the exceedingly small size of particle elements of the gel aggregates in this paste are characteristic features. The tendency to formation of fibrous habits is small. The large and thin plates also visible in this micrograph are crystals of the C–A–H hexagonal-plate phase.

FIGURE 15 *Representative aggregates from lightly ground hydrated Type I cement paste*

w/c=0 65, age=5½ yr

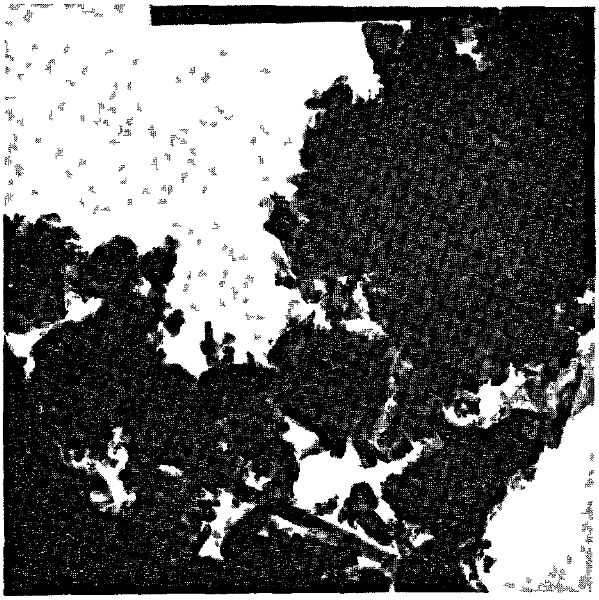


FIGURE 17. *Gel-structure elements from Type IV cement paste.*

w/c=0 6, age=7½ yr

FIGURE 16 *Relatively rare fibers from lightly ground hydrated Type I cement paste*

w/c=0 55, age=5 months

FIGURE 18 *Representative gel aggregate from Type III cement paste*

w/c=0 6, age=7½ yr

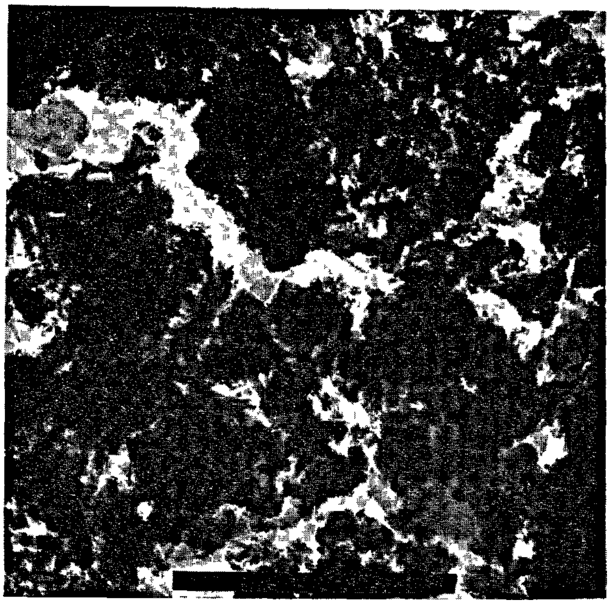


FIGURE 19. *Representative gel aggregates from a paste prepared from the 8,000-cm²/g fraction of Type I cement.*

w/c=0.7; age=2½ yr.

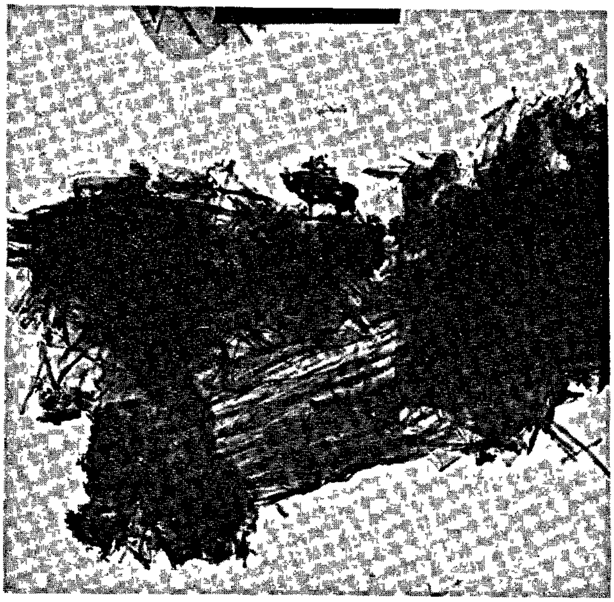


FIGURE 20. *Representative fiber bundles from a paste prepared from the 8,000-cm²/g fraction of a Type I cement.*

w/c=1.5; age=3 yr.

The same high-surface-area cement was used in preparing paste samples with the exceedingly high w/c ratio of 1.5, hydrated for more than 3 yr at the time of examination. The resulting paste was of course very soft and had a consistency resembling talc stone. Microstructurally, it consisted almost entirely of bundled and intertwined, very fine fibers, some of them only about 50 A across, as shown in figure 20, and in figure 5a. Figure 5b also shows the ED pattern given by such fibers, which agrees with that of well-crystallized CSH(B) tobermorite.

The oldest pastes examined were two samples of w/c 0.70 and 0.35 which had been kept in sealed vials for nearly 10 yr. Figure 4a is a micrograph from the former sample containing, in addition to the C–A–H plate, some irregular, flaky gel clumps. The latter paste was very hard and difficult to grind. Both pastes were composed chiefly of dense gel aggregates of small flakes, with only minor amounts of fibrous phase visible.

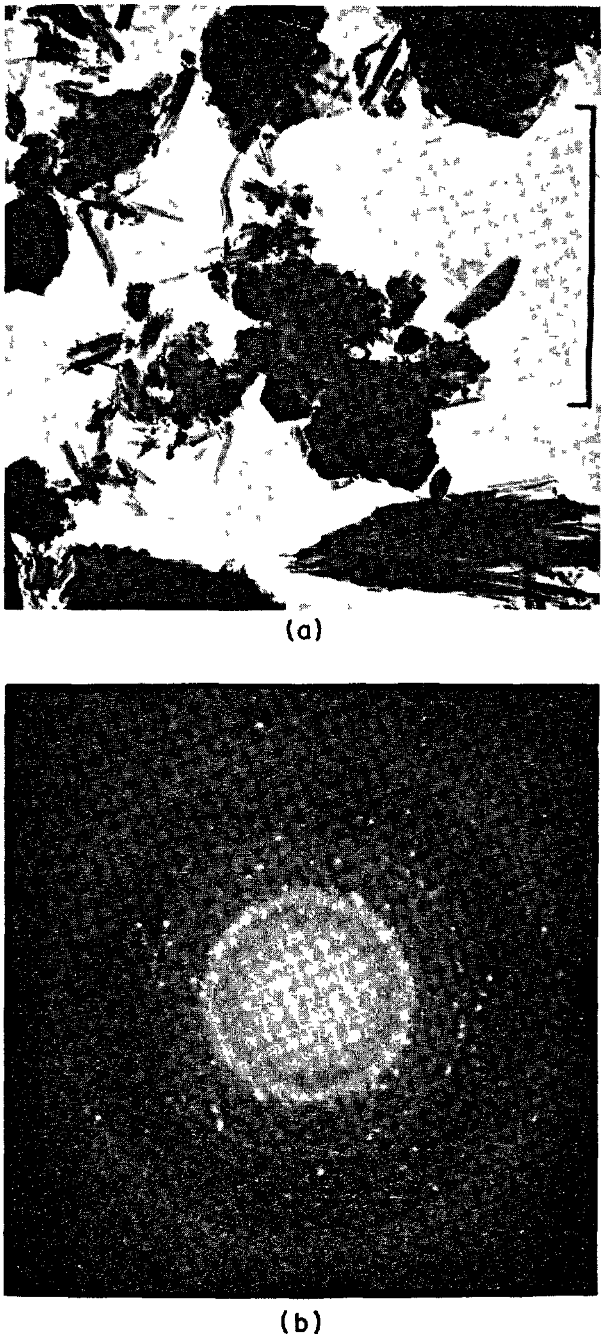
Observations on Pastes Cured at Elevated Temperatures

Hydrothermal curing of pastes for periods of short duration (less than a few days) at temperatures below about 150° C does not, as a rule, yield products of microstructural properties very different from those observed in pastes cured at normal temperatures. Kalousek and Prebus [30] show electron micrographs of the gel material in paste samples of cement and of a 60–40 percent cement-silica mixture, cured at 80 to 50° C for 15 hours. The complex XD pattern of the former product indicated, among other compounds, the formation of $C_2SH(B)$ (hillebrandite) and possibly some $C_2SH(A)$. The electron micrograph for this sample shows particles of various morphologic habits, tentatively identified by the authors, a few rod-like or tubular particles as hillebrandite, gel aggregates of partly fibrous appearance as C_2SH_2, thin plates as CH or $C_2SH(A)$. The cement-silica mixture consisted exclusively of irregular masses composed of small globules or plates.

The author examined a cement paste of w/c 0.46, autoclaved for 24 hours at 97° C and a pressure of about 700 kg per cm², then stored for about 7 years. No difference in appearance of the gel fragments in this paste and in those shown previously in this review could be detected.

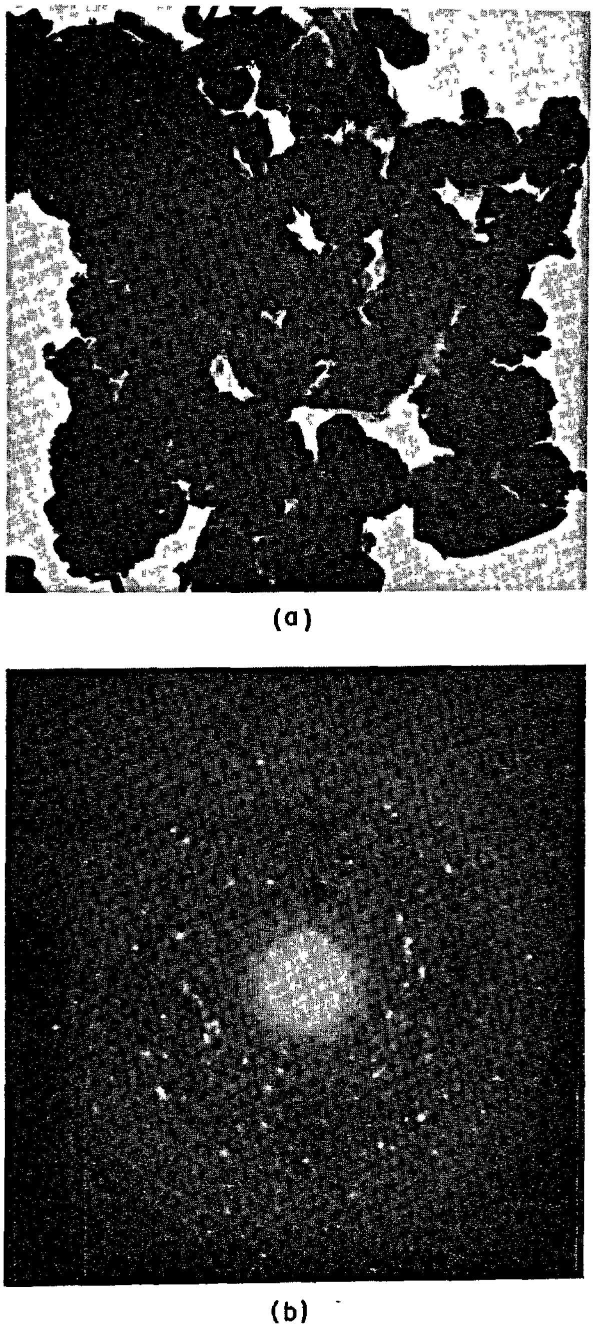
In another paste, cured at 177° C, but under otherwise equal conditions, the tendency to formation of fibrous structures was noticeable (fig. 21 a, b). The somewhat higher degree of crystallization is reflected in the increased intensities of the diffuse 2.7- to 3.1-A ring and the fiber reflection at 1.82 A. The spot reflections originate mainly from CH crystals, while C–A–H plates of the hexagonal C_4AH_{13} type could not be found in the specimen. Some lathlike or rodlike particles were identified, by means of their single-crystal ED patterns, as $C_3SH_{1.5}$.

A third paste examined, of Type I portland cement, w/c 0.40, had been autoclaved at 215° C for 24 hr, and then kept refrigerated for about 1 yr. The major part of this paste was found to be recrystallized, appearing as rather large, nontransparent crystal fragments together with CH crystal flakes (fig. 22 a, b). The ED pattern in figure 22 b shows a great number of irregularly distributed spots, considered to be the characteristic ED pattern from large and well-crystallized particles of a compound of low crystallographic symmetry. It is believed that the compound predominant in this paste is $C_2SH(A)$. Other constituents, present in minor quantities, were bundles of long rods or laths, identified by ED as $C_3SH_{1.5}$, and aggregates of thin, rounded flakes (fig. 23 a, b) giving an ED pattern of spot rings, corresponding to the (hk) crossgrating reflections from a hexagonal unit cell of $a_H = 5.33$ A. This compound can probably be identified as a synthetic clay (Al-Mg-silicate hydrate), formed from the cement constituents under the prevailing hydrothermal conditions.


(a)

(b)

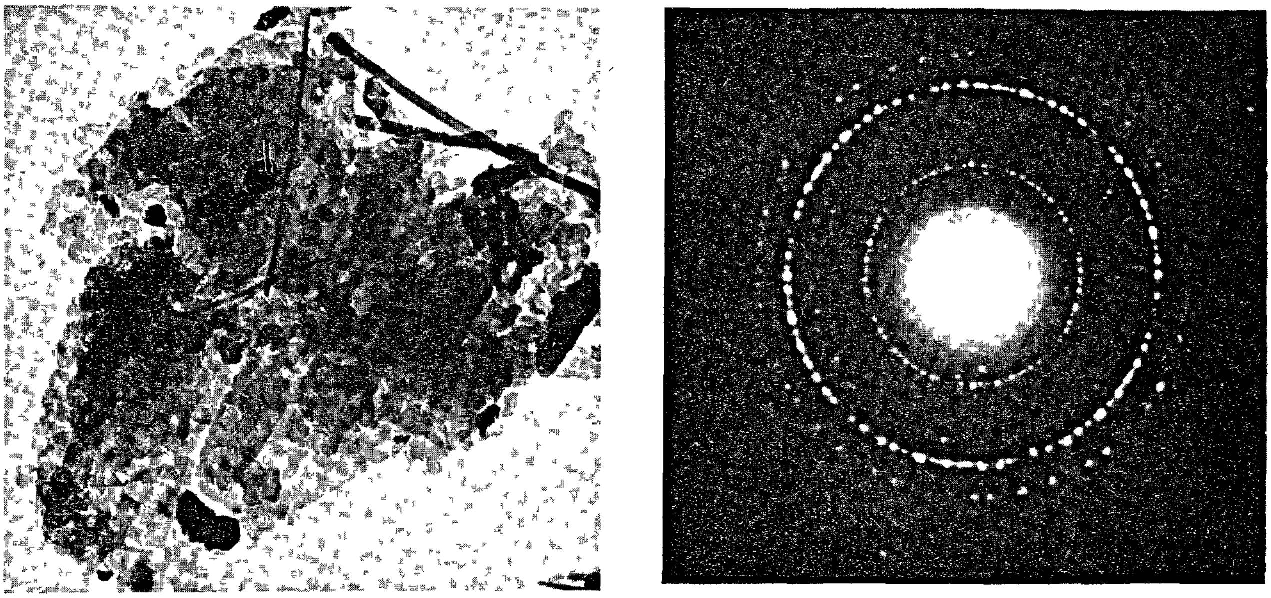
FIGURE 21. *(a) Representative fibrous structure from a cement paste autoclaved 24 hr at 177 °C and a pressure of about 700 kg/cm², stored for about 7 yr. (b) Electron diffraction pattern of material shown in figure 21a.*


(a)

(b)

FIGURE 22. *(a) Crystal fragments believed to be* C SH(A), *together with* $Ca(OH)_2$ *flakes from Type I cement paste autoclaved at 215 °C for 24 hr and kept refrigerated for 1 yr. (b) Electron diffraction pattern of material shown in figure 22a.*

w/c=0.4.



(a) (b)

FIGURE 23. *(a) Laths of* $C_3SH_{1.5}$ *and aggregates, probably synthetic clay* (Al-Mg-*silicate hydrate*), *present in minor quantities in Type I cement paste autoclaved at 215 °C for 24 hr and kept refrigerated for 1 yr.*

w/c=0.4.

Observations on Cement Paste by Replica Methods

A number of investigators in later years [93, 94, 95, 96, 97, 15] have reported electron-optical observations on thin replica films, of amorphous carbon or other materials, evaporated onto the surfaces of cement paste samples, and then stripped off or isolated by dissolution of the base material.

It is not surprising, considering the general lack of structure in cement gel particles as revealed in direct observations, that the replica studies have met with considerable difficulties of resolving the finer details of paste surfaces and of identifying various paste constituents from the appearance of their impressions in the replica film. In the opinion of the author, the employment of replica methods will be justified only if the results can be used to confirm or refute theories on the microstructural properties of hardened paste, based on data obtained in direct EM and ED observations of dispersed paste particles. As far as is known to the author, comparative EM studies of this kind, using both replication and direct observation, have not yet been attempted in any great extent. The particular branch of research on paste microstructure represented by EM replica techniques is in a state of rapid evolution. For this reason, it seems advisable, at the present time, to defer the discussion on this subject until it can be more clearly surveyed

Experimental Data and Theories

The data presented here on the general morphologic character of ordinary cement pastes do not confirm the theories on paste structure advanced by Bernal [8] at the London Symposium. According to these theories, which were based on the information then available on the microstructural properties of C–S–H compounds (given, among many others, also by this author), the paste structure was visualized as a network of fibers which thickened in the course of hardening to a dense, feltlike mass, thus imparting a steadily increasing mechanical strength to the paste. According to the data given in this review, such a model can be applicable to special cases of cement hardening, but it seems that in ordinary pastes the fibrous structures are not formed in quantities large enough to make it safe to assume that a framework of fibrous structures could be mainly responsible for the strength and dimensional stability of the hardened paste.

It has been shown previously, that at least the various pastes examined by the author seem to have a nearly amorphous structure even after many years of curing at normal temperatures. This observation is contradictory to the views expressed by Rehbinder [42], and by Strelkov [13], in developing the theories originally formulated by Baikov on the course of paste hydration of cement. The opinion held by these authors is, briefly stated, that the first products of hydration formed during setting are precipitated as highly colloidal masses, and that these products are, in later stages of prolonged hardening, converted into crystalline products of continuously increasing degree of crystallization, forming in the end product a monolithic structure of intergrown crystals.

The statement that the fibrous constituents are unlikely to contribute much to the structural rigidity of certain types of pastes is also partly opposed to some views on cement hardening put forth tentatively in a recent report by the author [34]. These views were based on observations of hydration processes in cement slurries. However, taking all available evidence into account, it seems that the structures formed in the presence of an excess of liquid phase may be essentially different from those formed during setting of fresh paste of low w/c ratio, which material, as far as is known to the author, has not yet been studied with respect to microstructure.

A reconsideration of current ideas on paste microstructure is obviously needed, but the experimental material on the systematic influence of a number of different factors must be enlarged considerably, before any definite statements can be made.

Considerations on Microstructure in Relation to Physical Properties

It is evident that there are still a great number of problems concerning the microstructure of cement pastes remaining to be solved. Therefore, it would be very difficult, with the present set of data, to establish any functional relationship between microstructure and, e.g., mechanical strength, or other important physical properties such as creep under load, permeability, etc. However, it is not necessary to know in detail the molecular microstructures of various components of the cement gel, in order to develop, in mathematical terms, far-reaching theories on the general physics and the mechanical behavior of hydrogels, specifically cement paste, as is demonstrated by Powers and by L'Hermite, in their review papers of this Symposium. In view of the great variability of microstructures in different cement pastes, it seems that the only property remaining for a characterization of cement gel is the enormous specific surface area developed in the collapsing anhydride structures due to the penetration of water through them. The importance of the evolution of large surface areas in materials possessing hydraulic properties has been particularly stressed by Powers [98], and by Brunauer [99]. However, as is also emphasized by these authors, it is not only the development of surface, but also the nature of links formed between surfaces that determines the properties of cohesion and strength development in a paste. These links or bonds between surfaces may be largely of physical nature (absorption forces), possibly acting via intermediate layers of water molecules, but in view of the dimensional stability of hardened paste it seems that some parts of the interacting surfaces must be connected by means of strong chemical bonds (valence forces) formed in the process of a direct superposition and intergrowth of surface lattice structures. One of the objects for future cement research is to establish the nature of these links between surfaces, and the relative preponderance of different types of forces at various stages of hardening. The application of results obtained in structural studies on more well-crystallized materials may prove helpful in solving this problem.

Another question pertinent to the relationship between structure and mechanical strength, is whether the presence of any particular habit of the crystal elements (e.g., fibers) in a paste structure is more favorable for the development of strength than others. The evidence on this point given in the literature related to the subject is rather confusing. It has been reported that paste products consisting of, e.g., well-crystallized tobermorite plates show high strength, whereas pastes composed of fibers or crinkly foils may be poorly integrated. In other cases highly colloidal structures are observed in paste products of high mechanical strength. In still other cases a fibrous microstructure is associated with high strength, while a recrystallization of the structure leads to disintegration. Obviously such quantities as initial w/c ratio and porosity, curing and mixing conditions, etc., are also factors which influence the ultimate result as much as does the habits of gel particles. However, it would seem that in further research on the hardening of pastes the formulation of some fundamental theories on the influence of the shape and size of gel particle elements must also be included.

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Discussion

L. E. Copeland and Edith G. Schulz

Mr. Grudemo has presented a comprehensive review of the microstructure of hardened pastes, and in his review has pointed out certain areas where little or no work has yet been reported. He has concluded that "by far the largest part of the cement pastes examined consists of exceedingly ill-formed, colloidal products, in which it is sometimes difficult to discern any definite morphology". He further concludes that the data he has examined do not support the theory of paste structure proposed by Bernal [1][1] nor the views of Rehbinder [2] and Strelkov [3].

We have done some work in one of the areas of ignorance pointed out by Mr. Grudemo, the nature of the structures formed during the setting of cement pastes. The primary purpose of our work has been to see if we can learn more about the microstructure of hardened paste by following the development of structure in the paste from the time of the first addition of water to the cement until it is completely cured. We can now present some data on the morphology of fresh pastes.

Pastes were mixed with a water-cement ratio of 0.4 by weight using a procedure previously described [4], except that the pastes were mixed at atmospheric pressure and poured into covered plastic containers for curing. The treatment of the paste after it was mixed depended upon whether samples were to be taken before setting or after setting occurred. Curing times after mixing ranged from 1 min to 2 months.

Samples to be taken before setting occurred were sealed in air-tight containers and at the prescribed time the hydration process was stopped by placing the container in a freezing mixture of dry ice and alcohol. The frozen sample was then transferred to a vacuum desiccator and the ice was sublimed. If samples were to be taken after setting occurred excess water was added before the container was closed. At the prescribed time the sample was crushed and then dried in the vacuum desiccator.

Specimens for the electron microscope were prepared by grinding the dried samples in a synthetic-sapphire mortar, with pestle, suspending the ground material in 1,1,1-trichloroethane and subjecting the suspension to ultrasonic vibration for two min. A drop of the suspension was then placed on a carbon-covered parlodion film supported by a copper grid. The liquid was evaporated in a current of air free of carbon dioxide and the specimen was transferred immediately to the microscope.

Pastes were prepared from two commercial cements, lot Nos. 15754 and 15669, the phase compositions of which (by X-ray diffraction analysis) are:

	Cement lot No.	
	15754	15669
Alite, %	53.1	29.6
Belite, %	25.9	56.0
C_3A, %	6.9	1.0
Ferrite, %	9.7	5.8
Ferrite A/F	1.44	1.22

A series of electron micrographs of pastes made from each of the two cements has been selected to illustrate the development of structure in the colloidal masses of the paste. The micrograph for each time of curing was selected to represent the major products of hydration, so for the most part the series does not give a complete representation of hydration processes. For example, for the purpose of this work the formation of well-crystallized phases was of little interest, so no effort was made to include their development in this series. These same pastes will be reexamined later for this latter purpose.

Figure 1a is a micrograph of unhydrated cement 15754, 1b is a micrograph of cement 15669. The magnification is the same as that of the hydrated pastes which follow. The particles have smooth edges and sharp corners, and show little evidence of surface hydration. Hydration of the cement starts immediately upon contact with water. Within 1 min after adding water to the cement, small plates develop on the surfaces of the particles, and within 6 min small rodlike particles appear as the small plates increase in number. Some of the plates are hexagonal, others appear square. We shall try to identify these plates by electron diffraction in the future.

After 14 min, the hydrated layer is thick enough to cover the surfaces of the original grains of cement 15754 with the small, almost square plates, figure 2a. The hydration of cement 15669 proceeds more slowly, the surfaces of the cement grains being partially covered with a product having the same appearance as that described above, figure 2b. Acicular crystals of gypsum are present—probably formed during the quick freezing of the paste in the sample preparation. These crystals have a characteristic form and are easily recognized. Their identity was established by their electron diffraction pattern. The hexagonal plates are larger than those observed in paste samples taken at shorter times.

After 1 hr the layer of hydration products on the grains of cement 15754 no longer appears to be composed of small plates, figure 3a. The form of the particles cannot be distinguished. The appearance of the grains of cement 15669 hydrated for one hour is about the same as in pastes hydrated only 14 min, figure 3b.

Figure 4a is an electronmicrograph of a paste of cement 15754 after 2 hr of hydration. During the second hour, clusters of acicular particles have developed, along with the platelike particles. Clusters of acicular particles that do not seem to be associated with grains of cement are present.

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[1] Figures in brackets indicate the literature references at the end of this paper.

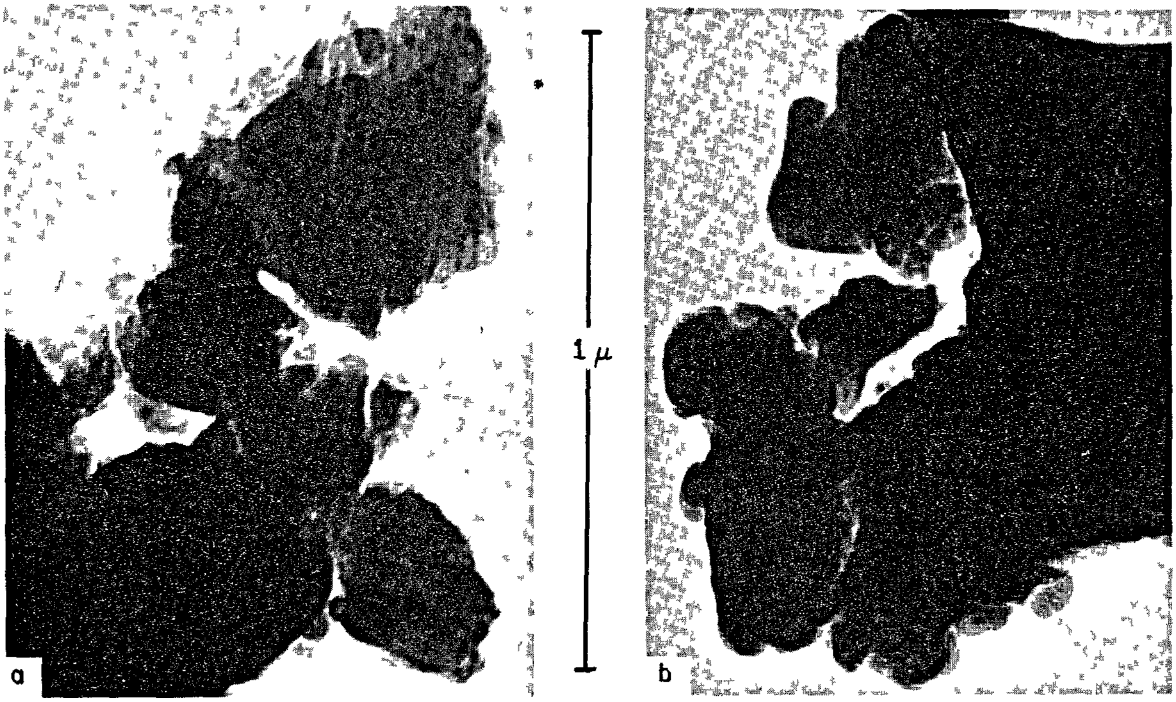

FIGURE 1. *Unhydrated cements*
(a) Cement No 15754, (b) Cement No 15669

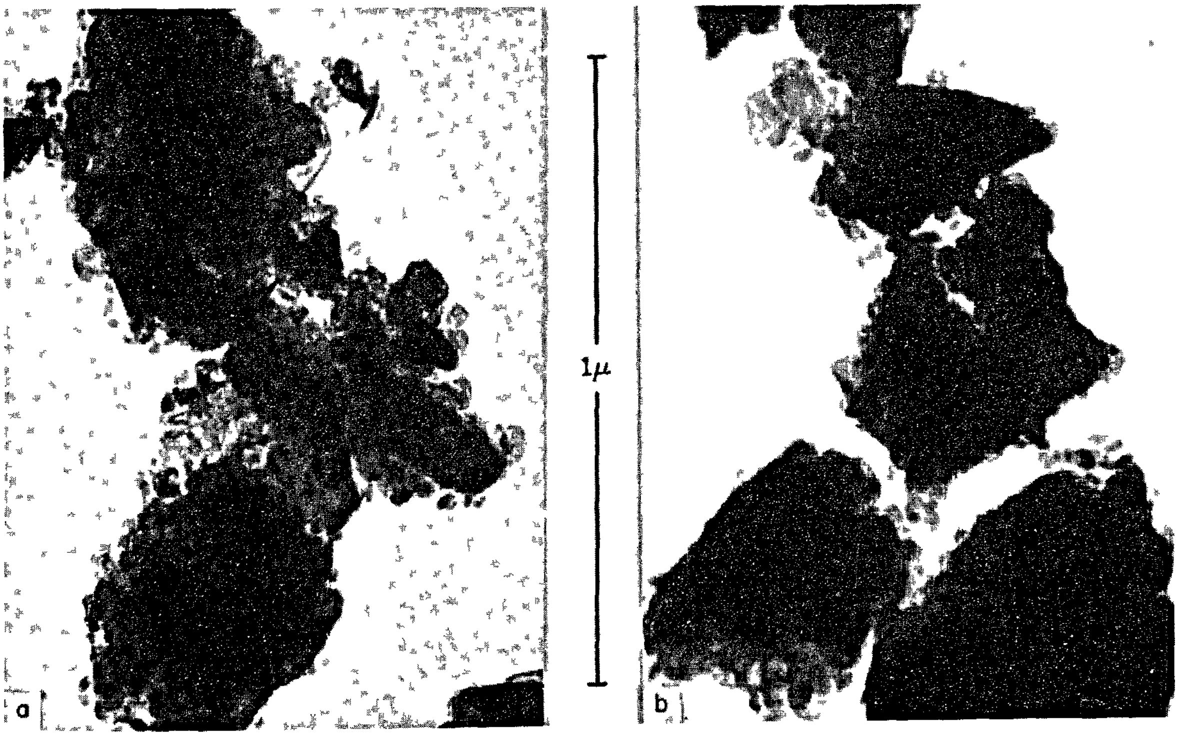

FIGURE 2. *Pastes hydrated 14 min.*
(a) Cement No 15754, (b) Cement No 15669

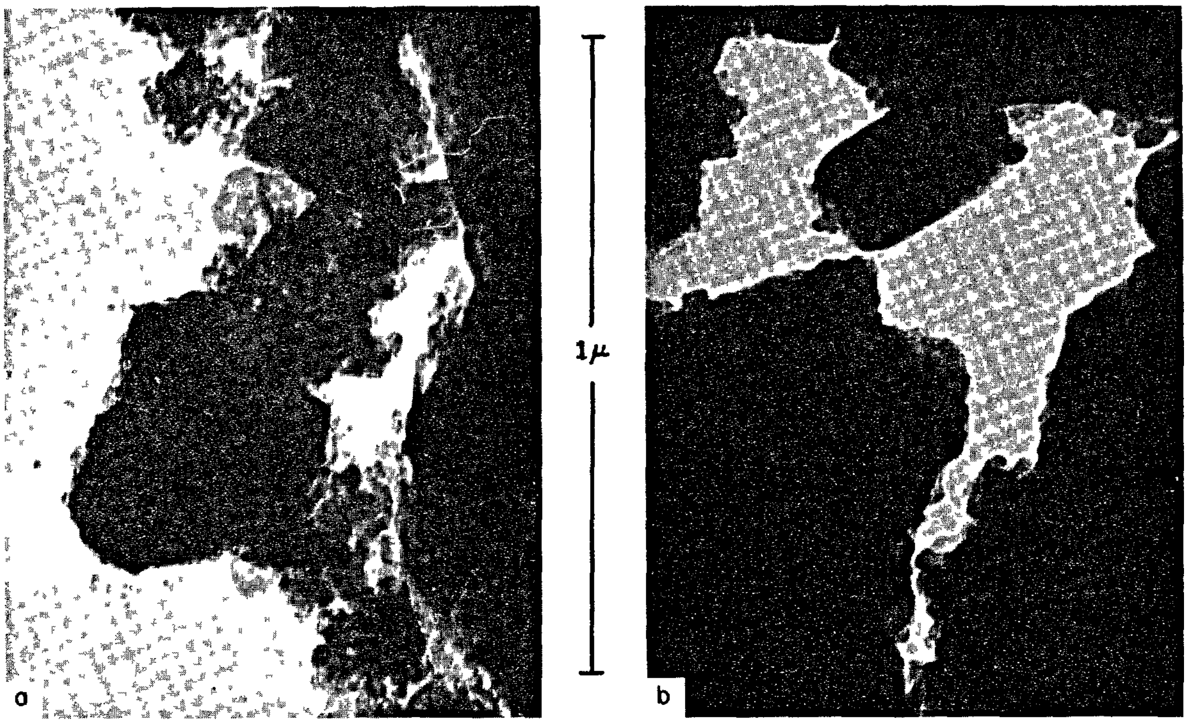

FIGURE 3. *Pastes hydrated 1 hr.*
(a) Cement No. 15754, (b) Cement No. 15669

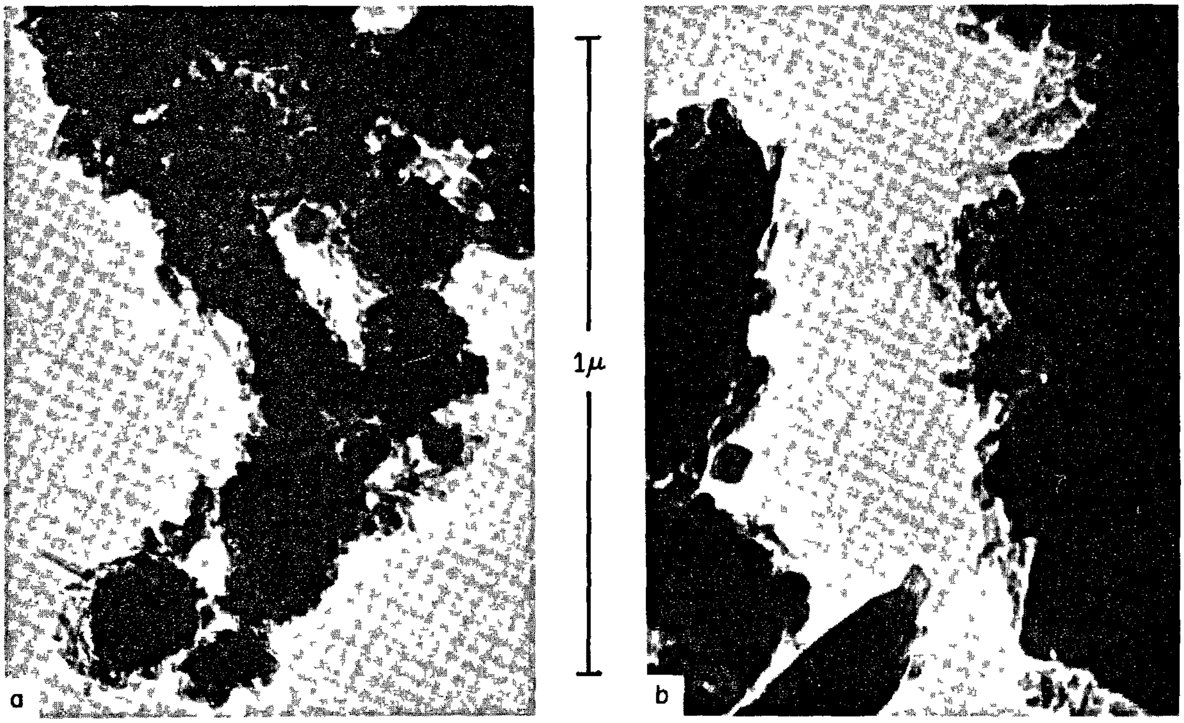

FIGURE 4. *Pastes hydrated 2 hr.*
(a) Cement No 15754, (b) Cement No. 15669.

These may have precipitated from solution, or may have started on very small grains that are now completely covered or completely hydrated. Alternatively these clusters may have been broken from larger clusters formed on grains of cement.

No acicular products are present in the paste of 15669 after 2 hr of hydration. The small platelets continue to form on the surfaces of the grains, and the hexagonal plates are larger than before.

After 4 hr, the clusters in pastes of cement 15754 have grown larger, but the shape of some of the particles seems to have changed, in that some of the particles do not have as sharp points as others; the blunt particles are shaped more like laths, figure 5a. In pastes of cement 15669 clusters of acicular-shaped particles have appeared, and look much like the acicular particles present in pastes of 15754 after 2 hr hydration, figure 5b. However, in addition to the acicular particles one occasionally sees a particle embedded in the acicular clusters that looks very much like the rolled foils or tubes that are found in pastes of β-C_2S and C_3S. These rolled foils do not appear in pastes of cement 15754.

Figure 6a, from a specimen of paste made from cement 15754, shows that after 6 hr hydration the clusters have become larger, but the individual particles seem also to be getting broader. Acicular particles, lathlike particles, and broader platelike particles can be seen in the same cluster. The texture of surface is the same in all these particles, and makes them appear to be aggregates of exceedingly fine fibers. Figure 6b shows a small aggregate or a particle from a paste of cement 15669 cured 6 hr. The mass seems to be a single star-shaped particle, identical in appearance with the product formed in the hydration of cement 15754.

After 16 hr hydration the clusters of acicular particles have disappeared completely from the hydration products of cement 15754; a typical field is shown in figure 7a. The irregular aggregates appear to be formed by flat, thin plates which can be seen at thin edges of the aggregates. The surface texture of these plates is the same as that of the particles seen at earlier ages. The paste of 15669 hydrated for 16 hr, figure 7b, still shows clusters, but many lathlike particles and flakes are now evident. The outlines of larger lathlike or rodlike particles imbedded in the clusters can also be seen.

After 24 hr hydration, pastes of cement 15754 cannot be dispersed sufficiently to show individual particles. The thin edges of the irregularly shaped aggregates that one can see seem to be composed of thin plates or flakes. The surfaces of these plates are striated as if they were fibrous. Figure 8a shows one such aggregate with a pronounced fibrous appearance. The thin foil on the upper edge of the aggregate appears to be a continuous sheet even though striations are seen on it too. This micrograph is slightly underfocus, and the diffraction line around the particle indicates that the edge of the sheet is smooth—that the striations are not separated individual fibers. The appearance of this sheet is very much like that of crepe paper.

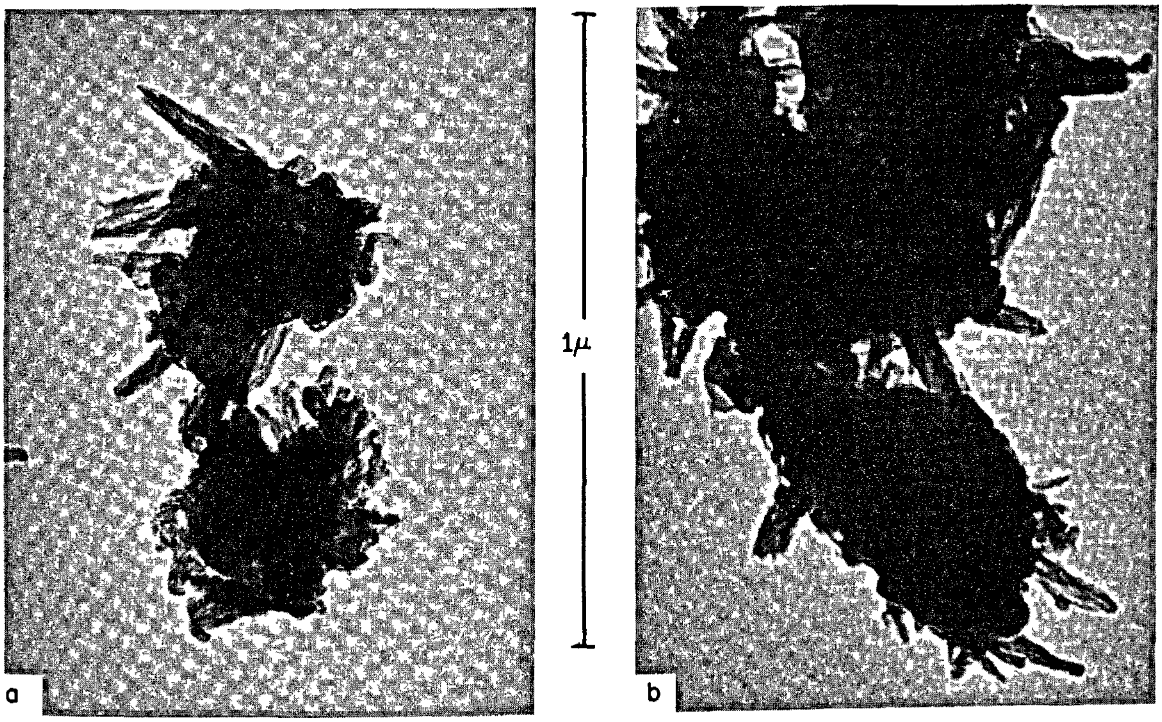

FIGURE 5. *Pastes hydrated 4 hr.*

(a) Cement No. 15754; (b) Cement No. 15669.

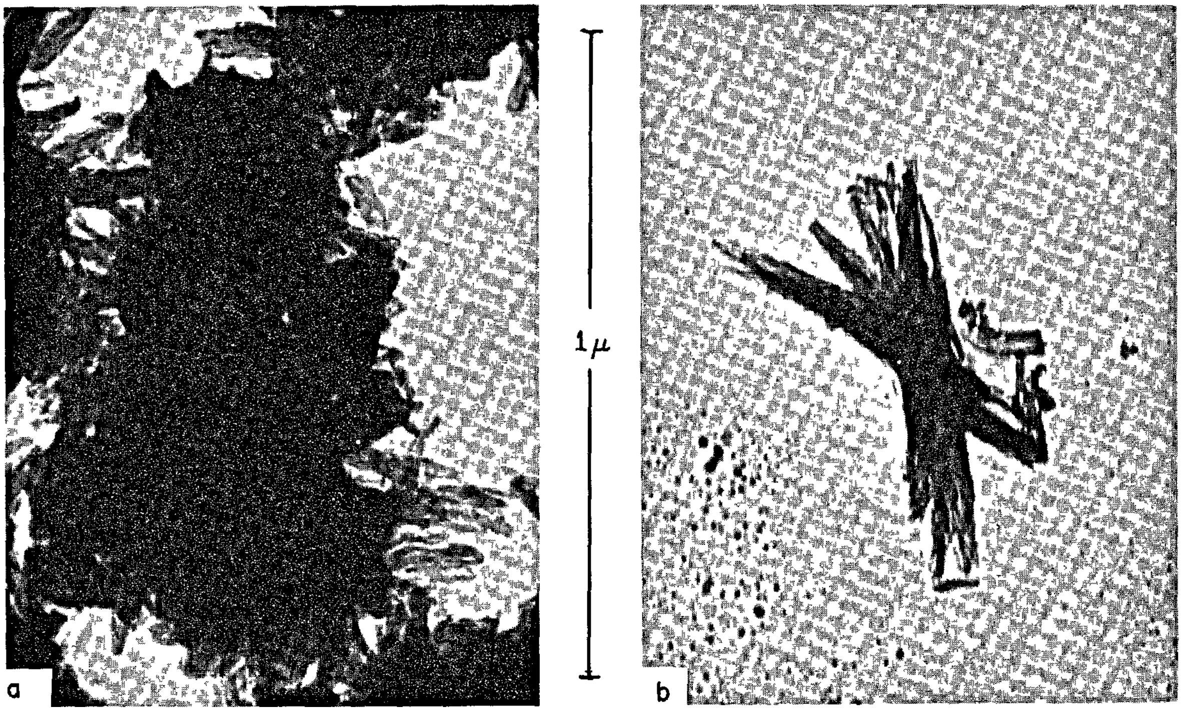

FIGURE 6. *Pastes hydrated 6 hr.*
(a) Cement No. 15754; (b) Cement No. 15669.

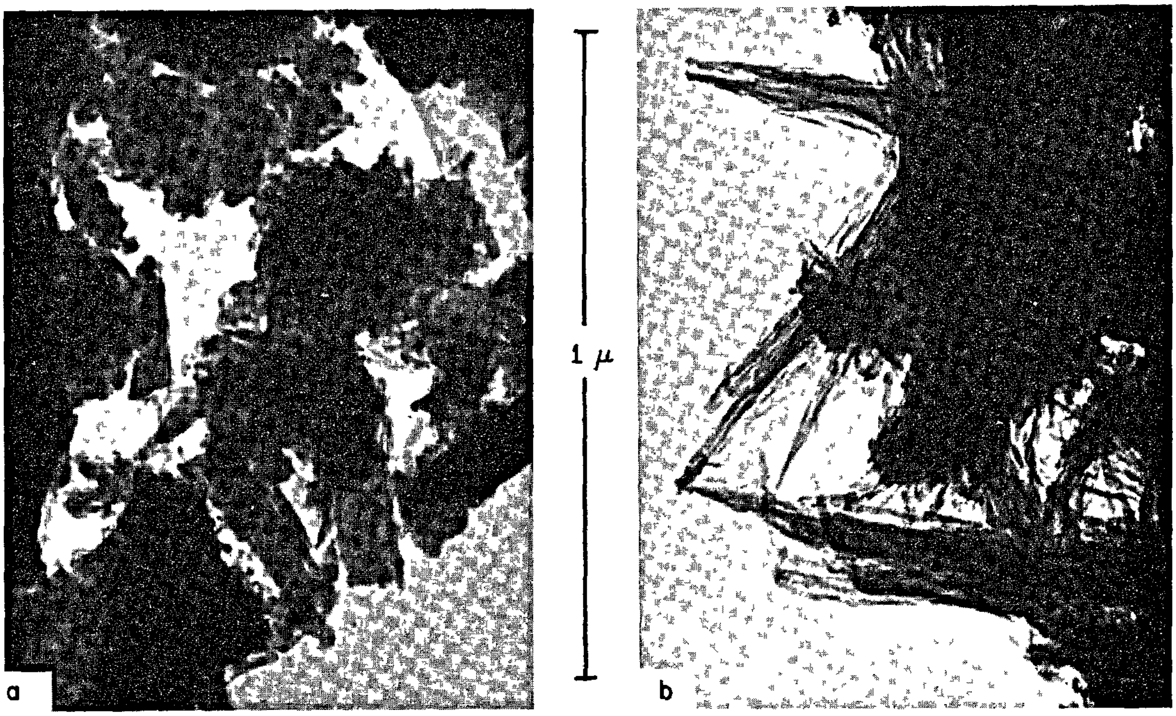

FIGURE 7. *Pastes hydrated 16 hr.*
(a) Cement No. 15754; (b) Cement No. 15669.

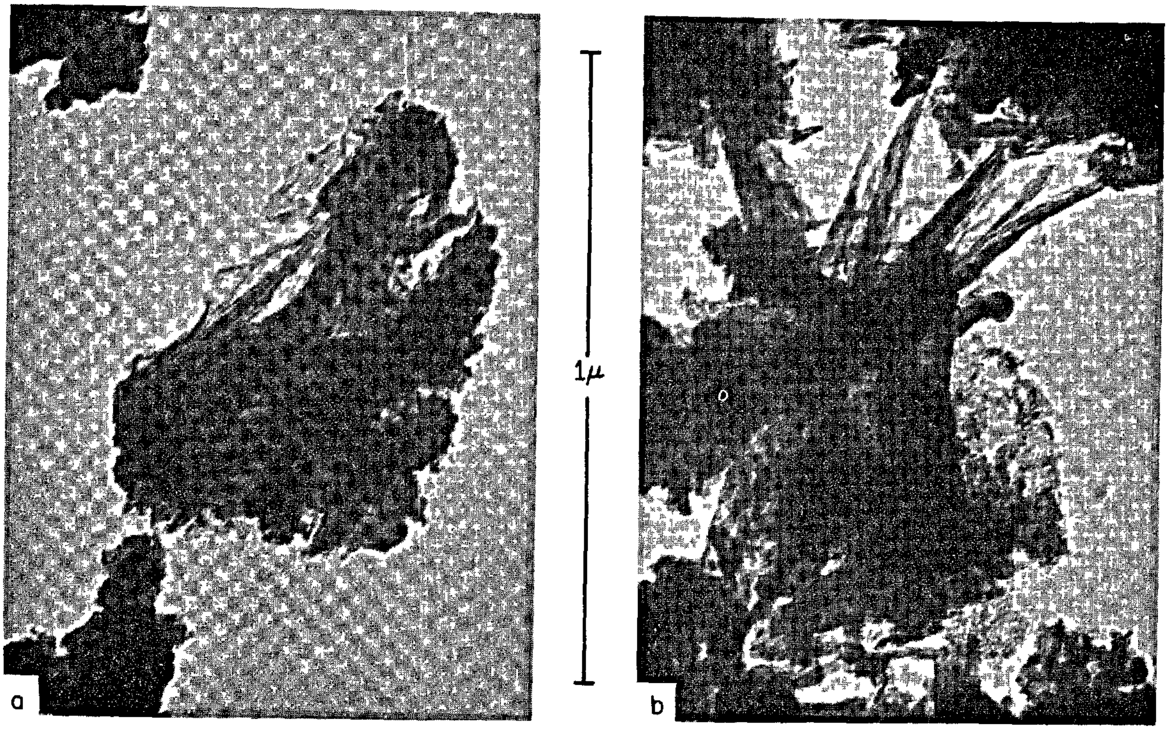

FIGURE 8. *Pastes hydrated 1 day.*

(a) Cement No. 15754; (b) Cement No. 15669.

The clusters of acicular and lathlike particles are still present in pastes of cement 15669 after 24 hr hydration. In the field shown, figure 8b, a cluster of acicular particles can be seen, in other fields particles similar to rolled sheets, so predominant in C_2S pastes, and sometimes thin sheets of flakes, can also be seen.

Figure 9a is a characteristic micrograph of a paste of cement 15754 hydrated for 2 days. The aggregates are too thick to show detail except at thin edges. Thin foils are visible with surface striations similar to those found in younger pastes. Occasionally one can find small thin, fragments like that appearing in this field. These have the same characteristic appearance of the hydration products seen in all these pastes.

The paste of cement 15669 after 2 days hydration is a mixture of rolled sheets or tubes and the irregular striated sheets seen in pastes of 15754. The particle at the right of the aggregate of particles shown in figure 9b has a thin sheet attached to it as if it were part of an outer layer of the roll that had been torn away. The surface texture of this sheet is similar to that of the striated sheets.

With longer curing times it becomes increasingly difficult to disperse the pastes sufficiently to see much detail in the structure. Pastes cured 7 days are shown in figure 10; figure 10a is a micrograph of paste from cement 15754, 10b that of a paste from 15669. Not much structure can seen be in 10a except that thin parts of the aggregate seem to be composed of sheets much like those seen in other micrographs. The striated sheets are more pronounced in 10b. A significant number of tubes or rolled sheets, were found in other fields.

No more details can be seen at 28 days hydration than can be seen in pastes hydrated several years. Figure 11a is a micrograph of a typical field from a paste of 15754. Thin regions of the aggregates appear very much like the product that can be seen in less well-hydrated pastes. Figure 11b is from a paste of 15669 cured 28 days The thin regions of aggregates again appear to be made of striated sheets. In other fields relatively large particles, shaped like rolled sheets seen in younger pastes, are embedded in the aggregates.

The effect of the difference in the rates of hydration of these two cements is evident in this work. The main characteristics of pastes of cement 15669 are about the same as those of pastes of cement 15754 at an earlier age. There is one important difference between the two sets: in pastes of cement 15669 many particles appear which are similar to those found in pastes of pure C_3S and β-C_2S, whereas these particles were not found in pastes made from cement 15754. It will be interesting to discover whether this difference is the result of the high belite content or low C_3A content of cement 15669.

The progress of hydration as seen in these micrographs suggests that the silicates in portland cement hydrate to form, at first, clusters of acicular particles. These clusters of acicular particles

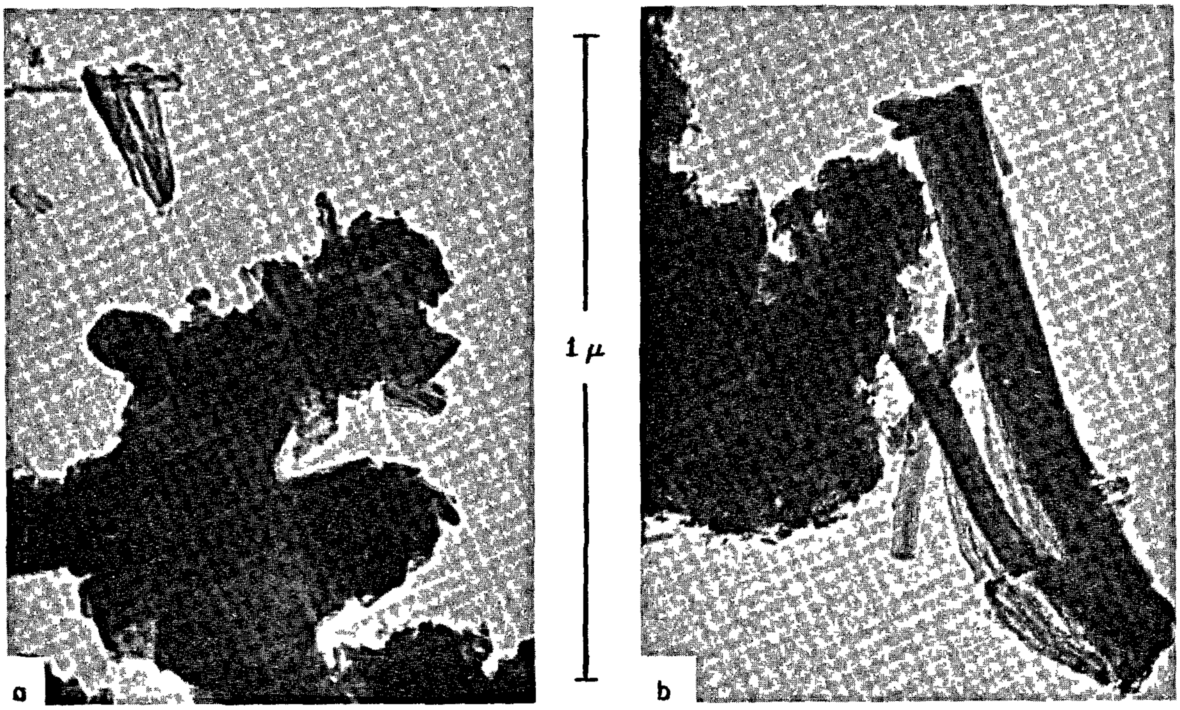

FIGURE 9. *Pastes hydrated 2 days.*
(a) Cement No. 15754; (b) Cement No. 15669.

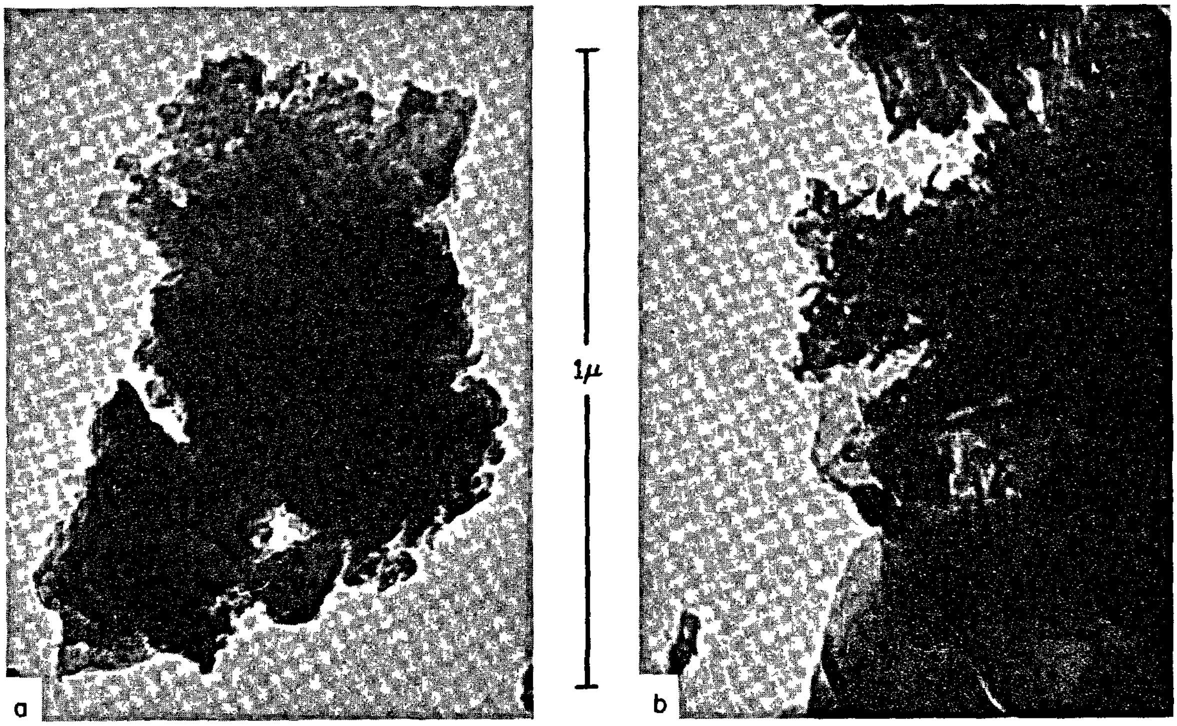

FIGURE 10. *Pastes hydrated 7 days.*
(a) Cement No. 15754; (b) Cement No. 15669.

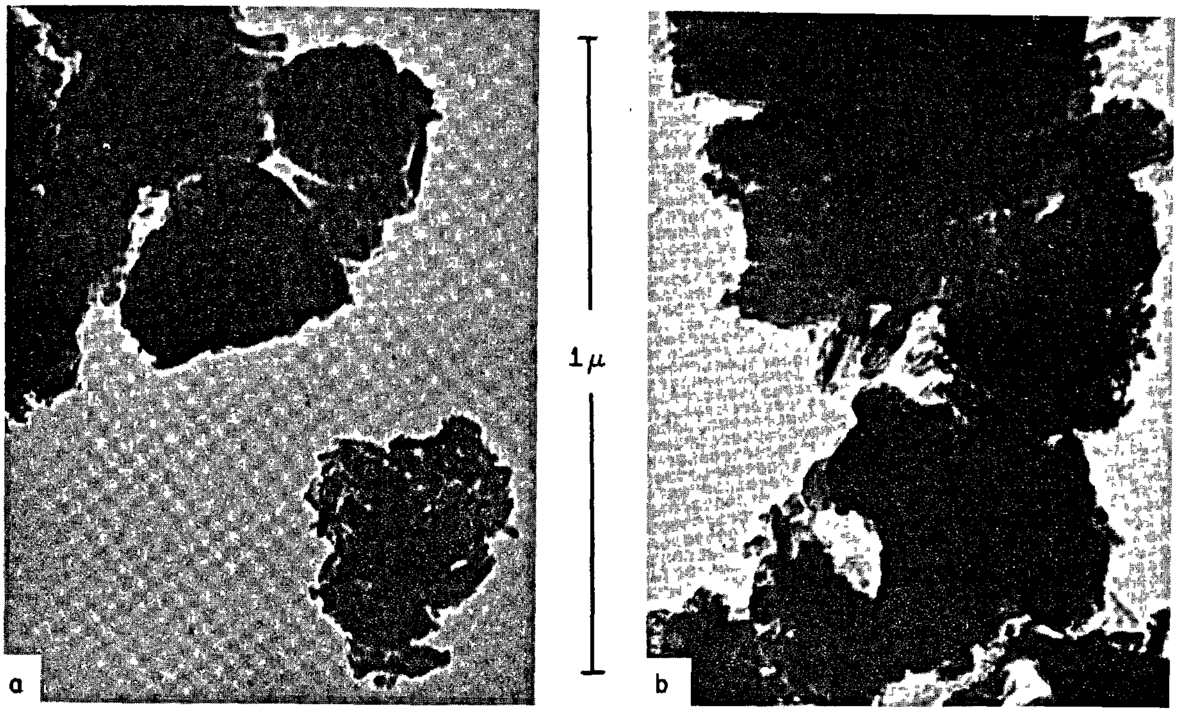

FIGURE 11. *Pastes hydrated 28 days.*

(a) Cement No. 15754; (b) Cement No. 15669.

are formed at about the time of the initial set of the paste. The clusters become larger and denser, and it seems logical to suppose that interlocking and growing together of the clusters of acicular particles causes final hardening. The absence of acicular particles and the presence of laths and sheets, or flakes, in the more hydrated pastes indicates that growth of the particle transverse to the axis of the needle formed initially must take place. The surface texture can be explained by strong orientation of the silica chains within the sheets.

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Discussion

Levi S. Brown

In discussion of the microstructure of hardened cement paste, there necessarily enters the particular concept of something happening in between the cement particles. The cement mix initially is a concentrated suspensoid of independent solid particles in water; shear resistance of the bulk mass is substantially zero. Within a time interval of minutes to hours the mass has become a single solid unit with very substantial shear resistance. The transformation results primarily from chemical reactions within the mass. It is known that the chemical reactions continue long after the arbitrary time defined as final set. It is known that cement still unhydrated is of common occurrence in good concretes after many years in service. In the light of these observations, the concept of something happening in between the grains becomes the central feature in investigations of the microstructure of hardened cement paste.

Being mechanical in nature, direct perception of the structure involves some sort of optical approach. The problem is especially elusive because (a) some 20 percent of the cement particles are individually in the size range of the wave length of light or below and (b) at the usable suspensoid concentrations the distances between the grains are of similar magnitude. Since this also is the limit of resolution by microscopy it follows that separate distinction of the fine particles, to say nothing of more specific identification, and the intervening spaces ranges into the impossible. The electron microscope of course notably extends the range, but at the disadvantage of interpretation of necessarily specialized subject preparation.

Cement particles actually are clinker particles. It is only in the size range of 5 to 7 μ and below that the particles tend to become monomineralic. Since 75 percent of the cement is above this size range, it follows that most of the cement particles, particularly the larger individuals, can be separately perceivable, as such, and further the clinker mineralogy recognized.

Observation of cement still unhydrated after many years in concrete of course means observation of the larger particles or, better, residuals of larger particles. The reason that these particles can persist for many years is, of course, in part because of their relatively large size. Far more importantly, however, it is because of very slow access of moisture. Significantly, such residuals are formed only in good concretes, that is, concretes that must be called good because of many years of satisfactory and unimpaired service in designed capacity.

In considering the microstructure of hardened cement paste, one may inquire as to the manner of long time hydration of these larger units. The question is easily subject to answer by direct visual microscopic observation of the initial and the altered material, by means of thin sections, powder mounts, or polished sections of the hardened cement paste or concrete. It is no trick at all to reveal the centers or cores of unhydrated clinker which, incidentally and by techniques well known, reveal also the clinker mineralogy. It is hardly more difficult to perceive in the altered material the initial boundary of the particle of clinker.

That is because the initial clinker structure is observed to be perfectly preserved. The initial structure, in brief, showed (a) angular crystals of C_3S and (b) nests of orbicular C_2S, together making up some 80 to 85 percent of the whole, enclosed within the (c) remaining 20 to 15 percent, which thereby is called "interstitial material", and which shows (d) itself to be made up usually of two components, one colorless (or dark, on polished sections) recognized as C_3A and one a dark brown (or bright, on polished sections) recognized as C_4AF. These, in some variation, are always perceivable. These initial minerals may be completely altered, yet these shapes, features, and mutual relations are seen to be perfectly preserved, and without evidence of mechanical distortion or volume change through the process of alteration.

The structure of the altered material is a perfect pseudomorph of the initial clinker. It is appropriate further to designate or to label the manner of alteration as pseudomorphous hydration. For this purpose, and for its significance, it is unnecessary to identify the secondary substances. That can be difficult. The best defined component is the interstitial material, which from location, isotropism, and refractive index can be identified as $C_3A{\cdot}6H_2O$ or, with Fe_2O_3, as a hydrogarnet. The pseudomorphs of former C_3S or C_2S are variable, for reasons or under conditions not known.

It is the size of these larger particles that clearly defines this pseudomorphous hydration. Once recognized as such, it is relatively easy to recognize the remains of progressively smaller particles, though with progressively lesser clarity and security.

This manner of hydration holds, for the writer, yet more structural significance. As noted earlier, the mass of fresh concrete in the form comes into existence as a competent structural unit through a complex sequence of chemical reactions. The usefulness of concrete as constructional material rests on the fact that this profound and pervasive chemical alteration occurs without significant changes in imposed external dimensions. It is indicated thereby that the alteration must be pseudomorphous. That is to say that, if the cement particles in the mix ever lost significantly their mechanical resistance or rigidity, the external boundaries of the mass could not be expected to remain fixed.

It is appropriate, in conclusion, to offer a thought relating this pseudomorphous hydration to the more common concept of cementitious bond by something happening between the grains. The fluid in the cement mix, the continuous phase, initially is water. The cement minerals are unstable in contact with water. Initially the range of disequilibrium is extreme. Discussion of hydration processes usually centers about reactions through this disequilibrium period, for that generally is the period of set, with interest primarily in what happens in between the grains. The liquid in time, and perhaps not too long a time, approaches an equilibrium composition. Though never in equilibrium with the unhydrated cement minerals, the manner of interaction may be expected to be different from that of the earlier period, and likewise to be affected by the progressively lesser availability of the liquid.

Closure

Åke Grudemo

It is clear that the microstructure of hardened paste is conditioned by the processes taking place in the chemical reaction between the different cement components and water. A number of observations certainly indicate a high degree of interaction between the products of hydration of the various minerals in cement; nevertheless, the development of structure in cement paste is closely related to similar phenomena taking place in the hydration of the pure components.

In my paper, therefore, I found it necessary to summarize what is known about the microstructures of a number of materials of interest in cement hydration, and to give the essential features of the cement hydration chemistry in general, especially in what regards the microstructural aspects of this subject. Such reviews have been given more ably and much more in detail earlier in the Symposium.

Also Mr. Powers, of course, in his unique representation of the physical properties of cement paste, has had occasion to deal with a number of problems connected with microstructure.

In view of this I will confine myself to touching upon a few specific points of interest. It was a pleasant surprise to find that a comparison of the data given and the opinions expressed on microstructural problems in the independently written review papers seems to show that, at least in a broad sense, all of them tend to converge to give one and the same reasonably well-resolved picture of paste structure and properties. There are discrepancies and disagreement on some points, but in such cases the need of further research is clearly indicated.

What is then, in general, the picture of the paste microstructure that has emerged, especially out of electron microscope studies? First, it must be stated that the hardened paste does not consist of an integrated mass of uniform composition, but is a composite material containing several ingredients, some of them well crystallized, others with severely restricted or deformed crystal lattices. Most particles or aggregates of particles in cement paste of ordinary water-cement ratios fall in the latter category. In other words, the structural elements are exceedingly small, most of them in the truly colloidal size range, and of ill-defined outer shape. The habit of thin plates predominates, but the tendency to fibrous growth is quite noticeable in most pastes, and seems to be promoted by a high water-cement ratio, by steamcuring at not too high temperatures, and by a high C_3S content in the cement.

The phase now described is generally recognized to be mainly a calcium silicate hydrate, of a C/S ratio somewhere between 1.5 and 2, and structurally related to tobermorite. This is clearly brought out in electron microscopy studies of C_3S and C_2S pastes, which are somewhat better crystallized, at least partly, than the C–S–H component of cement pastes. In the pure pastes, fibrous or needlelike particles are commonly found, which in electron diffraction diagrams show a series of diffuse spot patterns, of a modified single-crystal type, clearly identifying these particles as being structurally intermediate between a disorganized C–S–H gel, and well-crystallized tobermorite. Similar particles are seen occasionally also in ordinary cement pastes. In special cases of paste hydration, such as in high-porosity pastes with finely ground cement, there may be an extensive formation of well-crystallized fibers of tobermorite.

The generally lower degree of crystallinity of cement gel particles can probably be ascribed to structural disturbances caused by the incorporation of aluminum ions in the lattice, probably substituting for silicon in tetrahedral positions, as was shown by Kalousek, in the case of well-crystallized, platy tobermorite, where a diminution of crystal size was observed. In this connection we must also consider the phenomenon of increased fibrosity and more regular crystallization of tobermorite (G) observed in the vicinity of C–A–H plates of hexagonal crystal symmetry, slowly crystallizing out in pastes. The segregation of such particles may be associated with a transport of aluminum ions from the C–S–H gel phase to the C–A–H plates, causing the lattice disturbances in C–S–H to disappear. However, if such a process occurs, it is still only a local, diffusion-controlled reaction, and probably leaves most of the gel unaffected.

Similar slow processes of segregation may occur in hardened pastes in the case of the crystallization of large CH plates. It can be imagined that the material required is taken from the residue of amorphous material of composition CH, the existence of which has been evidenced in studies made by Brunauer and his coworkers. In any case, the hardened paste is a remarkably stable system, and the possibly occurring processes of recrystallization certainly proceed at a very slow speed, after the paste has reached a certain age.

Concerning the question of the lattice structure of tobermorite gel, and its modification with increasing C/S ratio up to 1.5 or 2, I would like to draw your attention to a number of conflicting ideas. Gard, Howison, and Taylor, as well as myself, describe the change taking place as probably caused by the gradual stripping off of metasilicate chains from the tobermorite layer, resulting ultimately in unsymmetrical 1:1 layer units instead of the symmetric 2:1 layers. Alternatively, Buckle and Taylor advanced the theory of the formation, in C_3S pastes, of an inhomogeneous C–S–H material, in which there is a short-range variation of structure between the extremes given by low-lime tobermorite, and calcium hydroxide. Kurczyk and Schwiete give a model of high-lime tobermorite consisting of low-lime tobermorite layers alternating with complete layers of CH, of distorted or disorganized structures. Brunauer and Greenberg, finally, conclude from certain rate-of-solution experiments, that the incorporation of excessive amounts of lime in the tobermorite gel structure is accompanied by a gradual breaking up and depolymerization of the metasilicate chains. They arrive at a silicate chain model resembling the one given by Bernal at the London Symposium, in which an important feature is the presence of hydrogen bonds connecting silica groups in the direction of the chain. Clearly, the question of the tobermorite gel structure cannot be solved without much further work.

In this connection, I would like to point out another interesting observation made by Gard, Howison, and Taylor. They noticed that unimolecular layers of well-crystallized tobermorite sometimes overlap, not with their fiber axes in parallel, but rotated at approximately hexagonal angles to each other. Such a process of overlapping might account for the appearance, in less well-crystallized tobemorite gels, of particles of the habit of small plates, rather than fibrous or needlelike crystals.

The ultimate paste structure is obviously conditioned by the prehistory of the material, that is, the course of development of the microstructure during the early period of cement hydration, in which a number of processes involving rearrangement of the structural elements proceed simultaneously at comparatively high rates of speed. There are many indications, among others some derived from electron microscope studies of cement slurries, that the development of the hydrated phases is not a straightforward process, as perhaps the continuously and uniformly increasing stiffness and strength of the cement paste might indicate. Transient phases may develop, only to disappear at later stages. The balance in the solution phase between the amounts of the more easily hydratable compounds of cement clinker, together with the effects of sulfate and other admixtures, are obviously decisive factors in the development of microstructures in setting pastes. However, the relationships involved here have not yet been studied in a very systematic way with respect to microstructure, but remain as very important problems for future research.

A valuable contribution to our knowledge of the internal microstructure at different early stages of paste hydration was presented by Dr. Copeland and Mrs. Schulz. Some observations that I have made recently on similar materials are in very good agreement with those made by Copeland and Schulz. It also seems to me that in future work on the development of colloidal hydrate structures, attempts should be made to correlate data on microstructure with the observed rheological properties of different pastes, as described in the paper by Dr. Ish-Shalom and Dr. Greenberg.

It can be stated, as a conclusion, that in applying our knowledge of paste structure in the study of the mechanical properties of cement paste, we must concern ourselves with the formation and spatial distribution of different types of bonds between the surfaces of gel particles. To the experimenting chemist, at least, it seems to be an extremely difficult problem to treat theoretically the relationship between bond formation in a colloidal system of particles, and the mechanical behavior of construction elements.

Paper V-3. Volume Changes of Concrete*

Robert G. L'Hermite

Synopsis

The purpose of the present report is to give an up-to-date account of the present state of knowledge on the deformation of concrete.

The following phenomena have been examined: hygrometric, thermal, chemical, and dynamic phenomena (*action of forces*) *in relation to the nature of cement, of aggregates,* and the composition of the concrete.

A certain number of questions remain unanswered, in connection with which certain hypotheses have been put forward:

Is the internal mechanism of shrinkage a hydroconstrictive phenomenon due to an equilibrium between the liquid phase and the vapor phase, or does it arise from the crystalline phase in the form of physically bound layers of water?

Does creep continue indefinitely though at a continuously reduced rate or is creep a *phenomenon of limited amplitude?*

Are creep and shrinkage two aspects of a single phenomenon or are they two distinct phenomena linked by correlation?

What is the explanation of creep on the scale of the structure?

Is the phenomenon of the resumption of creep in water after a pseudostabilization under dry conditions linked to the movement of the water or to the resumption of hydration of the cement?

The report has appended to it a specially prepared bibliography containing 230 references.

Résumé

Ce rapport constitue un document de mise à jour quant aux connaissances actuelles sur la déformation du béton.

Ont été évoqués les phénomènes suivants : hygrométriques, thermiques, chimiques et dynamiques (action des forces) en relation avec la nature du ciment, celle des agrégats et la composition du béton.

Un certain nombre de questions restent posées à propos desquelles ont été émises certaines hypothèses :

Le mécanisme interne du retrait est-il un phénomène hydro-constrictif dû à un équilibre entre la phase liquide et la phase vapeur ou prend-il son siège dans la phase cristalline sous forme de couches d'eau liées physiquement?

Le fluage se poursuit-il indéfiniment quoiqu'à vitesse continuellement réduite ou le fluage est-il un phénomène d'amplitude limitée?

Le fluage et le retrait sont-ils deux aspects d'un même phénomène ou sont-ils deux phénomènes distincts liés par corrélation?

Quelle est l'explication du fluage à l'échelle de la structure?

Le phénomène de reprise du fluage à l'eau après une pseudo-stabilisation à sec est-il lié au mouvement de l'eau ou à la reprise de l'hydratation du ciment?

Le rapport est suivi d'une bibliographie spécialement réunie et qui contient 230 références.

Zusammenfassung

Dieses Referat gibt den heutigen Standpunkt der Kenntnisse was die Verformung des Betons-anbetrifft.

Die folgenden Vorgänge wurden behandelt : Feuchtigkeitsgehalt, thermisches, chemisches und dynamisches Verhalten (Wirkung der verschiedenen Kräften) in Verbindung mit der Beschaffenheit des Betons.

Eine gewisse Anzahl Fragen stehen noch offen und folgende Vermutungen wurden angestellt:

Ist der innere Vorgang des Schwindens eine wasser-zusammenziehende Erscheinung abhängig von dem Gleichgewicht der Wasser- und der Dampfphase oder befindet sich der Sitz dieses Vorganges in der Kristallphase in der Form von physikalisch gebundenen Wasserschichten?

Ist das Kriechen ein zeitlich unbegränzter Vorgang obwohl mit beständig verminderter Geschwindigkeit oder ist das Kriechen eine begränzte Grösse?

Sind Kriechen und Schwinden die beiden Erscheinungen eines selben Vorganges oder sind diese beiden Vorgänge verschieden und in Wechselbeziehung stehend?

Welches ist die Erklärung des Kriechen was die Struktur anbetrifft?

Hängt das Wiedereinsetzen des Kriechen unter Einfluss von Wasser nach einer pseudo-Stabilisierung unter trockenen Verhältnisse mit der Wasserbewegung zusammen oder mit der, wieder in Gang tretender Wasseraufnahme des Zements?

Dem Referat folgt eine speziell zusammengestellte Bibliographie mit 230 Referenzen.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from Laboratories du Bâtiment et des Travaux Publics, Paris, France. (This paper was presented at the Symposium by H. Woods).

Introduction

Variations in the volume of concrete may be due to a variety of factors: hygrometric, produced by a variation in water content; thermal, produced by temperature changes; chemical, produced by variations in structure; dynamic, produced by applied loads.

In general, the effects to which these factors give rise are not cumulative or commutative, yet while they may be studied separately, their combinations have a complex aspect that is as yet little known.

In a necessarily limited account it is not possible to enter deeply into details, and we shall do no more than examine the state of present knowledge, attempt to make a synthesis, and indicate the areas still to be explored. A broad bibliography will enable readers to discover the elements requiring further study.

Thermohygrometric Variations in the Volume of Young Concrete (First Shrinkage)

The setting and hardening of a hydraulic binder is accompanied by a variation in its apparent volume. When a pure cement paste is cured from the time of its mixing in an excess of water in the form of a de-aired slurry, the whole undergoes a contraction in absolute volume. This phenomenon has been brought out by Le Châtelier who has shown that the volume of hydrates is always less than the sum of the absolute volumes of the anhydrous components and the water. At 7 days this contraction is of the order of 12 percent of the volume of anhydrous portland cement [1, 2][1]. It is higher for aluminous cement. While the absolute volume diminishes, however, the apparent volume of the paste cured in the presence of an excess of water increases in a continuous manner. During the first hours this swelling is augmented by a thermal dilatation due to the release of heat produced by the chemical reaction of setting.

In air, cement and concrete begin to show a shrinkage before setting begins. Since the binder does not yet have any other than a capillary cohesion, this shrinkage can give rise to cracks. Several optical methods have been used to make such measurements [3, 4]. The results of tests show that during the first hours shrinkage depends on the conditions affecting evaporation of the mix water: humidity, temperature, rate of flow of air, absolute volume of test piece. Rapid shrinkage generally manifests itself between 1 and 2 hr, often preceded by a slight swelling. After 6 to 10 hr, it slows down to assume the habitual course of hardened cement.

On slabs of pure cement paste 2 cm thick the influence of the speed of ventilation of air at 50 percent relative humidity, temperature 20 °C, gave the following shrinkage results for a portland cement, after 8 hr: without forced ventilation, $1{,}700\times10^{-6}$; ventilation at 0.6 m/s, $6{,}000\times10^{-6}$; ventilation at 1 m/s, $7{,}300\times10^{-6}$. R. Dutron's tests confirm these results and indicate a shrinkage of $14{,}000\times10^{-6}$ for ventilation speeds of 7 to 8 m/sec of air at 20 °C. For air at 100 °C he obtained figures of the order of $19{,}000\times10^{-6}$ [5]. A 7-cm layer of pure paste without forced ventilation gave at the same time 850×10^{-6}. These figures, which differ by an order of magnitude, show the importance of ventilation.

The nature of the cement is of importance, since with a speed of aeration of 1 m/sec, blast-furnace cement gives $4{,}100\times10^{-6}$, portland cement $7{,}300\times10^{-6}$ supersulfated cement $10{,}000\times10^{-6}$.

The shrinkage of concrete at an early age is less than that of pure paste. Figure 1 shows the appearance of the shrinkage curves and indicates that shrinkage is increased with the proportioning, Rilem-Cembureau mortar having a cement content halfway between mortar and pure paste.

For a series of concretes, the first shrinkage varied between 800×10^{-6} with a content of 200 kg/m^3, $1{,}600\times10^{-6}$ with a content of 350 kg/m^3, and $2{,}300\times10^{-6}$ with a content of 500 kg/m^3. The quantity of mix water has an influence on concretes, shrinkage at an early age increases with the water/cement ratio, passes through a maximum, and then diminishes.

For a concrete proportioned at 350 kg/m^3, the following results were obtained:

w/c	0.45	0.50	0.55	0.60
shrinkage$\times10^6$	1,000	1,550	1,600	1,350

The influence of plasticizers is marked, the addition of these having the effect of increasing the initial shrinkage.

The initial shrinkage can be explained only in part by the loss of water. A shrinkage is in fact equally to be observed in the absence of any evaporation, which appears to be due to a settling by gravity and the action of capillary forces [6, 7]. In any case, the first cause is dominant and, by the time the surface becomes dry, the loss in volume is of the order of magnitude of the loss of water up to the time when the grains enter into contact and a structure is established; then the law of shrinkage assumes a different form. It is observed that the bleeding of the water in part opposes the first shrinkage by producing a wet surface which prevents internal evaporation.

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[1] Figures in brackets indicate the literature references at the end of this paper.

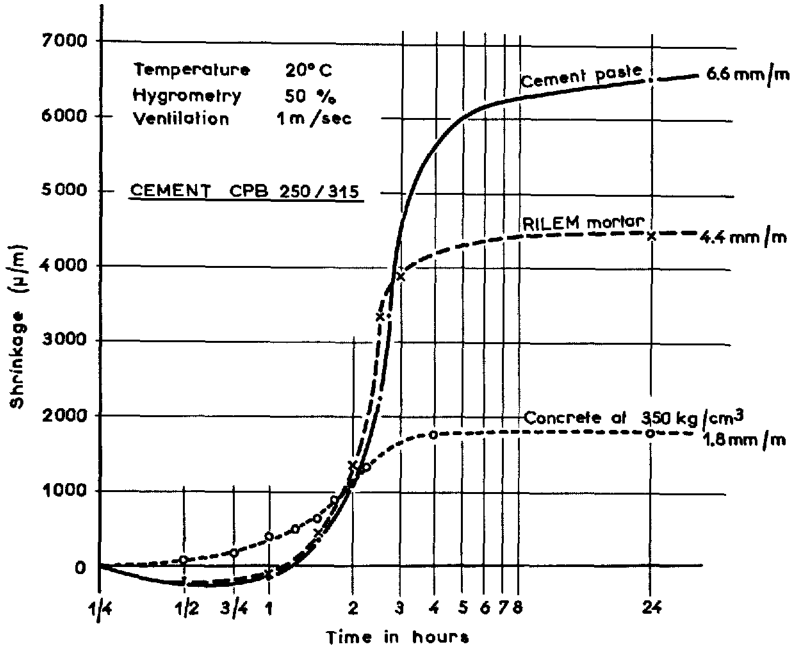


FIGURE 1. *Shrinkage from 0 to 24 hr after placing.*

This first shrinkage can have awkward consequences for building, for the decrease in dimensions contrasts with a reaction of the adjoining parts composed either of the parts of the volume having lost less water, or by the support. There may result cracks on the surface or in depth [8]. A familiar illustration is the cracking of the pavement · of concrete roads, the cracking of plaster, etc. The behavior of cements, however, is as we have seen rather different, depending on their nature, that of concretes or mortars depending on their proportions, their water/cement ratio, and the addition of products like plasticizers. This is why cracking tests have been devised. One of these consists in applying a 2-cm coating to the surface of a concrete beam, and ventilating it at a speed of 1 m/sec with air at 50 percent relative humidity. The mortar having 1:1 portland cement cracks after 20 min, 1:2 mortar cracks after 1 hr 10 min, and 1:2.5 mortar does not crack. The adding of a plasticizer accelerates the cracking, but the corresponding risk appears only in the first hours; after setting this risk diminishes. For concrete, the test consists in grinding a flat test piece held in place at its broadened ends in fixed heads. The first cracking can be counteracted by preventing or slowing down the evaporation of the water either by protective membranes (curing compounds), or by artificially keeping the surfaces moist [9, 10].

Thermohygrometric Variations in the Volume of Concrete in the Course of Hardening

This dimensional variation is usually called shrinkage. It constitutes a different phenomenon from that dealt with in the preceding paragraph in that it applies to a material that is solid, even though porous, having a structure that is continuous while it is at the same time in evolution.

We may note that the term shrinkage generally includes swelling due to physical and chemical causes independent of the hydroconstrictive movement. We shall therefore speak first of this phenomenon.

Hygrometric Swelling of Cements and Concretes

A cement cured uninterruptedly in water from the time of its molding swells. The initial measurement being made at 24 hr after mixing, this swelling continues at a reduced rate. For a portland cement paste we found, for example, the following linear elongations [7]: at 100 days, $1{,}300\times10^{-6}$; at 1,000 days, $2{,}000\times10^{-6}$; and at 2,000 days, $2{,}200\times10^{-6}$.

Generally speaking, cements of this kind have at 3 yr a linear swelling of from 0.6 to 1.5 percent. According to Dutron [11] the quantity is thus quite variable. An increase in weight accompanies the swelling which occurs with an absorption of water greater than that which would correspond to the increase in volume. This result therefore means that there is in fact contraction in the liquid-solid combination at the same time as an increase in the apparent volume. The increase in weight after curing in distilled water, for portland cements, is between 3 and 5 percent, from 1 to 1,000 days, which would correspond to an increase in voids of 8 to 10 percent of the volume of the sample, 12 to 16 percent of the volume of the anhydrous cement; this figure corresponds to that given by Le Châtelier's method. It thus seems that swelling is indeed a phenomenon of chemical origin that accompanies hardening.

The swelling of concrete in water is much less than that of a neat paste. For a concrete proportioned at 300 kg/m^3 the linear expansion at 1,000 days is 100 to 120×10^{-6}, with an increase in weight of 1 percent at 1,000 days. The mortars have an expansion of 150 to 300×10^{-6} for a cement content of 500 kg/m^3. Dutron [11] has studied the influence of the nature of the cement and demonstrated a greater expansion of aluminous cement and a lesser expansion of slag cement (at 275 days): aluminous cement, 300×10^{-6}; rapid-hardening portland, 240×10^{-6}; ordinary portland, 230×10^{-6}; slag cement, 160×10^{-6}. Mixes of slag and portland cements, however, may give an expansion greater than that of portland cement alone. These differences are greatly reduced in the case of concretes. The law of swelling in terms of time is difficult to define precisely. At the outset it often appears to have the form $\Delta = Q \log t$ where Δ is the linear expansion, t the time, and Q a constant. It should not be deduced from this equation, however, that cement swells indefinitely, but if there is a limit, Δ_m, the latter cannot be derived from tests even extended over several years. Tests of paste carried out over 6 yr have not reached a stable value, the annual variations being of the order of magnitude of the experimental errors. For concrete, moreover, the swelling phenomenon stabilizes much more rapidly than for neat cement paste. It practically stops between 6 months and 1 yr, although the increase in weight appears to persist over a longer period. It is to be noted that at the beginning of hardening a shrinkage under water may be observed [11], but this varies with the dimensions of the test piece, the proportions, and the grain size. It is very visible on neat pastes, attenuated on mortars, and disappears for concretes except in the case of aluminous cements. The shrinkage appears to be due to the internal desiccation brought about by such rapid hydration that the supply of outside water cannot compensate because of the impermeability of the mix. Attempts made on very fine sheets of cement appear to tend to make this phenomenon disappear, and it might be considered to be an "effect of volume".

Chemical Expansion of Cements and Concretes

Although the hygrometric swelling may be explained as having a chemical origin, it is possible to separate the factors due to the normal hydration from those due to another influence either in the composition itself of the curing water or in that of the product itself aside from its fundamental components, the silicates and aluminates. The swelling of ordinary portland cement after about 2 yr is three times greater in sea water than in distilled water. A portland slag cement swells three times less than a portland in a 5 percent magnesium sulfate solution.

Is such swelling bound to lead to disaggregation? Not if it becomes stabilized below a limit within which the mechanical properties are not affected. It is possible to know this fact through the measurement of vibratory modulus of elasticity which shows a diminution at the beginning of disaggregation.

It seems that disaggregation is due to a discontinuous swelling in the volume on a microscopic or macroscopic scale. The former case is, for example, one in which the surface swells much more than the interior; it is subjected to considerable compression and disaggregation through flaking. The latter case is brought about when there are nuclei of expansion within the volume, discontinuous and distributed microscopic nuclei. Such is the case where there is free lime and also where there is an attack by lime sulfate. There is a combination of this salt with the lime aluminate in the cement and a formation of sulfoaluminate. If the sulfate combines with the aluminate without previous dissolution of the latter, swelling results, and regular clefts are formed in the mortar [2] due to the presence of expansion nuclei.

A thoroughgoing study of swelling in terms of composition has been made by R. H. Bogue [12] who draws a number of conclusions, including the following: expansion increases with the free lime content, the effect of which is especially appreciable between one month and three months; and it increases with the magnesia content, but the effect is much slower. The presence of magnesia makes cements more sensitive to the action of sulfates [13]. Goggi [14] indicates that expansion increases with the content of aluminate in the crystalline form.

Another highly important contribution is that of L. Blondiau [15] who used mainly the autoclave test advocated by the A.S.T.M. for accelerating the phenomenon, and, like R. H. Bogue, he deduces therefrom a justification for this method. He indicates in particular that the addition of pozzolanic materials to the slag markedly diminishes the swelling.

The boiling-water test long advocated by Le Châtelier has the advantage of bringing out very rapidly the presence of free lime and free magnesia, provided the treatment is prolonged for at least 5 hours.

Finally an expansion may be produced by the reaction between the cement and the aggregates. We merely call attention to it here for it is dealt with elsewhere in this symposium (N. Plum et al.). It may likewise be due to mixes of cements reacting chemically [16]. A mix of portland cement and aluminous cement gives, for 30 percent of the former and 70 percent of the latter, a swelling in water at the end of a year three times the average of those of the two components.

Thermal Dilation of the Concrete

Thermal dilation is generally expressed in the form of a coefficient of expansion. In the case of concrete, this coefficient is a function of numerous factors such as composition, age, water content, temperature, etc.

Tests on neat paste [17] show a very marked influence of the curing hygrometry preceding the test according to the age of the concrete at the moment when it is carried out. At 20 days for example the coefficient in microns per meter and per degree, $\frac{\Delta l}{lt}\times 10^6$, increases from 14 for a humidity of 35 percent, to 22 for a humidity of 50, and drops back to 12 for a humidity of 100 percent. At 200 days, the corresponding figures are 14, 15, and 10. The matured cements thus have a lower coefficient of expansion than cements cured in humidities between 50 and 75 percent which at every age present a maximum that appears, moreover, to diminish with time. In any case, if the coefficient of expansion diminishes with age, it is always lower for curing in water than in air.

The coefficient of expansion is not independent of temperature, the average coefficient measured between 60° and 20° (return) is always less than that which is measured between 45° and 60° (outward); the dilation-temperature curves for outgoing and for return cannot be superposed except for a cement cured in water for a very long time. This phenomenon is probably due to the factor of physico-chemical transformations stimulated by the increase in temperature. For a normal portland cement, the extremes are a coefficient of 26×10^{-6} at the age of 20 days (between 45 and 60 °C) for a previous curing at 50 percent humidity and a coefficient of 10×10^{-6} at the age of 200 days and beyond for a previous curing in water. For a portland cement having a high initial strength, the maximum coefficient of 39×10^{-6} occurs between 45 and 60 °C at about 40 days for curing at 50 percent humidity; for a slag cement it is 25×10^{-6} at approximately the same age under the same conditions. The coefficient of expansion after long maturing in water is in both cases between 10 and 13×10^{-6}.

It is interesting to note that the average coefficient of expansion on the return between 60 and 20 °C of a paste aged 200 days varies with the quantity of water included, which depends on the previous state of curing. Figure 2 relative to a portland cement shows an increase with the water content followed by a decrease. This phenomenon has been observed by various authors, including D Bonnel and F. C. Harper [18] who in addition note that the desiccation of a concrete previously cured in water increases its coefficient of expansion and that the modulus of dilation of a saturated concrete is independent of its previous states of curing. It is therefore clear that the phenomenon is reversible and does not depend on the solid structure but solely on the presence of water. There is probably an interference between dilation and the phenomena giving rise to the hygrometric movement. It can be imagined that the diminution of the surface tension of the water with the temperature diminishes the shrinkage pressure [19] or that the increase of the vapor pressure of the water in the voids with the temperature produces a swelling pressure. These phenomena cannot occur in a saturated medium nor in the absence of free water. There must therefore be a maximum of swelling for an intermediate value (70 percent according to S. L. Meyers [20]). But this hygrometric swelling does not constitute a state of equilibrium and must disappear through the balancing of the water with its vapor at the same temperature. If we assume a swelling pressure given by Kelvin's expression $f=A\log\theta$, where θ is the relative humidity, the variation in pressure corresponding to a variation in temperature dt is:

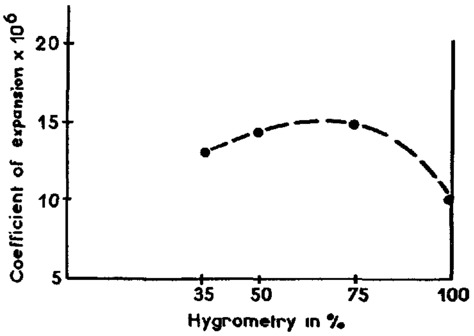


FIGURE 2. *Coefficient of expansion of a portland cement paste in relation to water content.*

$$\frac{df}{dt}=\frac{A}{\theta}\frac{d\theta}{dt}.$$

Now $\frac{d\theta}{dt}$ is nil for $\theta=1$ and nil for $\theta=\theta_l$, a humidity of equilibrium below which there is no longer any free water. We can write an approximate but simple function:

$$\frac{d\theta}{dt}\approx Q(1-\theta)(\theta-\theta_l).$$

Moreover, the swelling Δ must be proportional to the product of the swelling pressure by the quantity of water under pressure, $\frac{d\Delta}{dt}=s\theta E_0\frac{df}{dt}$ where E_0 is the water contained for $\theta=1$. Finally the expression of the instantaneous thermohygrometric swelling coefficient has the form:

$$\frac{d\Delta}{dt}=Q(1-\theta)(\theta-\theta_l)$$

which passes through a maximum for $\theta=\frac{1+\theta_l}{2}$.

If θ_l, the limit humidity of the free water, is 0.40, we find the maximum for $\theta=0.70$, which corresponds approximately to the tests and shows in any case that the reasoning is plausible.

Powers [21] finds an equally plausible explanation in saying that there is a capillary water and a water fixed in the gel that is constituted by the hydrated phase, the entropy of the capillary water and that of the gel being different. When the equilibrium is established, a change in temperature destroys this equilibrium and requires a transfer of water between the two phases. The delay in this transfer between the gel and the capillary water determines an additional dilation that disappears after reestablishment of the equilibrium. The same author indicates that cements autoclaved under steam pressure have a coefficient of expansion independent of the degree of humidity, which would be due to the replacement of the gel by a crystalline phase.

The coefficient of expansion of concrete depends on that of the aggregates. The variations in terms of age and of the curing medium are reduced in comparison with those that are found for the neat cement paste. The experiments that we have made show that the coefficient of expansion obeys the law of mixtures, taking account of the moduli of elasticity E_c of the pure paste cement and of the aggregate E_a:

$$\alpha_b=\frac{\alpha_a V_a E_a+\alpha_c V_c E_c}{V_a E_a+V_c E_c}$$

where α_a is the coefficient of expansion of the aggregate, α_c that of the pure paste, V_a the volume of aggregates and V_c that of cement.

For a concrete with limestone aggregate at 400 days of curing in air, the coefficient of expansion was 6.9×10^{-6}, that of the aggregate 5.5×10^{-6}, and that of the cement 14×10^{-6}. A similar concrete having quartz aggregate with a coefficient of expansion of 11.3×10^{-6} gave for the concrete 11×10^{-6}. A third concrete with mixed siliceous and Seine limestone aggregates had an expansion coefficient of 8.8×10^{-6}. The considerable importance of the role played by the aggregate in thermal expansion is apparent. This role has been recognized and studied by various authors, including D. Bonnel and F. C. Harper [18] and L. Mitchell [22] who have achieved results similar to ours—concretes with siliceous gravel, 13.2; granite, 8.6; sandstone, 11.7; crushed slag, 10.6×10^{-6}. It also appears that the coefficient of expansion diminishes with the cement content in a manner that also corresponds to the law of mixtures, taking account of the unpredictable deviations that this approximation entails.

It should be noted that the indications provided here concern only relatively low temperatures; beyond 200 to 250 °C we get a contraction due to dehydration followed by a fresh swelling from 400 °C on [23].

Shrinkage and Desiccation

A cement paste, or a concrete cured in humid air or in water, then placed in a dry atmosphere, will shrink and at the same time lose weight through evaporation of water. Replaced in water, they swell and regain weight through imbibition. There is thus a relation between the movement of the water and shrinkage that does indeed appear to be a cause-and-effect relationship. Various investigators have concerned themselves with this relationship [1, 24, 25, 26, 27, 28, 29, 30].

For a compact neat cement paste the relation appears to be linear (fig. 3) for an advanced age (OA). For a young paste, it is curvilinear (OB), the curve OB tending toward OA when the age of beginning desiccation increases. For a mortar and a concrete, the relation takes the form OCD. Up to a certain loss of water, of which the abscissa corresponds to OC, there is only a slight shrinkage; beyond this the deformation is proportional to the loss of water for an old cement and follows a certain curve for a concrete that has not completed its hardening.

But we are now concerned with an initial shrinkage of a cement paste or a concrete that has had no previous desiccation. Repeated cycles of desiccation-humidification show a residual shrinkage *Os* (fig. 4) taking account of a hysteresis of which the effect may increase or decrease according

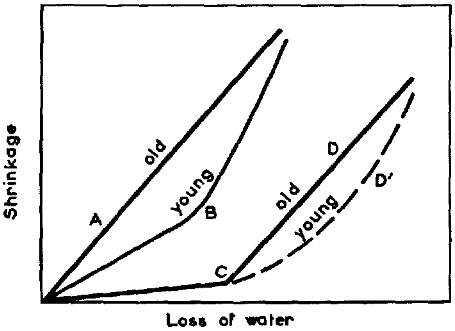


FIGURE 3. *Relation between loss of water and shrinkage of a cement paste.*

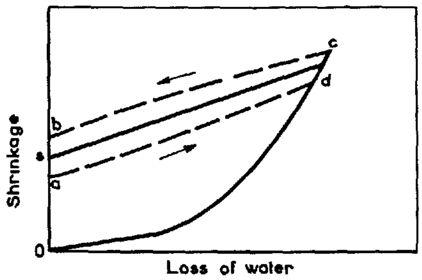


FIGURE 4. *Residual shrinkage after desiccation-humidification cycles.*

to the nature of the concrete and the degree of humidification. It can probably be explained as an effect of adjustment compensated by an effect of fatigue, both having a mechanical origin [28].

Beyond a certain degree of desiccation that practically can be obtained only by treatment at a temperature above 200 °C, it seems that a new relation can be attained in which shrinkage increases more rapidly in relation to loss of water.

All this seems to mean that, leaving aside possible transitions, what we have is different forms of water in regard to the shrinkage evaporation relation:

(a) a free water having little or no influence on the dimensional variations;

(b) a physically held water that is primarily involved in these variations;

(c) a water held at a higher degree that can be evaporated only under exceptional conditions of time or of temperature.

In the diagram of figure 5, the loss of water in terms of the degree of humidity of the curing medium can be expressed schematically by three straight lines: AB, free water whose quantity depends on the volume of the large voids in the paste; BC, water linked to shrinkage; CD, nonevaporable water [31].

It is interesting to know that a sample of cement protected against any evaporation by an impermeable coating during curing nevertheless shows shrinkage after a slight initial swelling [1]. This phenomenon shows that hydration has the effect of diminishing the internal humidity and leads to the same consequences as a progressive desiccation. This "adiabatic" desiccation, however, should not modify the hardening when the quantity of mixing water is such that $\frac{w}{c}>0.5$ [32]. It thus seems that the potential energy of hydration is higher than that which corresponds to evaporation above a certain hygrometric degree. The limit appears to be around 40 percent relative humidity for portland cement. The effect of diminution of humidity by hydration can occur only when the quantity of water chemically absorbed becomes greater than the quantity of free water. This effect is appreciable for pure pastes that contain little free water; after a year, the internal humidity can descend to 95 percent, a relatively slight drop [32]. (Lucas [33] indicates a limit of 85 percent for pure portland cement paste at 150 days.) For ordinary concrete such an effect is scarcely measurable.

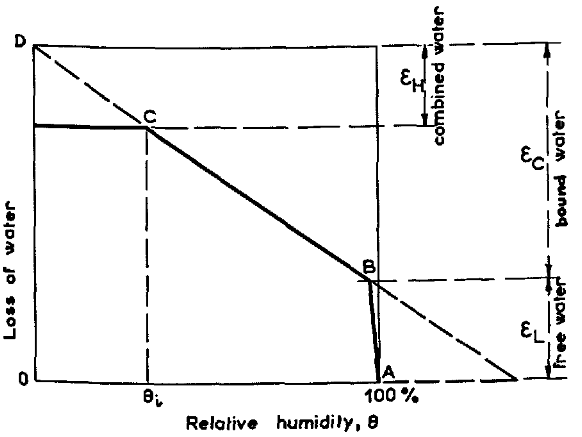


Figure 5. *Loss of water as a function of relative humidity.*

Since shrinkage is for the major part conditioned by evaporation, it is interesting to know the laws that govern the latter. Figure 6 shows curves of variation in weight of concrete cured in different humidities, θ [31]. It might seem that we here have a phenomenon of capillary evaporation in which the latter would be zero at 100 percent humidity and total at 0 percent. Experience shows that the phenomenon is much more complicated. Atmosphere in which $\theta=0.99$ (we shall assume $\theta=0.99$, an arbitrary figure, and not $\theta=1$, for complete saturation leads to condensations impossible to control experimentally; here we have a discontinuity) may determine an evaporation or an increase in weight but never leaves the weight constant. Let us assume a spongy medium with large pores and such that the solid part has only a negligible affinity for water. Let us saturate it with water and place it in air. All the water will eventually evaporate, whatever may be the humidity, on condition that it is less than saturation. The water cannot subsist in the liquid state in the presence of an indefinite volume of air. There is in concrete a certain quantity of water that can be evaporated under these conditions. This quantity, in figure 6, is comprised between curve A of curing in water and the curve $\theta=99\%\simeq 100\%$, and is the value AB of figure 5.

It is difficult to define the law of this evaporation in terms of time. It begins with the wet surface where the speed of evaporation is constant,

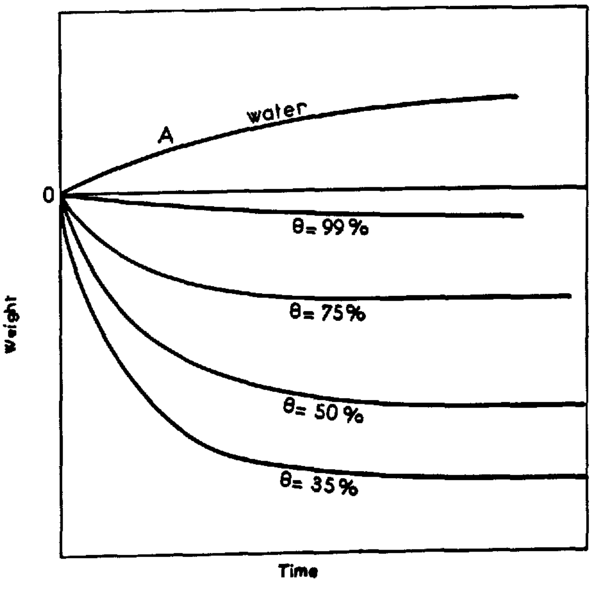


Figure 6. *Weight change of concrete cured at different relative humidities.*

then it diminishes until the concentration at the surface reaches a value in equilibrium with air. Finally, in a third period, a movement of diffusion of the internal water toward the surface begins. It is in fact this third phase that becomes all-important for the solid pieces in which the water from surface wetting is in small quantity compared with the free water of the pores.

In a one-dimensional medium, the movement of water at every point is defined by an equation $\frac{dE}{dt}=q(E)\frac{d^2E}{dx^2}$ where E is the quantity of water, x a normal geometric coordinate on the surface and $q(E)$ a function of E that remains to be specified and that represents a coefficient of diffusivity.

For a three-dimensional medium:

$$\frac{dE}{dt}=q(E)\left(\frac{d^2E}{dx^2}+\frac{d^2E}{dy^2}+\frac{d^2E}{dz^2}\right). \tag{1}$$

It is a Fourier's equation with variable coefficients. It is difficult to find a solution to this equation. By operating empirically, one observes that the mean evaporation of a piece corresponds to an expression of the form:

$$\frac{dE}{dt}=-(E_L-E)\gamma(t) \tag{2}$$

where γ is a function of time t elapsed since the beginning of the operation and E is the evaporated water.

If D is the designation given to the average dimension $D=\frac{\text{volume}}{\text{surface}}$, and K a coefficient of diffusivity peculiar to the solid, we observe that $\gamma(t)$ can be replaced by a function $\lambda\left(\frac{K}{D},t\right)$ that is to say that the time necessary to obtain a determined evaporation is proportional to a certain function of the average dimension. We may write λ more simply in the form $\lambda\left[\frac{K^u}{D^u}t\right]$ where u is between 1 and 2.

By making $\tau=\left(\frac{K}{D}\right)^u t$, the preceding expression becomes:

$$\frac{dE}{d\tau}=(E_L-E)\left(\frac{K}{D}\right)^u\lambda(\tau) \tag{3}$$

and the evaporated water:

$$E=E_L[1-e^{-\mu(\tau)}]$$

with $\lambda(\tau)=\frac{d\mu(\tau)}{d\tau}$.

This expression shows that the speed of evaporation is proportional to the quantity of remaining free water and appears to indicate that the movement of the water outward occurs within the liquid phase and not the vapor phase, at least for the most part. Equation (1) should then be written:

$$\frac{dE}{dt}=Q(E_L-E)\Delta^2_{xyz}E$$

and would have as a consequence that a perfectly dry barrier would oppose a transfer of humidity. Indeed the quantity of water that passes through a surface is $\left(\frac{dE}{dt}\right)_n=QE\frac{dE}{dn}$ where n is the direction of the normal. An experimental verification of this has been made on very fine sands [34], which appears to show that the transfer as the vapor phase is much slower than the transfer as the liquid phase, so that in order to take both into account we might write eq (1) in the form, from the saturated state:

$$\frac{dE}{dt}=[Q(E_L-E)+Q'E]\Delta^2E$$

with $Q'<<Q$.

Let us go back to eq (2) which indicates the speed of evaporation. Experience shows that the latter increases when the vapor stress diminishes, hence the function γ must include a term in θ, the relative humidity of the surrounding medium. For $\theta=0.99\simeq 1$ the speed of evaporation is not zero.

In a first approximation, it seems that eq (3) can be written in the more precise form:

$$\frac{dE}{d\tau}=(E_L-E)\left(\frac{q}{D}\right)^u(A-B\theta)\lambda(\tau) \tag{4}$$

in which now

$$\tau=\left(\frac{q}{D}\right)^u(A-B\theta)t \text{ and } \lambda(\tau)=\frac{d\mu(\tau)}{d\tau}$$

or

$$E=E_L[1-e^{-\mu(\tau)}], \tag{5}$$

an expression still valid in a more general way if we write $\tau=\left(\frac{q}{D}\right)^u\varphi(\theta)$; $\varphi(\theta)$ being a decreasing monotonic function when θ increases, having a positive value for $\theta=0$ and a value, not zero, less than the preceding for $\theta=1$.

All this is very theoretical and in fact presents only a phenomenological aspect, but one that it is interesting to consider for it will guide us in the realm of bound water. If we call the bound water E_c, whether it be capillary, adsorbed, or colloidal, it slowly gets into equilibrium with the relative humidity θ. Between certain limits, $\theta=0.99$ and $\theta=0.4$ for example, $E_c=\theta E_C$ when equilibrium is reached (fig. 5). However the evaporation of the bound water and that of the free water are not totally separate; they partly overlap, for concrete is a heterogeneous medium both in its structure and in the mechanism of evaporation which is itself heterogeneous in the volume once the surface has reached a sufficient dryness: $\theta<0.99$.

By analogy with the evaporation of free water but knowing that the evaporable part of the bound water diminishes when the humidity increases, we can write:

$$E=E_c(1-\theta)[1-e^{-\eta(\tau)}] \qquad (6)$$

where E_c represents the bound water and $\tau=\left(\frac{K}{D}\right)^u t$ so that the speed of evaporation is:

$$\frac{dE}{dt}=[E_c(1-\theta)-E]\left(\frac{K}{D}\right)^u \nu(\tau);$$

$$\nu(\tau)=\frac{d\eta(\tau)}{d\tau}. \qquad (7)$$

The only distinction that can be made in relation to eq (4) is that $\frac{dE}{dt}$ is annulled for $\theta=1$ and $E=0$.

Even more generally, we could write:

$$E=E_c\Phi(\theta)[1-e^{-\eta(\tau)}]$$

but it is possible, in a first approximation, to let Φ keep a linear form.

The function $\eta(\tau)$ remains to be defined. It is easy to represent it in an empirical manner as a power of τ, or $\eta(\tau)=\left(\frac{K^u}{D^u}t\right)^{1/n}$. But K itself is a function of age a since the concrete hardens and becomes less permeable; we shall write:

$$K=\mathrm{K}\left[\frac{\alpha}{(a+t)^{1/m}}+\beta\right].$$

Experiments show [31, 34] that n is close to 2; as for the variation of K, it is different depending on the composition. For a pure paste, we find that β is small compared with $\frac{\alpha}{(a+t)^{1/m}}$, with m close to 3, whereas for a concrete the variation of K is slight, m is above 12.

Finally, we shall write:

$$E=E_c(1-\theta)\left[1-e^{-\left[\frac{K(t)}{D}\right]^{u/2}\sqrt{t}}\right]$$

where $K(t)$ is a decreasing function during hardening, tending toward a constant value with age.

The quantity of bound water evaporated, E_c, at a given moment, may be determined by placing the test piece in a saturated atmosphere and maintaining it long enough (fig. 7). The gain of weight corresponds to E_c. A similar test piece placed in water takes on greater weight and joins the curve that corresponds to the permanent maintenance in water. The difference corresponds to the evaporated free water E_l.

We must now go on to the relation $\Delta(E_c)$. If we represent in juxtaposition figure 6, which gives the water variation, and figure 8, which indicates the volume or average length variation, and we look for a correlation between these two magnitudes for each value of t, we find that the correlation is approximately linear. We do not want to say here that a better approximation is impossible, but in the present state of knowledge it is difficult to do better.

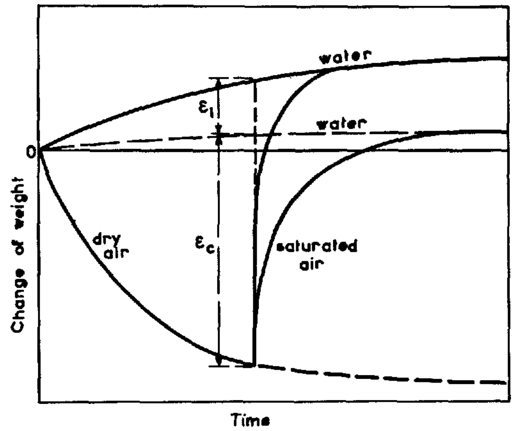


FIGURE 7. *Determination of bound and free water evaporated.*

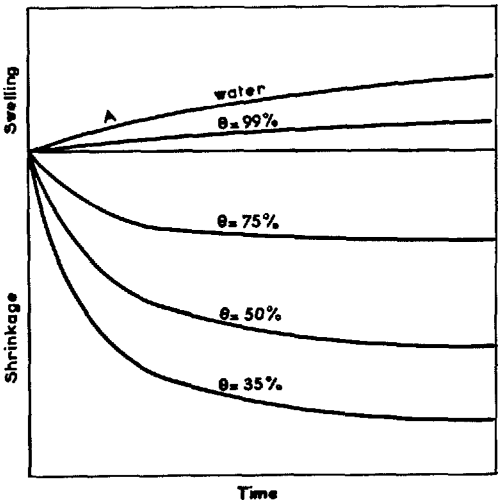


FIGURE 8. *Volume change of concrete cured at different relative humidities.*

We shall thus write:

$$\Delta=\rho(E_l-E_L) \qquad E_l>E_L$$

where E_l is the evaporated water, E_L the total free water, and ρ a coefficient of shrinkage. This relationship leaves out of account other influences such as the action of carbon dioxide and that of the internal stresses produced by shrinkage. Experiment shows that the coefficient of shrinkage varies with age a and increases with time t. An identical loss of water gives a greater shrinkage at 1,000 days than at 7 days. This result, surprising at first sight, can be explained if we recall that the quantity of hydrated cement also increases with time and we can admit the hypothesis that ρ is proportional to the volume of the hydrated phase or, if one prefers to reason from the gel, to the volume of gel formed. We shall say more simply by taking water as a variable that ρ is proportional to E_h, the quantity of water absorbed by hydration.

Finally, it must be possible to express the law of shrinkage in the form:

$$\Delta(t)=QE_h(E_t-E_L) \tag{8}$$

$$\Delta(t)=QE_h(t)E_c(1-\theta)[1-e^{-\eta(\tau)}] \tag{9}$$

with $\tau=\left(\frac{K}{D}\right)^u t$.

We may note that this gives for the differential element:

$$\frac{d\Delta}{dt}=QE_h\frac{dE}{dt}+QE\frac{dE_h}{dt}.$$

If we consider the proportionality to the differential element only, this leads us to write:

$$\frac{d\Delta}{dt}=QE_h\frac{dE}{dt} \tag{10}$$

and the speed of shrinkage is less.

This proposition appears more correct but leads to an equation difficult to integrate in an analytical manner, especially as $E_h(t)$ is inexactly known. In any case, the final shrinkage remains the same and proportional to $(1-\theta)\frac{K}{D}$. In order to avoid having to make calculations on hypothetical bases, it appears possible and especially prudent to write simply:

$$\frac{d\Delta}{dt}=[\Delta_m(\theta)-\Delta]\left(\frac{K}{D}\right)^u\chi(\tau)$$

where χ is a function to be determined experimentally, and if we admit the linearity of the final shrinkage in terms of θ: $\Delta_m(\theta)=\Delta_M(1-\theta)$ where Δ_M is a reference value for $\theta=0$. We shall see later that it cannot be affirmed that this last relation is correct.

Finally:

$$\Delta(t)=\Delta_m(\theta)[1-e^{-\Phi(\tau)}] \tag{11}$$

where $\chi(\tau)=\frac{d\Phi(\tau)}{d\tau}$.

In the case of application of eq (8): $\chi(\tau)=\nu(\tau)$ (see eq (7)), the form of the shrinkage curve would be the same as that of the curve of evaporation of the bound water. So it is for aged concretes, but young concretes diverge slightly (fig. 3), which appears to justify eq (10).

A consequence of the theory that has just been put forward is that the final shrinkage in atmosphere θ must be independent of the previous curing up to an age a (this is confirmed by Dutron [11]). Only the speed of shrinkage from the age beyond which θ is constant is modified. Figure 9 which results from our tests shows the shape of the shrinkage curves. We see that the low shrinkage rate at advanced ages can partially mask the phenomenon. It is, moreover, possible that in solid pieces the development of internal stresses may lead to irreversible plastic deformations whose resultant opposes contraction. It may be supposed that the final shrinkage somewhat diminishes with the age of loading, all the more so as the mean dimension D is greater. It will be further remarked that if the measured swelling in water is important the shrinkage can diminish after a certain time. We have observed this phenomenon after several years of curing [7], indicating, therefore, that the physico-chemical swelling referred to above persists even in dry air.

We have already given a function of shrinkage depending on the time in which we find in the e power another function $\Phi(t)$ which governs the whole phenomenon. This function must depend on the age a of placing in dry air and on the time t, in other words on the two variables t and $(t+a)$.

It seems that they can be given the same form as that which we had recourse to for the evaporation, so that, finally:

$$\Delta=\Delta_m(\theta)\left[1-e^{-\frac{K(t)}{D}\sqrt{t}}\right]$$

An important phenomenon to consider is the reversibility of shrinkage. By contrast with what we observe for the variation in weight, the reversibility is not complete even after a prolonged immersion in water. A permanent deformation δ subsists, such that $\frac{\delta}{\Delta}$ varies between 0.3 and 0.6. We are entitled to wonder to what this is due. It immediately suggests a plastic phenomenon, but it is not certain that this similarity is in fact representative. If such were the case the deformations would be due to a shrinkage pressure

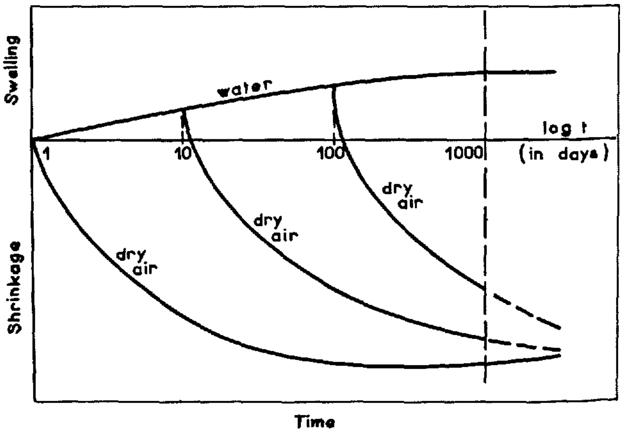


FIGURE 9. *Drying shrinkage in relation to previous curing.*

resulting from inner stresses but which would modify the rupture conditions. Now, these do not appear to be affected by the shrinkage in an appreciable manner before the stresses that would enter into play. An explanation must therefore probably be sought elsewhere. The question has not yet been answered, but it seems that it may be at least partially answered by the introduction during shrinkage of additional links due to the progress of hydration in the condensed medium, that is to say to the creation of new links through the coming together of the crystallites that oppose swelling, at the moment of the return to the wet medium. In favor of this explanation we observe that the residual shrinkage disappears when concretes have undergone a prolonged hardening in water (180 days for example) before placing in dry air [1]. In addition to which we shall see later that carbonation, which generates a structure insensitive to moisture, increases the residual shrinkage considerably.

This theoretical part which we conclude herewith and which rests on our personal investigations [35] must be compared with the studies of other authors. Those of Lucas [33] appear to indicate that between relative humidities of 40 and 99 percent, evaporation and shrinkage are approximately linear functions of θ; below 40 percent, the curves assume a somewhat irregular appearance. It is observed, moreover, that swelling in water becomes more pronounced after desiccation at less than 40 percent, which seems indeed to show a cessation of hydration in these very low humidities. Haller [36] clearly brings out the linear relation between the evaporated water and the humidity, but this relation does not appear precisely for the shrinkage, whereas it is more or less observed in Dutron's tests [11].

Finally it may be said that the assumption of linearity between certain limits of humidity $\theta=0.4$ and $\theta=0.95$ appears to be approximately acceptable for evaporation.

On the other hand, it is not certain that this is always the case for shrinkage. The curves obtained in terms of θ are in general of the form given by figure 10 in relation to the saturated state in water. AD represents the swelling in water in relation to curing at 99 percent rh. But nothing tells us that for $\theta<99$ percent there is not a swelling being deducted from the shrinkage, such swelling being always possible in the presence of free water so long as any subsists in a part of the volume. The theoretical shrinkage curve BC is thus modified by the swelling s which is greater as the value of θ is higher.

This point of view appears to be confirmed by the fact that concretes cured for a very long time (more than a year) in water show a shrinkage, when placed in air, that is really proportional to $(1-\theta)$; the swelling then becomes negligible in relation to the shrinkage that subsequently occurs.

Finally it is necessary to explain why certain cements such as slag give in neat paste and in rich mortar a marked shrinkage at 99 percent of relative humidity. We believe that this shrinkage is due to the inner desiccation caused by hydration which produces a shrinkage without variation in weight of the parts furthest removed from the surface. The straight line i of figure 10 which represents the initial length passes below D.

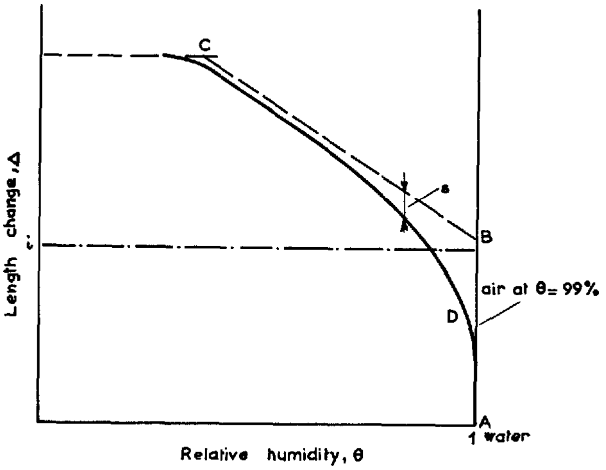


FIGURE 10. *Combination of swelling and shrinkage.*

A natural factor that plays an important role in shrinkage is atmospheric carbon dioxide. It has been studied in particular by Meyers [37], Leber and Blakey [38], and Verbeck [39]. Prisms of mortar placed in an atmosphere of carbon dioxide at the same relative humidity show an increase of shrinkage and an increase in weight. This increase is zero for saturated atmosphere, approximately double the normal shrinkage for $\theta=50$ percent where it reaches a maximum, and tends toward 0 for $\theta<25$ percent. We see that this influence is far from negligible and must be appreciable even for atmospheric air. It seems, moreover, that this effect increases with the dimension of the sample and thereupon decreases. It is therefore not surprising that such a phenomenon should modify the aspect of the theoretical curve of shrinkage and give it different shapes according to the experimental method used.

It appears moreover that carbonation diminishes the reversible part of the shrinkage and subsequently gives it a greater stability during the alternations of drying and moistening. This is the proof of the presence of a supplementary solid structure that does not have the hydroconstrictive properties of the hydrated phase of the cement. We therefore recommend to experimenters that they carry out shrinkage measurements in atmospheres free of carbon dioxide which may distort the results in a manner that is unexpected and difficult to control; this is now the procedure in our laboratory.

The volumetric coefficient has been studied by Ross [40], Haller [36], Glanville [41], and Carlson [42]. It is found that the shrinkage in dry air of prisms of pure paste having section ratios of

1 to 2 is in the ratio of 1.3 to 2.3 at 1 yr and tends toward 2.5 for section ratios of 1 to 8. Ross's tests show how the shrinkage propagates from a free surface in a plate made impermeable at all the other surfaces. At 200 days, the shrinkage at a distance of 4 in from the surface is still only one-third of the surface shrinkage. This delay is considerable, and its order of magnitude can be roughly fixed as proportional to the square of the distance to the surface of evaporation. If we compare the shrinkages as well as the losses in water of different test pieces of the same concrete tested by Ross [35], we find that the values align themselves along a single curve in relation to the variable $t\left(\frac{s}{v}\right)^2$. This means that the time necessary to produce a given shrinkage is proportional to the ratio $\left(\frac{v}{s}\right)^2$, other things being equal as far as the composition and the curing medium are concerned. Karapetian [79] indicates that for a block dried at 50 percent rh desiccation reaches 8 cm in depth at the end of a month and 60 cm at the end of 10 yr (the term "dried" probably means that the concrete has lost its free water).

Our tests confirm this point of view insofar as atmospheres of high humidity are concerned. On the other hand, for shrinkages carried out at a low humidity, lower than 50 percent rh, the exponent u of formula (3) and the following appears to tend toward unity [80]. This is why we wrote above that the exponent u was between 1 and 2.

We may note that Weil [81] gives shrinkage values in terms of the dimension which bring out exponent u close to 1.5 while Karapetian's results [79] give a value close to 2. Practically, apart from exceptional desiccations, it seems that we may take $u=2$ as a first approximation.

Composition

The part played by the composition of the concrete is very important in creating shrinkage. First of all the nature of the cement has a considerable influence. Roughly speaking, shrinkages increase in the following order: ordinary portland, aluminous cement, slag, and portland with high early strength. In each category, they are very variable. According to Cocagne [35] an ordinary portland gives 0.22 percent shrinkage in neat paste at 1,000 days, a portland having high early strength 0.35 percent. Dutron [11] indicates for ordinary portland a figure of the same order of magnitude, for aluminous cement, 0.25 percent. The same author shows that in portland and slag mixtures, the shrinkage increases with the proportion of the latter. Figure 11 gives a number of average curves relating to cements manufactured in France.

Graf [43] seems to have been the first to concern himself with the influence of the grain size of the cement on shrinkage by bringing out the increase of the latter when the specific surface increases. Haller [36] has shown that shrinkage increases from 0.117 to 0.169 percent in 90 days when the specific surface increases from 1,355 cm²/g to 2,280 cm²/g for the same portland cement. Jaspers [44] finds a linear relation between the specific surface and shrinkage at 90 days. Lafuma [45] likewise

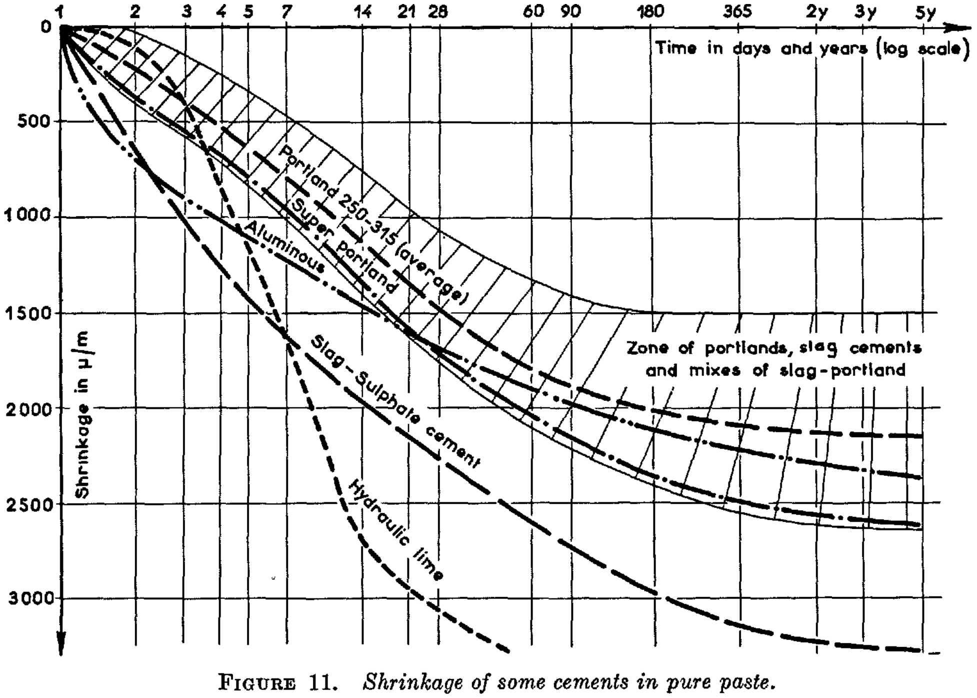


FIGURE 11. *Shrinkage of some cements in pure paste.*

According to Centre d'Etudes des Liants Hydrauliques, Paris. Tests on samples 4 x 4 x 16 cm at 50 percent rh and temperature 20 °C.

brings out a variation of the same kind on mortar: from 2,000 to 5,500 cm^2/g obtained with the same clinker the shrinkage increases from 0.05 to 0.17 percent while the losses in weight are less for the highest specific surfaces. The latter fact confirms what we had already established, that with an identical quantity of evaporated water, shrinkage increases with the volume of the hydrated phase, and this volume does increase with the specific surface.

The addition of mineral powders to the cement may have variable effects; certain authors [11] indicate a marked increase. Our tests carried out with mixtures of cement and basalt powder [1] have indicated, on the contrary, an increase in shrinkage with the cement/powder ratio. There is accordingly an influence exerted by the mineralogical nature of the filler.

The introduction of soluble salts into the mixing water, apart from a chemical reaction of expansion, has the effect of increasing the shrinkage [46]. The salts dissolved in the city water contribute an appreciable increase. Sodium carbonate at 0.4 percent in the mixing water increases the shrinkage at 1 month by 40 percent, sodium nitrate at 6 percent doubles the shrinkage. But the most specially studied influence was that of calcium chloride habitually used as an antifreeze and hardening accelerator [47]. The experiments that we have made [7] have shown a marked increase in the shrinkage of an ordinary portland measured at 5 months from the introduction of a quantity of $CaCl_2$ equal to 0.5 percent of the weight of cement. This increase of approximately 50 percent persists without great variation to 2 percent of $CaCl_2$, then from this quantity the shrinkage suddenly increases, its increase amounting to 110 percent for 2.5 percent of added $CaCl_2$ and 165 percent for an addition of 3 percent of $CaCl_2$.

Let us now examine the influence of the quantity of mixing water in mortars and concretes. Certain authors, including Haller [36] and Cocagne [48], indicate a rather important increase in shrinkage with the ratio $\frac{\text{water}}{\text{cement}}\left(=\frac{\text{w}}{\text{c}}\right)$. But this increase occurs with neat pastes. In the case of a concrete, our tests have shown a very slight influence both on shrinkage and on swelling when it is considered after a day of hardening, the first shrinkage being on the contrary influenced by variation of this ratio as was said at the beginning of this paper and as Pickett [49] confirms. For a portland concrete with a cement content of 350 kg/m^3 and Seine aggregates, the shrinkage at 1,000 days was 0.045 percent for $\frac{\text{w}}{\text{c}}=0.47$, 0.048 for $\frac{\text{w}}{\text{c}}=0.52$, and 0.05 percent for $\frac{\text{w}}{\text{c}}=0.57$. Which is to say that the variations are of the order of magnitude of the experimental errors while the limits of $\frac{\text{w}}{\text{c}}$ correspond to the extreme possibilities of placing. Another series of tests covering several thousand concretes studied from the statistical point of view have shown that the variation of $\frac{\text{w}}{\text{c}}$ possible for the range of cement contents extending from 250 to 500 kg/m^3 had an influence on shrinkage amounting to less than 10 percent [50].

As the losses in weight, moreover, are approximately proportional to $\frac{\text{w}}{\text{c}}$ this result seems to mean that beyond a certain quantity of mixing water, the incorporated water becomes free water without appreciable influence on shrinkage. The same is obviously not true for neat paste, where the $\frac{\text{w}}{\text{c}}$ ratio is less at normal consistencies.

The cement content, on the other hand, has a very marked influence. Many authors have studied it [48, 11, 36, etc.].

It seems that a usable empirical expression is here possible. Dutron indicates for the shrinkage of concrete:

$$\Delta_b=\gamma(e+c+v+f)^n$$

where e=volume of water, c=volume of cement, v=volume of voids, f=volume of fines. If the volume of the aggregate is written $a=[1-(e+c+v+f)]$ and if $a=0$ we obtain the shrinkage of the neat paste Δ_c and this expression becomes transformed into $\Delta_b=\Delta_c(1-a)^n$. We find that n is between 1.20 and 1.70 when the tests of the different authors are interpreted. (Pickett [49], who has established this formula theoretically, finds $n=1.7$.) Our measurements on siliceous Seine aggregates (silex) gave $n=1.24$ with a maximum spread of 10 percent.

Another semiempiric expression proposed by us [31] has the form:

$$\Delta_b=\Delta_c\frac{c}{c+[1-(c+e+v+f)]\mu_{ca}}=\Delta_c\frac{c}{c+a\mu_{ca}}$$

where μ_{ca} is a coefficient that represents the relation between the coefficient of compressibility of the aggregates and that of the cement paste. For a siliceous aggregate we find that $\mu_{ca}=0.88-0.53\ \frac{\text{w}}{\text{c}}$. The mineralogical nature of the aggregate has a marked effect on the amount of the shrinkage as may be expected from the above formula. Numerous investigators among those already quoted have taken this factor into consideration. Figure 12 shows the results of tests on a concrete with a cement content of 350 kg/m^3 with an identical quantity of water $\left(\frac{\text{w}}{\text{c}}=0.55\right)$ and aggregates of different mineralogical natures. This variation is quite adequately expressed in the preceding formula by the variation in the modulus of compressibility.

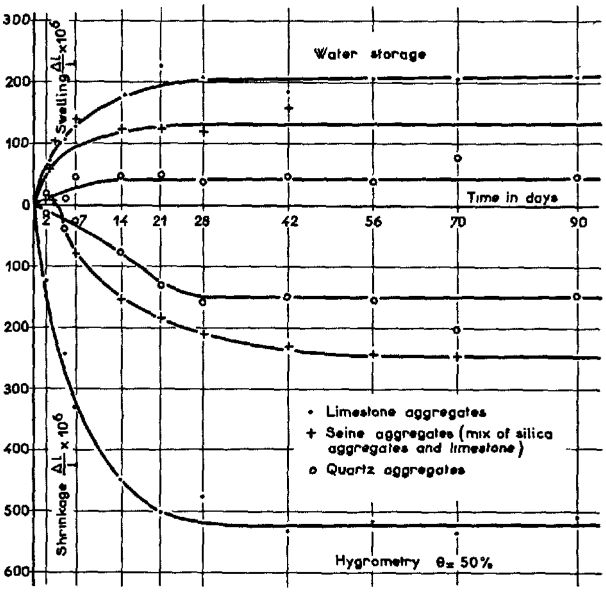


FIGURE 12. *Swelling and shrinkage of concrete with different aggregates.*

Theories

How is shrinkage to be explained? The answer to this question appears not an easy one.

One of the first theories is that of shrinkage stress (or of swelling stress) in which the liquid phase is placed under stress in relation to its initial state. Let F be this stress, e the liquid volume, v the total volume of the solid phase. The shrinkage should be:

$$\Delta=F\frac{e}{v}\chi_b$$

where χ is a coefficient of compressibility of the solid.

In order to determine F it is assumed that the stresses that can be developed are capillary stresses. This idea appears to have been put forward initially by Freyssinet [51]. It has since been adopted by various authors and almost completely abandoned [19]. The force F in this case should be proportional to the surface tension σ of the liquid that fills the capillaries and inversely proportional to the radii of curvature r_1 and r_2 of the menisci that limit the liquid phase, or

$$F=\sigma\left(\frac{1}{r_1}+\frac{1}{r_2}\right).$$

If the quantity of water diminishes, the radii do likewise and F increases.

Kelvin's equation, moreover, gives

$$\frac{1}{r_1}+\frac{1}{r_2}=\frac{AT}{\sigma}\log\theta$$

where T is the absolute temperature, and

$$F=AT\log\theta,$$

which makes it possible to set aside the artifice of capillarity, and finally the shrinkage would be:

$$\Delta=ATe\log\theta.$$

But such a relation can be considered valid only between certain limits, for if θ diminishes, e likewise diminishes, and Δ must pass through a maximum for the decreasing θ, which is contrary to experience. Calculation shows without difficulty that if we write $e=e_i+e_j(1-\theta)$, $\frac{e_i}{e_j}$ must be greater than 0.40 in order that the shrinkage may be stabilized approximately within $\theta=0.25$, and under these conditions the calculated shrinkage varies but slightly from linearity up to $\theta=0.5$.

If e_i is a kind of nonevaporable water, hence of hydration water or water fixed in such a way that it cannot escape for very low humidities, it must itself be placed under the same stress as evaporable water. This hypothesis remains to be proved and has a somewhat artificial aspect. Nevertheless, such a mechanism is not in contradiction with the hypothesis that presents the hydrated phase in the form of a gel.

The other hypothesis that assumes that the water is deposited on the solid crystallites having great surface development in adsorbed layers is likewise plausible. The evaporation of the outer layers, the least bound, develops forces of attraction on the inner water layers, by liberation of the Van der Waals forces, which place the adjacent solid in compression, by reaction, the last layers being too tightly bound to the solid to be extracted. The mass of water thus conserved may be sufficiently small to be confused with the hydration water. We may then attempt to get an idea of the magnitude of these forces of attraction by suction measurements. We know that a porous body placed in the presence of free water absorbs this water by exerting a tension on it that depends on the quantity of water e already contained in this body [52]. This force F can be measured by preventing the penetration of the water by means of a reduced pressure exerted on the latter. We then find that F is a function of the water contained in the body at the moment when the measurement is made; $F(e)$. The suction is generally expressed as a decimal logarithm of the height of water in cm corresponding to the suction F: $pF=\log_{10}H$. Beyond $pF=3$, that is to say beyond atmospheric pressure, the device using suction on the liquid phase is no longer usable. We then use a drier in which the sample is suspended in the void above a solution of sulfuric acid of known density which, at equilibrium, gives a relative humidity θ. The value of the suction is then given by Kelvin's formula, and for a temperature of 20 °C

$$pF=6.5+\log_{10}(2-\log_{10}\theta).$$

We then obtain for the cement a curve of the form given by figure 13. One can also attempt to extract the water and measure the necessary force by proceeding according to one of the two above methods and, further, by centrifuging. The $pF(e)$ relation found then gives a curve that is above the previous one (fig. 13). It is to be regretted that very few attempts have been made to connect suction with the variation in the volume of the cement.

What we observe, however, is that drying develops a higher pF than moistening, the quantity of water being equal, and this effect may be favorable to the creation of a residual shrinkage. It is nevertheless possible to examine whether the order of magnitude of the suction forces is sufficient to explain the shrinkage deformation. Let us assume that we have reached $pF=5$ for 50 percent of evaporated water; this gives $F=100$ kg/cm^2. Let us further assume that the water that remains at this humidity represents 50 percent of the volume of the cement. The hydrostatic pressure on the solid part is then at the maximum: $p=100\times 0.4=40$ kg/cm^2. The elastic deformation that corresponds to the saturation of the paste is of the order of

$$\Delta=p\frac{1-2\sigma}{E}$$

With $E=200{,}000$ kg/cm^2 and $\sigma=0.2$, we should find

$$\frac{\Delta l}{l}=80\times 10^{-6}=0.008\%.$$

The order of magnitude of the deformations measured is more than 0.1 percent. The part of shrinkage deformation corresponding to the suction forces is of the order of one-tenth of the total deformation, and the suction forces cannot alone explain the shrinkage.

An interesting remark to be made derives from the observations of shrinkage on cements and concretes treated by heat. A treatment at 80 °C for 3 hr does not markedly modify the resulting shrinkage, whereas a treatment at 185° for 8 hr under a pressure of 10 atm of saturated steam completely changes the phenomenon. We first observe in neat paste a very considerable swelling during the treatment (between 0.1 and 0.6 percent) if the test piece remains free to dilate. But whether the freedom is allowed or the mortar is kept in a closed mold, we find that the shrinkage measured upon drying after cooling becomes very slight, between 1.0 and 2.0 percent of the shrinkage measured on an untreated control concrete [53].

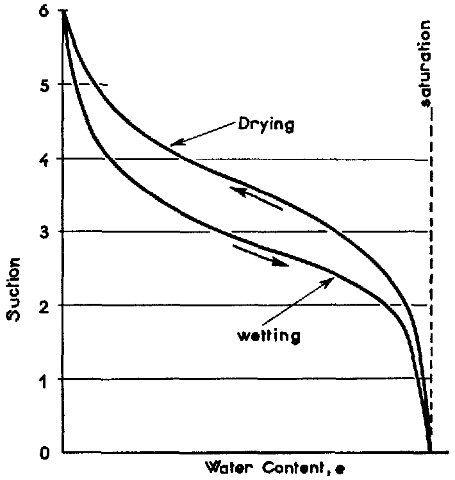


FIGURE 13. *Form of curves of wetting and drying of cement.*

This shrinkage is then of the order of magnitude of that indicated above under the influence of the suction forces alone. Now, we know that the silicate crystals hydrated at high temperature have a different structure and a greater volume stability. It is then possible that the origin of the shrinkage is to be found in large part in the crystalline structure and that in the case of treatment by autoclave the crystals formed are no longer sensitive to variations in humidity. It is well then to look for the origin of this sensitivity.

In his work on the structure of hydrated cements, Bernal indicates [54] the presence of tobermorite in fibrous form and, in the direction normal to the fibers, of layers of water the thickness of which varies from 14 to 9 A during drying. This is no longer a simple phenomenon of adsorption but of layers of zeolitic water of dimensions varying with the humidity of the medium. It is Bernal's opinion that we must look here for the origin of the shrinkage properties of cement. In concretes hydrated under heat, tobermorite crystallizes mainly in the form of slabs and no longer in the form of fibers, such slabs being probably less sensitive to the hydroconstrictive movement. Powers [21] appears to be of a different opinion and finds an explanation by saying that for setting at normal temperature the hydrated phase appears in a colloidal form highly sensitive to humidity whereas the treatment by steam under pressure gives a crystallized and not a colloidal phase. He bases this explanation on the fact that cements treated in this manner have a coefficient of thermal expansion independent of humidity.

Volume Variations of Concrete Under Load

Under a progressive loading applied at a given age, concrete undergoes a deformation. Let us call this deformation Δ measured in a part uniformly stressed and T the corresponding homogeneous stress, whether of tension or compression. T is shown as the ordinates and Δ as the abscissas of a system of rectangular coordinates (fig. 14), and we get a curve of deformation. This curve OA is tangential to, or one with, a straight line OE over a certain length (an inflection at the

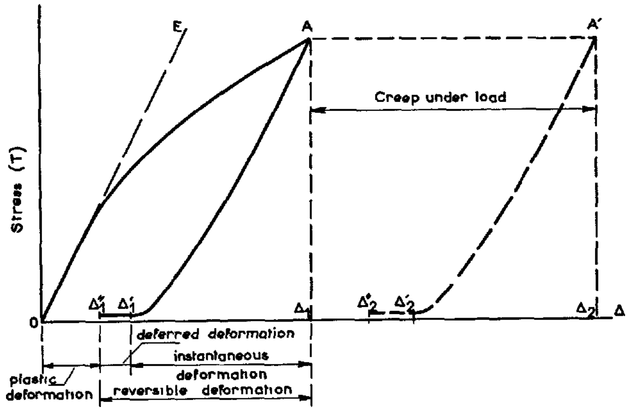


FIGURE 14. *Stress-deformation relations for concrete.*

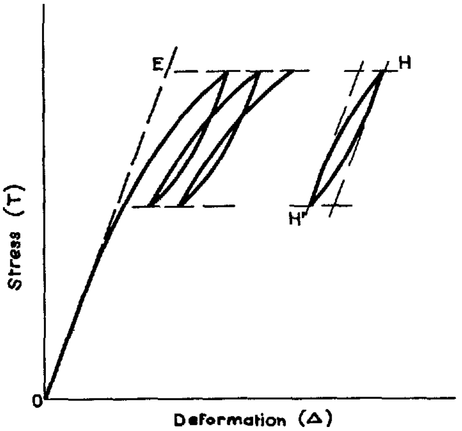


FIGURE 15. *Stress-deformation relation on cyclic loading.*

beginning of the compression curve can sometimes be observed; this is the sign of a preexisting internal microfissuration).

After having applied the load as far as A, let us remove the load. The unloading curve is close to a straight line but very slightly incurved in the opposite direction. After complete removal of the load, there remains a deformation Δ_1' and, after a time of rest, the residual deformation diminishes by a slight amount and tends toward Δ_1''. If the load removal is sufficiently rapid, the instantaneous reversible deformation is called $\Delta_1-\Delta_1'$, the reversible total deformation $\Delta_1-\Delta_1''$, and the reversible deferred deformation $\Delta_1'-\Delta_1''$, while the permanent residual deformation or plastic deformation is Δ_1''. If the solid is maintained under load a sufficiently long time, the deformation increases from A to A′ and reaches the value Δ_2. The magnitude $\Delta_2-\Delta_1$ is the creep under load, while $\Delta_2''-\Delta_2'$ is the residual creep. If instead of completely unloading the test piece the stress is partially decreased and load is again applied, and the process is repeated a certain number of times, one obtains a series of loops that finally stabilize in the form of a very flattened loop HH′ practically identical with a straight line (fig. 15). The inclination of this straight line is the same as that of the original tangent OE. This property is verified when the maximum load is less than 6/10 of the breaking load. The modulus of elasticity thus defined, or fundamental modulus, is the same as the one found by means of the measurement of the speed of propagation of shock waves [55]. Because of this it is called "modulus of dynamic elasticity".

As the total deformation of a concrete includes an elastic and reversible part and a plastic part, it is necessary in order to recognize the relative parts to operate through successive and increasing loadings with intervals of unloading. Three curves can thus be established (fig. 16): the curve of total deformationΔ_T, the curve of plastic or residual deformation Δ_R and the curve of elastic deformation $\Delta_E=\Delta_T-\Delta_R$.

Finally, if for a compressive or tensile stress the deformation δ is measured in the direction normal to that of the applied total stress, the latter has a sign which is the contrary of the longitudinal deformation Δ. We can recognize in δ a total deformation δ_T, a residual deformation δ_R and a reversible elastic deformation δ_E. From which we obtain three values to be considered:

—the total Poisson's ratio, $\sigma_T=-\dfrac{\delta_T}{\Delta_T}$

—the plastic Poisson's ratio, $\sigma_R=-\dfrac{\delta_R}{\Delta_R}$

—the elastic Poisson's ratio, $\sigma_E=-\dfrac{\delta_E}{\Delta_E}$.

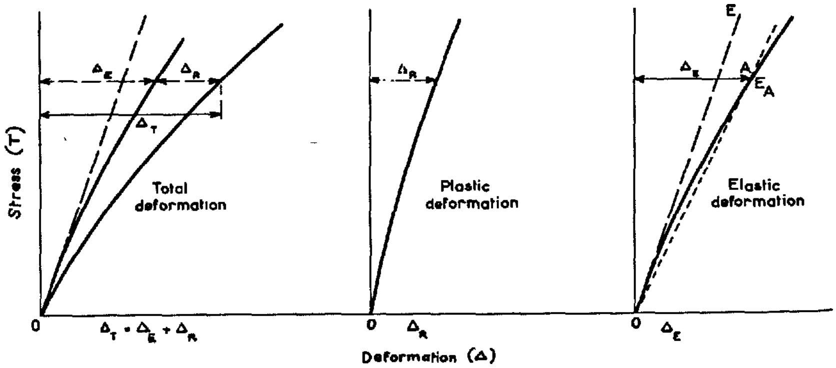


FIGURE 16. *Curves of total, plastic, and elastic deformation of concrete.*

These preliminaries having been effected in order to narrow the definitions, we shall successively examine the elastic deformation of concrete, its rapid plastic deformation, and its slow plastic deformation or creep in terms of the variables already considered for the study of shrinkage, to which is added the variable stress T.

Elastic Deformations

Experience shows that $\Delta_E(T)$ is not a straight line and that concrete has an elasticity that is not perfectly linear, but this lack of linearity is not very great and diminishes when the concrete ages. If we define the modulus of elastic deformation or secant modulus $E_A=\frac{T}{\Delta_E}$ (fig. 16) as the inclination of the straight line OA that joins the origin to point A considered on the curve, it is possible to examine its relative variation in terms of the stress T and its relation to the classical instantaneous breaking load R (on cylinder). The experimental work done on this subject is rather limited, for the authors have neglected, in most cases, to separate the reversible elastic deformation from the total deformation.

It is recognized that $\frac{E_A}{E}$ remains constant up to one-tenth of the rupture load. Le Camus [56] has found that $\frac{E_A}{A}=0.95$ for $\frac{T}{R}=0.2$, 0.90 for $\frac{T}{R}=0.33$, and 0.75 for $\frac{T}{R}=0.5$.

The Federal Laboratory of Zurich gives the formula:

$$\frac{E_A}{E}=\frac{1}{1+K\frac{T/R}{1-T/R}}$$

with $K=0.10$ (it seems that for young concretes, K should be higher, close to 0.25). Santarella [57] indicates that the modulus of elasticity diminishes in an almost linear manner till it reaches one-half the breaking load. Vivian [58] gives for the modulus E_A a formula that leads to $\frac{E_A}{E}=0.97$ for $\frac{T}{R}=0.10$, 0.94 for $\frac{T}{R}=0.20$, and 0.92 for $\frac{T}{R}=0.30$. We see that all these results do not greatly differ. When concrete is loaded at increasing speed, the modulus E_A measured at 50 percent of the breaking load increases to join the modulus of dynamic elasticity E [59]. This behavior appears to show the presence of a viscous elasticity, the ratio of viscosity depending on the load, the curve of elastic deformation approaching a straight line for increasing speeds of stress.

For a given concrete, the modulus of elasticity increases with age during hardening in accordance with a law that is approximately proportional to the square root of the compressive strength, and it is greatly influenced by the humidity of the curing medium. Our tests have shown, for example, on a concrete containing 350 kg of cement per m^3, with siliceous aggregates, the following moduli at 200 days:

Relative humidity of curing medium	Modulus of elasticity
%	kg/cm^2
35	340,000
50	365,000
75	385,000
99	450,000
Water	450,000

It is to be noted that a concrete cured in dry air and subsequently exposed to humidity does not recover the modulus of elasticity of the same concrete cured uninterruptedly in moist air; the modulus does increase, but remains definitely lower. It is therefore probable that the mode of hardening of a concrete cured in dry air does not lead to the same structure of the hydrated phase. The formation of gel or of crystals cannot occur in voids from which water is absent. A curing in water for a week followed by exposure to dry air does not appear, on the other hand, to modify substantially the subsequent increase in the modulus that proceeds as for a curing in water. It must be, then, that the curing during the early stage is predominant, permitting the creation from the beginning of a more compact structure that subsequently becomes consolidated.

The modulus of elasticity of concrete is influenced by the variations in composition, in compactness, and in physical or chemical decomposition. This sensitivity, bearing in mind the scatter, is at least as great as that observed in tests for mechanical strength. In addition, it confers upon the measurement the advantage of applying to a volumetric mean, and in the case of the use of dynamic methods (speed of sound) it brings out a localized modification such as a crack capable of forming a transmission barrier.

The modulus of dynamic elasticity of a normal hardened concrete varies between 200,000 and 600,000 kg/cm². It varies with the actual quality of the aggregates, being higher for concretes with siliceous aggregates than for concretes with limestone. The modulus E_b conforms approximately to the law of mixtures for a relatively compact concrete;

$$E_b=\frac{AE_a+ME_m}{A+M+O}$$

where E_a is the modulus of the aggregate of volume A, E_b is the modulus of the mortar of volume B, O is the volume of the voids.

The order of magnitude of the modulus of a hardened mortar is approximately 200,000 kg/cm², that of a river siliceous aggregate (Seine aggregate) 630,000 kg/cm²; that of quartz 800,000 kg/cm²; for limestone, it .varies between 55,000 kg/cm² for very soft limestones to 250,000 kg/cm^2 for average limestones and 700,000 kg/cm^2 for very hard limestones such as marbles.

The Poisson's ratio of concrete has received attention in only a few studies [56, 60]. At first we find that for a stress below half the breaking load the transverse deformations are wholly reversible to within the precision of the measurements. Beyond this, irreversible deformations begin to occur which are due in part to microfissuring. It is found that Poisson's ratio varies between 0.10 and 0.30; it is higher as the concrete is younger or less strong. For a hardened concrete, 0.20 ± 0.02 is currently found. By using the dynamic method, we nevertheless obtain a higher ratio, close to 0.30 [60, 61].

Rapid Plastic Deformations

We shall use the term rapid plastic deformations to distinguish such deformations *a priori* from creep produced over a prolonged period. The deformations we are here considering are those that are due to a loading of duration less than 1 hr, a time which corresponds to the practical duration of a loading and unloading experiment in a laboratory. The plastic deformation, moreover, varies little between 1 min and 1 hr in the light of the deformation that subsequently appears in the course of time [62]. In any case, the creep that we shall later consider takes these "instantaneous" deformations into account. This being said, let us examine the curve that represents deformations of this kind in the coordinates T and Δ_P (fig. 17). This curve is concave toward the abscissa, passes through a maximum T_R corresponding to a deformation Δ_R which corresponds to the rupture in the sense usually given to this term, that is to say at the maximum load that the solid can bear. In the course of a test of this kind, it is possible to make a number of supplementary measurements on a fairly slender prism. In addition to the longitudinal and transverse deformations it is possible to place at mid-height a microphone connected to an amplifier and a device capable of recording the sound characteristics, that is to say the sounds that are produced in the concrete under the action of loading. In addition, it is further possible to set up an apparatus for measuring the speed of the shocks along a diameter (normal to the direction of the load applied). The test piece being loaded, the microphone records multiple feeble sounds, and beyond a load T_i very different noises are heard, which are crackings. They increase in frequency and in intensity when the test piece reaches the breaking point (fig. 18). For a load below T_i the speed of sound is constant, and drops beyond this. The crackings are thus indications of internal ruptures that disturb the continuity of the structure. These ruptures have been observed by Berg [63], Freudenthal [82], Rusch, and ourselves. Their length is a few millimeters and their thickness a few microns. The increase in the load augments the density of this cracking and enlarges the cracks which, as they join, lead to rupture.

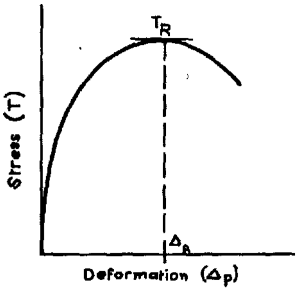


FIGURE 17. *Curve for rapid plastic deformation.*

The transverse swelling is likewise characteristic; Poisson's ratio remains constant up to T_i, then increases to reach 0.5 and beyond shortly before rupture. This transverse swelling appears to be due to the establishment and the dilation of microfissures, the privileged direction of which is parallel to the axis of the compressive stress. To summarize, we see that the rupture properly speaking is preceded by a "pre-rupture" which appears rather early, between 50 and 75 percent of the standard breaking load. What we then measure is no longer a simple plastic deformation since there is added to it the effect of a disorganization.

In general, it seems that no measurable instantaneous plastic deformation is found in compression below ½₀ of the breaking load. Here are a few figures obtained by Le Camus:

$\frac{T}{T_R}$	0.05	0.10	0.20	0.30	0.50
$\frac{\Delta_R}{\Delta_E}$	0	0.10	0.18	0.22	0.26

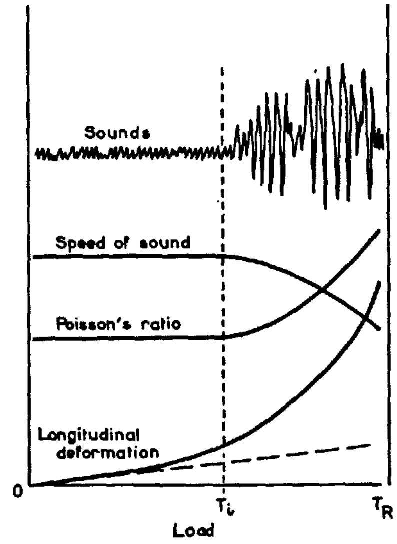


FIGURE 18. *Changes in mechanical and sound characteristics on loading.*

Glanville [41] has given deformation curves of concrete under loads maintained for variable periods from 5 to 60 seconds on a concrete containing 350 kg of portland cement per m^3, loaded at 28 days. The plastic deformation increases with time. At about 30 percent of the breaking load, $\frac{\Delta_R}{\Delta_E}=5$ percent at 15 sec, 10 percent at 30 sec, and 15 percent at 60 sec.

Deformation under heavy loads has been specially studied by Shank [64]. His paper appears to lend itself to the interpretation provided by the following table for measurements at 1 hr:

$\frac{T}{T_R}$	0.855	0.88	0.905
$\frac{\Delta_R}{\Delta_E}$	0.30	0.45	0.55

For $\frac{T_E}{T_R}=92$ percent the rupture occurs before 1 hr. It occurs at 7 hr for $\frac{T_E}{T_R}=0.905$. The author proposes representing the rapid plastic deformation in the form $\Delta_R=cT^{1/n}$. We may mention that Blakey [65] proposes an expression $T=E\Delta e^{-\Delta/\Delta_m}$ where Δ_m is the deformation at the maximum of the curve. Smith and Young [66] propose the formula: $\frac{T}{T_R}=\frac{\Delta}{\Delta_m}e^{1-\Delta/\Delta_m}$.

But finally, it must be confessed that we do not know a great deal about rapid plastic deformation in terms of the age, the curing medium, etc. We know only that it is less than the elastic deformation and negligible up to 10 percent of rupture. As for the plastic Poisson's ratio, we know practically nothing about it.

In tension, rapid plastic deformation tests are few in number. Our tests and those of Grassam and Fisher [67] indicate a total linear deformation up to 85 percent of the breaking load in tension, with the plastic deformation preceding rupture not exceeding 8 percent of the elastic deformation. Todd [68] on the contrary indicates a few experiments in which the plastic elongation obtained beyond 75 percent of the tensile strength exceeds a quarter of the elastic deformation. These involve prisms containing a longitudinal steel bar, however, and it is recognized that the rupture or cracking elongation of a concrete is increased in the proximity of a reinforcement. As sudden cracking cannot occur, it is replaced by a microfissuring that may look like plastic deformation. In order to check this, we have used a device composed of a tube of steel within which concrete was poured [31, 62], an inside thread ensuring adherence between the two. The tensile stress was applied to the tube by means of threaded sleeves. Under these conditions the tube stretched, along with the concrete, to the same amount. The elongation Δ was measured on the outside of the steel tube, in the central area, by means of strain gages. If Ω_a is the section of the tube having a modulus of elasticity E_a and Ω_b the section of the concrete having a modulus of elasticity E_b, the stress must be $F=\Delta(E_a\Omega_a+E_b\Omega_b)$. The curve that represents the relation $F(\Delta)$ must be included between two straight lines of inclinations $\frac{F}{\Delta}=E_a\Omega_a+E_b\Omega_b$ (a perfectly elastic system) and $\frac{F}{\Delta}=E_a\Omega_a$ (the concrete no longer reacts, it is broken, fig. 19). We find that the experimental form is OAB. It is identical with the upper straight line as far as A, then bends. If there were a sudden break at a given moment, we should find a drop CC′, and the reaction of the concrete should instantly be equal to zero. Yet not only is there no sudden break, but the reaction of the concrete does not become equal to zero. This result may suggest plasticity, but in order to decide the matter another experiment was indicated. This time the concrete was not bound to the tube except at its extremities; it was separated from it by a sheath of foam rubber. The CC′ reactions of the concrete were then the same up to A, then less, equaling zero shortly thereafter, but this time also without suddenness. If we record both types of reactions F_R=CC′ in figure 20 we see that the maximum reaction of the free concrete, that is to say its strength, occurs near A and equals zero shortly thereafter as soon as cracking has crossed the section. For concrete supplied with a steel guide the reaction in M′ is greater than in M.

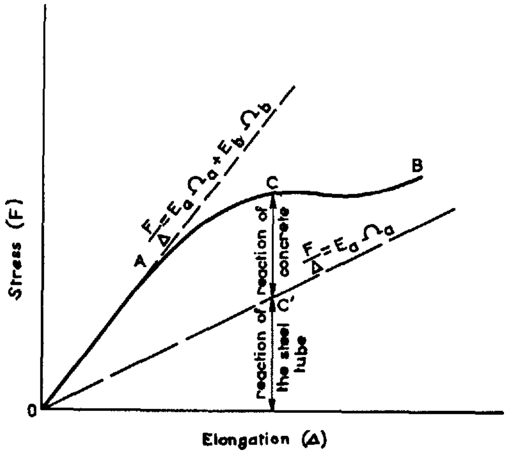


FIGURE 19. *Elongation of concrete in a threaded steel tube.*

All this shows that the apparent plasticity of concrete in tension is improved by the presence of a reinforcement.

Tests of the plasticity of concrete have been made by bending, strain gauges being placed on the strained surface of joists poured without reinforcement. On neat paste, at 3 months, our tests showed that up to 90 percent of the breaking load no measurable residual deformation occurs. At 95 percent of this load, the plastic deformation

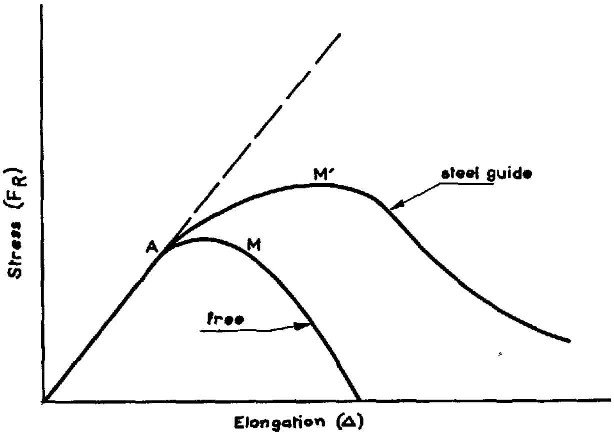


FIGURE 20. *Behavior of concrete unrestrained in a steel tube compared with that in a threaded tube.*

was 2 to 5 percent of the elastic deformation at 1 hr and 6 to 11 percent at 4 hr. The few experiments made in torsion [56] seem to show that plastic deformation appears earlier than in tension; close to rupture $\left(\frac{T}{T_R}=0.9\right)$ it amounts to 10 percent of the elastic deformations, but it is possible that errors due to the friction of the supports may account for this figure. Such measurements should be undertaken on tubes.

Creep—Slow Plastic Deformations

When concrete, after having been loaded, remains under the influence of this load over a long period, it continues to become deformed. It is this slow plastic deformation that we call creep. It appears to approach a limit to the extent to which the load is maintained constant for a very long period. We say that it appears to approach a limit without being really able to affirm this. The tests begun by R. Davis [69] some 30 yr ago have not yet brought out this stabilization. Creep in 1 yr being taken as a unit, it becomes after 2 yr 1.14, after 5 yr 1.20, after 10 yr 1.26, after 20 yr 1.33 and after 30 yr 1.36. These are the longest tests known; no one knows what happens to the concrete at the end of 100 yr, and there is no chance of my finding out. I therefore suggest that Davis' measurements be carefully continued by his successors in order that our scientific heirs may some day be able to settle this important point. To build a sealed room where the atmosphere is fixed at 50 percent humidity and into which one will enter religiously every 20 yr does not appear to me to constitute an expense incompatible with the financial means used in other fields for scientific research in a country like the United States of America.

Having said this, let us remove a load from a test piece after a time *t*. The test piece becomes deformed in the opposite sense instantaneously, then it continues to be deformed for a certain time (fig. 21). Without concluding as to whether what we have is a deferred elasticity or a reaction of the elastic aggregates on the plastic phase that the binder may constitute, we shall say that, finally, a permanent deformation remains. But this includes in part the shrinkage that the concrete would have undergone during the same period. The permanent deformation, the one due to creep, which is a consequence of the applied load, thus appears to be the difference between the permanent deformation and the shrinkage.

If at the moment $t'>t$ the creep test piece and the shrinkage test piece are both placed in water, they swell. The test piece that has been subjected to a load swells more than the one that was cured without load and more markedly so to the extent to which the load applied has been greater.

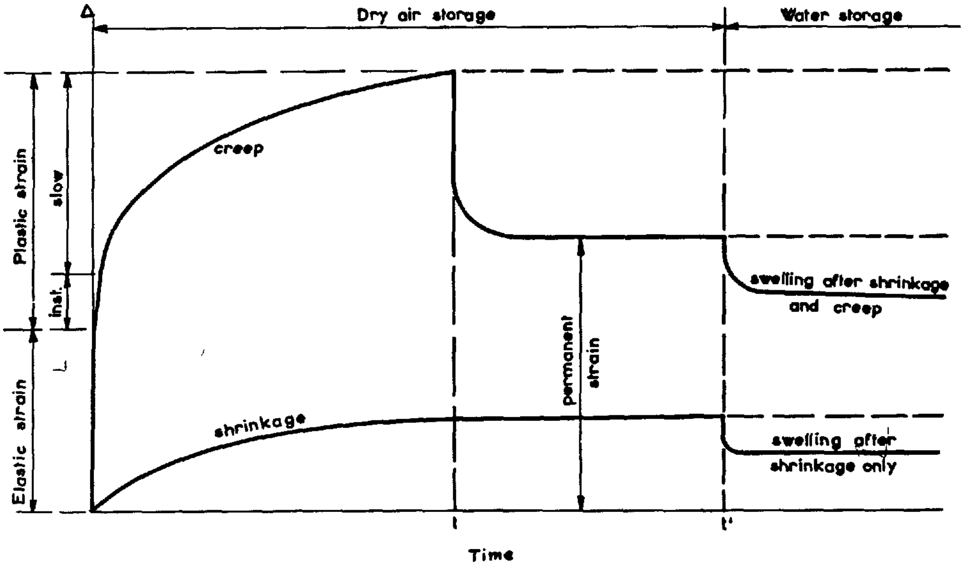


FIGURE 21. *Creep and shrinkage as affected by conditions of loading and storage.*

Such are the rough outlines of the phenomenon that we shall examine in detail. The first known study of creep is the one published by Woolson in 1905 [70]. We shall mention further, among the precursors, W. K. Hatt in 1907, E. Freyssinet in 1907, F. R. McMillan in 1915. A fairly complete bibliography will be found in the paper presented before the Munich symposium in 1958 [62.]

Creep in Compression

Most creep curves in terms of time have an asymptotic shape; they appear, under constant load and other things being equal, to show an increase in deformation Δ toward a limit value which can be reached after several dozen years. In any case the magnitude $\frac{d\Delta}{dt}$ has a decreasing value with t. Many authors have tried to give an empirical form to the curves obtained. Lorman [71] gives the function $\Delta(t)=T\frac{mt}{n+t}$ in which m and n are two constants. The final value of the creep is thus $\Delta=mT$ where m is called ratio of creep and T the applied stress. There is found the concept of period, the time at the end of which Δ reaches half its final value Δ_m, this time being $t=n$.

We may note that this expression can be written in the differential form:

$$\frac{d\Delta}{dt}=(\Delta_m-\Delta)\,\frac{1}{n+t}.$$

Lee [72] gives a differential expression:

$$\Delta=\Delta_m[1-e^{-F(t)}]$$

whence:

$$\frac{d\Delta}{dt}=(\Delta_m-\Delta)\,\frac{dF(t)}{dt}.$$

Ross [73] uses a simple rheological model and gives:

$$\frac{d\Delta}{dt}=(\Delta_m-\Delta)K$$

a simple equation of viscosity. Torroja and Paez [74] use a more complete model with springs, dashpots, and dry friction in parallel and in series. It is difficult to derive a simple general equation from it. Freudenthal and Roll [83] also use a rheological model which leads to an expression:

$$\Delta=C\left[1-e^{-\frac{t}{t_m}}\right]+T\alpha\left[2-e^{-\frac{t}{t_1}}-e^{-\frac{10t}{t_2}}\right].$$

t_m, t_1, and t_2 are the times of relaxation of three visco-elastoplastic systems considered. α and C are constants characteristic of the solid, and T is the applied load. There is therefore a term independent of the load which represents shrinkage, creep properly speaking being the sum of two viscous deformations. McHenry [75] gives a relation composed of two exponentials:

$$\Delta=\alpha(1-e^{-rt})+\beta e^{-pa}(1-e^{-mt})$$

where a is the age of loading, α, β, r, m, and p constants. What we have is the superposition of two different creeps $\Delta_1+\Delta_2=\Delta$, both simply viscous, so that:

$$\frac{d\Delta}{dt}=\frac{d\Delta_1}{dt}+\frac{d\Delta_2}{dt}=(\Delta_{m_1}-\Delta_1)K_1+(\Delta_{m_2}-\Delta_2)K_2(a)$$

Thomas [76] proposes an equation $\frac{d\Delta}{dt}=\frac{A}{(B+t)^n}$ which also leads to an exponential form of Δ. All authors, however, have not accepted the assumption of limited creep, and Straub [77] in particular indicates the relation $\Delta=Kt^{1/n}$, a purely logarithmic form. We shall not endorse this proposal which if need be can represent the beginning of creep but which does not seem able to maintain itself indefinitely, and we shall come back to the simple equation:

$$\frac{d\Delta}{dt}=(\Delta_m-\Delta)\,\frac{dF}{dt}$$

although for very young concretes, Delarue [78] believes it is necessary to add a term of consolidation of form $\frac{A}{\sqrt{t}}$ which would tend toward a finite limit after a few days. It appears not impossible to introduce such an influence into the function F, however, for if one takes into account the form of the deformation curve there is nothing to prevent looking for its derivatives. Finally, it is convenient and probably correct to represent creep by an equation stating that the speed of deformation at a given moment is proportional to the deformation that remains to be accomplished and to a function $\Phi(t)=\frac{dF}{dt}$ which takes into account the state of the concrete at the moment considered. If we set aside the instantaneous plastic deformation $t>1$ hr, we find that Φ is the sum of a constant and of a function of time, or $\Phi=K_1(a,t)+K_2$ where a is the age of loading from the beginning of setting. For concretes loaded beyond 1 week, it appears that:

$$K_1(a,t)\simeq\frac{K_1}{a+t}$$

or $\frac{d\Delta}{dt}=(\Delta_m-\Delta)\left(\frac{K_1}{a+t}+K_2\right)$ when the applied load is less than half the breaking load, the usual area of use of concrete.

This leads us to write:

$$\Delta=\Delta_m\left[1-e^{-\left(K_1\log\frac{a+t}{a}+K_2t\right)}\right]$$

and

$$\log\frac{\Delta_m-\Delta}{\Delta_m}=-\left[K_1\log\frac{a+t}{a}+K_2t\right].$$

If we set down $\log \frac{\Delta_m-\Delta}{\Delta_m}$ as ordinates and $\log \frac{a+t}{a}$ as abscissas, we get a diagram like that in figure 22. The curve is tangential and for a long time close to the straight line

$$\log \frac{\Delta_m-\Delta}{\Delta_m} = -K \log \frac{a+t}{a}$$

from which it subsequently separates [62]. This allows calculation of K_1 and K_2. We have found for a series of concretes that K_1 is in general between 0.60 and 0.80 and K_2 between 0.0005 and 0.0015, much lower than K_1.

We shall see further that it is possible to have a different conception of shrinkage in which it is possible to separate basic creep from a deformation favored by the movement of water.

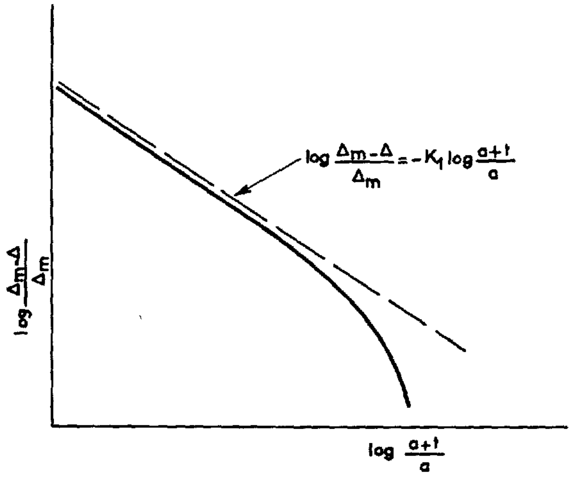


FIGURE 22. *Relation of* $\frac{\Delta_m-\Delta}{\Delta_m}$ *to* $\frac{a+t}{a}$.

Size of Load

Certain authors claim that the final deformation of a concrete, after prolonged creep under constant external conditions, is proportional to the load: Glanville [41], L'Hermite [31], Mamillan [84], Neville [85], etc. Others appear to be certain of the contrary: de la Peña [86], etc.

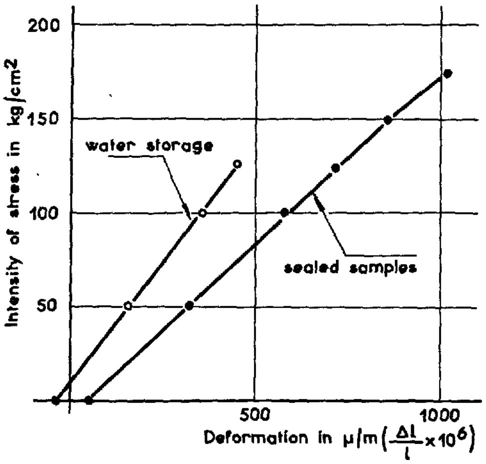
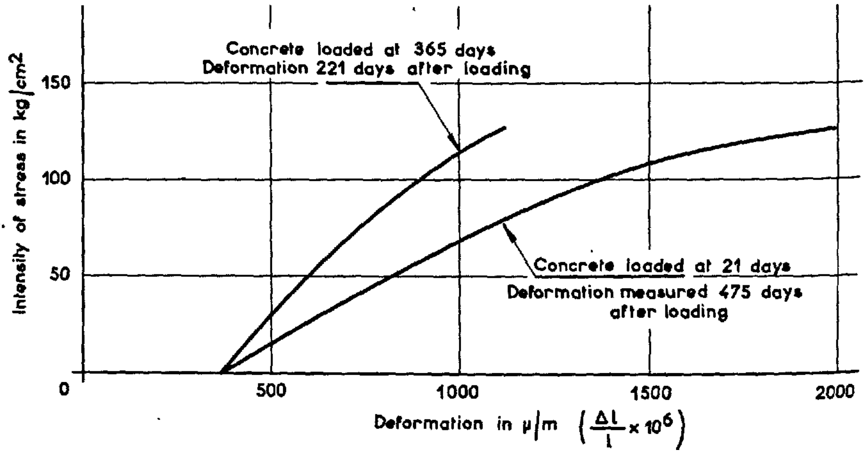


FIGURE 23. *Portland cement concrete loaded at 28 days; creep measured 70 days after loading (shrinkage or swelling included).*

Our experiments have shown an almost perfect proportionality for samples cured in such a way that there can be no exchange of water with the outside up to 50 percent of the breaking load. The same holds for concretes cured in water (fig. 23). On the other hand, for curing in dry air, the linearity appears less clearcut (fig. 24). However, it can be allowed that below 100 kg/cm², or one-third of the breaking load, the creep, deducting shrinkage, is proportional to the applied load to within less than 10 percent.

Certain tests suggest that the total deformation becomes linear and proportional to the load, shrinkage included, when the influence of the latter, considerable for slight loads, becomes negligible for higher pressures [62] (fig. 25). But in view of the slight deviation that this involves in relation to linearity, it seems that the latter can be considered as practically acceptable for engineering calculations for an intensity of stress below 50 percent of the breaking limit.

FIGURE 24. *Creep at 50 percent rh.*



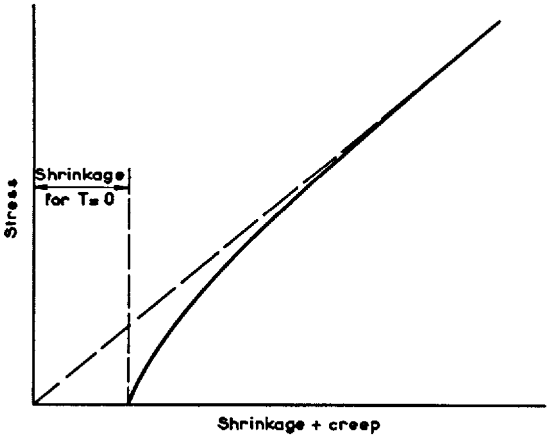


FIGURE 25. *Deformation, including shrinkage, in relation to stress.*

Age of Concrete at the Moment of Loading

Experiments made on this subject are relatively few in number when great differences in age are involved. What is certain, in any case, is that the creep after several years of loading is less as the age at which the loading has been effected is more advanced.

Let us call $\Delta_n(7)$ the creep after several years of a concrete loaded at 7 days and $\Delta_n(a)$ the creep after an equally long time of a concrete loaded at the same rate at any age a. The relation $\frac{\Delta_n(a)}{\Delta_n(7)}$ is a decreasing function. Figure 26, drawn from the results of experiments of which we have had knowledge and of experiments which we have carried out, shows that, aside from the scatter, the relation $\frac{\Delta_n(a)}{\Delta_n(7)}$ diminishes in a practically linear way with the logarithm of the age. It seems that this must approach a limit, but nothing in the data at present available allows us to establish it. It is believed that the total creep deformation varies inversely with the mechanical strength of the concrete at the time of loading, but the precise form of this relation remains to be found.

Mode of Curing

Davis [69] was the first to bring out the important influence of the humidity of the curing medium on creep. By way of example, we may indicate that after 1,600 days the following creeps were obtained on a portland cement concrete loaded at 28 days at 65 kg/cm^2:

Relative humidity	Total creep	Shrinkage without load	Calculated creep
	μ/m	μ/m	μ/m
Water	180	−120	200
Air 99 percent	250	−100	240
Air 70 percent	1,450	+750	1,460
Air 50 percent	2,100	+1,200	2,100

We observe the enormous influence of the humidity. The interdependence or at least the correlation between creep and shrinkage appears positive. We have proposed [31] relating these two phenomena by a formula:

$$\Delta_m = \Delta_{mi}(1 + Q\Delta_r)$$

where Δ_{mi} is the creep in the absence of shrinkage, Q a constant depending on the concrete and Δ_r the shrinkage with the corresponding humidity. This relationship indicates that creep in a constant atmosphere is a linear variable of the absolute shrinkage measured in relation to the swelling curve. The fourth column of the preceding table gives the result of the calculation which indicates a good correlation.

The mode of curing that precedes loading likewise has a great influence. R. Davis has shown that curing in water before loading may greatly diminish the outer creep. Curing in water for 28 days instead of in dry air (50 percent rh) reduces the creep (shrinkage being deducted) from 550 to 175 μ/m at 350 days. It is possible to bring in the mechanical strength R reached at the moment of loading and to add a correcting term to the empirical formula already established:

$$\Delta_m = \Delta_{mi}(1 + Q\Delta_r)f(R)$$

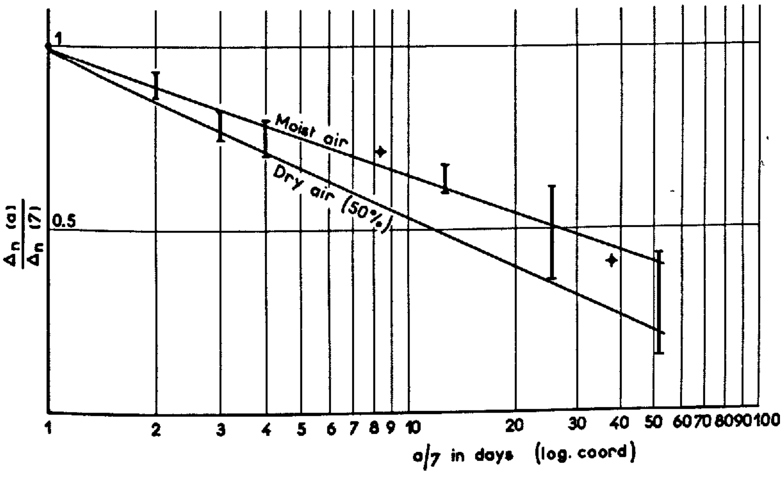


FIGURE 26. *Variation of creep in terms of age of loading.*

where $f(R)$ is a variable to be determined; for instance as a first approximation $f(R)=A/R$.

But an unexpected phenomenon was brought out at the last RILEM symposium in Munich (Oct. 1958): "alternations of humidification and of drying produce an increase in creep". In order to check this fact, we used a certain number of samples having stood for 600 days in dry air under a series of permanent loads: 0, 50, 100, 150, 200 kg/cm^2. We then placed them in water. Some swelled, others continued to contract; but the absolute difference between the swelling of the nonloaded control and the deformation under load was positive and spectacular. For 28 days, the creep of the sample exposed to a compression of 150 kg/cm^2 was 300 μ/m (figs. 27 and 28). After this period, the test pieces, still loaded, were replaced in dry air for 70 days. We then witnessed a general shrinkage, independent of the load but without creep, properly speaking. Next, the samples were again placed in water for 90 days: there was again creep amounting to approximately 180 μ/m per 150 kg/cm^2. A fresh exposure to dry air for 28 days gave rise only to a shrinkage independent of the load. These unsystematic experiments, which must be considered merely as a first attempt, appear to show that creep as it is usually considered—the difference between shrinkage and deformation—increases rapidly through humidification and remains stable during subsequent drying. Similar results were likewise obtained by Hansen [87]. It is possible, however, to consider another aspect of the phenomenon as it is indicated by figure 27. Without load, the concrete swells in water, shrinks in dry air, and so forth. Under load, the swelling is reduced and varies inversely with the compressive load. It may be said that under a pressure p equal to 100 kg/cm^2 in the case considered, the swelling in water is compensated. It is not far from this conception to that of swelling pressure put forward by certain authors, including Powers. In any case, it would be interesting to pursue investigations of this kind.

Tests by Seaman [88] have borne on the influence of the preliminary treatment of concrete by steam. The treatment in autoclave at 180 °C under steam pressure gives a modulus of elasticity 30 percent lower than that of a concrete hardened in moist air at 30 °C. But at 70 days, the creep of the treated concrete is approximately one-quarter that of the other. Moreover, it seems that this creep is very rapidly stabilized (in approximately 30 days). When one tries the silico-calcareous reaction with introduction of powdered silica, the creep becomes very slight after treatment, namely 50 μ/m at 90 days, and is stabilized after 2 weeks. This diminution of the deformation corresponds to that of shrinkage. There is probably a relation with the structure of the hydrates.

We call attention also to Ross's original article [89] in which he proposes treating the concrete before loading by heat and vacuum in order to produce a rapid drying. Placing in a damper atmosphere at the moment of loading determines a swelling that at least partly compensates the subsequent creep.

The influence of temperature on creep has been studied by Serafim [90], who indicates that this factor is appreciable in the first days of loading (4 to 7 days); afterwards the deformation curve remains parallel. The difference for 45 °C that persists to 60 days under a load of 25 kg/cm^2 applied at 8 days of age without exchange of water with the outside (coated test pieces) is 160 μ/m as against 400 μ/m of total creep at 20 °C.

Composition of the Concrete

The effect of the cement content has been studied by Davis, Glanville, and others. The grain size plays a role as well as the water/cement ratio. We find upon examination of these test results that there is a lessening of creep when the cement content increases; a lessening compensated by the increase in shrinkage. However, it is possible to observe a new increase for rich mortars, and beyond question a considerable creep for neat pastes. This seems to mean that there is a concrete composition with minimum creep which is likely to be found with an aggregate having a special mineralogical composition (quartz or very hard limestone) and for a rather high cement content, which it would be presumptuous to try to specify at this point but which must take into account the grain size of the aggregates and the nature of the cement. The influence of the nature of the aggregates is in fact really appreciable when their modulus of elasticity is very low or when they can be subjected to actual plastic deformations. The tests made by Davis [69] give the following creep values (shrinkage included) at 25 yr for 50 percent rh; sandstone, 2,600 μ/m; basalt, 2,100 μ/m; granite, 1,700 μ/m; and quartz, 1,300 μ/m. He also indicates that creep increases especially at the beginning when the size of the aggregates increases. Kordina [91] produced eight concretes of identical cement content with different aggregates. He obtained two families of concretes: the one includes aggregates of the following types: siliceous gravel, quartz, marble, granite and basalt; the other includes the sandstones. After 1 yr of curing at 65 percent rh, the first family gives a specific creep in relation to 1 kg/cm^2 which varies between 1.7 and 2.3 $\times 10^{-6}$; the second family gives a creep which varies between 6 and 7×10^{-6}. We may note further that the creep increases only slightly but in a manner corresponding to the water/cement ratio, approximately following the concomitant variations of shrinkage without load.

The influence of the nature of the binder has been studied by Neville [85, 92]. It appears that, generally speaking, shrinkage under a given load diminishes when the strength of the cement increases (the creep under this constant load

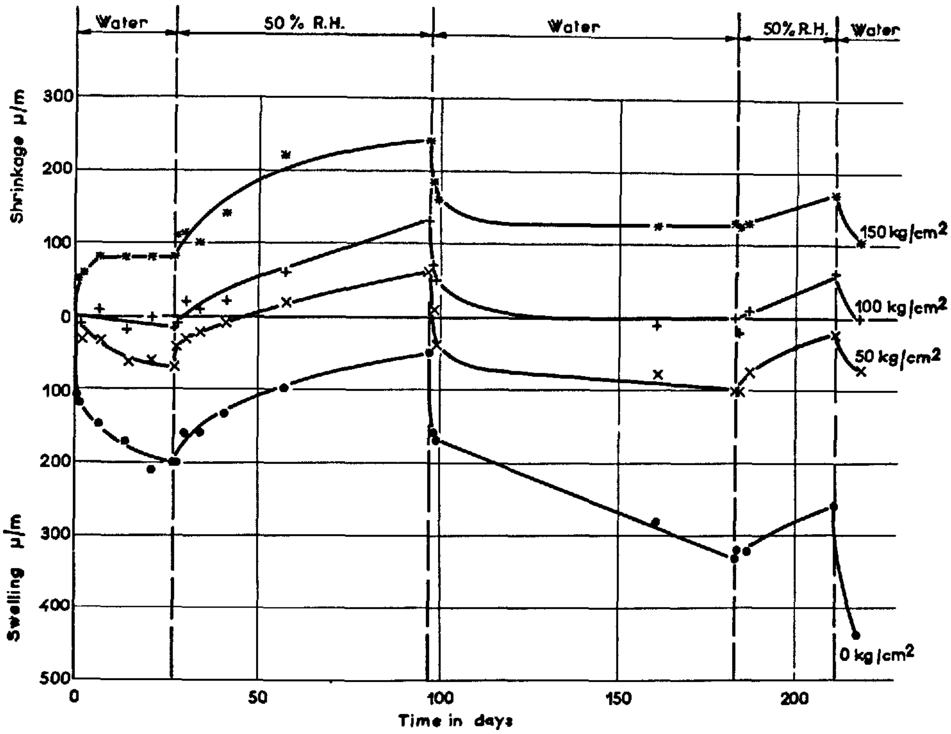


FIGURE 27. *Deformations due to alternations in humidity in relation to the deformations of test pieces loaded under the same stresses and cured continuously at 50 percent rh.*

Series loaded at 7 days. Initial recording at first placing in water after 600 days of loading. Creep at this time:

0 kg/cm²:	280 μ/m
50 kg/cm²:	1,000 μ/m
100 kg/cm²:	1,800 μ/m
150 kg/cm²:	2,900 μ/m

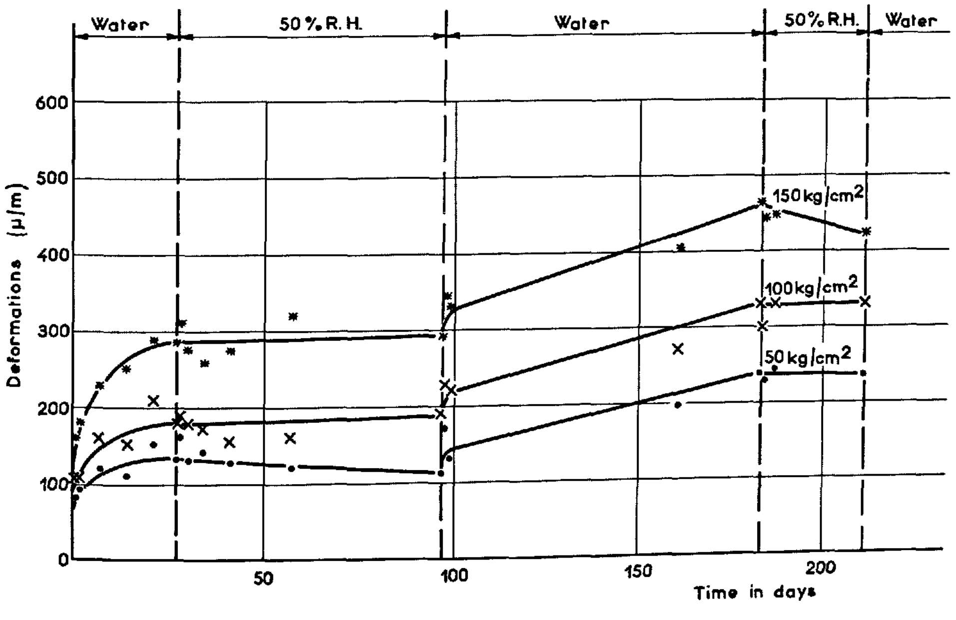


FIGURE 28. *Increase in creep in relation to the nonloaded test piece.*

being, moreover, inversely proportional to the strength). The author indicates further that aluminous cement has a lower creep than portland, that creep increases with the fineness at the same time as the shrinkage. The influence of the chemical composition of the clinker has not yet been studied and is a subject well worth looking into. Indeed certain works like prestressed concrete bridges require a concrete having low creep, whereas works such as gravity dams where the structure must adapt itself to the movement of the foundations should use concretes with a relatively higher creep. The adaptation of the binder and the composition to the liability to plastic deformation seems to be a problem of construction that has not yet been sufficiently considered.

The Influence of Volume

The dimensions of the test piece have a bearing on the speed of creep and perhaps also on its final value. Davis' tests [69] show at 10 yr creeps that decrease with the dimension for curing in air. Gwosdew [93] has studied prisms whose dimension ranged from 1 to 8. For an intensity of stress equal to one-half the breaking load, the creep after a few years was approximately three times greater for the small test piece than for the large one. Results of the same kind were obtained by Karapetian [79]. The Russian school advocates the use of the parameter $\tau=t\left(\frac{K}{D}\right)^2$ by analogy with what has been indicated above for shrinkage.

However, it appears certain that for concretes cured within a membrane preventing any exchange of water with the outside, creep is independent of the dimensions. The supplementary creep that accompanies drying occurs after a period proportional to $\left(\frac{R}{K}\right)^u$ where u varies between 1 and 2, so that the parameter τ which defines the time of equal creep must be of the form $\tau=t\left[a+b\left(\frac{K}{R}\right)^u\right]$ with u included between 1 and 2. However this may be, it is indispensable that in experiments relative to the influence of the dimensional scale on shrinkage, comparisons should be made with the adiabatic shrinkage or basic shrinkage, in the absence of evaporation or water absorption. Only under these conditions can useful comparisons be obtained.

Effect of Load Removal

When the load is removed from a test piece that has been placed for some time under a permanent load, it undergoes a partial instantaneous recovery, followed by a further deferred recovery, during a visco-elastic period, that augments the instantaneous elastic recovery by 15 to 30 percent (fig. 21). The magnitude involved is thus appreciable.

When the recovery is effected in the same medium as the loading, the phenomenon appears to be markedly viscous, for it corresponds to an equation $\Delta=\Delta_v(1-e^{-Qt})$ where Δ_v is the total recovery and Q a constant. Representation with the coordinates log $(\Delta_v-\Delta)$ and t gives straight lines (fig. 29).

The question arises as to what this recovery is due to: perhaps to a reabsorption of water from the surrounding air, but the measurements of weight that we have made have been absolutely negative (if there is recovery of weight, it is negligible); perhaps to a movement of the water in the hydrated phase; perhaps again to a reaction of the elastic aggregate phase on the viscous hydrated-cement phase (this last assumption appears the most probable).

McHenry [75] gives a hypothesis on the reversibility of creep (fig. 30). Let us consider a creep curve obtained after age a_1: curve A. Let us now consider a creep curve after age a_2: curve B. If we unload test piece A, the unloading curve after time a_2 is obtained by subtracting from the

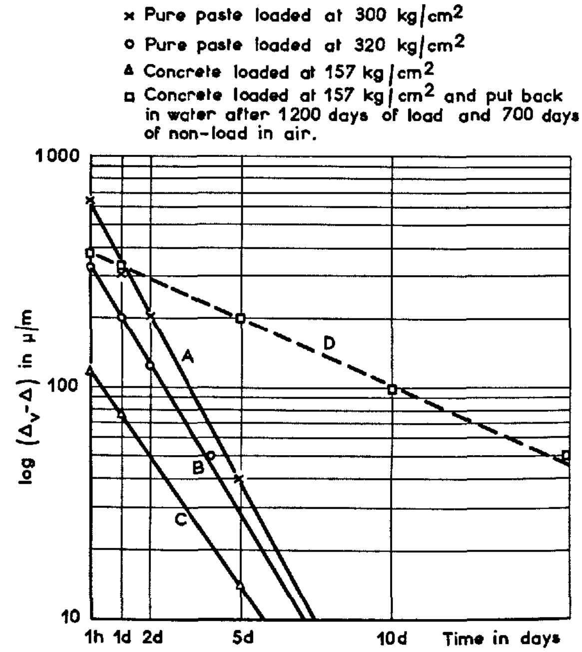


FIGURE 29. *Elastic aftereffect.*

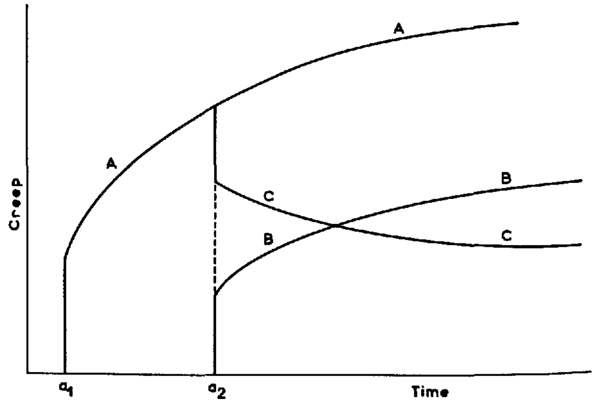


FIGURE 30. *Representation of the hypothesis on the reversibility of creep.*

ordinates of curve A those of curve B, to form C. This hypothesis is attractive in its simplicity, and it appears to have been verified in several cases [94]. We have observed that it gives an acceptable approximation for some 50 days at a maximum when the creep occurs in water but that it remains uncertain for creep in dry air ($\theta=50\%$). The postelastic effect is rapid and viscous, whereas creep does not conform to a simple law of viscosity. It may be said, however, that McHenry's hypothesis is a convenient approximation.

We may say further that if the concrete is placed in water after removal of the load, it swells more than a test piece that has never been loaded placed under the same conditions, and all the more as the load applied has been greater (fig. 31). But, the weight measurements do not on this account appear to indicate an increased reabsorption of water. It is also to be observed that this swelling appears only if the load applied exceeds a certain magnitude (in the case of figure 31, above 45 kg/cm^2). This is a very puzzling phenomenon and invites further scrutiny. Figure 32 shows the changes in length of a concrete and indicates in particular that the residual deformation after unloading and placing in water is much less than the maximum deformation. It will likewise be observed that if placing in water under load gives rise to an increase in creep, the placing in water after unloading gives rise, on the contrary, to a higher elastic recovery. I should like to see this lead to a few experiments such as, for example, the reloading at the moment of placing in water to compare it with the effect of unloading. This procedure might give indications as to the influence of water on viscosity and an estimate of the forces of elastic recovery.

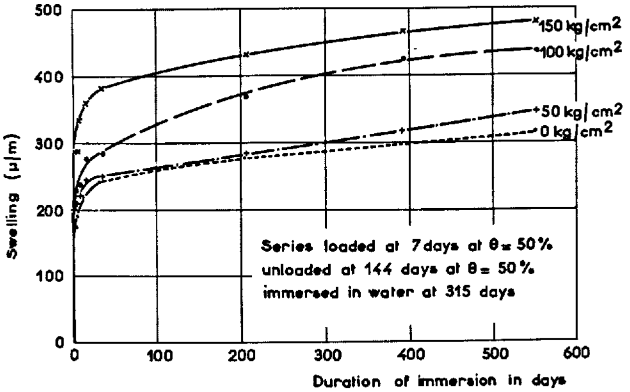


FIGURE 31. *Swelling due to water immersion after unloading.*

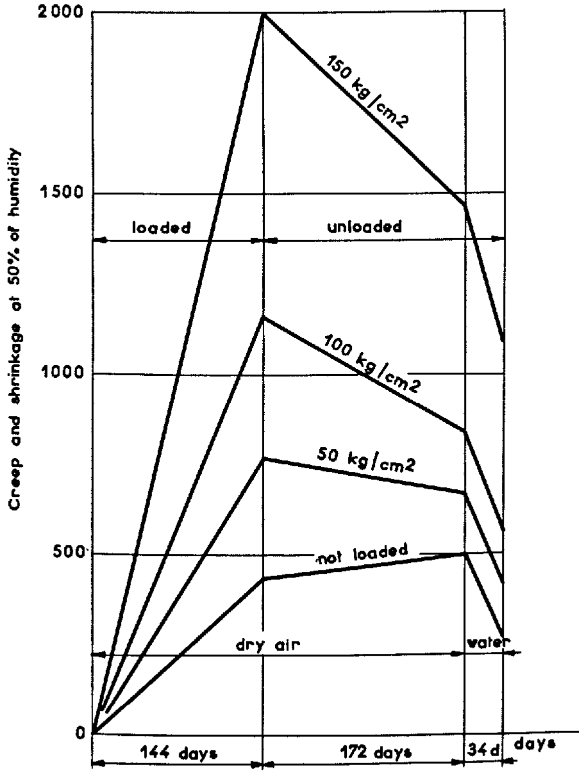


FIGURE 32. *Deformation of a concrete loaded at 7 days unloaded at 144 days, and submerged at 316 days.*

Transverse Deformation of Concrete (Poisson's ratio)

We have noted that under instantaneous loadings the reversible transverse deformation was 10 to 30 percent of the longitudinal deformation and that this ratio diminishes with age. If we call $\sigma_p=\frac{\Delta'_p}{\Delta_p}$ the ratio of the longitudinal and transverse plastic deformations, we call this "the plastic Poisson's ratio". Certain authors consider it to be equal to 0 or in any case much lower than Poisson's ratio relative to elastic deformations. This conclusion is at all events in contradiction with the classical theory of plasticity which indicates $\sigma_p=0.5$, showing thereby that plasticity is a phenomenon which occurs without change in volume. Our tests made recently and very carefully to clarify this question have shown the existence of a plastic Poisson's ratio very close to or equal to the purely plastic Poisson's ratio for instantaneous deformations (fig. 33). Up to 200 days, this ratio appears to hold, making allowance for shrinkage, which incidentally is not always the same per unit of length along the axis and the side of a prism. In our experiments we have found it close to 0.2 (Mamillan, to be published in the Annales de l'Institut Technique du Bâtiment et des Travaux Publics). Kordina [91] has found Poisson's ratio varying with the various types of aggregates. For rolled quartz and basalt he obtains a value close to 0.30, for river siliceous aggregates, granite, and crushed quartz, the values are grouped around 0.20, and, finally, for sandstone the Poisson's ratio becomes less.

It therefore seems that creep does occur with a lessening in volume and is governed by the elastic skeleton. If this hypothesis is confirmed the conclusion is of great interest, for it would make it possible to relate the transverse deformation to the longitudinal deformation in a biunivocal way.

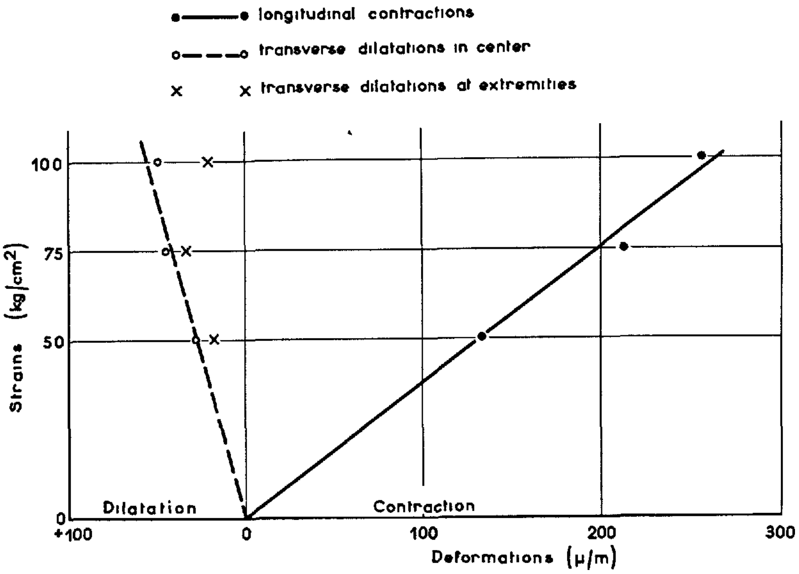


FIGURE 33. *Instantaneous deformations of test pieces.*

Curing: 50 percent rh.
Age of loading: 30 days.

However this may be, creep occurs with a lessening in volume, which appears undeniable, and if this phenomenon is produced by the displacement of a viscous phase it cannot occur without an increase in compactness. Apparently this increase exists and must be confirmed by experiments on strength. Washa and Fluck [95] have operated for more than 10 yr and have shown that at the present date the increase does not exceed 5 percent of that of the nonloaded control concretes. On the other hand, the modulus of elasticity increases from 20 to 30 percent between the nonloaded test pieces and the loaded ones. This result appears to be confirmed by R. Davis' tests (verbal communication). Finally, while one cannot anticipate an appreciable increase in strengths as a result of creep, the increases that are observed below 50 percent of the breaking limit are *always* positive and clearly show the effect of an increase in compactness.

Creep Under Repeated Loads

If instead of leaving a permanent load resting on the test piece one repeats the same load at a rather rapid rate (several times per minute), one observes an acceleration in plastic deformation. Tests have been made by Le Camus [56] on two groups of identical test pieces. One of these was subjected to a permanent compressive stress of 126 kg/cm^2 and the other to the same load repeated at a rate of 500 times per minute. After 24 hr of treatment (720,000 repetitions), the permanent deformation observed was the same as for 28 days of permanent load. After 3,600,000 repetitions (5 days) the effect was identical with that of 180 days of static load. After 10 million repeated loadings the deformation was the same as that resulting from 600 days of permanent load.

We wanted to find out if a concrete already deformed by creep was sensitive to the effect of repeated loads in order to ascertain whether the deformation by repeated load was of the same nature as deformation under permanent load. (We already knew that it was not produced by microfissuring for the transverse modulus of elasticity had not been lowered in the course of the treatment). Thus a test piece loaded for 1,000 days was unloaded, placed at rest, and reloaded under repeated stresses. At the end of 3 million repetitions the plastic deformation had increased by a maximum of 6 percent.

Creep under permanent load and plastic deformation under repeated load do not have a cumulative action. A concrete adapted under permanent load is no longer apt to be deformed under repeated load (if we neglect the 6 percent indicated above which perhaps is due to shrinkage resulting from heating through mechanical hysteresis).

Creep in Tension and in Torsion—Combined Stresses

Tension creep devices are more difficult to make than those for compression. The laws, however, appear to be similar. There is a continuity between elastic and plastic deformations. As the tensile strength is very low as compared to the compressive strength, however, the creep that it is possible to measure is very slight and is limited by rupture to a short time.

It is possible to see that the creep is proportional to the applied load, but it appears at least that the creep is more rapid, and because of this in a bent beam the neutral fiber rises toward the compressed surface and subsequently descends again. We may recall in this connection the tests by Bingham and Reiner [96] on cement joists 1 in. on the side and 34 in. in length subjected to a bending moment. The deformation curve in relation to time has at the outset the form of a parabola and then becomes linear in relation to time; the speed of creep becomes constant. The tests were ended too soon to bring out the possible stabilization and the hygrometric conditions were not well defined.

The simplest combination of stresses is provided by torsion which is a combination of tension and of compression at 90°. The only experiments of this kind that I have come across are those that were carried out in my laboratory by Le Camus [56]. The method has the advantage of eliminating shrinkage, since the latter can apparently not produce a torsion. Tests carried out over 400 days showed that the permanent deformation is proportional to the applied couple. Another observation not devoid of interest is that the shrinkage along the axis is the same for the loaded and the nonloaded test pieces. This identical shrinkage can occur only if the tensile and compressive creeps compensate each other exactly for equal loads of contrary sign.

Dukes and Davis [97] have carried out creep tests on compressed cylinders subjected to a lateral stress. The longitudinal creep deformation measured after 3 months of loading in a damp medium is approximately proportional to the difference in the chief stresses, a result which appears to extend the application of the linear law of deformation. Poisson's ratio, according to the authors, appears to be of the order of 1/6, but the interpretation of the tests is difficult in this case.

Ross [98] has carried out very interesting tests in the case of creep under double stresses. Square test pieces left free in the direction normal to their plane were stressed on the other two pairs of sides. The author believes that from this test could be deduced the linearity of deformation in relation to load and a very low value of the plastic Poisson's ratio.

Theories and Conclusions on Creep

Theories on creep are numerous and varied if not contradictory, which is characteristic of a young science. Some of these theories are simply explanatory or phenomenological; others are quantitative and are aimed at permitting calculation and extrapolation for the needs of builders. As it is difficult to summarize them all and in any case impossible to bring them all together in this report, we shall examine their main features in what is to follow, and we shall begin by asking a few questions.

Where does creep have its seat?

Concrete is composed of two essential parts: a skeleton of aggregates and a phase composed of a more or less hydrated cement with generally an excess of water. The aggregates are in most cases much more rigid than the binding phase and have little susceptibility to plastic deformation. Creep thus appears to have its seat in this binding phase and in its bond with the aggregates.

Why and how does the cement paste creep?

According to certain authors the binding paste is a gel, hence a viscous body, but in continual evolution by virtue of hydration, hence of variable viscosity. Under these conditions, the effect of external forces is to put this gel into movement in such a way that it fills the voids in the concrete. The elastic skeleton follows the movement in the direction of the forces applied with the transverse deformations that are peculiar to it, which conforms to the conservation of the elastic Poisson's ratio observed by different authors insofar as creep is concerned.

According to other authors, the binding paste is composed of a padding of crystals forming no longer a viscous body but a plastic solid with a deformation which is viscous, to be sure, but having cohesion and rigidity, these two characteristics evolving with the degree of hydration. It is possible, for that matter, that the two forms of binding paste coexist, the proportion of the second in relation to the first increasing with time according to conditions of hydration.

Can several forms of creep be distinguished?

In this case there would have to be an indefinite viscous creep and a limited plastic creep.

Viscous creep must be in part reversible upon unloading by virtue of its association with an elastic skeleton. And unloading does have a character of viscosity (fig. 29).

Plastic creep cannot be reversible upon unloading so long as the reaction of the elastic skeleton is less than the stress applied upon loading, which is the case.

Apparently, one can only separate the reversible part of creep from the permanent part, which last can include the plastic creep, plus a part of the viscous creep. This separation is what was done by Freudenthal and Roll [83] and by Glucklich [99], proceeding by unloading at different ages as indicated in figure 34, determining for each age of unloading the irreversible deformation. Leaving out of consideration the creep and the possible evolution of the concrete during unloading, the curve obtained represents the irreversible part of creep that has been called secondary shrinkage by contrast with the primary creep or viscoelastic creep.

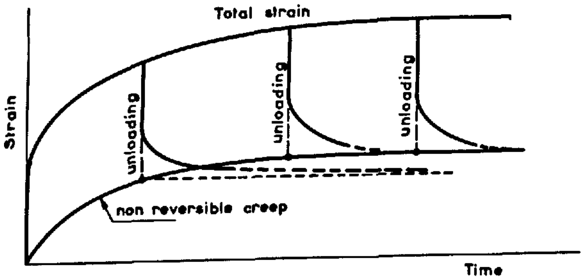


FIGURE 34. *Irreversible deformation after unloading at different ages.*

Is creep indefinite?

This question is highly important and not yet resolved. For this to be so, there must subsist a permanent viscous phase not included in the visco-elastic behavior associated with the elastic skeleton. This phase would then have as its law of deformation:

$$\frac{d\Delta_v}{dt}=a(t)$$

where $a(t)$ is a decreasing function with t. In order to know whether $a(t)$ approaches zero for t approaching infinity, one would have to know the evolution of creep over a period of tens of years.

What do we know about the law of creep with constant load, humidity, and temperature?

This law may be the combination of three phenomena:

—an elasto-plastic creep that is partially reversible:

$$\frac{d\Delta_p}{dt}=\dot{C}(t)(\Delta_{mp}-\Delta_p) \qquad \Delta_p=\Delta_{mp}e^{-C(t)}$$

—an irreversible viscous creep:

$$\frac{d\Delta_v}{dt}=\dot{A}(t) \qquad \Delta_v=A(t)$$

—a wholly reversible visco-elastic creep:

$$\frac{d\Delta_e}{dt}=\dot{B}(t)(\Delta_{me}-\Delta_e) \qquad \Delta_e=\Delta_{me}e^{-B(t)}.$$

The interaction of these phenomena which we qualify in rheology as laws of Newton and of Kelvin justifies the use of models in which one combines springs, dash-pots, friction, and return valves. This procedure leads to calculations that are extremely complicated and at the same time of great interest. Their practical use, however, remains uncertain [83, 99, 100].

If we simply superpose the three types of deformation, we find:

$$\Delta=A(t)+\Delta_{me}e^{-B(t)}+\Delta_{mp}e^{-C(t)}.$$

Now $B(t)$ must be a function similar to $A(t)$ to within one factor. The form of this function must be deducible from the unloading curve. Its form is viscous but depends on age, so that:

$$A(t)=\frac{\alpha t}{f(a)}$$

where $f(a)$ is an increasing variable of time, thus:

$$\Delta(t)=\left[\Delta_{me}e^{-\frac{\alpha t}{f(a)}}\right]+\left[\beta\frac{\alpha t}{f(a)}+\Delta_{mp}e^{-C(t,a)}\right].$$

The first term between brackets represents the continuous part of the creep and the second term the part limited to Δ_{mp}. This relationship is not very different from what McHenry proposes [75].

There is nothing, moreover, to prevent seeking an empiric variable

$$F(t) \text{ with } \Delta(t)=\beta\frac{\alpha t}{f(a)}+\Delta_m[1-e^{-F(t)}]$$

where the second term includes the viscous elasticity, the latter effect not being separated during loading. If, in addition, we consider that the first term is negligible compared to the second, we come back to the equation $\frac{d\Delta}{dt}=(\Delta_m-\Delta)F(t)$. For the moment, it does not seem possible to go much further in these calculations.

Is creep linked to shrinkage?

This question is both simple and complex. Without any doubt the concretes that have the greatest shrinkage have the most marked creep. But to say that creep is a shrinkage under load is in a sense a play on words. From the hygrometric point of view there is certainly a dependency between creep and shrinkage, while it is not certain that this relation is biunivocal; it is probably more correlative than functional. In other words, the two phenomena appear more precisely linked to a form of the hydrated phase that leads both to a similar evolution, that of a viscosity depending on time both for the one and for the other.

Concretes cured without a possibility of appreciable shrinkage nevertheless have a marked creep (adiabatic curing without exchange of water). This means, in any case, that there can be creep without shrinkage. A number of authors have considered this creep as a basic creep. But nothing, on the other hand, proves that creep in a dry atmosphere leads to a higher evaporation of the enclosed water as compared to a loaded test piece. The basic creep may be a factor of comparison that eliminates the dimensional parameter but does not appear to have any other effective value. We have seen, finally, that a concrete cured dry over a long period may, when placed in water, undergo a swelling without load and a supplementary shrinkage under load while the deformation remains the same, with or without load, over a period of drying that follows the placing in water (figs. 27 and 28). It is probable that placing in water leads either to an increase in the volume of the hydrated phase for a concrete cured dry or to a continuation of hydration, which endows the latter, through the lessening of its viscosity and its rigidity, with a new possibility of deformation. This hypothesis would likewise explain the increase in the elastic recovery for a test piece that is unloaded and placed in water (fig. 32). Let us not forget, however, that the creep of a concrete cured in water is less than for dry curing, and this appears contradictory. We must then suppose that curing in dry air does not permit a complete hydration and that it is the resumption of this hydration that gives rise to a new creep. This hypothesis does appear to be confirmed by the measurements of strength and of modulus of dynamic elasticity. We should then have to know whether a concrete hydrated permanently in water for a long period presents or does not present a resumption of creep after drying and fresh humidification. But we have no knowledge of any such experiment. T. C. Hansen [87] puts forth the hypothesis that creep is encouraged by any movement of dampness; alternate wetting and drying should give a higher and more rapid creep. This would mean that concrete is a thixotropic material.

Pickett [49] suggests that creep constitutes an accleration of shrinkage, which accordingly would have the effect of separating certain groups of particles and thus diminishing the rigidity. But this mechanism does not, apparently, explain the resumption of creep upon placing in water.

We see, finally, that the detailed explanation of the mechanism of creep on the scale of structure has not yet been given without possible challenge.

How does creep depend on humidity, on evaporation, and hydration?

Creep increases when evaporation occurs in dry air, that is to say when the evaporation is greater, no matter what may be the state of curing, hence of previous hydration. We have seen, however, that the creep deformation under load that is added to that of shrinkage without load does not lead to loss of weight, or therefore to a measurable supplementary loss of water. The explanation for this behavior is not easy to find. T. C. Hansen's surmise is very ingenious, but it does not explain the cessation of creep in a period of drying after wetting, if this fact remains confirmed by other experiments. But instead of saying, as does this author, that the diffusion of water favors movement, we might suppose that the chemical phenomenon of hydration by the molecular movement that it produces is a factor in softening of the binding phase. There may thus be a visco-plastic creep of which the speed is all the more limited, given equal hydration, as the hydrated phase is more considerable, and a viscous and visco-elastic creep of which the speed increases at the same time as the speed of hydration. We might describe this in a simplified and phenomenological way such as:

$$\frac{d\Delta}{dt}=\frac{A(t)}{H}+\frac{B(t)}{H}\frac{dH}{dt}$$

where H represents the volume of hydrated binder, the first term indicating the plastic creep and the second the viscous creep.

I hope I may be allowed an approximation suggested solely by the drafting of this report and which so far has benefited by no direct verification. Such a hypothesis, however, makes it possible to interpret several apparently contradictory phenomena such as:

—the more rapid stabilization of creep in a damp medium for a lesser final value,

—the increase of visco-elastic recovery by placing in water,

—the resumption of creep by humidification and its stoppage by drying.

The maturing of a concrete represents, in a sense, its degree of hydration, whether it be represented in volume, in mechanical strength, in rigidity, etc. It is dependent upon time, temperature, the medium in general. In fact it is homologous to the variable H indicated above. An excellent interpretation of it is to be found in a recent report by Ross [101] and we believe that herein may be found matter for broad interpretations.

We said earlier that creep may increase indefinitely so long as a viscous phase subsists, and we wrote $\frac{d\Delta_v}{dt}=a(t)$. We can compare this point of view with what has just been set forth and write: $a(t)=\frac{b(t)}{H}\frac{dH}{dt}$. Viscous creep of the Newton type disappears only when hydration is completed. It disappears more rapidly in curing in water than in dry air where the hydration is considerably slowed down; in the latter case, it resumes upon placing in water.

In the case of curing in constant atmosphere and taking $\beta(t)=\beta$ as a constant, we find that the final viscous deformation is:

$$\Delta_{mv}=\beta\log\frac{H_m}{H_0}$$

where $\frac{H_0}{H_m}$ represents the relative hydration at the moment of loading compared to the total hydration. If we assume that the relative hydration is proportional to θ, or $H_0=H_{m0}\theta$ where H_{m0} is the degree of hydration at time $t=0$ of the piece cured in water, we find:

$$\Delta_{mv}=\beta\left[\log\frac{H_m}{H_{m0}}+\log\frac{1}{\theta}\right].$$

The first term between brackets represents the effect of viscosity for curing in water, the second represents the additional deformation for curing in air in an atmosphere of relative humidity θ. Now $\frac{\log 1/\theta}{1-\theta}$ varies between 1 and 1.20 for θ included between 0.99 and 0.6. This means that the viscous creep must be approximately proportional to $(1-\theta)$; which is not in contradiction with the experiments.

This calculation has been made without any other pretension than to show the comparability of its principle with the results already known and to propose to investigators a line of reasoning.

How does creep depend on volume?

The influence of the absolute volume on creep is undeniable; it is generally explained by the rapidity of evaporation. Concrete cured in water has less creep than that cured in a closed medium, and creep in a closed medium is less than in a dry atmosphere.

Two explanations are then possible, if not complementary. The first involves the internal stresses [102, 79]. Creep and shrinkage begin on the surface and lead to a concentration of stresses toward the core. The latter then undergoes a creep in a moist medium less pronounced than the surface creep. If the effects were simply compensated there would result a delay in the deformation, but as the compensation does not occur for bulky pieces, there results likewise a lessening in the final creep. The second explanation derives from the interpretation of what we have just said in connection with hydration. The bulkier a piece is, the slower its mean evaporation is, and the closer, at the beginning, it comes to curing in a closed space. When desiccation reaches the core, the hydration is far advanced, H is large and $\frac{dH}{dt}$ is slight. We know that a preliminary curing in moist air diminishes the final creep in dry air. Here this process is progressive but leads to similar effects. Finally, the bulky pieces creep less because they are better hydrated. The pieces protected from evaporation by surface humidification or by a protective device maintained for a sufficiently long time must have a lower and more rapidly stabilized final plastic deformation.

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Discussion

E. Torroja and C. de la Peña

Introduction

The shrinkage and creep of the gel constituted by cement and water are better studied when:

(a) No gravel and coarse sand are present, because the stones restrain very much the free deformations of the paste and put it in tension, and

(b) The specimen has a thin section, because the differences in humidity and temperature between its core and surface give rise to internal stresses.

In the testing procedure described here, we use mortar specimens having the form of a tube with a very thin wall.

The surface per unit of volume of these pipes is 10 cm^2/cm^3, which amounts to 9 times that of the 4 x 4 x 16-cm prisms and 30 times that of cylinders 15 cm in diameter and 30 cm in length.

Using pipes of such a high specific surface speeds up the process of exchanging water between the specimen and the surrounding air, and so it is possible to reach the final equilibrium in a short time.

The results of the first tests carried out with these pipes were submitted to the RILEM Colloquium upon Shrinkage and Creep of Mortars and Concretes held in Munich. The paper was published in Bulletin No. 3 of RILEM (July, 1959).

Just a few more results are now available, but we think the procedure may be of interest to the attendants at the Symposium, because it seems a proper method for studying among other things the relationships between the composition, fineness, etc., of cements and their shrinkage and creep.

Specimens

Form and Dimensions

The specimens are pipes with the dimensions given in figure 1. The walls of the tubes are a little thicker at their ends in order to prevent the anomalous failures observed when these pipes are made of constant wall thickness throughout their length and tested in compression.

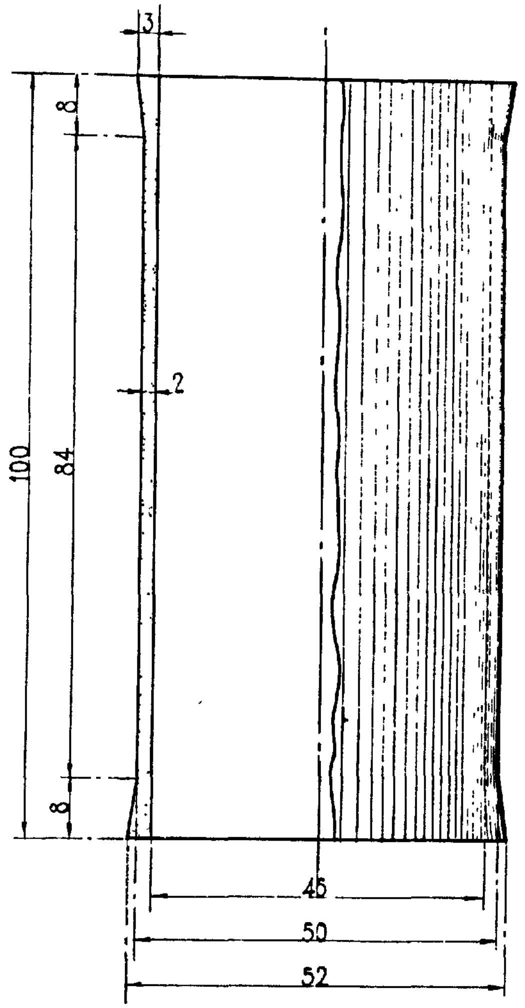

FIGURE 1. *Dimensions of pipe specimen.*
(Dimensions in mm.)

Molds

Figure 2 shows the mold employed. All the molds are made of stainless steel in order to prevent any corrosion, which would be more harmful in this case than in others because of the thinness of the specimen wall.

The side wall of the molds is a tube divided in two halves lengthwise. These two halves are

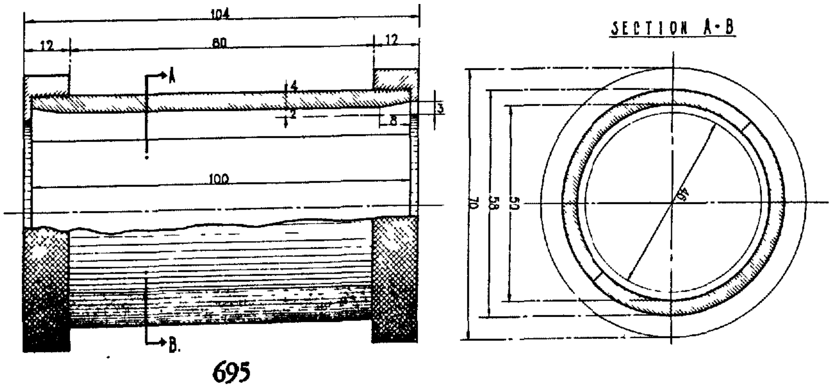

FIGURE 2. *Specimen mold.*
(Dimensions in mm.)

held together by two like pieces, one on each end of the tube. Both pieces have a 46-mm central circular hole which provides, with the 50-mm inside diameter of the steel tube, a 2-mm mortar wall.[1]

Mortar

In the tests referred to in this paper we have used a common portland cement and a very pure siliceous sand in which the particles ranged from 0.15 mm to 0.30 mm in diameter. The proportions by weight of the mortar were 1:1.

The mixing water was adjusted in order to obtain a flow of 40 ± 5 percent on the RILEM flow table for mortars. This flow corresponds to a workable plastic consistency.

The resulting water/cement ratio was 0.34.

Molding

The essentials of the procedure are the following:

The mold is held by the left hand, with the palm upwards and the axis of the mold practically horizontal. With a tool that is a sort of a sharpened straight rule, a small amount of mortar is put in on the lower part of the mold, evenly distributed throughout the length of the steel tube, gently pressed and tapped with the tool and made level with its sharpened edge, which is moved meanwhile as it bears upon the edges of both holes of the mold. The mold is then turned through a small angle around its axis with the left hand, and another portion of mortar is placed inside in the same way. The filling goes on until the whole interior surface of the steel tube is properly covered by a 2-mm layer of mortar (fig. 3).

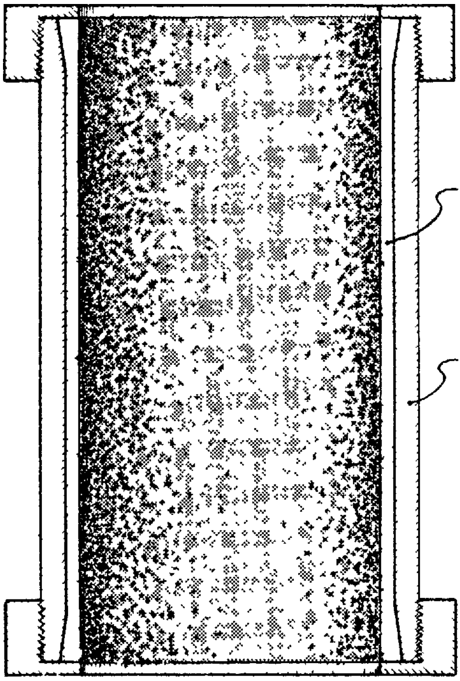

Figure 3. *Longitudinal section of specimen in mold.*

With mixes neither too dry nor too wet, such as that of mean consistency, which we have used, the procedure described works well, though some training of the laborer is necessary anyway.

The molding is performed in a room at 20 ± 2 °C and 98 ± 2 percent rh.

Curing

The mortar pipes are left in their molds for 24 hr in the same room where they are molded. Then the molds are removed, and the specimens are immersed in water at 20 ± 1 °C until just the moment of their test.

Apparatus

All apparatus is in a room whose temperature is 20 ± 1 °C.

Device for Measuring Shrinkage

The apparatus to measure the shrinkage of the pipes is shown in figure 4. It has a central airtight chamber which includes the specimen under test and a hollowed ring container at the bottom for the moisture-conditioning water-glycerine solution.[2] The top of the chamber is a thin sheet of rubber to allow the stainless steel block that rests on the upper end of the pipe to descend as the pipe shrinks.

A dial gage is rigidly attached to the beam at the upper part of the apparatus. The tip of its stem, which is in contact with the center of the block, follows the shortening of specimen.

In order to make possible the changing of the water-glycerine solution during the tests, the container has a hole in its lower part through which, when it is necessary, the already altered solution can be extracted; meanwhile another open hole in the glass tube lets air in and so prevents any vacuum in the chamber.

Once the container is empty, a fresh solution is injected through the same hole, with the vent valve open as before, to prevent any unwanted pressure in the specimen chamber.

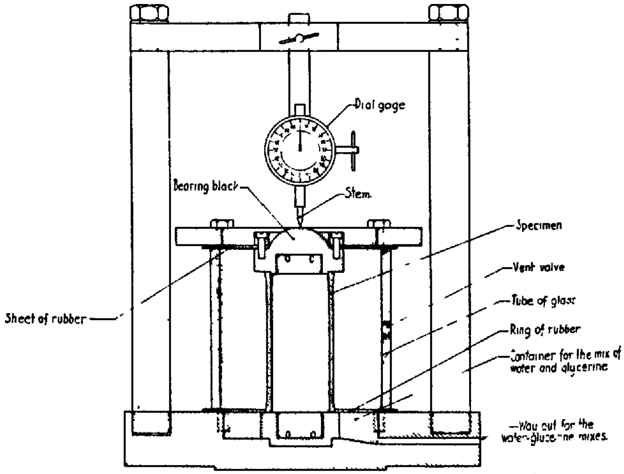

Figure 4. *Apparatus for measuring shrinkage.*

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[1] The mortar pipe wall thickness equals half the difference of the two before-mentioned diameters, as will be seen in a following paragraph.

[2] The solutions of water and glycerine are prepared and checked in accordance with the ASTM Recommended Practice for Maintaining Constant Relative Humidity by Means of Aqueous Solutions (E 104–51).

Device for Measuring Creep

The apparatus used to measure the creep is essentially the shrinkage device mounted in a framework which has a rubber cylindrical pneumatic chamber at the bottom and a big steel beam at the top to compress between them the specimen under test.

As can be seen in figure 5, the dial-gage stem is not now in contact with the bearing block as before, but with the big beam of the charging framework. Therefore, it is in this case the body of the gage that moves, going up as the specimen shortens with time under the load applied.

Before the tests were started, a graph was drawn plotting the kg/cm² of air pressure in the pneumatic chamber against the kg of compression between the bearing blocks.

To carry out the third group of tests described below, the creep devices were somewhat modified. No water-glycerine mix was used in these tests, and the whole chamber with the specimen was filled with water whose temperature was raised to and maintained at the specified figure. For this purpose, an electric resistance, a thermoregulator, and a thermometer were put inside the chamber of each apparatus. The variations registered about the desired temperature were never greater than ± 1 °C.

Tests

Three groups of tests were carried out in order to see the following things:

(1) The reproducibility of the results of shrinkage and creep measurements,

(2) The relation between load and creep, and

(3) The influence of temperature upon creep.

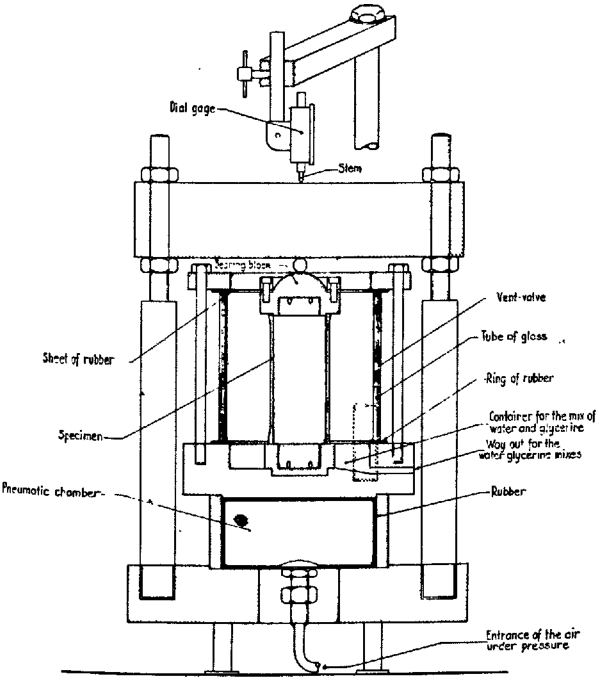

Figure 5. *Apparatus for tests of creep.*

Reproducibility of Results

Shrinkage. After a curing time of 28 days in water at 20 ± 1 °C, 15 pipes made with the mortar and in the conditions described above were put for 21 days in the shrinkage devices with the proper water-glycerine mix to maintain a relative humidity of 50 percent in the specimen chamber. The room with the apparatus was kept at 20 ± 1 °C.

The shrinkages were measured every 24 hr, and it was observed that the major part of the shrinkage of the pipes takes place in the first week, as can be seen in figure 6, where the curve of the mean values has been drawn, as well as the curves joining the points of minimum and maximum shrinkage.

The shrinkage of each pipe appears in table 1, as well as the mean values, the standard devia-

Table 1. *Shrinkage of pipe specimens at ages up to 28 days*

Pipe No.	Shrinkage in ‰		
	At 1 day	At 7 days	At 28 days
1	0.81	1.19	1.28
2	.78	1.16	1.28
3	.82	1.16	1.31
4	.58	1.08	1.16
5	.68	1.07	1.14
6	.81	1.19	1.23
7	.80	1.21	1.31
8	.81	1.14	1.18
9	.79	1.19	1.30
10	.82	1.21	1.27
11	.80	1.17	1.25
12	.75	1.15	1.25
13	.71	1.13	1.23
14	.70	1.15	1.18
15	.74	1.18	1.16
Mean value	.75	1.16	1.24
Standard deviation	.066	.040	.052
Coefficient of variation, %	8.80	3.44	4.19

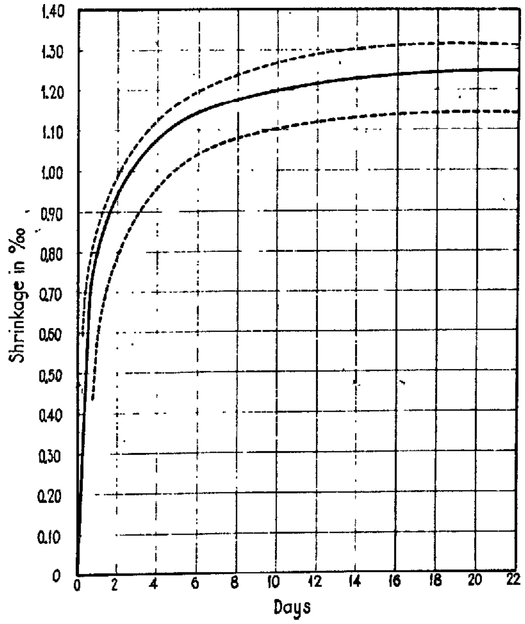

Figure 6. *Shrinkage of specimens in relation to period of storage at 50 percent rh.*

tions, and the coefficients of variation (relative deviations).

The results show that:

(a) The final value of shrinkage is reached very quickly, and

(b) The different final values obtained are rather alike.

Creep. Once the final value of shrinkage was practically reached, the 15 pipes were removed from the shrinkage apparatus, put in the creep devices, where the temperature and relative humidity were the same as before (20 °C and 50 percent rh), and loaded at 50 percent of their compressive strength.

The shortenings were measured every 24 hr. In figure 7 appear the curve of the mean values as well as the curves joining the points of minimum and maximum shortening.

The creep of each pipe can be seen in table 2, as well as the mean values, the standard deviations, and the coefficients of variation. The results obtained show that the relative differences are of the same order as in other tests of cements.

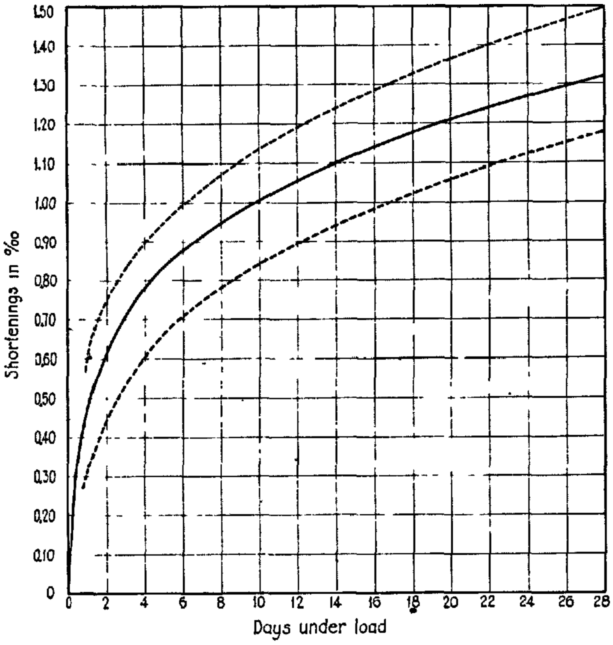

FIGURE 7. *Creep of specimens in relation to period under load.*

Loads and Creep

Twelve pipes made and cured as before (28 days in water at 20 °C) were allowed to shrink for 21 days in air (20 °C temperature and 50 percent rh) and then put for 28 days in the creep devices. Three specimens were under each of the following loads: 20, 30, 40, and 50 percent of their compressive strength. The temperature and relative humidity of the air surrounding the specimens while being tested for creep were as before (20 °C and 50 percent rh).

TABLE 2. *Creep of pipe specimens at ages up to 28 days*

Pipe No.	Creep in ‰					
	At 1 day	At 3 days	At 7 days	At 14 days	At 21 days	At 28 days
1	0.47	0.70	0.91	1.12	1.25	1.35
2	.46	.66	.80	.93	1 05−	1.18−
3	.58	.83	1.02	1.23+	1 36	1 48
4	.53	.77	.99	1.21	1.37+	1.50+
5	.59+	.83+	1 03+	1.13	1.26	1.35
6	.52	.74	1.00	1.15	1 29	1 39
7	.49	.68	.89	1.04	1.14	1.25
8	.45	.70	.92	1.12	1.26	1.33
9	.47	.70	.92	1.14	1.25	1.34
10	.39	.68	.89	1.05	1.16	1.25
11	.44	.69	.89	1 11	1.23	1.34
12	.32−	.53−	.74−	.94−	1.11	1.28
13	.42	.64	.83	.99	1.09	1 19
14	.55	.81	1.00	1.21	1.32	1.39
15	.47	.69	.85	1.07	1.16	1.25
Mean value	.48	.71	.91	1.10	1.22	1.32
Standard deviation	.069	.075	.082	.089	.094	.090
Coefficient of variation, %	14.37	10.56	9.03	8.09	7.70	6.81

Figure 8, drawn with the mean values of the shortening at 1, 2, 3, and 4 weeks, shows that the creep is practically proportional to the load applied when this is not greater than 50 percent of the compressive strength of the pipes.[3]

Temperature and Creep

Thirty pipes cured as in the two previous groups of tests (28 days in water at 20 °C) were put in the creep devices and tested under water for 7 days, as follows:

Number of pipes	Temperature of the water	Load applied (percentage of the compressive strength)
	°C	%
5	20	20
5	20	40
5	35	20
5	35	40
5	50	20
5	50	40

With the mean values of the results obtained after 7 days of testing we have drawn figures 9 and 10 where it can be seen that:

(a) Regardless of temperature, the deformation of the pipes after 7 days of testing is proportional to the load applied up to 40 percent of their compressive strength, and (b) Creep under water is also proportional to temperature in the range from 20 to 50 °C, after 7 days under load.

Final Considerations

We realize that the limits of our conclusions are very narrow, because of both the small number of tests and the very short time under load of the pipes.

For instance, the effect of temperature may be quite different if the specimens are tested in dry hot air instead of under hot water.

On the other hand, it is very probable that the influence of temperature upon creep becomes less

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[3] This conclusion seems to be in contradiction with the statement that appears in our previous paper; but it is necessary to take into account the differences in the procedures followed then and now in testing the pipes as well as in the form of presenting the results.

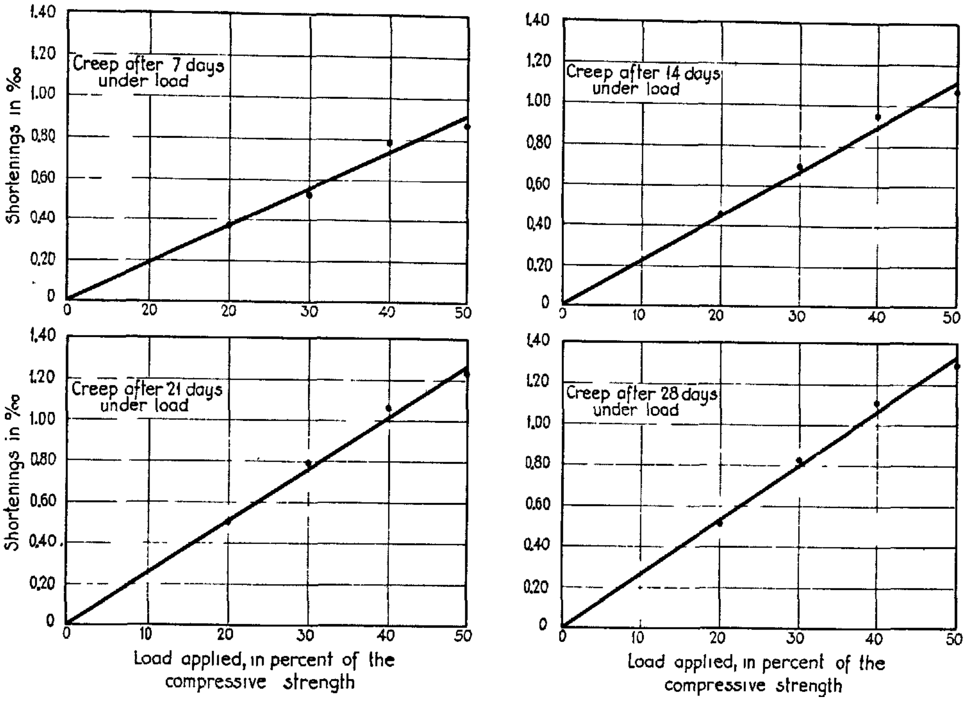

FIGURE 8. *Creep as function of load for various periods under load.*

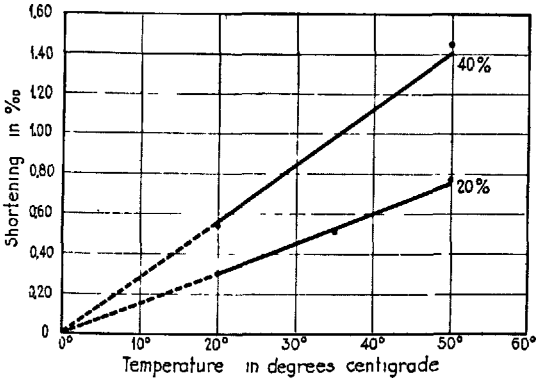

FIGURE 9. *Creep under water with two different loads, in percent of the compressive strength.*

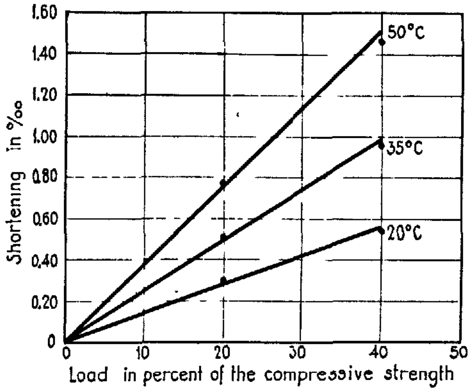

FIGURE 10. *Creep under water at three different temperatures.*

and less important as the time under load increases.

Therefore, much further research is necessary before coming to firm conclusions upon the matters dealt with in this paper; especially, as far as the effect of temperature upon creep is concerned.

We hope that this paper will give to the members of the Symposium a guess about the possibilities of the testing procedure employed in carrying out studies of the shrinkage and creep of cements, not only without the microcracking caused by gradients of humidity and temperature between core and surface, but also without the uncertainty about the real humidity and true temperature of the different parts of the commonly used thick specimens. In order to obtain reliable results, the conditions of humidity and temperature of not only the surrounding air, but, above all, of the specimen under test, need to be well defined.

Discussion

R. R. Hattiangadi and P. J. Jagus

The swelling of cement under hydration is a chemical phenomenon accompanying hardening. It has been observed that swelling continues for a longer time and is also of greater magnitude in those cements which harden or hydrate slowly than in rapid-hardening cements. It would be of interest to know whether or not the internal buildup of strength plays a part in resisting the apparent increase of volume through swelling.

The observation regarding the boiling water test for cement, popularly known as the Le Chatelier test, being advocated for the rapid determination of chemical unsoundness of cement is of significance. It is mentioned that the test brings out very rapidly the presence of unhydrated

CaO and MgO if the boiling is continued for 5 hr. Contrasted to this, the British Standard Specification B.S. 12, which has adopted this test, specifies the boiling period of the specimen at 1 hr. In our Indian Standard Specification for ordinary and rapid-hardening cements, this boiling time was originally prescribed at 30 min but on later consideration it was increased to 3 hr in the subsequent revisions of the standard. If a longer period of boiling is observed to bring about reliable results with greater rapidity, it is worth considering whether standard specifications which stipulate the Le Chatelier test for determining the soundness of cement should revise upwards the period of boiling on the basis of any standardization work that may have been done in this direction.

It would also be worthwhile to look comparatively at the two parallel tests for soundness of cement, namely, the Le Chatelier test and the autoclave expansion test. Whereas autoclaving the specimen at a high temperature and a pressure of 310 psi for 3 hr can bring about a rapid hydration of the CaO and MgO, one wonders whether the full physical effects of this hydration in terms of the accompanying volume change will be brought about in the specimen, since it is simultaneously being subjected to such a high pressure. The Le Chatelier test, on the other hand, permits an almost unrestricted swelling of the specimen. This test, which is easier to adopt, is generally prescribed more frequently than the autoclave test, and if any further advantage in reliance and rapidity of the test could be secured by increasing the period of boiling, such a change would be worthy of adoption in the specifications.

The paper brings out important aspects of the physical properties of concrete in respect to the volume changes under varying conditions. Cements which have been matured under water show lower coefficients of thermal expansion than those cured under lower relative humidities of 50 and 75 percent.

The observation is made that cement paste protected against evaporation by an impermeable membrane shrinks due to the internal desiccation of the mass by hydration of cement consuming the internal humidity. This phenomenon has a practical significance in respect to concretes which are cured with the help of solid and liquid membranes. In the absence of replacement of that part of the free water which is chemically taken up for hydration, the mass will tend to shrink, developing distress in the body of the concrete at an early age when it has very little strength to resist the stress.

The work of Meyers, Verbeck, and others has shown that carbonation of a concrete specimen diminishes the reversible shrinkage and gives it greater stability against volume variations due to changes in relative humidity. It may be of interest to note that this fact is now being usefully exploited by several American manufacturers of concrete products and masonry block. It has also been found in practice that the strength of carbonated concrete increases with the amount of carbon dioxide absorbed and the amount absorbed increases in turn with the amount of water present. The industrial application of this idea is made possible at very little extra cost with the help of waste flue gases which are diverted into the curing chamber. This treatment is also known to help in reducing the permeability and efflorescence of the concrete.

The author, in the latter part of his paper, has dealt with load-deformation characteristics of cement and concrete. I am sure that exhaustive information compiled on elastic, and plastic, creep behavior of concrete will be of immense value to the men in research as well as in construction.

Discussion

Myron A. Swayze

In his paper on "Volume Changes in Concrete", Robert L'Hermite is concerned with all phases of change in volume; not only in concrete, but in mortars and cement pastes as well. This discussion is limited to the consideration of the shrinkage due solely to drying of these three types of specimens in air of 50 percent rh for various types of portland cement.

It has long been considered that increasing the fineness of cements leads to higher drying shrinkages in pastes, mortars, and concretes. It has also been assumed that when differences in the shrinkage characteristics of a group of cements are found in neat pastes or rich mortar specimens, proportionate differences will be found in the shrinkage of concretes made with these products. It is the purpose of this discussion to show that neither of these assumptions is tenable, so far as the behavior of portland cements in normal concrete is concerned.

The Lone Star Cement Research Laboratory at Hudson, New York, has been conducting volume-change tests on 3 x 3 x 10-in concrete specimens for many years, using mixtures of cement and nonreactive siliceous sand and gravel aggregates ranging from 329 to 846 lb of cement per cubic yard (195 to 500 kg/m^3) with water sufficient to produce slumps of 2 and 6 in. Up to this year we have not made similar tests on mortar or neat-cement specimens, due to the tendency of some otherwise well-informed engineers to translate the higher shrinkages exhibited by such specimens into terms of contraction in inches per 100 feet of concrete pavement, and to draw erroneous conclusions from these figures.

This year two proposals to limit volume changes of portland cements by specification were proposed in the United States. One test consisted of molding a normal consistency neat paste in 1 x 1 x 10-in molds moist curing for 24 hr., measuring, and then storing in air of 50 percent rh for 48 hr. A limit of 0.10 percent shrinkage at the age of 72 hr. was suggested. The second proposal was to use a 1:2 graded Ottawa sand mortar, cured in 1 x 1 x

10-in molds for 24 hr, then measured and immersed in water for 48 hr. Expansions were then measured, after which specimens were placed in 50 percent rh air storage for an additional 4 days. The proposed limits were 0.01 percent on 48 hr expansion in water and 0.04 percent on subsequent shrinkage after 4 days of drying. Both types of test would reject a majority of cements tested under their conditions and limits.

To check the volume changes obtained by these methods against similar data on concrete specimens, cement samples of all ASTM Types, except IV and V, were used for production of neat and 1:2 mortar bars. These samples had been preserved in sealed metal cans and represented cements in a comprehensive series of concrete tests, started in 1957 and now nearing completion, on some 56 cements of different types. The 42 cements included in this discussion are those on which we have information through the age of 1 yr.

Our figures on concrete shrinkages are based on averages of 18 concrete specimens for each cement. These 3 x 3 x 10-in specimens represented three rounds of batches mixed on successive days with cement contents of 423, 564 and 705 lb of cement per cubic yard (250, 334, and 417 kg/m^3) with 2- and 6-in slumps. Past experience has shown that the 1-yr tests on such specimens are at or very close to their ultimate shrinkage. Design of all concrete mixes was based on a total fineness modulus of 4.85 (including the cement volume as 0.00 FM) for normal concretes, and 5.00 for air-entraining varieties. Aggregate grading was from 0 to 1½ in, all of siliceous sand and gravel. Gravel larger than 1½ in was discarded in molding volume change specimens. Curing of all concrete specimens was in molds for 24 hr, 2 days in fog at 23 °C, followed by continuous storage in air of 50 percent rh.

Data on neat pastes and 1:2 mortars are on averages of three specimens for each cement. Curing of neat bars was 24 hr in molds, followed by immediate storage in air at 50 percent rh after removal from molds and initial measurements. The mortar bars were cured 24 hr in molds, 48 hr in water and then in air at 50 percent rh until 28 days after molding. Finally, all neat paste and mortar bars were subjected to 48-hr drying at 105 °C, then returned to 50 percent rh storage for 24 hr before final measurements at 31 days.

The following table shows average percentages of linear dimensional change for each type of cement in the three types of test. In all cases shrinkages are related to the initial measurements after removal from molds, rather than to those made after the 48 hr of fog or water curing. The ages relate to ages of specimens after casting. Details on individual cements in each type classification are too lengthy to be discussed here, but will be published in the ASTM Bulletin early in 1961, following presentation of the data before ASTM Committee C-1 on Cement in December, 1960.

TABLE 1. *Dimensional changes of concretes, neat pastes, and 1:2 mortars after indicated time of storage at 50 percent* rh

Concrete Tests

Type of cement	No. of cements	w/C	% shrinkage after 1 day in molds, 2 days in fog				
			3 day	7 day	28 day	3 mo	1 yr
		%					
I	10	54.6	+0.001	0.012	0.035	0.048	0.060
IA	7	49.6	+.001	.012	.036	.050	.062
II	8	53.6	+.001	.009	.032	.047	.060
IIA	3	48.3	+.001	.009	.033	.046	.062
III	12	54.4	+.001	.011	.033	.047	.061
IIIA	2	51.1	+.001	.011	.035	.048	.062

Neat Pastes

			% shrinkage after 1 day in molds				
			2 day	3 day	7 day	28 day	Dried
I	----------	24.6	0.061	0.092	0.152	0.221	0.428
IA	----------	24.3	.077	.112	.180	.255	.459
II	----------	24.6	.058	.090	.152	.211	.414
IIA	----------	23.5	.062	.095	.159	.221	.425
III	----------	26.5	.078	.122	.172	.243	.525
IIIA	----------	26.0	.088	.125	.184	.255	.542

1:2 Mortars

			% shrinkage after 1 day in molds, 2 days in water			
			3 day	7 day	28 day	Dried
I	----------	38.5	+0.002	0.055	0.096	0.139
IA	----------	38.1	+.002	.058	.102	.152
II	----------	38.3	+.002	.040	.075	.116
IIA	----------	37.1	+.002	.046	.087	.131
III	----------	38.7	+.005	.050	.089	.140
IIIA	----------	38.0	+.002	.053	.093	.144

Considering these data, it becomes immediately apparent that the effect of type of cement on ultimate shrinkage of concrete is insignificant. The very finely ground Type III and IIIA products display no more shrinkage than normal-fineness cements, if differences of one or two thousandths of a percent can be neglected. On the other hand, specimens made with neat pastes would lead one to believe that Type II cements should display some 5 percent less shrinkage than Type I products, and 22 percent less than Type III cements, if we consider the data on dried specimens after 28 days of 50 percent rh storage as a measure of the ultimate shrinkage of neat pastes.

In a somewhat similar comparison in mortars, Type II cements again appear to have an advantage over Type I products in developing lower ultimate shrinkages. On the other hand, the high-fineness Type III cements display no significantly greater shrinkages than Type I cements, either at the age of 28 days or after drying.

The moral to be derived from these data is obvious. If we are interested primarily in reducing drying shrinkage due to cement in structures, we should always use the cement in concrete mixes—never in mortars or neat pastes that are subject to drying. Second, although molding and testing of concrete specimens with their larger bulk is more expensive and time-consuming, we should confine our testing to this medium if we are to avoid the arrival at erroneous conclusions from data derived from tests on neat pastes or rich mortars.

Discussion

T. C. Powers

Prof. L'Hermite is to be thanked for his prodigious task of assembling facts and ideas pertaining to volume changes of concrete. The scope of his discussion contributes toward a unified understanding of the various phenomena embraced by the subject.

Prof. L'Hermite refers to the observation that concrete shrinks or swells when its water content is decreased or increased, and says, "There is thus a relation between the movement of water and shrinkage that does indeed appear to be a 'cause-and-effect' relationship." At this point the wording suggests some reservation regarding the actual relation of cause and effect, but in other parts of the paper the widely held belief that water removal per se is the cause of shrinkage is adopted. For example, it is said that shrinking or swelling cannot occur when a specimen is kept in the saturated state. In another connection, it is indicated, correctly, that a sealed specimen may shrink because some of the water in it is effectively removed by chemical reaction—"self-desiccation"—but it is indicated that a sealed specimen cannot shrink in the absence of self-desiccation. In connection with the relation between shrinkage and creep, it seems to be suggested that since loaded and unloaded specimens lose the same amounts of water under the same conditions of drying, the extra time-dependent deformation of the loaded specimen cannot be ascribed to extra shrinkage caused by the load.

It is indubitably a fact that if the water content of cement gel changes, the volume of the gel will change too, but it is incorrect to say that if the water content of the gel does not change, the specimen cannot shrink or swell. This was proved from experiments carried out in this laboratory by R. A. Helmuth. He found that when a saturated specimen of cement paste was cooled at a steady rate, its *initial* rate of contraction was about 3 times as great as the normal rate of thermal contraction—29 millionths per degree as compared with 11 millionths per degree. The difference, 18 millionths per degree, represented shrinkage of the gel occurring while its water content was constant. Such shrinkage is caused by the appearance of tension in the water, related directly to the decrease of temperature. In a saturated specimen, the effect is transient because the tension induced by the drop of temperature becomes released by transfer of water from the capillary spaces (eventually from water outside the specimen) to the gel.

When Helmuth cooled a sealed specimen in which the water content was below the saturation point, the specimen contracted about 25 millionths per degree, of which about 14 millionths per degree was due to shrinkage, as discussed above. In this case, nearly all the evaporable water was in the gel pores to begin with, and thus there was not enough capillary water to relieve the increase in tension caused by the drop of temperature. The shrinkage caused by cooling in this case was therefore not transient, as it was for a saturated specimen.

In recent studies of old data I found that for all relative humidities above 50 percent the final amount of shrinkage of a laboratory specimen of mature paste (no unhydrated cement) is the product of internal hydrostatic tension and the mechanical compressibility of the specimen. The amount of shrinkage is nearly the same as would be produced by an externally applied, sustained, hydraulic pressure of the same intensity as the internal tension. The intensity of internal tension, that is the tensile stress, is given with adequate accuracy by Kelvin's equation. For example, at a humidity of 50 percent, the amount of shrinkage is the same as that which would be caused by an external hydraulic pressure of about 900 atm applied at the specimen boundaries. When the internal tension becomes canceled, as by saturating the specimen, the specimen expands *elastically* the same amount that it would from the removal of an equal external pressure. (The first shrinkage is greater than the first swelling because of irreversible changes in gel structure that are produced by the first loading of the structure by the internal tension.)

Such results are to be expected from the theory that Prof. L'Hermite ascribes to Freyssinet, called the Capillary Theory. As commonly given, this theory ascribes the state of water tension to the presence of curved water surfaces—meniscuses. However, it now appears that meniscuses should be regarded as the *result* of water tension, rather than the cause, and when this concept is adopted, the capillary theory and its apparent rival are in harmony under the limited range of conditions within which the capillary theory is applicable.

Since shrinkage is mechanical, partly elastic compression, a cylindrical specimen subjected to an axial load and to drying simultaneously is being subjected to a uniaxial pressure and a triaxial pressure simultaneously. Each pressure is capable of producing elastic, time-dependent, and irreversible deformations. This should be taken into account in attempting to discover the relationship between shrinkage and creep.

Shrinking, swelling, creep, and all such words do not correspond to intrinsic properties of a material. They are terms we have adopted to designate certain modes of behavior, usually of laboratory specimens, under changing internal and external forces. I believe we are now in a position to establish a unified picture of such behaviors in terms of known forces and corresponding displacements.

Paper V–S1. Creep of Aluminous Cement Concrete*

A. M. Neville and H. W. Kenington

Synopsis

Data on creep of aluminous-cement concrete are presented, and it is shown that the order of magnitude of creep is the same as that of portland-cement concrete, when compared on the basis of the stress-strength ratio. Ambient humidity is also shown to have a similar effect on both types of cement.

These similarities, and the influence of the strength of concrete on creep, are thought to suggest that the gel-space ratio of the hydrated paste is the primary factor in creep.

Résumé

Des données sur le fluage du béton de ciment alumineux sont présentées, et il est indiqué que l'ordre de magnitude du fluage est le même que celui du béton de ciment Portland, quand on les compare sur la base du rapport contrainte-résistance. Il est prouvé également que l'humidité ambiante a un effet semblable sur l'un comme sur l'autre ciment.

Ces similitudes, et l'influence de la résistance du béton sur le fluage semblent pouvoir suggérer que le rapport gel-espace de la pâte hydratée est le facteur principal dans le fluage.

Zusammenfassung

Werte für das Kriechen des Tonerdezementbetons werden angegeben, und es ist angedeutet, daß die Größenordnung des Kriechens dieselbe wie für Portlandzementbeton ist, wenn der Vergleich auf der Basis des Verhältnisses Spannung/Festigkeit gezogen wird. Die Umgebungsfeuchtigkeit hat einen ähnlichen Einfluß auf beide Zementarten.

Diese Ähnlichkeiten und auch der Einfluß der Betonfestigkeit auf das Kriechen werden so gedeutet, daß das Verhältnis Gel/Volumen der hydratisierten Paste den größten Einfluß auf das Kriechen ausübt.

Introduction

Recent advances in the study of creep of concrete have brought us closer to a full understanding of the nature of creep and thus to a better appreciation of the physical and chemical factors in the behavior of hydrated cement paste. A study of creep [1] [1] and of creep recovery [2] of sand-cement mortars made with cements of different compound compositions, has been reported earlier; in this paper the results of creep tests on aluminous-cement concrete are presented. In addition to widening the field of study of the influence of the type of cement, the data presented here give some indication of the creep behavior of aluminous-cement concrete—a material used structurally under conditions in which creep may be of great importance.

Comparatively little is known about the creep properties of this cement; Glanville [3] reported his pioneer tests in 1930, and their long-term extension was described in 1939 by Glanville and Thomas [4]. Only one mix was used in those tests, and, of course, at the time the various factors in creep were not realized. This remark must not be construed as a criticism of Glanville's work, as, indeed, it was he in England and Davis in the United States who brought to our notice the entire problem of creep and its wide implications.

One important feature of Glanville's tests is that he found the creep of aluminous-cement concrete when stored dry to be less than when stored wet; this behavior would appear to be contrary to that exhibited by all portland cements, and probably for this reason it has been quoted again and again during the last 30 yr. A probable explanation of this anomaly will be given in this paper.

Test Details

Cylindrical concrete specimens were subjected to a sustained load in a simple lever-frame apparatus, operating on the principle of a nutcracker. This apparatus as well as the storage cabinets and the method of loading and the various details of procedure have all been described in a previous paper [5]. The specimens were stored at 20± 0.1 °C, and for the main series of tests at a relative humidity of 95 percent.

The cement used was of English manufacture; its properties are listed in table 1, and it can be

TABLE 1. *Properties of cement*

Setting time (Vicat): initial, 4 hr 15 min; final, 4 hr 35 min
Specific surface (Lea and Nurse): 2910 cm²/gm

	Oxide composition							
Oxide	SiO_2	Al_2O_3	CaO	Fe_2O_3	FeO	TiO_2	MgO	Loss on ignition
Percent	4.87	38.35	38.35	9.43	6.00	1.99	0.74	0.16

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the University of Manchester, England.

[1] Figures in brackets indicate the literature references at the end of this paper.

seen that it is a fairly typical aluminous cement, although perhaps with a rather low alumina-lime ratio.

The aggregate was of siliceous origin; well rounded gravel for the 3/16 to 3/8-in. fraction, and crushed gravel for the sand fraction. The grading curve is given in figure 1.

Table 2 lists the mix proportions of the various mixes used, and also the values of compressive strength of 3-in. test cubes and of cylinders. It should be noted that the cylinders, which were of the same dimensions as those used in the actual creep tests, were not of standard proportions, but were 9¼ in. long and 2 in. in diameter. These dimensions were governed by the limitations of the creep apparatus [5]. Since, however, the strength data are mainly of comparative value, the high height-diameter ratio used is not thought to be of importance.

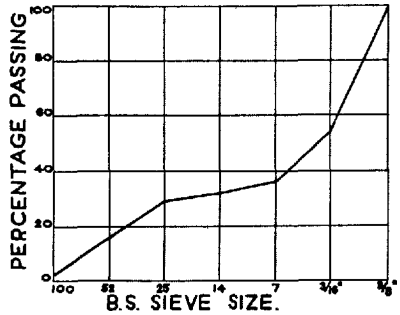

FIGURE 1: *Grading of aggregate.*

TABLE 2. *Mix details*

Maximum aggregate size is 3/8-in.

Mix	Aggregate-cement ratio	Water-cement ratio	Cement content	Compressive strength at 24 hr.	
				2 x 9¼-in. cylinder	3-in. cube
			lb/yd³	*psi*	*psi*
A	4	0.35	760	4,850	10,250
B	4	.40	750	4,550	9,550
F	4	.45	740	4,200	8,850
G	4	.55	730	3,700	7,550
J	6	.55	520	3,750	7,600

Factors Affecting Creep

Age at Loading

One of the outstanding features of aluminous cement is its extremely rapid development of strength (see fig. 2). For this reason aluminous-cement concrete can be subjected to load at an age of 24 hr or even less, and it was therefore considered of interest to establish the creep characteristics of concretes loaded at different ages. Figure 3 shows the creep after a given time under load for concretes loaded between the ages of 18 hr and 11 days.

It can be seen that up to the age of about 2 days an increase in the age at loading results in a very considerable decrease in creep after any given time under load, and probably also in the ultimate creep. At later ages the influence of age at loading on creep becomes progressively smaller.

This behavior is interpreted to indicate the influence on creep of the degree of hydration of the cement paste, and it may be interesting to note that the creep-age at loading curve of figure 3 is very similar in form to a strength-age curve of figure 2 (the two curves being mirror images of one another).

In the past there was a tendency to explain the influence of age on creep in terms of the

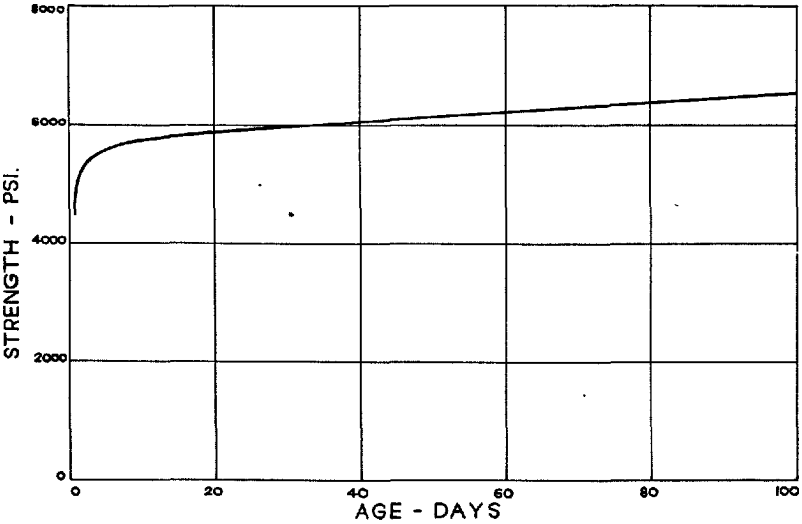

FIGURE 2: *Strength development of aluminous-cement concrete (mix A) stored at 95 percent rh; 2 by 9¼-in. cylinders.*

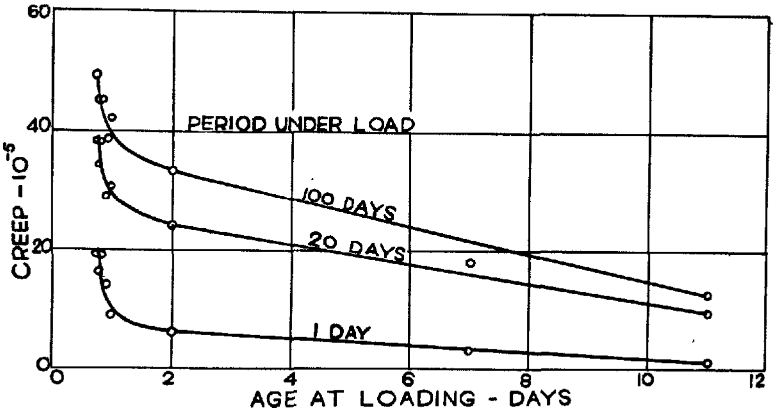

FIGURE 3: *Creep for different ages at loading.*
(Mix A, applied stress=2150 psi)

quantity of water available in the paste, but in the authors' opinion it is primarily the strength of the concrete at the time of application of the sustained load that affects the magnitude of creep. This influence of strength was established on the basis of tests on mortars differing only in the properties of the portland cement used [1]. Further evidence is given below.

Water-Cement Ratio

If, as suggested above, strength is the primary factor in creep, it would be expected that varying the strength of a mix by altering its water-cement ratio should be clearly reflected in the magnitude of creep. To check this hypothesis a series of mixes were made with values of the water-cement ratio between 0.35 and 0.55, the aggregate-cement ratio being kept constant at 4.0. All specimens were subjected to constant stress of 2,150 psi. The resulting relationship is most conveniently plotted as creep against $\frac{1}{\text{strength}}$, as an approximately straight line is then obtained (fig. 4). It is not thought, however, that a linear extrapolation into the range of higher strengths is justified: such a line would indicate a zero creep (after 100 days) for a strength of about 7,000 psi, while concrete of that strength would, of course, exhibit creep under the given load. It may be noted that the elastic strains on the application of the load, similarly plotted, also give a straight line which, if extended, would indicate no strain at approximately 6,500 psi. As mentioned before, such extrapolations are unwarranted, but the similarity between the elastic and creep curves is of interest.

In passing, it may be noted that, unlike the case of portland cement, the relation between the compressive strength of aluminous-cement concrete and the water-cement ratio is linear. This relationship is shown in figure 5 for the 2 by 9¼-in. cylinders of the present series and also for 3 by 9¼-in. cylinders made with the same cement as well as for standard 6 by 12-in. cylinders

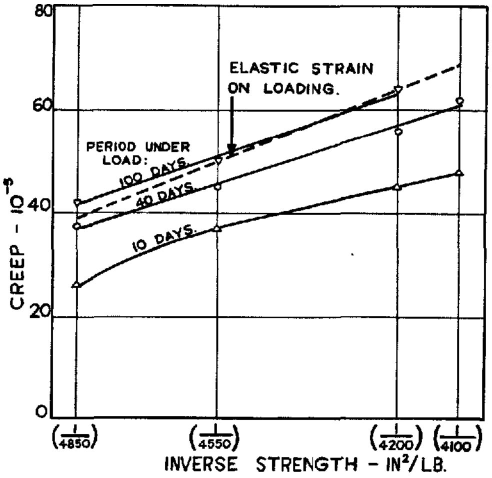

FIGURE 4: *The relation between creep and inverse strength at the time of application of load for mixes with different water-cement ratios.*
(Applied stress=2,150)

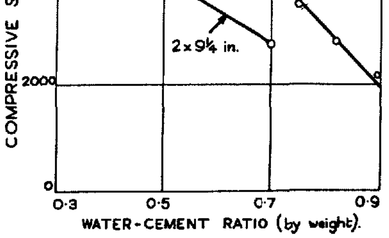

FIGURE 5: *The relation between 24-hr compressive strength and water-cement ratio for cylinders of different proportions.*

of another study, i.e., made with a different batch of aluminous cement.

Table 2 shows that the basic mixes had an aggregate-cement ratio of 4. Increasing this ratio to 6 (Mix J) has not affected the magnitude of creep, but pilot tests on much leaner mixes indicate that the aggregate-cement ratio may not always be disregarded.

Stress-Strength Ratio

In the present investigation, the majority of specimens were subjected to a sustained stress of 2,150 psi, this being the order of working stress for aluminous-cement concrete used, for instance, in a prestressed member. Only one series of specimens was used to check the relation between creep and stress, and this relationship was found to be linear, as is the case with portland-cement mortar and concrete. The stresses applied did not exceed 60 percent of the ultimate strength.

It is thus possible to express creep in terms of the ratio of the stress applied to the strength at the time of application of the load, or, in brief, the stress-strength ratio. Figure 6 shows a plot of the relevant data for the various specimens of the present investigation, and, for the limited range of variables involved, the significance level of this apparently linear relation is considerably better than 0.1 percent. It is clear, however, that this line would indicate no creep after 20 days under load for values of the stress-strength ratio below about 0.3. A similar pattern has been found for some tests of other investigators, as shown in an earlier paper [1].

The lower range of values of the stress-strength ratio has unfortunately not been investigated, as in the time available it was essential to concentrate on stresses and strengths used in practice. However, the behavior of concrete subjected to low stresses should be studied, particularly because a lowering of stress appears to decrease the creep less than a corresponding decrease in the stress-strength ratio obtained by an increase in strength. It is hoped to perform the necessary tests in the near future.

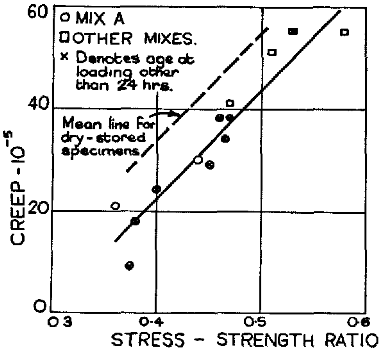

FIGURE 6: *The relation between creep after 20 days under load and the stress-strength ratio for wet-stored specimens.*
(Regression line shown)

Ambient Humidity

All the data presented so far referred to specimens stored at a relative humidity of 95 percent. Another series of tests was performed at a relative humidity of 32 percent and a temperature of 20 °C. The specimens were subjected to these dry conditions from the time they were stripped (at 24 hrs), and they exhibited, therefore, a considerable shrinkage. It was thus not possible for the specimens to achieve hygral equilibrium with the surrounding medium prior to the application of the load, so that some shrinkage-creep interaction was inevitable. Since, however, these conditions of early loading and simultaneous drying out are often encountered, it was considered worthwhile to obtain some test results, particularly in view of the belief, already mentioned, that the creep of aluminous-cement concrete in air is smaller than in water.

Under the circumstances it was necessary to distinguish between creep and shrinkage and, although the two are known not to be additive, there was no alternative but to subtract the shrinkage of unloaded companion specimens from the total-time deformation of specimens under load. (This makes the present results comparable in form with the older test results.) The resulting relation between creep and the stress-strength ratio is shown in figure 6, and it is clear that the creep of drying specimens stored at a relatively humidity of 32 percent is somewhat higher than that of humid specimens at 95 percent rh. After 20 days under load the difference was of the order of 0.0001 (strain), which represents an increase in creep of approximately 20 percent in a specimen with a stress-strength ratio of 0.5.

It appears then that the creep of a drying specimen is greater than the creep of humid specimens, and indeed this is the normal behavior of concrete made with portland cement. How then are Glanville's [3] results explained? It seems that his specimens were loaded at the age of 28 days, and their strengths at the time were 3,340 psi for the wet and 4,640 psi for the dry specimens. No explanation of this difference is available. If a loss of strength had occurred, the reason is not known, as the temperature was 10 °C [6]. It is also interesting to note that Glanville's data show an increase in the elastic strain with time for air-stored concrete. It is not clear whether this increase is related to a retrogression of strength.

In any case, taking the actual values of strengths at the time of application of the load, the creep should be adjusted in proportion to $\frac{1}{\text{strength}}$. It is more convenient to plot a product of creep and strength against time, and this relationship is shown in figure 7. It can be seen that, on this basis, there is very little difference between the creeps of dry and wet specimens, although at periods under load greater than 14 days the latter show a slightly higher creep. It should be remembered that in Glanville's investigation the load was applied at the age of 28 days, so that the pattern of shrinkage development was possibly quite different from that in the present experiments.

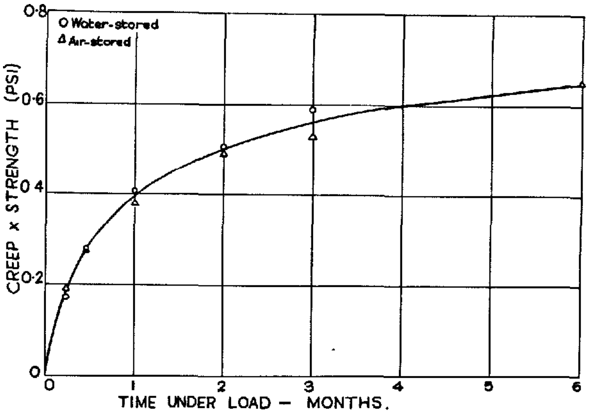

FIGURE 7: *Creep times strength for Glanville's [3] air- and water-stored aluminous-cement concrete.*

Creep Recovery

Upon release of load the specimens of aluminous-cement concrete exhibited an instantaneous recovery corresponding to the modulus of elasticity of concrete at that time, and this elastic recovery was followed by a gradual creep recovery. These movements are similar to those characteristic of portland-cement concrete, and in particular the very rapid completion of creep recovery can be observed. Figure 8 shows a typical deformation-time curve for mix A specimens loaded at 18 hr to a stress of 2,150 psi; both the creep and the creep-recovery are shown.

No clear trend in the values of the creep recovery has been observed. It can, therefore, be tentatively concluded that creep recovery is not a simple function of the strength of concrete, but the factors influencing it have not been recognized. As a corollary, it would appear that the nature of creep recovery is not necessarily the same as that of creep; a similar conclusion was drawn in the case of portland cement mortars [2].

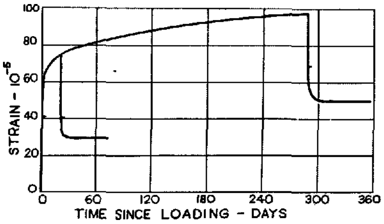

FIGURE 8: *Elastic strain, creep, and creep recovery for mix A under 2,150 psi.*

Comparison With Portland Cement

In a previous investigation [1] of creep of mortars made with portland cements of different compositions, one mortar made with aluminous cement was included, and in a comparison on the stress-strength basis there was no apparent difference between the two types of cement. In the present tests a few check mixes made with rapid-hardening portland cement (Type III) again showed that on the basis of the stress-strength ratio at the time of application of the load, the creep of concretes made with the two cements appears to be of the same order of magnitude, although the actual values are affected by the varying rates of strength development of the two cements. This lack of an inherent difference between the creeps of portland and aluminous cements is of considerable interest in the study of the nature of creep; it would appear to be at variance with Bernal's [7] suggestion that creep is related to the movement of zeolitic water in calcium silicate hydrates. Since the products of hydration of aluminous cement and of portland cement are largely dissimilar, it is much more likely that creep is related to the grosser structure of the cement gel—a suggestion supported by Powers [8], and intimated in an earlier study [1].

Summary and Conclusions

Although the tests reported here cover only a limited field, they are the first set of data on the creep of aluminous-cement concretes of different mixes, and thus enable us to obtain a general picture of the behavior of that cement.

The age at loading appears to affect very strongly the magnitude of creep after any time under load and probably also the magnitude of the ultimate (limiting) creep. This influence is particularly strong at ages below about 2 days: by delaying the application of the load from the age of 18 to 48 hr creep can be reduced by about one-third. The magnitude of creep appears to be related inversely to the strength of concrete at the time of application of the load.

A similar relation is found when the strength of concrete is varied by a change in the water-cement ratio for a constant cement content. There is thus a linear relation between creep and the inverse of strength over the range of strength values investigated: this relationship covers water-cement ratios between 0.35 and 0.55, and would correspond to 24-hr strengths of standard 6 by 12-in. cylinders between about 5,500 and 8,000 psi.

It is possible thus to express creep as a linear function of the stress-strength ratio, but for values of this ratio below about 0.3 the behavior is not clearly established. It is likely that, as suggested by Evans [9], another relation exists in the lower range of stress-strength ratios; there are some indications of this from specimens subjected to low stresses.

The ambient humidity has been shown to affect creep comparatively little, the creep of drying specimens being somewhat higher than the creep of wet-stored concrete. This is in agreement with the pattern of behavior of portland-cement concretes but directly opposite to previous results on aluminous-cement concrete [3]. This apparent anomaly is explained by the very much higher strength of dry specimens as compared with humid specimens in those earlier tests. The clarification of this point is believed to be of considerable interest.

The pattern and magnitude of creep and of creep recovery of aluminous-cement concrete appear to be similar to those of concretes made with portland cements. Since the chemical compositions of the products of hydration of the two basic types of cement are largely different, it can be inferred that creep is related to the grosser structure of the hydrated paste rather than to the crystal structure of calcium silicate hydrates. The close relation between creep and strength can be interpreted to mean that the gel-space ratio, established by Powers [10], is a primary factor in creep. The mechanism of creep is likely to be bound up with the volume of pores not filled by the hydrated cement paste: a further investigation of this physical aspect of concrete is essential in improving our knowledge of the engineering properties of this material.

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Paper V-S2. Strength, Elasticity, and Creep as Related to the Internal Structure of Concrete*

Torben C. Hansen

Synopsis

On the basis of that conception of the microstructure of cement paste which has recently been presented by Powers, Grudemo, and others, it has been possible to derive an interrelation between the elasticity of cement paste and concrete and the gel space ratio or gel density (as defined by Powers). When applied to concrete, an approximate theoretical interrelation between strength and elasticity is obtained which is in good agreement with experimental results.

Following the same lines the two components of creep, delayed elasticity and viscosity, could be related to the gel density at any age of the cement paste, and to the volume concentration of cement paste in concrete. Even the effect of the time under sustained loading could be taken into consideration when applying certain standard time functions for the two components of creep (established on the basis of a rheological model).

The sum of the theoretical terms for delayed elasticity and viscosity gave the final creep equation for concrete, not exposed to any drying or wetting during the time of sustained loading. It has been shown that the creep calculated according to this equation is in good agreement with the creep determined in 42 creep tests found in the literature. The general creep equation which is based on our knowledge of the internal structure of cement paste can be directly applied for a practical calculation of the creep of any water-stored concrete, cement mortar, or cement paste, under the above-mentioned conditions when the age at loading, the time under sustained loading, the chemical composition of the cement, and the composition of the concrete (water-cement ratio and volume concentration of cement paste) are known.

Résumé

En s'appuyant sur la conception de la microstructure de la pâte de ciment—laquelle a été récemment présentée par Powers, Grudemo, et par d'autres auteurs—, il a été possible de dériver une interrelation entre l'élasticité de la pâte de ciment et du béton, et le "gel-space ratio" ou "gel density" (comme le définit Powers). Quand on l'applique au béton, on obtient une interrelation théorétique approximative entre la résistance et l'élasticité, qui est en bon accord avec les résultats expérimentaux.

Suivant les mêmes idées, on pourrait établir un rapport entre (1) les deux composants du fluage: l'élasticité retardée et la viscosité, et (2) le "gel density" de la pâte de ciment à l'âge choisi et la concentration volumétrique de la pâte de ciment dans le béton. On pourrait même tenir compte de l'effet du temps pendant la charge de longue durée quand on applique certaines fonctions de temps pour les deux composants du fluage (établies sur la base d'un modèle rhéologique).

La somme des expressions théorétiques pour l'élasticité retardée et la viscosité donnèrent l'équation finale du fluage pour le béton qui n'est pas exposé au séchage ni au mouillage pendant la période de charge de longue durée. Il est démontré que le fluage calculé suivant cette équation est en bon accord avec le fluage déterminé par 42 essais de fluage trouvés dans la littérature. Cette équation générale du fluage, qui est basée sur notre connaissance de la structure interne de la pâte de ciment, peut être utilisée directement dans le calcul pratique du fluage de tout béton, mortier et pâte de ciment conservés dans l'eau sous les conditions mentionnées ci-dessus, quand on connaît l'âge à la mise en charge, la période de charge de longue durée, la composition chimique du ciment et la composition du béton, c'est à dire le rapport eau-ciment et la concentration volumétrique de la pâte de ciment.

Zusammenfassung

Auf der Grundlage des Begriffs der Zementpastenmikrostruktur, wie er neulich von Powers, Grudemo und anderen Forschern ausgearbeitet worden ist, bekam es möglich, eine Beziehung zwischen der Elastizität der Zementpaste und des Betons und dem Gel-Volumen-Verhältnis oder Geldichte, wie von Powers definiert wurde, aufzustellen. Wenn man diese für Beton anwendet, bekommt man eine ungefähre theoretische Beziehung zwischen Festigkeit und Elastizität, die mit den experimentellen Ergebnissen gut übereinstimmt.

Durch Weiterentwicklung dieses Begriffs war es möglich eine Beziehung zwischen den beiden Kriechkomponenten, d.h. der verzögerten Elastizität und der Viskosität, und der Geldichte für jedes Alter der Zementpaste, und auch der Volumenkonzentration der Zementpaste im Beton aufzustellen. Auch die Zeitwirkung bei fortgesetzter Belastung konnte erklärt werden, wenn gewisse genormte Zeitfunktionen für die zwei Kriechkomponenten, wie sie von einem rheologischen Modell abgeleitet worden sind, angewandt werden.

Die Summe der theoretischen Ausdrücke für die verzögerte Elastizität und die Viskosität lieferte die endgültige Kriechgleichung für Beton, wenn dieser während der Zeit der ununterbrochenen Beladung keinem Trocknen oder keiner Naßmachung ausgesetzt ist. Es

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Swedish Cement and Concrete Research Institute, Stockholm, Sweden. (The author was with the Portland Cement Association, Skokie, Illinois, at the time of the Symposium.)

wurde gefunden, daß das Kriechen, wie sie nach dieser Gleichung berechnet wurde, vorzüglich mit dem Kriechen, das in 42 Kriechprüfungen in der Literatur beschrieben worden ist, übereinstimmt. Die allgemeine Kriechgleichung, welche von der Kenntnis der inneren Struktur der Zementpaste abgeleitet worden ist, kann direkt auf das Kriechen unter praktischen Bedingungen eines jeden unter Wasser aufbewahrten Betons, eines Zementmörtels und einer Zementpaste angewandt werden, wenn die obigen Bedingungen erfüllt sind; man muß als Parameter die Zeit der ununterbrochenen Beladung, die chemische Zusammensetzung des Zements und die Betonzusammensetzung, d.h. das Verhältnis Wasser / Zement und die Volumenkonzentration der Zementmasse, kennen.

Introduction

For many years concrete research has dealt with engineering aspects, that is, so to say, with the external behavior of the material when loaded in different ways or exposed to various conditions. Very little has been known about the internal mechanism which is the basis of the external behavior of concrete. However, our knowledge concerning the physical structure of cement paste and concrete increases, and a gap has quickly developed between the physical discoveries and the engineering aspects. In this paper the author has tried to relate certain external phenomena to the internal structure of concrete, and thus bridge that gap.

The Microstructure of Cement Paste

Basic studies of the physical chemistry of hardened cement paste have established that the structure of paste is an agglomeration of unhydrated grains of cement which are joined by an aggregation of colloid or microcrystalline particles, the so called cement gel.

Electron-micrographs obtained by Grudemo [1] [1] in the laboratories of the Portland Cement Association revealed to some extent the physical mechanism of the hydration of cement. Grudemo found that when cement grains start hydrating, a coarsely fibrous structure of slender rods grows radially from the grains into the outer solution. In the areas of contact between cement particles the rodlike formations grow in between each other and bonds are formed by superposition of the atomic structure in the contact areas, this probably causing the first binding in the cement paste. Subsequently the rodlike or partly fibrous elements gradually grow out to fill all the interstitial spaces, and simultaneously a steadily increasing number of bonds are formed in the areas of intersection between them. The bonds in these contact points are probably one of the sources of strength and rigidity of cement paste.

The formation of an increased amount of colloidal material on the surfaces makes the interior parts of the cement grains less easily accessible to attack by the outer solution, thus leading to a decrease in the rate of hydration. The slowing up of the process of hydration seems to produce conditions favorable for the generation of another component which is composed of a felted mass of extremely thin wrinkled foils. In the second stage of hydration in ordinary paste, this component grows out, in the course of time filling all meshes in the network formed by the coarsely fibrous structural elements. On account of the cohesive forces in the network, this mass finally becomes so strongly compressed that its character of a layer structure is no longer discernible. In this way a stationary third stage is reached in which all possible changes proceed at a very slow rate.

The strength as well as the deformational properties of cement paste and concrete is probably determined by the molecular structure in the surfaces of these colloidal particles and the bond between them.

Strength and Elasticity

Strength as Related to the Internal Structure of Concrete

Both the rodlike structure and the felted mass probably contribute to the strength and rigidity of cement paste. If this is true, three different stages should be observed when strength is plotted against age of cement paste or concrete. P. G. Hansen [2] found that the graph of strength versus age of concrete plotted logarithmically shows the strength-age curve from 0 to about 30 hr as a straight line, from 30 to 72 hr as another straight line and from 72 hr to 28 days as a still different straight line (see fig. 1). These time intervals are in accordance with Grudemo's observations of the different stages of hydration.

Reinius [3] developed a theory which gives an explanation of the mechanism of short-time deformation and failure of concrete on the basis of a mechanical model of cement paste which is principally in accordance with Grudemo's observations.

It was suggested that the force acting upon a concrete specimen is transmitted from particle

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[1] Figures in brackets indicate the literature references at the end of this paper.

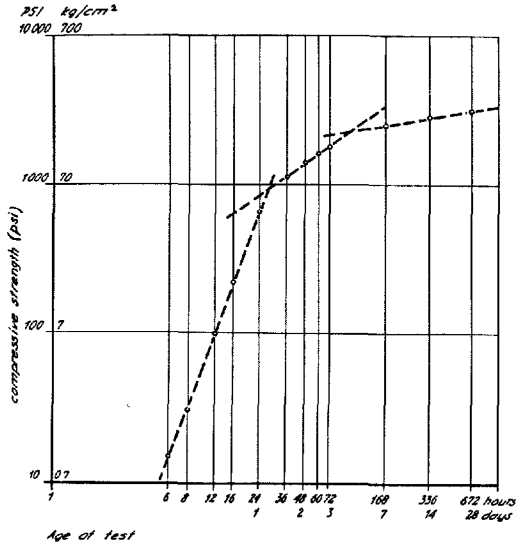

FIGURE 1. *Graph of ultimate compressive stress vs. age of concrete showing the three stages of hydration.*

(Experimental data obtained by P. G. Hansen [2].)

to particle by a lattice of more or less needle-shaped crystals. Some of the crystals are oriented in the direction of the acting load and some are inclined and try to push the particles aside. Other crystals, perpendicular to the direction of the load, hold the particles together by tension. The elongation of these crystals results in a lateral expansion when the concrete is subjected to axial compression.

Since the tensile strength of the crystal lattice structure is much less than the compressive strength, a progressive fracture starts when the tensile strength of the crystals perpendicular to the applied load is reached. The weak crystals fail first, and the stronger at greater loads, and tension cracks appear parallel to the load, as observed when concrete cubes or cylinders are loaded and the friction at the end surfaces is eliminated.

Reinius suggested that the bond of needle-shaped crystalline cement gel particles between two unhydrated grains of cement, as well as the bonds between grains of aggregate, could be replaced schematically by two bars in the plane of the force. As a result of an extensive theoretical analysis of this mechanical model of concrete, Reinius was able to explain not only the nature of rupture and crack formation in concrete under different types of load, but also the deformational behavior up to rupture, the variation of Poisson's ratio under increasing load, etc.

Reinius' theory is restricted to the mechanism of deformation and strength, and does not take into account the influence of the composition of concrete on these properties. However, our present knowledge concerning the physical structure of the material is sufficient to extend the theory and take these factors into account.

An increase in the water content of concrete increases the distance between cement grains in the paste, and therefore decreases the number of welding points and gel connections between unhydrated grains of cement. Since the strength as well as the rigidity depends on the number of such connections, strength decreases and short-time deformations increase with increasing water content, that is to say with increasing water-cement ratio.

It is reasonable to believe that strength as well as rigidity is proportional to the degree of hydration of cement paste, since a certain change in hydration means the formation of a certain amount of new gel (Powers and Brownyard [4]) and thus a certain amount of new connections and contact points between unhydrated cement grains.

It is remarkable the Grudemo [1] found that even large variations in the mineral composition of cement do not cause substantial changes in the microstructural composition of the final product. Powers, Mann, and Copeland [5] later stated that the specific surface of the hydration products only varies little with the chemical composition of the cement, thus indicating that these products are the same for all cements. Therefore it may be expected that the strength and rigidity are not influenced by the type and composition of the cement in any other way than through the amount of gel formed per degree of hydration.

Consequently the strength and rigidity of concrete should depend on the water content and the age in the following way

$$F_c = f\left(\frac{V_{hc}}{w_o}\right)$$

where F_c=strength of cement paste, mortar or concrete; V_{hc}=total volume of the gel (depending on the type of cement and the age); w_o=weight of original water content after bleeding.

Powers and Brownyard [4] showed empirically that the strength of cement mortar is approximately proportional to the gel space ratio, i.e.,

$$\frac{\text{volume of gel}}{\text{original space available for the increase in volume of gel phase}} = \delta\,\frac{V_m}{w_o} = \delta\,\frac{kw_n(t)}{w_o}$$

where V_m=constant, proportional to the surface area of the gel, w_o=weight of original water content after bleeding, g/cc, $w_n(t)$=weight of nonevaporable water, g/cc, k=constant, characteristic of the cement. k is related to the computed compound composition as follows: $k=0.230\ (C_3S)+0.320\ (C_2S)+0.317\ (C_3A)+0.368\ (C_4AF)$ where the symbols in parentheses represent the computed weight proportions of the compound indicated. δ=proportionality factor between V_m and total volume of gel V_{hc}.

In a later paper Powers [6] reported that the strength of cement mortar more correctly is a function of another ratio or what we may call the gel density V_5.

$$V_5 = \frac{V_{hc}}{V_{hc} + p_c}$$

where V_{hc}=volume of gel; p_c=volume of capillary pores.

Powers found that the strength F_c could be represented by the expression

$$F_c \cong a V_5^d. \qquad (1)$$

Both a and the order of V_5 vary somewhat from cement to cement.

When considering the strength of concrete, some other factors are also of importance, such as the quality and grading of the aggregate material, and the bond between aggregate and cement paste. Therefore eq (1) will only apply as a very rough approximation.

Elasticity as Related to the Internal Structure of Concrete

It has been suggested by the author [7] that the internal structure of a heterogeneous material like concrete can be built up in two quite different ways.

The *ideal combined hard material* has a continuous lattice of an elastic component with a high modulus of elasticity, and the voids are filled up with another component with a lower modulus of elasticity.

The *ideal combined soft material* has grains of an elastic component with a high modulus of elasticity embedded in a continuous component with a lower modulus of elasticity.

The author has derived fundamental equations for calculating the moduli of elasticity of the two types of structures when the moduli of elasticity of the components and their volume concentrations are known.

For a *combined hard material* the modulus of elasticity can be calculated from the assumption that the strain is the same over a whole cross section.

Let a material of this type be represented by a unit volume (see fig. 2) composed of two parallel columns consisting of a hard and a soft component. The modulus of elasticity for the material can then be calculated as follows:

$$\epsilon = \frac{\sigma_s}{E_s} = \frac{\sigma_h}{E_h} \qquad (2)$$

where ϵ=elastic strain of the combined material; E_s=the modulus of elasticity for the soft component; E_h=the modulus of elasticity for the hard component; σ_s=stress on the soft component; σ_h = stress on the hard component.

Since the sum of the forces over the section must equal the total external force $\sigma \cdot 1$

$$\sigma_s V_s + \sigma_h V_h = \sigma \cdot 1 \qquad (3)$$

where V_s=area of cross section of column consisting of soft material=volume concentration of the soft component; V_h=area of cross section of column consisting of hard material=volume concentration of the hard component.

From eqs (2) and (3)

$$\frac{\epsilon E_s V_s}{\epsilon} + \frac{\epsilon E_h V_h}{\epsilon} = \frac{\sigma}{\epsilon} = E$$

or the fundamental equation for a *combined hard material:*

$$E = V_s E_s + V_h E_h \qquad (4)$$

where E=modulus of elasticity for the combined material, E_s=modulus of elasticity for the soft component, E_h=modulus of elasticity for the hard component.

For a *combined soft material* the modulus of elasticity can be calculated from the assumption that the stress is the same over a whole section.

Let a material of this type be represented by a unit volume (see fig. 3) composed of two layers consisting of the hard and the soft component. The modulus of elasticity can then be calculated as follows

$$\epsilon_s V_s + \epsilon_h V_h = \epsilon \cdot 1 \qquad (5)$$

where V_s=depth of layer consisting of soft material=volume concentration of the soft com-

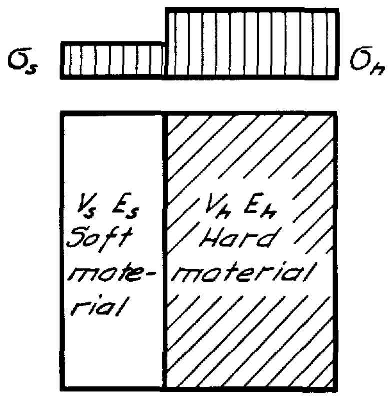

FIGURE 2. *Stress distribution over a unit volume of a combined hard material.*

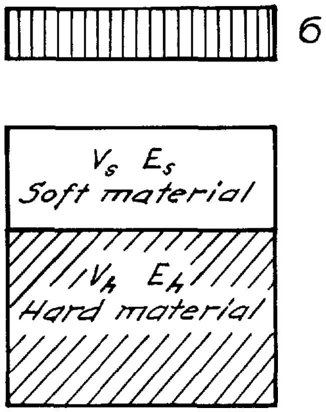

FIGURE 3. *Stress distribution over a unit volume of a combined soft material.*

ponent, V_h=depth of layer consisting of hard material=volume concentration of the hard component, ϵ_s=strain of soft component, ϵ_h=strain of hard component.

$$\epsilon_s=\frac{\sigma}{E_s} \tag{6}$$

and

$$\epsilon_h=\frac{\sigma}{E_h}. \tag{7}$$

By substituting eqs (6) and (7) in eq (5)

$$\epsilon=\frac{\sigma V_s}{E_s}+\frac{\sigma V_h}{E_h}=\frac{\sigma}{E}$$

or the fundamental equation for a *combined soft material:*

$$E=\frac{1}{\frac{V_s}{E_s}+\frac{V_h}{E_h}} \tag{8}$$

where all symbols are the same as the ones used in the previous calculation of the modulus of elasticity for a *combined hard material.*

Generally, cement paste or mortar is the continuous component in concrete while the stone particles are embedded in this mass. If the modulus of elasticity of the stones is higher than that of the mortar, as in most cases, it is possible to calculate the modulus of elasticity of concrete from the moduli of elasticity of the components and their volume concentrations on the assumption that concrete is a combined soft material, that is from the following equation:

$$\frac{1}{E}=\frac{V_1}{E_1}+\frac{V_2}{E_2} \tag{9}$$

where V_1=volume concentration of cement paste or mortar in concrete, V_2=volume concentration of aggregate in concrete, E=modulus of elasticity of concrete, E_1=modulus of elasticity of cement paste or mortar, E_2=modulus of elasticity of aggregates.

This has been done by the author in table 1 (experiments 1–27) on the basis of the experimental results of Dantu [8] and La Rue [9].

If, however, the modulus of elasticity of the stones is lower than that of mortar, then the modulus of elasticity should be calculated on the assumption that concrete is a combined hard material or from the following equation:

$$E=V_1E_1+V_2E_2 \tag{10}$$

where all symbols are the same as used above.

This has been done by the author in table 1 (experiments 28–30) on the basis of the experimental results of La Rue [9].

It will be seen that there is excellent agreement between the calculated and the experimentally determined moduli of elasticity (see table 1, column 11). Only in experiment 16 is the agreement not so good. This is due to the fact that the glass balls here are very densely packed. The volume concentration is 64 percent. The most dense packing gives a volume concentration of 74 percent. The glass balls are so densely packed that many of them must touch each other and thus we are in a transition zone between a combined soft and a combined hard material. As a matter of fact, in a real material some embedded particles will always touch each other. Therefore the experimentally determined moduli will generally lie between the results obtained by the two ideal equations (see table 1, columns 8, 9, and 10). In most cases there will be no doubt, however, as to which group a material should be assigned.

The author has tried to analyze the behavior of the cement paste according to the same principles.

The cement paste is to be regarded as a combined soft material consisting of hard grains of unhydrated cement embedded in a continuous soft component of cement gel and pores. The modulus of elasticity of cement paste can therefore be determined from eq (11),

$$\frac{1}{E_1}=\frac{V_3}{E_3}+\frac{V_4}{E_4} \tag{11}$$

where V_3=volume concentration of gel and capillary pores in cement paste, V_4=volume concentration of unhydrated cement grains in cement paste, E_3=modulus of elasticity of gel and pores, E_4=modulus of elasticity of unhydrated cement grains.

The phase consisting of gel and pores is to be regarded as a continuous hard material and the modulus of elasticity can therefore be determined from the following equation:

$$E_3=V_5E_5+V_6E_6=V_5E_5 \tag{12}$$

where V_5=volume concentration of gel in the component consisting of gel and capillary pores; V_6=volume concentration of pores in the component consisting of gel and capillary pores, E_5=modulus of elasticity of cement gel, E_6=modulus of elasticity of capillary pores=0.

By substituting eqs (11) and (12) in eq (9) we get *the fundamental equation*

$$\frac{1}{E}=\frac{V_3V_1}{V_5E_5}+\frac{V_1V_4}{E_4}+\frac{V_2}{E_2} \tag{13}$$

from which it should be possible to determine the modulus of elasticity of concrete when the moduli of elasticity and the volume concentrations of components are known.

Grudemo [1] found that even large variations in the mineral composition of cement do not cause

Table 1. *Comparison between calculated and experimentally determined moduli of elasticity for some heterogeneous materials*

1	2	3	4	5	6	7	8	9	10	11
Exp. no.	Source	Aggregate	Mortar	$V_2=$ vol. % agg.	$E_{2(\text{agg})}$ kg/cm^2 $\times 10^{-3}$	$E_{1(\text{mortar})}$ kg/cm^2 $\times 10^{-3}$	E_{exp} for concrete kg/cm^2 $\times 10^{-3}$	$E'_{\text{calc}}=\frac{1}{\frac{V_1}{E_1}+\frac{V_2}{E_2}}$ kg/cm^2 $\times 10^{-3}$ soft material	$E''_{\text{calc}}=V_1E_1+V_2E_2$ kg/cm^2 $\times 10^{-3}$ hard material	$\frac{E_{\text{exp}}}{E'_{\text{calc}}}$ or $\frac{E_{\text{exp}}}{E''_{\text{calc}}}$
1	Dantu [8]	20–40 mm Diorite	Cement 700 kg/m^3 Sand 1,260 kg/m^3 Water 300 kg/m^3	0.40	1,041	346	495	475	624	1.04
2				.50	1,041	346	550	520	694	1.05
3				.55	1,041	346	568	548	728	1.04
4		10–20 mm Diorite	Cement 700 kg/m^3 Sand 1,260 kg/m^3 Water 300 kg/m^3	.33	1,041	337	425	433	575	0.98
5				.42	1,041	337	471	471	638	1.00
6				.52	1,041	337	527	520	707	1.01
7		10–20 mm Diorite	Cement 700 kg/m^3 Sand 1,260 kg/m^3 Water 300 kg/m^3	.33	1,047	326	419	421	564	1.00
8				.42	1,047	326	475	459	629	1.04
9				.52	1,047	326	518	509	701	1.02
10		Glass spheres 17–18 mm Ø	Cement 700 kg/m^3 Sand 1,260 kg/m^3 Water 300 kg/m^3	.35	742	313	399	393	463	0.99
11				.45	742	313	431	422	506	1.02
12				.55	742	313	467	458	549	1.02
13		Pieces of glass 12.5–22 mm	Cement 700 kg/m^3 Sand 1,260 kg/m^3 Water 300 kg/m^3	.35	742	313	393	392	463	1.00
14				.45	742	313	426	422	506	1.01
15		Steel cylinders 5 mm Ø $h=5$ mm	Cement 700 kg/m^3 Sand 1,260 kg/m^3 Water 300 kg/m^3	.55	2,200	313	600	592	1,350	1.01
16		Glass spheres 5 mm Ø	Araldite	.64	720	39	175	99	475	1.57
17		10–20 mm Diorite	Gypsum	.59	1,047	374	638	602	771	1.06
18		Steel balls 5 mm Ø	Alliage-lino	.54	2,200	289	650	545	1,320	1.19
19	LaRue [9]	Limestone (Plattin) Graded	Cement: Sand: Water: 1:2.19:0.77 by volume	.43	795	374	485	484	557	1.00
20				.47	795	374	529	499	572	1.06
21				.52	795	374	472	519	592	1.10
22		Limestone (Burlington) (RM Carthage) Graded	Cement: Sand: Water: 1:2.19:0.77 by volume	.43	632	374	417	454	486	0.92
23				.47	632	374	411	464	496	0.89
24				.52	632	374	465	478	507	0.97
25		Limestone (Burlington) (LM Carthage) Graded	Cement: Sand: Water: 1:2.19:0.77 by volume	.43	473	374	356	411	417	0.87
26				.47	473	374	347	415	420	0.84
27				.52	473	374	399	422	425	0.94
28		Limestone (Bowling Green) Graded	Cement: Sand: Water: 1:2.19:0.77 by volume	.43	131	374	272	222	268	1.01
29				.47	131	374	275	199	258	1.07
30				.52	131	374	284	192	248	1.14

substantial changes in the microstructural composition of the cement gel. Therefore it may be expected that the modulus of elasticity of the gel component is rather constant and independent of the type and composition of the cement used.

A Relationship Between Strength and Elasticity

Powers [6] showed that the following relationship exists between strength of mortar F_c and gel density of cement paste,

$$F_c = aV_5^d$$

where a can vary between large limits with the type of cement used. However,

$$a \sim 1{,}160 \text{ kg/cm}^2$$

is a reasonable average value. The value of d can vary somewhat from cement to cement, but for an average cement we get:

$$d \sim 2.5.$$

When applying the following average values for concrete, $E_5=300{,}000$ kg/cm^2, $E_2=600{,}000$ kg/cm^2, $V_1=0.3$, $V_2=0.7$, $V_3=1.0$, $V_4=0.0$, we get from eq (13):

$$E=\frac{1}{\frac{V_1}{V_5E_5}+\frac{V_2}{E_2}}=\frac{1}{\frac{0.3}{300{,}000V_5}+\frac{0.7}{600{,}000}}=\frac{600{,}000}{\frac{0.6}{V_5}+0.7}. \qquad (14)$$

By substituting eq (14) in eq (1) we get the following approximate relationship between strength and modulus of elasticity of an average concrete:

$$E=\frac{600{,}000}{0.6^{-2.5}\frac{F_c}{1{,}160}+0.7}.$$

From figure 4 it is seen that this relationship covers reasonably well the experimental results obtained by Roš [10] and C.U.R. [11].

The apparent correlation between modulus of elasticity and strength of concrete, which has so often been observed, is explained by the fact that both properties depend on the gel density.

The large scatter of the experimental results around the theoretical curve in figure 4 is probably due to the actual variation in type of cement, modulus of elasticity of aggregates, volume concentration of cement paste, and other factors which have been regarded as invariables for different concretes when establishing eq (1) and eq (14).

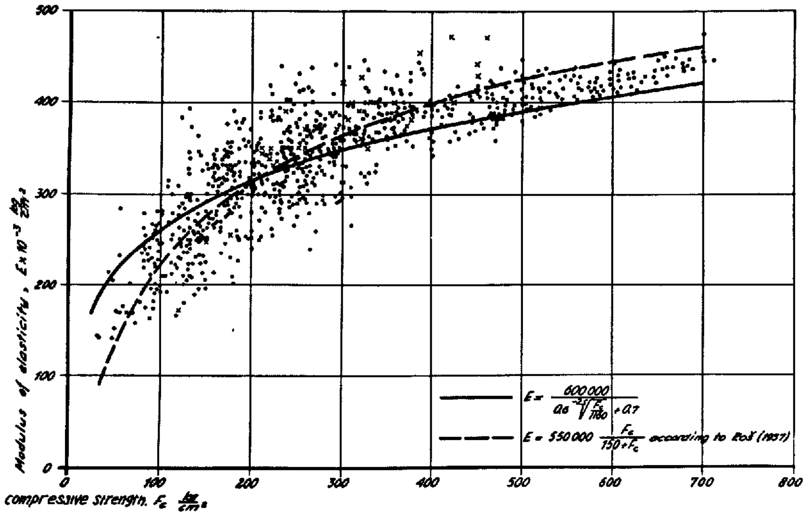

FIGURE 4. *Graph showing theoretical and experimental correlation between strength and modulus of elasticity of concrete.* (The experimental data have been collected by Roš [10] and C.U.R. [11].)

Creep

The Internal Mechanism of Concrete Creep

According to Flügge [12], Reiner [13], and T. C. Hansen [7], the viscoelastic behavior of concrete can be described by means of a rheological model, a Burgers body as shown in figure 5, where the four rheological constants vary with the age of concrete.

A rheological model is a combination of ideal elastic and viscous elements in series or parallel, which represents the behavior of actual materials under load or deformation.

The element E_M describes the instantaneous elastic deformation of concrete, λ_M the viscous part of creep; E_K and λ_K in series describe the delayed elastic part of creep.

It should be emphasized that the use of this model is to give a phenomenological description of the viscoelastic response of concrete, but it does not necessarily imply anything about the molecular mechanisms responsible for the observed behavior. Several attempts have been made to develop a molecular theory of viscoelastic behavior of concrete, but no theory is commonly accepted. During the last few years our knowledge of cement paste has been extended so far that it should be possible to give at least a tentative explanation of creep.

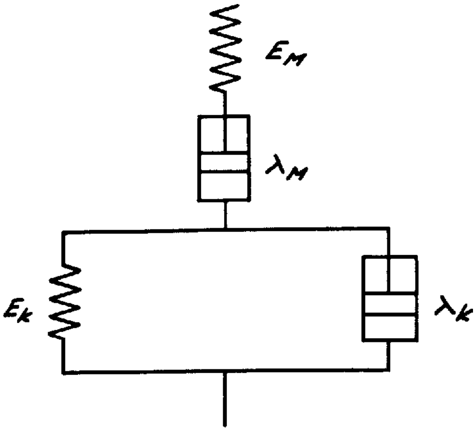

FIGURE 5. *Suggested rheological model for concrete.*

Cement gel shows a remarkable structural stability as compared with other hydrogels, when exposed to external load or to changes in moisture content and consequential shrinkage or swelling. According to Grudemo [1] the principal cause of this dimensional stability is to be sought in the presence of the framework of fibrous particles. It can be presumed that the units of this framework have a comparatively great flexural rigidity on account of their tubular structure.

The more amorphous part of cement gel, the felted structure of crumpled sheets and foils, probably contains the main part of the absorbed water after the cement has hardened. The number of gel particles is about 7 x 10^{16} per cc, and the interstitial spaces are therefore minute. They are of the order of a few molecular diameters. When two particles are in such proximity, they exert a mutual attraction, the "van der Waals" forces. When the paste is thoroughly dried out, the van der Waals forces and, to some extent, chemical bonds are the only bonds between the gel particles. When the paste is wetted, the water molecules spread all over the gel surface because of mutual attraction between them and the molecules composing the solid surface. The water molecules act against the above-mentioned bonds between adjacent surfaces, thus forcing the surfaces apart and weakening the bonds. The result of the wetting is a swelling and a reduced strength compared with that of dry paste. When the paste dries, the water evaporates and the paste shrinks.

Creep of concrete is a sum mainly of two different types of deformation, the viscous time-dependent deformation and the delayed elasticity. Grudemo [1] has suggested that these deformations take place as lateral or angular displacements in the points of intersection of the gel framework of the cement paste.

It was mentioned earlier that the bonds between the solid gel particles probably are van der Waals forces, hydrogen bonds, and chemical bonds. The author suggests that the viscous deformation of cement paste is a viscous flow in the grain boundaries or welding points. While the van der Waals forces as well as the hydrogen bonds are forces of the same type as the forces which hold the molecules of a liquid together, there has been some doubt whether solid bonds like chemical or crystalline bonds can behave in a viscous manner. Usually dislocations and consequential plastic deformation properties are attributed to solid bonds. However, lately Kê [14, 15, 16] has shown that the grain boundaries in polycrystalline metals, where the atom positions represent a compromise between the crystalline arrangements in two adjoining grains, can behave in a viscous manner. Hence cement gel is not unique in showing viscous flow in grain or particle boundaries. It is recognized, however, that time-dependent permanent set due to collapse of the gel structure, when submitted to a sustained load, may also contribute somewhat to the nonreversible part of creep. This may be the case specially when concrete is exposed to simultaneous drying or wetting.

So far, no theory has been presented which can conclusively explain the delayed elastic part of creep. However, the retardation of deformation in solid materials is often thought to be due to internal diffusion processes.

The cement paste consists of a solid network of particles which are loosely linked and may be capable of orientation. The response of this structure to stress is probably diffusion controlled, and molecular orientation is induced by stress due to external load. This means that a less probable state is induced by the application of stress. The configurational entropy is decreased so that release of stress results in an attempt by the molecules to restore maximum entropy and hence produce a definite restoring force.

The sources of delayed elasticity of concrete are probably the same, in the main, as in glass (Douglas [17]). In addition to a chemical diffusion, a certain amount of segmental diffusion of the solid particles, the slender ribbons and the crumpled sheets and foils, might occur. Each individual chain molecule, or whole conglomerations of molecules of the intertwined assembly, wriggle around from one configuration to another. The higher the temperature, the faster is this diffusional motion. When a stress is imposed on the system, this intermolecular Brownian motion is biased, and oriented molecular configurations are favored. When the load is released, the segments will tend to return to the original positions and the retardation will be the same on unloading as during the time of sustained loading.

The new equilibrium distribution of configurations (under stress) due to chemical and segmental diffusion corresponds to the equilibrium elastic strain of the delayed elasticity. The retardation time is determined by the rate of the diffusional motion.

It has been suggested by other authors that the water molecules absorbed on the surfaces of the gel particles will start moving from the more-stressed areas to less-stressed areas when an external load is applied on cement paste. When the stress is released, the water tends to return to the original position. The result is a complete recovery unless the internal structure has in some other ways been modified by the sustained load. It is an important objection against this theory that no exchange of water takes place between a concrete specimen and the surroundings, due to sustained loading. It has been possible to prove neither that a large scale migration of water molecules takes place within the cement paste after application of an external load, nor that the internal relative humidity is altered when the external load is applied. If such a migration really occurs, it does not seem to imply any disturbance in the moisture equilibrium of the concrete but only a movement of gel water from one location to another.

In an earlier paper the possible relations between creep and shrinkage were discussed (T. C. Hansen [7]).

It was concluded that some process in connection with the water diffusion during the period of drying influences the creep properties of concrete. Therefore, it is believed that there is an interrelation between creep and shrinkage. These two concrete properties are probably both influenced by a common process taking place in the concrete during the period of drying. But it is not necessarily true that the shrinkage in itself influences creep or vice versa.

To avoid the effect of this interdependence between shrinkage and creep, when experimentally studying creep, the concept of "basic creep" was introduced. Basic creep was defined as creep of concrete which is not exposed to any moisture diffusion and consequential shrinkage or swelling during the period of sustained loading. Since the effect of drying and wetting severely influences the experimental results, a connection between creep and the factors influencing creep (other than drying and wetting, see table 2), is more likely to be revealed if basic creep is investigated, than when creep of drying concrete is determined.

TABLE 2. *The internal primary variables for basic creep*

1. The cement quality.
2. The water-cement ratio.
3. The quantity of cement paste in the concrete.
4. The rheological properties of the aggregates.
5. Admixtures.
6. The intensity of the compaction process.
7. The type and importance of load.
8. The stage of hydration of the cement paste when load is applied.
9. The temperature.

Theoretical Equation Relating Basic Creep of Concrete to Water-Cement Ratio, Volume Concentration of Cement Paste, Type of Cement, Age at Loading and Time Under Sustained Loading

It is reasonable to believe that the modulus of viscosity λ_M as well as the delayed elastic modulus of concrete E_K increases with the amount of cement gel formed. The two moduli must also increase with decreasing distance between the cement grains, that is, with decreasing water-cement ratio. Thus it appears that the same factors influence the strength and elasticity of cement paste as well as the deformations under sustained load.

It is not obvious that the gel density which proved to be a useful parameter when dealing with strength and elasticity should also apply for creep, but on the other hand there are certain indications that it does.

On an experimental basis, Neville [18] suggested that the creep rate at any time after load application is inversely proportional to the strength of the cement mortar independently of the composition of the mortar and the type of cement used. This indicates a close relationship between creep rate and gel density.

However, if a relationship exists between creep and strength as suggested by Neville, this can only be true for cement paste but not for mortar or concrete. The creep properties are highly influenced by the volume concentration of the aggregate because it immobilizes part of the total volume. The creep is actually directly proportional to the volume concentration of cement paste in concrete (T. C. Hansen [7]), whereas the strength properties are far less influenced by the amount of aggregate, as long as the water-cement ratio is kept constant.

A similar relationship, as derived earlier in this paper, between the modulus of elasticity of concrete E and the moduli of elasticity of the components E_2, E_4, and E_5 as well as the volume concentrations V_1, V_2, V_3, V_4, and V_5, can probably be established between the moduli λ_M, E_K, and λ_K describing the viscoelastic creep of concrete according to the rheological model shown in figure 5, and the moduli and volume concentrations of the components.

Analogous to eq (13) which in terms of E_M can be written:

$$\frac{1}{E_M}=\frac{V_3V_1}{V_5E_{M_5}}+\frac{V_1V_4}{E_{M_4}}+\frac{V_2}{E_{M_2}} \tag{13a}$$

we get for λ_M

$$\frac{1}{\lambda_M}=\frac{V_3V_1}{V_5\lambda_{M_5}}+\frac{V_1V_4}{\lambda_{M_4}}+\frac{V_2}{\lambda_{M_2}}. \tag{15}$$

It is assumed that the aggregate is an inert material which influences the creep only by occupying part of the volume, thus λ_{M_2} and $\lambda_{M_4} \gg \lambda_{M_5}$. (It is further assumed that V_3 does not vary much from concrete to concrete.) As a rough approximation we get eq (16):

$$\frac{1}{\lambda_M}=\frac{V_1}{V_5\lambda_{M_5}} \tag{16}$$

and analogously for E_K and λ_K

$$\frac{1}{E_K}=\frac{V_1}{V_5E_{K_5}} \tag{17}$$

$$\frac{1}{\lambda_K}=\frac{V_1}{V_5\lambda_{K_5}}. \tag{18}$$

(While eqs (16) and (17) are theoretically correct, eq (18) is only a suggested approximation.)

Grudemo [1] found, as earlier mentioned, that even large variations in the mineral composition of cement do not cause substantial changes in the microstructural composition of the cement gel. Therefore it may be assumed that the moduli of deformation of the gel component are rather constant and independent of the type and composition of cement used, and eqs (16), (17), and

(18) can be written

$$\frac{1}{\lambda_M}=\alpha\frac{V_1}{V_5} \tag{19}$$

$$\frac{1}{E_K}=\beta\frac{V_1}{V_5} \tag{20}$$

$$\frac{1}{\lambda_K}=\gamma\frac{V_1}{V_5} \tag{21}$$

where α, β, and γ=coefficients; V_1=volume concentration of cement paste in concrete; V_5=gel density. This factor is actually a function of time, $V_5(t)$.

If the rheological model shown in figure 5 is subjected to a constant stress we find

$$\frac{d\frac{\epsilon}{\sigma}}{dt}=\frac{1}{\lambda_M}+\frac{1}{\lambda_K}\exp\left(-\frac{E_K}{\lambda_K}\cdot t\right) \tag{22}$$

or integrated from the time of load application $t_1-t_1=0$ to the time $t-t_1$

$$\epsilon\ \text{creep}=\frac{\epsilon_{\text{del. el.}}}{\sigma}+\frac{\epsilon_{\text{visc.}}}{\sigma}=\int_{t_1-t_1}^{t-t_1}\frac{1}{\lambda_K(t)}\exp\left(-\frac{E_{K(t)}}{\lambda_{K(t)}}\cdot t\right)dt+\int_{t_1-t_1}^{t-t_1}\frac{1}{\lambda_{M(t)}}dt \tag{23}$$

where t=age of concrete at time t, in days; t_1 =age of concrete at load application, in days.

Evaluation of the First Term in Eq (23), the Delayed Elasticity

If it is assumed that the delayed elastic deformation takes place so quickly that the influence of time upon $\lambda_K(t)$ and $E_K(t)$ is the same, and small during this period, the first term in eq (23) can be written as follows:

$$\frac{\epsilon_{\text{del. el.}}}{\sigma}=\frac{1}{E_K}\left(1-e^{-m(t-t_1)}\right) \tag{24}$$

where m is a coefficient.

It was experimentally shown by L'Hermite [19] that an equation of this type very well describes the delayed elastic recovery of concrete which is actually equivalent to the pure delayed elasticity without any influence of viscosity. Thus the form of this equation is experimentally verified.

The gel density is defined according to Power's [6] (Copeland and Hayes [20] have later modified Powers' results, but this is without any importance here):

$$V_5=\frac{V_{hc}}{V_{hc}+p_c} \tag{25}$$

where V_{hc}=volume of gel, p_c=volume of capillary pores, or since

$$V_{hc}=(N+n)w_n,\ \text{and}\ p_c=w_o-Nw_n$$

we get

$$V_5=\frac{(N+n)w_n}{n\cdot w_n+w_o}$$

where w_n=weight of nonevaporable water, in g/cc, w_o=weight of original mixing water corrected for bleeding, in g/cc, and $N=0.75(1+4k)$, where $k=0.230\ (C_3S)+0.320\ (C_2S)+0.317\ (C_3A)+0.368\ (C_4AF)$. The symbols in parentheses represent the computed weight proportions of the cement compounds indicated, and

$$n=\frac{v_c}{\frac{w_n}{C}}=\frac{v_c}{k_1}$$

where v_c=specific volume of the original cement, in cc/gram≅0.31, $k_1=\frac{w_n}{C}$=weight ratio of nonevaporable water to cement when all the cement is hydrated, $k_1=0.187\ (C_3S)+0.158\ (C_2S)+0.665\ (C_3A)+0.213(C_4AF)$. Since $w_n=g(t_1)k_1\cdot C$, where $g(t_1)$=degree of hydration of cement at time t_1, C=weight of cement, in g/cc, we get from eq (25)

$$V_5=\frac{(N\cdot k_1+v_c)g(t_1)}{v_c g(t_1)+\frac{w_o}{C}} \tag{26}$$

or since $v_c\sim0.31$,

$$V_5=\frac{(N\cdot k_1+0.31)g(t_1)}{0.31g(t_1)+\frac{w_o}{C}}. \tag{27}$$

Substituting eq (27) in eqs. (19), (20), and (21) gives

$$\frac{1}{\lambda_M}=\alpha\frac{\left(0.31g(t_1)+\frac{w_o}{C}\right)V_1}{(Nk_1+0.31)g(t_1)} \tag{28}$$

$$\frac{1}{E_K}=\beta\frac{\left(0.31g(t_1)+\frac{w_o}{C}\right)V_1}{(Nk_1+0.31)g(t_1)} \tag{29}$$

$$\frac{1}{\lambda_K}=\gamma\frac{\left(0.31g(t_1)+\frac{w_o}{C}\right)V_1}{(Nk_1+0.31)g(t_1)}. \tag{30}$$

Substituting eq (29) in eq (24) gives

$$\frac{\epsilon_{\text{del. el.}}}{\sigma}=\beta\frac{\left(0.31g(t_1)+\frac{w_o}{C}\right)V_1}{(Nk_1+0.31)g(t_1)}\left(1-e^{-m(t-t_1)}\right). \tag{31}$$

Evaluation of the Second Term in Eq (23), the Viscosity

Substituting eq (28) in the viscosity term of eq (23) gives

$$\frac{\epsilon_{\mathrm{visc.}}}{\sigma}=\int_{t_1}^{t}\frac{1}{\lambda_M(t)}\,dt=\int_{t_1}^{t}\alpha\,\frac{\left(0.31g(t)+\frac{w_o}{C}\right)V_1}{(Nk_1+0.31)g(t)}\,dt \tag{32}$$

or possibly

$$\frac{\epsilon_{\mathrm{visc.}}}{\sigma}=\int_{t_1}^{t}\alpha(t)\,\frac{\left(0.31g(t)+\frac{w_o}{C}\right)V_1}{(Nk_1+0.31)g(t)}\,dt. \tag{32a}$$

Not knowing the functions $g(t)$ and $\alpha(t)$ with any accuracy is a serious obstacle against an integration of eq (32a). It is known, however, that the creep curves obtained when creep is plotted against the logarithm of time are approximately straight lines at later stages when all the delayed elastic deformation has taken place (see Hanson [21], Bäckström [22], and Serafim and Guerreiro [23]. Moreover, the curves obtained when creep is plotted against time are parallel at later stages for concretes made at the same time but loaded at different ages (see, e.g., Glanville [24], McHenry [25], and Bäckström [22]). Therefore such creep curves must also be parallel at later stages in a semilogarithmic graph. Consequently, it is to be expected that the viscous part of creep can be approximated by the following function of time:

$$\frac{\epsilon_{\mathrm{visc.}}}{\sigma}=\mathrm{const}\cdot\ln\frac{t}{t_1} \tag{33}$$

where t=age of concrete at time t, in days; t_1=age of concrete when loaded, in days.

Considering the influence of composition of concrete, it is suggested that eq (32) or (32a) can be written as

$$\frac{\epsilon_{\mathrm{visc.}}}{\sigma}=\alpha_1\frac{w_o}{C}V_1\ln\frac{t}{t_1}. \tag{34}$$

It must be remarked that the linearity between specific creep (i.e., creep per unit stress) and time in a semilogarithmic graph is only valid up to about 1,000 days sustained loading of a young concrete. (Davis and Troxell [26].) Thereafter the creep rate is considerably reduced probably due to recrystallization in the cement gel, and the creep obtained after another 20 yr sustained loading is only slightly greater than the creep obtained after 1,000 days sustained loading.

Substituting eq (31) and eq (34) in eq (23) gives *the general rheological creep equation of all cement pastes, mortars, and concretes when cured and stored in water (or under other conditions where no drying or wetting can take place) and subjected to a constant compressive, tensile, or flexural load.*

$$\frac{\epsilon_{\mathrm{creep}}}{\sigma}=\beta\,\frac{\left(0.31g(t_1)+\frac{w_o}{C}\right)V_1}{(Nk_1+0.31)g(t_1)}\left(1-e^{-m(t-t_1)}\right)$$

(Creep per unit stress) (Delayed elasticity)

$$+\alpha_1\frac{w_o}{C}\cdot V_1\ln\left(\frac{t}{t_1}\right) \tag{35}$$

(Viscosity)

where t=age of concrete at time t, in days, t_1=age of concrete when loaded, in days, w_o/C=water-cement ratio by weight, corrected for bleeding, V_1=volume concentration of cement paste in mortar or concrete, $g(t_1)$=degree of hydration of cement at the time of load application, α_1, β, and m=coefficients to be determined experimentally, k_1=weight ratio of nonevaporable water to cement when all cement is hydrated. k_1 is a function of the proportions of cement components: $k_1=0.187\,(C_3S)+0.158\,(C_2S)+0.665\,(C_3A)+0.213\,(C_4AF)$. $N=0.75\,(1+4k)$, where $k=0.230\,(C_3S)-0.320\,(C_2S)+0.317\,(C_3A)+0.368\,(C_4AF)$.

The strain response of any stress, or the stress response of any strain, constant or varying, and applied at any time to any concrete, can be predicted from a similar analysis of the rheological model shown in figure 5. Due consideration should be paid to our present knowledge of the physical structure and properties of concrete. It must, however, be remembered that this model is only valid for normal working stresses under the plastic limit where no internal microcracking occurs (see T. C. Hansen [7] and [27]), and that the model does not take into account the phenomenon of permanent set.

Experimental Verification

All creep tests found in the literature which meet with the following two requirements are grouped in table 3.

1. Test specimens have been loaded in water after continuous storage in water. This provides us with results on basic creep under very well-defined conditions.
2. Test specimens have been loaded under the proportional or plastic limit where no microcracking has occurred, which, where no other information is available, is estimated to be at least 30–40 percent of the short-time strength.

The 42 creep tests listed, provide us with good material for experimental verification of eq (35).

In estimating the values of the parameters in eq (35) for all these creep tests, the following approximations have been made.

When the composition of the cement used is unknown, and therefore it has not been possible to calculate k and k_1, it has been assumed according to Powers and Brownyard [4] that $k=0.25$ and $k_1=0.23$.

Further it has been assumed according to Hummel [28] that the two curves a and b in figure 6

TABLE 3. *Concrete data for comparison between calculated and experimentally determined creep values*

	No.	Ser.	Type of test	Age at load application days	$g(t_1)$ degree of hydration at load application	$\frac{w}{c}$, $\frac{w_o}{C}$ by weight	V_1, vol. concentration of cement paste	Type of cement	k	k_1	N	$\frac{\epsilon}{\sigma}$ Specific creep after 50 days sustained loading		$\frac{\epsilon}{\sigma}$ Specific creep after 100 days sustained loading		$\frac{\epsilon}{\sigma}$ Specific creep after 200 days sustained loading		$\frac{\epsilon}{\sigma}$ Specific creep after 900 days sustained loading		Notes
												Calc. acc. to eq (35)	Measured	Calc. acc. to eq (35)	Measured	Calc. acc. to eq (35)	Measured	Calc. acc. to eq (35)	Measured	
1	Davis [29]	2	Compr.	2	0.2	0.64	0.330	Normal	0.25	0.23	1.50	8.35	10.00	9.99	11.50	10.93	12.50	12.71	13.70	
2	Davis [30]	2	do	7	.4	.64	.330	do	.25	.23	1.50	4.93	6.16	6.13	6.44	7.01	7.20	8.79	7.85	
3	do	2	do	7	.4	.64	.330	do	.25	.23	1.50									Loaded over plastic limit.
4	do	2	do	28	.7	.64	.330	do	.25	.23	1.50	2.78	2.88	3.64	4.00	4.39	5.05	6.09	5.70	
5	do	2	do	28	.7	.64	.330	do	.25	.23	1.50									Loaded over plastic limit.
6	do	2	do	28	.7	.64	.330	do	.25	.23	1.50									Loaded over plastic limit.
7	do	2	do	90	.9	.64	.330	do	.25	.23	1.50	1.83	2.02	2.44	2.50	2.98	3.10	4.44	4.30	
8	do	2	do	90	.9	.64	.330	do	.25	.23	1.50	1.83	2.34	2.44	2.78	2.98	3.50	4.44	5.15	
9	do	2	do	90	.9	.64	.330	do	.25	.23	1.50	1.83	2.96	2.44	3.33	2.98	3.92	4.44	5.25	
10	Davis [31]	Reinf. test.	do	28	.7	.76	.250	do	.25	.23	1.50	2.45	2.63	3.21	3.46	3.91	5.10			
11	do	Reinf. test.	do	28	.7	.49	.305	do	.25	.23	1.50	2.03	1.96	2.68	2.73	3.24	3.65			
12	do	3	do	28	.7	.55	.286	do	.25	.23	1.50	2.13	3.24	2.78	3.57	3.35	3.95			
13	Davis [30]	7	do	28	.7	.44	.330	do	.25	.23	1.50	2.04	2.08	2.65	2.50	3.19	3.50			
14	do	7	do	28	.7	.61	.255	do	.25	.23	1.50	2.07	2.53	2.72	2.82	3.28	3.20			
15	Davis [31]	14	do	90	.9	.57	.250	do	.25	.23	1.50	1.27	2.14	1.70	2.30					
16	do	16	do	28	.7	.71	.290	do	.25	.23	1.50	2.68	3.65	3.43	4.20					
17	Dutron [32]	PP350	do	60	.9	.69	.305	H.E. Str.	.25	.23	1.50	1.98	2.15	2.67	2.55	3.29	3.95	4.85	6.30	
18	do	PP350	do	60	.9	.69	.305	do	.25	.23	1.50	1.98	1.61	2.67	2.30	3.29	3.20	4.85	5.05	
19	do	PP350	do	60	.9	.69	.305	do	.25	.23	1.50	1.98	1.41	2.67	2.15	3.29	2.85	4.85	4.70	
20	do	GR300	do	60	.9	.56	.234	do	.25	.23	1.50	1.33	1.32	1.82	1.64	2.12	2.65	3.10	3.70	
21	do	GR300	do	60	.9	.56	.234	do	.25	23	1.50	1.33	1.26	1.82	1.58	2.12	2.35	3.10	2.75	
22	do	GR300	do	60	.9	.56	.234	do	.25	.23	1.50	1.33	.90	1.82	1.40	2.12	1.96	3.10	2.40	
23	do	GR300	do	60	.9	.56	.234	do	.25	.23	1.50	1.33	.88	1.82	1.30	2.12	1.83	3.10	2.45	
24	do	PP350	do	14	.7	.69	.305	do	.25	.23	1.50	3.32	2.20	4.32	3.72	5.11	5.13	6.85	7.22	
25	do	PP350	do	14	.7	.69	.305	do	.25	.23	1.50	3.32	2.15	4.32	3.32	5.11	4.66	6.85	5.90	
26	Bergstrom [33]	PH	Flex.	28	.7	.35	1.000	Normal	.23	.20	1.44	5.42	5.72	7.04	7.20					
27	do	PJ	do	28	.7	.25	1.000	do	.23	.20	1.44	4.22	4.15	5.44	5.36					
28	do	PM	do	28	.7	.30	1.000	do	.23	.20	1.44	4.81	5.25	6.24	7.15					
29	do	PN	do	28	.7	.30	.800	do	.23	.20	1.44	3.84	6.25	4.99	7.56					
30	Hansen (unpubl)	B	do	28	.7	.37	.590	do	.23	.20	1.44	3.32	3.71	4.33	4.83					
31	Neville [18]	Cem 1	Compr.	28	.7	.40	.377	do	.25	.24	1.50	2.06	2.95	2.69	3.50					$\frac{\epsilon}{\sigma}$ Meas. is corrected for shrinkage according to the capacity of creep.
32	do	do 2	do	28	.7	.40	.377	do	.25	.23	1.50	2.10	2.95	2.75	3.50					
33	do	do 3	do	28	.7	.40	.377	do	.25	.23	1.50	2.10	2.06	2.75	2.30					
34	do	do 4	do	28	.7	.40	.377	Sulph. res.	.26	.18	1.53	2.31	2.26	3.00	2.50					
35	do	do 5	do	28	.7	.40	.377	Normal	.25	.23	1.50	2.10	3.10	2.75	3.30					
36	do	do 6	do	28	.7	.40	.377	do	.26	.22	1.53	2.15	2.85	2.80	3.10					
37	do	do 7	do	28	.7	.40	.377	do	.26	.22	1.53	2.15	2.25	2.80	2.40					
38	do	do 8	do	28	.7	.40	.377	White	.24	.21	1.47	2.25	2.66	2.92	2.90					
39	do	do 9	do	28	.8	.40	.377	H.E. Str.	.24	.23	1.47	2.04	2.15	2.70	2.30					
40	do	do 10	do	28	.7	.40	.377	Low heat	.27	.18	1.56	2.27	2.85	3.17	2.90					
41	do	do 11	do	28	.7	.40	.377	Sulph. res.	.28	.19	1.59	2.28	2.30	2.97	2.30					
42	Serafim [23]	Stage 2	Saturated compr.	8	.45	.50	.257	Normal	.25	.23	1.50	2.84	3.40	3.55	4.0					

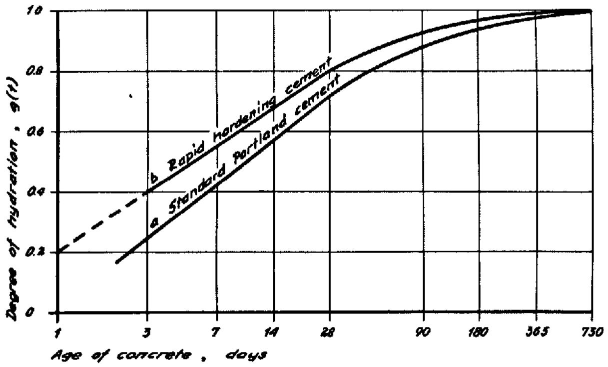

FIGURE 6. *Graph showing degree of hydration versus age of concrete.*
(Hummel [26].)

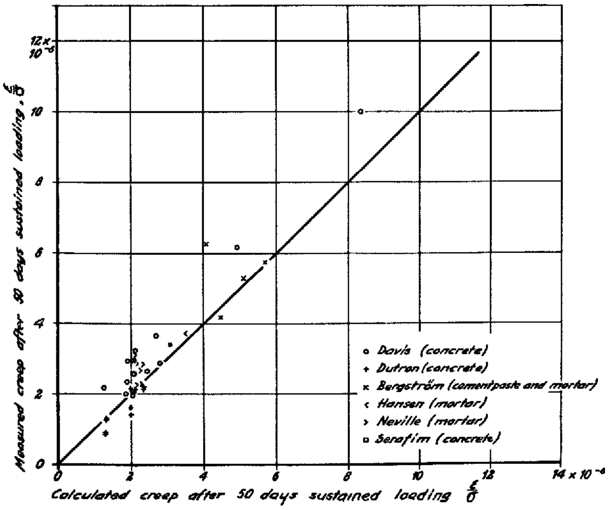

FIGURE 7. *Graph showing agreement between calculated and experimentally determined creep after 50 days sustained loading.*

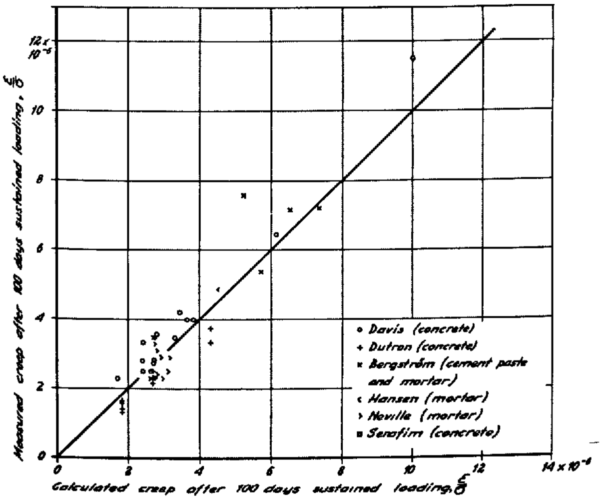

FIGURE 8. *Graph showing agreement between calculated and experimentally determined creep after 100 days sustained loading.*

give the increase in strength or in degree of hydration with time for average standard portland cement, and for rapid hardening cement.

Figures 7–10 show agreement between experimentally determined creep values after 50, 100, 200, and 900 days sustained loading, and creep values calculated from eq (35). (The full line curves correspond to the ideal case where the computed creep values are equal to the experimentally determined values.) The coefficients are

$$\beta=3.06\cdot10^{-6}$$

$$m=0.0333$$

$$\alpha_1=5.7\cdot10^{-6}.$$

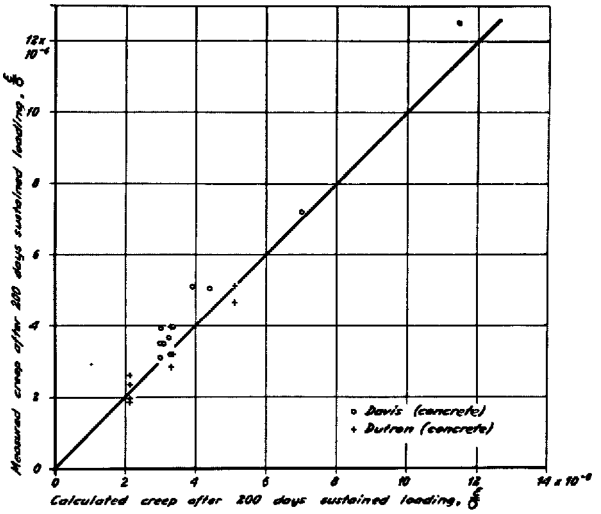

FIGURE 9. *Graph showing agreement between calculated and experimentally determined creep after 200 days sustained loading.*

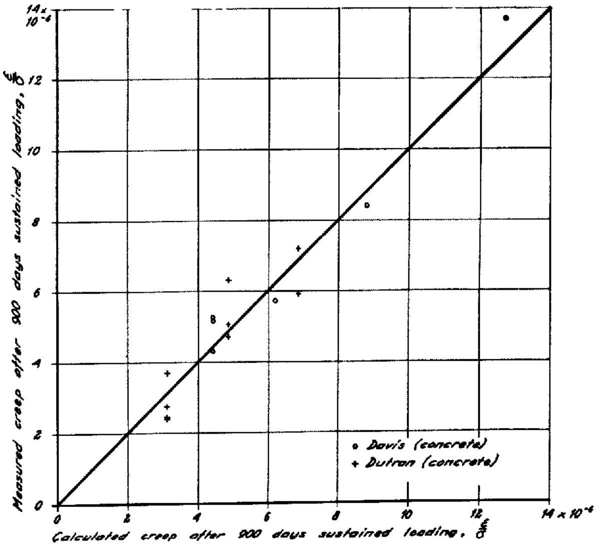

FIGURE 10. *Graph showing agreement between calculated and experimentally determined creep after 900 days sustained loading.*

Using these values, *the fundamental equation for creep of water-stored concrete, mortar, and cement paste can be written as follows:*

$$\frac{\epsilon_{\text{creep}}}{\sigma}=3.06\cdot10^{-6}\frac{\left(0.31g(t_1)+\frac{w_o}{C}V_1\right)}{(Nk_1+0.31)g(t_1)}(1-e^{-0.0333(t-t_1)})$$
$$+5.7\cdot10^{-6}\frac{w_o}{C}V_1\ln\left(\frac{t}{t_1}\right) \quad (35a)$$

where all symbols are defined as in eq (35).

It is remarked that the experimental creep values in table 3 include flexural and compressive creep tests on concrete, mortar, and cement paste made from different cements and different aggregate material in different laboratories all over the world in the years 1930–1958. Considering this fact and the large scatter found even in very well-controlled creep tests, the average percentage deviations of 12–16 percent between measured and calculated creep values in table 3 are not surprising.

The rather large deviations between our calculated creep values and some of Neville's experimental data on creep of mortars of the same composition but made with different cements indicate that part of the uncertainty in the calculated values can be explained by the fact that the degree of hydration of the different cements cannot be estimated accurately enough from the two average curves a and b in figure 6.

Appendix 1

List of Repeatedly Used Symbols

a = constant
α = constant
α_1 = constant
b = coefficient
β = coefficient
C = weight of cement, in grams per cc of paste
c = coefficient
d = coefficient
δ = proportionality factor between V_m and total volume of gel V_{hc}
$E_M=E$ = modulus of elasticity of concrete, kg/cm^2
$E_{M_1}=E_1$ = modulus of elasticity of cement paste or mortar, kg/cm^2
$E_{M_2}=E_2$ = modulus of elasticity of aggregates, kg/cm^2
$E_{M_3}=E_3$ = modulus of elasticity of gel and pores in cement paste, kg/cm^2
$E_{M_4}=E_4$ = modulus of elasticity of unhydrated cement grains in cement paste, kg/cm^2
$E_{M_5}=E_5$ = modulus of elasticity of cement gel, kg/cm^2
$E_{M_6}=E_6$ = modulus of elasticity of capillary pores $=0$
$E_{K_{1\text{to}6}}$ = modulus of delayed elasticity (see fig. 5) of the respective components, kg/cm^2
E_s = modulus of elasticity for a soft component of a combined material, kg/cm^3
E_h = modulus of elasticity for a hard component of a combined material, kg/cm^2
e = base of natural or Napierian logarithms
ϵ = elastic strain of a combined material
ϵ_s = strain of the soft component of a combined material
ϵ_h = strain of the hard component of a combined material
ϵ_{creep} = creep strain
$\epsilon_{\text{del. el.}}$ = delayed elastic strain
$\epsilon_{\text{visc.}}$ = viscous strain
F_c = strength of cement paste, mortar or concrete, kg/cm^2
$g(t_1)$ = degree of hydration of cement at age t_1 when concrete is loaded
γ = coefficient
k = constant, characteristic of the cement, related to the computed compound composition as follows: $k=0.230\,(C_3S)+0.320\,(C_2S)+0.317\,(C_3A)+0.368(C_4AF)$
$k_1=\frac{w_n}{C}$ = weight ratio of nonevaporable water to cement where all the cement is hydrated; k_1 is related to the computed compound composition of the cement as follows: $k_1=0.187\,(C_3S)+0.158\,(C_2S)+0.665\,(C_3A)+0.213(C_4AF)$
$\lambda_{M_{1\text{to}6}}$ = Troutons coefficient of viscous traction for Maxwell element (see fig. 5) of respective components, kg sec/cm^2
$\lambda_{K_{1\text{to}6}}$ = Troutons coefficient of viscous traction for Kelvin element (see fig. 5) of respective components, kg sec/cm^2
m = coefficient
N = $0.75(1+4k)$
p_c = volume of capillary pores, in cc/cc of cement paste
σ = stress, kg/cm^2
σ_s = stress on the soft component of a combined material, kg/cm^2
σ_h = stress on the hard component of a combined material, kg/cm^2
t = age of concrete, days
t_1 = age of concrete when loaded, days
V_s = volume concentration of the soft component of a combined material
V_h = volume concentration of the hard component of a combined material
V_{hc} = volume of hydrated cement = volume of gel, cc/cc of cement paste
V_m = constant, proportional to the surface area of the gel; theoretically the number of grams of water required to cover the surface of the hydrated cement in 1 cc of cement paste with a layer averaging one molecule deep
V_1 = volume concentration of cement paste in concrete
V_2 = volume concentration of aggregate in concrete
V_3 = volume concentration of gel and capillary pores in cement paste
V_4 = volume concentration of unhydrated cement grains in cement paste
$V_5=\frac{V_{hc}}{V_{hc}+p_c}$ = volume concentration of gel in the component of cement paste which consists of gel and pores = gel density
V_6 = volume concentration of pores in the component of cement paste which consists of gel and pores
v_c = specific volume of the original cement, cc/gram $\cong 0.31$
w_o = weight of original water content corrected for bleeding, g/cc of cement paste
w_n = weight of nonevaporable water, g/cc of cement paste

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Paper V–S3. A Few Unsolved Problems of Cement Hydration*

Wolfgang Czernin

Synopsis

The writer deals with some problems of cement hydration which have been mentioned in the papers and discussions of this Symposium.

The "Dormant Period". Although some facts seem to indicate that there exists a "dormant period" after the mixing of cement with water, the writer—on the basis of his own experiments and those of others—believes that the stiffening of cement pastes starts immediately after mixing. The stiffening phenomena can, however, be obscured in tests where the thixotropic properties or the "memory" of the paste can play their part.

Does Hydration Proceed by Solution and Precipitation or by Topochemical Reaction? The writer produces electronmicrographs obtained by use of carbon replicas of hydrating C_3S which seems to show that topochemical hydration reactions are accompanied by solution and precipitation reactions which lead to deposits in the capillary spaces. Thus it is indicated that both kinds of reaction take place during the hydration of cement.

The Constancy of Cement Gel Porosity. The assumption of a constant porosity of the cement gel independent of the water cement factor does not seem to be in accordance with Abrams' law: If the porosity of the hydrated parts remains the same, whatever the amount of unhydrated material distributed in the gel, then strength should remain at the same level or at least near it when we lower the w/c from 0.4 to the lowest possible ratio. This, however, is, as we all know, not the case.

Résumé

L'auteur traite certains problèmes de l'hydratation du ciment qui ont été mentionnés dans les exposés et discussions de ce Symposium.

La "Période dormante". Bien que certains faits semblent indiquer qu'il existe une "période dormante" après le mélange du ciment avec l'eau, l'auteur —s'appuyant sur ses propres expériences et sur d'autres— croit que le durcissement des pâtes de ciment commence immédiatement après le mélange. Cependant les phénomènes de durcissement peuvent être cachés dans les expériences où les propriétés thixotropiques ou la "mémoire" de la pâte peuvent jouer un rôle.

Est-ce que l'Hydratation procède par Solution et Précipitation ou par Réaction Topochimique? L'auteur présente des électronmicrographes obtenus au moyen de répliques au carbone de l'hydratation de C_3S qui semblent indiquer que les réactions topochimiques d'hydratation s'accompagnent de réactions de solution et de précipitation qui mènent à des dépôts dans les espaces capillaires. Ainsi il est indiqué que les deux sortes de réactions ont lieu pendant l'hydratation du ciment.

Constance de la Porosité du Gel de Ciment. L'hypothèse d'une porosité constante du gel de ciment indépendante du facteur de l'eau dans le ciment ne paraît pas conforme à la loi d'Abrams: Si la porosité des parties hydratées reste la même, quelle que soit la quantité de matière nonhydratée distribuée dans le gel, la résistance devrait rester au même niveau ou du moins très proche quand nous diminuons le e/c de 0.4 au rapport le plus bas possible. Ceci cependant, et nous le savons tous, n'est pas le cas.

Zusammenfassung

Der Autor beschäftigte sich mit einigen Problemen der Zementhydratation, die auch von anderen Forschern, die in diesem Symposium berichtet haben, untersucht worden sind.

"Dormant Period." Man kann aus einigen Beobachtungen schließen, daß nach dem Mischen des Zements mit Wasser eine Latenzzeit vorhanden ist, aber der Autor glaubt unter Bezugnahme seiner eigenen Arbeiten und die Ergebnisse anderer Forscher, daß Zementpasten doch sofort nach dem Anmachen zu härten beginnen. Dieses Härten kann in Fällen, in welchen sich die thixotropischen Eigenschaften oder das "Gedächtnis" der Mischung bemerkbar machen, häufig nicht durch Messungen veranschaulicht werden.

Wird die Hydratation durch ein Auflösen und Ausfallen, oder durch eine topochemische Reaktion hervorgebracht? Der Autor zeigte einige Elektronmikrographien, die er durch Kohlehüllenbilder des hydratisierenden C_3S erhielt, aus denen ersichtlich ist, daß Hydratationsreaktionen an der Oberfläche von Auflösungen und Ausfällungen die zu Ablagerungen im Kapillarraum führen, begleitet sind. Das heißt also, daß beide Reaktionsarten treten während der Zementhydratation auf.

Die Unveränderlichkeit der Porosität des Zementgels. Man hat angenommen, daß die Porosität eines Zementgels konstant ist und nicht vom Wasser-Zementfaktor abhängt; aber das scheint im Widerspruch zum Gesetz von Abrams zu sein. Wenn man nämlich annimmt, daß die Porosität der hydratisierten Anteile sich nicht ändert, ganz egal der Menge des unhydratisierten Materials das in dem Gel verteilt ist, dann sollte auch die Festigkeit unverändert bleiben, oder doch wenigstens ungefähr so, wenn das Verhältnis Wasser / Zement von 0,4 bis zum kleinstmöglichsten Wert erniedrigt wird. Aber, wie es ganz allgemein bekannt ist, das ist garnicht der Fall.

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* Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from Verein der Österreichischen Zementfabrikanten, Vienna, Austria.

Introduction

Although the papers on the hydration of cement as presented at this Symposium demonstrate in an impressive way the progress in the past decade of our knowledge of the behavior of cement, there still are many questions open to discussion which will have to be answered before we can say that we really understand cement.

Among these the writer wants to deal with the following items:

The "dormant period".

Solution-precipitation vs. solid-state hydration.

The constancy of cement gel porosity.

The "Dormant Period"

Discussing "Early Hydration Reactions," K. T. Greene [1][1] points out the conflicting facts that though the bleeding rate of cement pastes has been found to be remarkably constant for a considerable time, thus indicating a "dormant period" in the process of hydration, results of mechanical tests have been reported which seem to point to the contrary. These results indicating progressive stiffening of the pastes have, however, in their turn been contradicted by others showing that the paste does not change its physical characteristics to an appreciable degree for the first hour or so after mixing.

The writer's own experiments are in accordance with those of Dorsch [2], Humm [3] and Francardi [4]: Stiffening of cement pastes seems to begin immediately after mixing. Figure 1 shows the equipment used by the writer for his tests.

The cement paste is put on a balance in a Vicat-ring. A needle (3 mm in diameter) is then driven into the paste at a constant speed (10 cm/min) by means of a motor. The stiffer the mix, the more the balance will be deflected so that the resistance to the penetration of the needle can be read directly from the scale. Figure 2 shows a few test results obtained with two different cements. The tests started immediately after mixing, placing, and de-airing the paste, i.e., 7 min after the addition of water to the cement.

This kind of test is rather sensitive and shows among other things the surprising "memory" of pastes of normal consistency The penetration of the needle even into a fresh paste will cause a displacement of solid matter which seems to a considerable degree to be irreversible. Even after a long lapse of time the repenetrating needle does not find appreciable resistance.

Keil [5] and Kozlowski [6] as well as Greene [1] himself did not in their experiments find significant thickening up to 2 hr or so. But as Greene points out, his pastes were continuously agitated, while Keil agitated his prior to the consistency measurements. Kozlowski, while not actually agitating his sample, used a single paste specimen for measuring consistency at regular intervals with a penetration rod.

This writer believes that the stiffening of cement pastes starts immediately after mixing. This phenomenon however can be concealed in tests where the thixotropic properties or the "memory" of the paste can play their part.

It is therefore felt that the "constant bleeding rate" must find another explanation than that of a "dormant period"

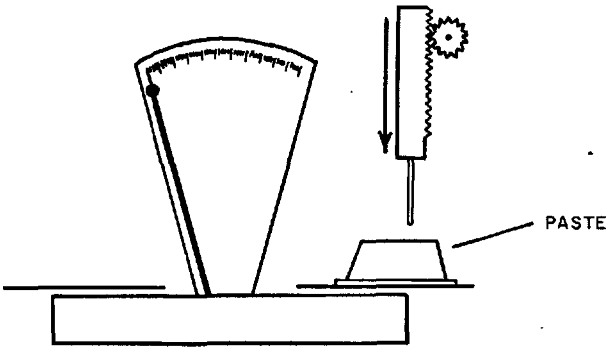

Figure 1. *Device for measuring the stiffening of cement paste at early ages.*

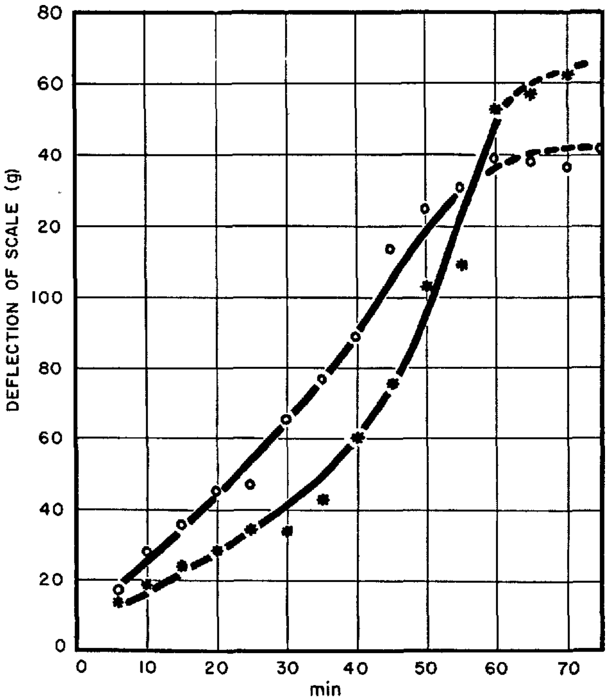

Figure 2. *Resistance to penetration of two portland-cement pastes of standard consistency at early ages.*

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[1] Figures in brackets indicate the literature references at the end of this paper.

Does Hydration Proceed by Solution and Precipitation or by Topochemical Reaction?

The accompanying electronmicrographs [2]—though published previously by the writer [7]—are presented here because they seem to show that topochemical reactions do not play an important part in cement hydration. The cement grains in figure 4, from 6 to 9 μ in diameter, have been obtained by sedimentation of a laboratory-made "alite" cement of the following composition: C_3S, 90 percent; C_2S, 1 percent; C_3A, 2.7 percent; C_4AF, 1.3 percent; free CaO, 1.4 percent. There was no need to add any gypsum as the cement was slow setting.

A paste corresponding to a w/c ratio of 0.6 was prepared with this cement and spread thinly on a microscope slide. The well-wetted grains then could be imagined standing in a "foot bath" as sketched in figure 3. When, immediately after the spreading of the paste, the slide was put in a desiccator over $CaCl_2$ it dried very quickly and cannot have been in contact with evaporable water for more than 5 min. This state of hydration is shown in figure 4. Though the reaction time was short, the film of evaporated water left a residue of well-developed hexagonal crystals, and on the grain surface left products of a topochemical reaction. If the paste is preserved in moist air for 1 hr, the picture—figure 5—looks different. The grains are covered by a growth of rolled and wrinkled foils, as can more distinctly be seen in the higher magnification in figure 6. But these foils can also be found in what might be called the capillary space. This deposit in the capillary space is much more strongly pronounced after 24 hr of moist curing (fig. 7). It seems difficult to imagine that such a deposit could have been produced in the capillary space if hydration had proceeded as a solid-liquid reaction. Figure 8, finally, shows the state of things after 28 days of moist curing. The darker and more uniform parts correspond to the original cement grains. Seen through a stereoscope they sharply protrude out of what was formerly the capillary space.

These pictures may not yet give an unequivocal answer to the questions at hand. But it is believed that we have here a technique which might be helpful in the future in solving this and other problems of cement hydration. (Notice for instance the remarkable change in the aspect of the cement grains during the first hour; surely this does not look like a "dormant period".) This writer is fully aware that identification of paste constituents must for the time being remain one of the main objectives of electron microscopy in this field of research. Grudemo's excellent paper on the "Microstructure of Hardened Paste" presented at this Symposium [8] is an outstanding example of that kind of work. Contrary to Grudemo's view, however, this writer believes that replica methods when handled with skill and experience can resolve the finest details of the paste surface.[3] This fact, together with the enormous depth of focus of the electron microscope which allows the most revealing stereoscopic observations, seem to be advantages of the replica technique well worth while following up in the study of cement hydration.

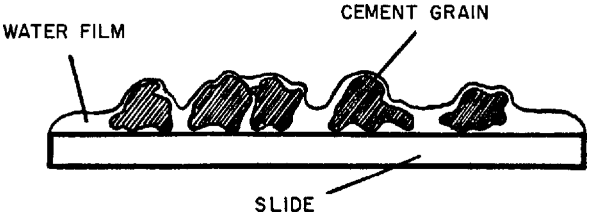

FIGURE 3. *Schematic drawing of portland-cement paste on microscope slide.*

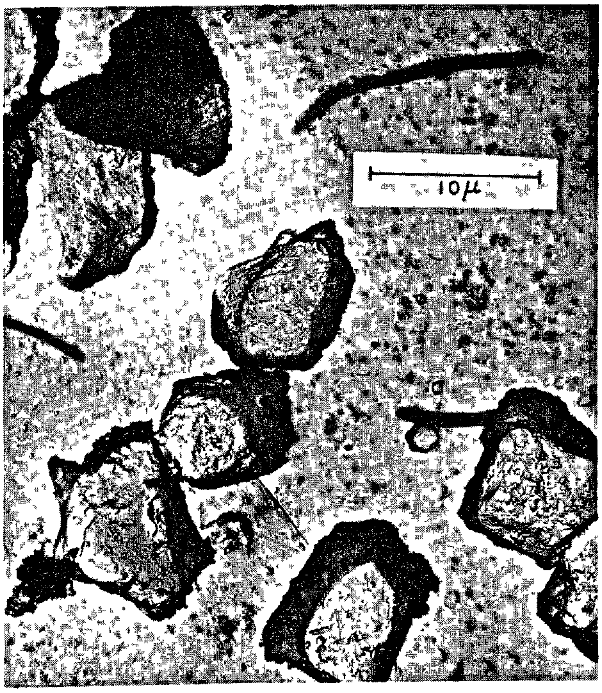

FIGURE 4. *Cement paste hydrated 5 min.*

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[2] The electronmicrographs have been obtained by use of carbon replicas in collaboration with F. Grasenick, director of the Electronmicroscopic Institute of the Technical University, Graz, Austria.

[3] See Grasenick's stereophotos of carbon replicas of periclase crystals, Zement u. Beton, No. 16 (July 1959), page 18.

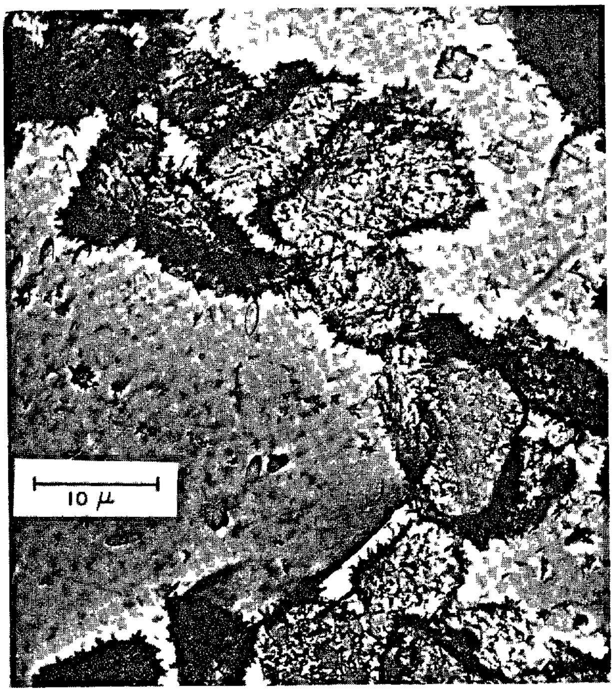

Figure 5. *Cement paste hydrated 1 hr.*

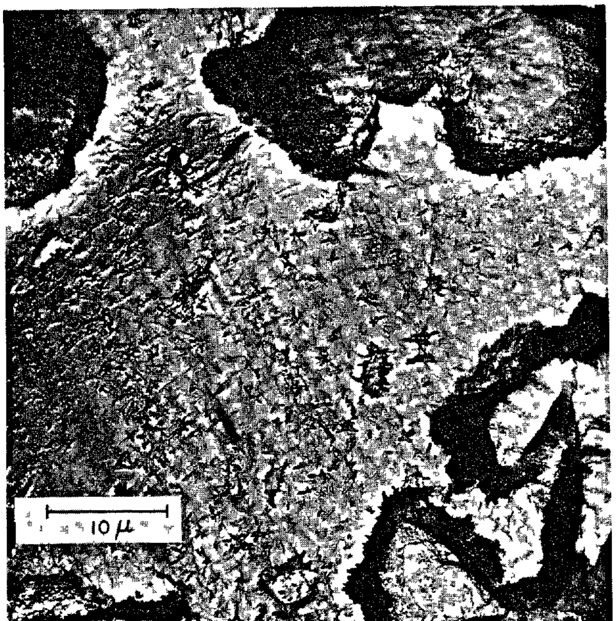

Figure 6. *Cement paste hydrated 24 hr.*

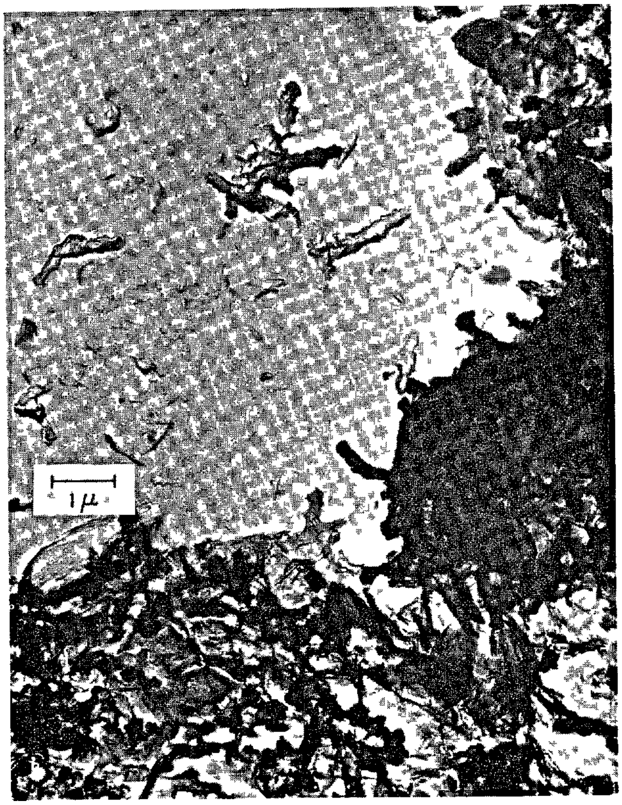

Figure 7. *Cement paste hydrated 24 hr (high magnification).*

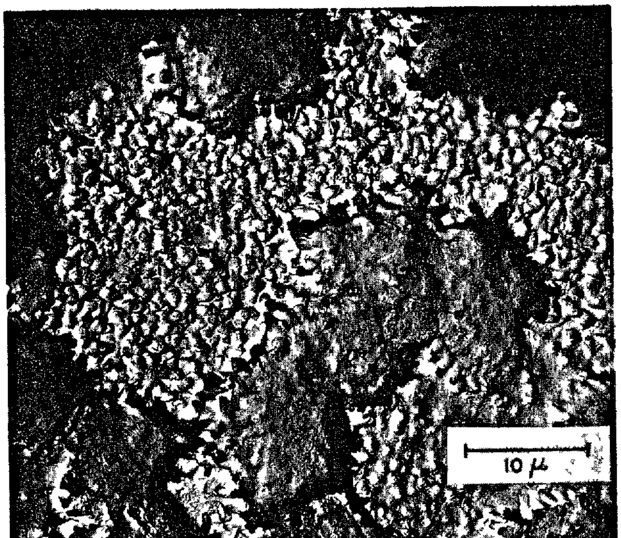

Figure 8. *Cement paste hydrated 28 days.*

In his paper "On the Physical Properties of Cement Paste" presented at this Symposium [9], T. C. Powers states that "when the cement content is at the limit for complete hydration the porosity of a completely hydrated specimen is at a minimum. At any higher cement content the porosity of the paste is lower only because of the presence of unhydrated cement; the porosity of the hydrated part remains the same." This means, inter alia, that the water in the gel pores, though evaporable and able to migrate, is unable to react with unhydrated cement. Powers, while raising the question whether stoppage of hydration is virtual or real, discusses a few of the present writer's experiments, which attempted to force the hydration of cement samples with water added in quantities not sufficient for the full hydration of the cement. This forced hydration was attempted through continued ball-milling of the mixture. By this procedure, however, the evaporable water could not be reduced below a certain level corresponding to a gel porosity of ~21 percent. Thus Powers' finding seemed to be confirmed qualitatively, but not quantitatively, as the minimum porosity found in the Portland Cement Association laboratories did not fall below 28 percent.

In trying to explain this divergence Powers reasons that self-desiccation as it happens in the ball mill must lead to a lesser amount of evaporable water than is present in a corresponding water-cured sample. While in the sealed container some capillary space will become empty through self-desiccation, that space will be filled with additional water in the case of the water-cured specimen. But in the opinion of the present writer this additional water will not remain capillary water but will react in its turn with unhydrated cement as long as capillary space is available. Thus it seems as if we could expect the same w_n/w_e values in both cases.

Even if this reasoning should be correct, the ball-mill experiment is of course not conclusive with respect to the validity of Powers' theory of constant gel porosity.

There is another point, however, which seems incompatible with the conception of a constant gel porosity. If the porosity of the hydrated parts remains the same, whatever the amount of unhydrated material distributed in the gel, then the strength should remain at the same level or at least near it when we lower the w/c ratio from 0.4 to the lowest possible ratio. But we know that the strength curve proceeds without a break as a straight line towards fabulous figures in accordance with Abram's law.

The writer is aware that his discussion of certain unsolved problems has not contributed much to their solution. He hopes nevertheless to have drawn the attention to a few points where further work seems needed.

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Paper V–S4. The Rheology of Fresh Portland Cement Pastes*

Moshe Ish-Shalom and S. A. Greenberg

Synopsis

The flow behaviors of fresh pastes were examined in order to obtain information on these properties and to try to correlate the properties with the physicochemical nature of the pastes. Rheological measurements were performed with a coaxial cylinder viscometer. With this instrument rpm-torque plots were determined as a function of several variables. Plots were made with increasing rpm (upcurve) and decreasing rpm (downcurve) as a function of torque. From these plots parameters related to yield values, *f*, and plastic viscosities, *U*, were evaluated. Among the variables studied were: (1) chemical compositions of cements, (2) mixing conditions, (3) surface areas of cements, and (4) temperature of hydration.

The data showed that three types of rheological behavior are frequently found in pastes: (1) antithixotropic, (2) reversible, and (3) thixotropic. Antithixotropic behavior was detected in pastes which had been vigorously agitated and were allowed to hydrate to a small extent. Antithixotropic behavior is characterized by a flow curve (rpm-torque) in which the descending portion (decreasing rpm) is to the *right* of the upcurve (increasing rpm). The reversible rpm-torque flow curves were exhibited by pastes which were allowed to hydrate for about 45 min. The predominant kind of flow curve was thixotropic. The pastes are essentially thixotropic in flow behavior, with the other types mainly deviations from this behavior. Thixotropy is characterized by a flow curve in which the descending branch is to the *left* of the upcurve.

It is proposed that thixotropy is characteristic of the hydrogel formed by hydration of the calcium silicates in cement. These gels are believed to be constructed of particles, which are plates or fibers, in contact only at certain points. This arrangement of flocculated particles leads to a loose three-dimensional network of solids in a liquid medium. Setting would occur when sufficient gel had formed to increase the yield values and viscosities of the pastes to a characteristic degree. Setting would also be aided by the removal of water by evaporation and by chemical reaction.

Tricalcium aluminates were found to increase the "strength" or consistency of the pastes. The rates of increase of the rheological coefficients were augmented by an increase in the temperature of hydration, alkai content and amount of initial mixing of the cement and water.

Résumé

Les comportements d'écoulement des pâtes fraîches ont été examinés dans le but d'obtenir des renseignements sur les propriétés en question et d'essayer de mettre celles-ci en corrélation avec la nature physico-chimique des pâtes. Des mesures rhéologiques furent opérées à l'aide d'un viscomètre à cylindre coaxial. Avec cet instrument des diagrammes de rotation-moment de torsion furent déterminés en fonction de différentes variables. Les diagrammes furent établis avec r.p.m. croissante (courbe ascendante) et r.p.m. décroissante (courbe descendante) en fonction de la moment de torsion. D'après ces diagrammes, des paramètres se rapportant aux valeurs de la limite d'écoulement *f* et aux viscosités plastiques *U* furent évalués. Parmi les variables étudiées se trouvaient: (1) les compositions chimiques des ciments (2) les conditions de mélange (3) les surfaces spécifiques des ciments et (4) la température d'hydratation.

Les données indiquaient que l'on trouve fréquement trois types de comportement rhéologique dans les pâtes: (1) antithixotropique (2) réversible et (3) thixotropique. Le comportement antithixotropique fut détecté dans les pâtes qui avaient été vigoureusement agitées et qui avaient pu s'hydrater quelque peu. Le comportement antithixotropique est caractérisé par une courbe d'écoulement (r.p.m.-moment de torsion) dans laquelle la portion descendante (r.p.m. décroissante) est á la *droite* de la courbe ascendante (r.p.m. croissante) Les courbes d'écoulement réversibles r.p.m.-moment de torsion étaient présentées par des pâtes qui avaient pu s'hydrater pendant 45 minutes environ. Le type de courbe d'écoulement prédominant était thixotropique. Les pâtes sont essentiellement thixotropiques dans le comportement d'écoulement avec les autres types qui sont surtout des déviations de ce comportement. La thixotropie est caractérisée par une courbe d'écoulement dans laquelle la branche descendante est à la *gauche* de la courbe ascendante.

Il est suggéré que la thixotropie est caractéristique de l'hydrogel formé par l'hydratation des silicates de calcium dans le ciment. On pense que ces gels sont formés de particules, qui sont des plaques ou des fibres, en contact seulement en certains points. Cet arrangement de particules floculées mène à un réseau lâche à trois dimensions de solides dans un milieu liquide. La prise se produit quand suffisamment de gel s'est formé pour augmenter les valeurs de la limite d'écoulement et les viscosités des pâtes à un degré caractéristique. La prise est également favorisée par l'élimination de l'eau par évaporation et par réaction chimique.

Les tricalciumaluminates augmentent la "résistance" ou consistance des pâtes. Les vitesses d'accroissement des coefficients rhéologiques étaient augmentées par l'accroissement de la température d'hydratation, la teneur en alcali et la quantité de mélange initial du ciment et de l'eau.

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Zusammenfassung

Das Fließverhalten frischer Pasten wurde mit dem Zwecke, mehr Kenntnisse über diese Eigenschaften zu erhalten, und auch für die Herstellung eines Zusammenhanges solcher Eigenschaften mit der physikochemischen Natur der Pasten, untersucht. Rheologische Messungen wurden mit Hilfe eines coaxialen Zylinderviskositätsmesser unternomnen. Mit einem solchen Instrument wurde das Drehmoment für verschiedene Umdrehungsgeschwindigkeiten als Funktion mehrerer Veründerlicher bestimmt. Kurven wurden für steigende Umdrehungsgeschwindigkeiten (die ansteigende Kurve) und für fallende Umdrehungsgeschwindigkeiten (die fallende Kurve), als Funktion des Drehmoments gezeichnet. Aus solchen Kurven wurden die Parameter, die zur *Fließgrenze f* und der *plastischen* Viskosität *U* gehören, ausgewertet. Zu den Veränderlichen, die untersucht wurden, gehörten: (1) die chemische Zusammensetzung des Zements, (2) die Mischbedingungen, (3) die Oberflächengrößen des Zements und (4) die Hydratationstemperatur.

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Die Data zeigten, daß drei typische Fließverhalten häufig in Pasten gefunden werden: das (1) antithixotropische, das (2) umkehrbare und das (3) thixotropische Verhalten. Antithixotropisches Verhalten wurde in Pasten, die heftig gerührt worden waren und ein wenig Wasser binden konnten, beobachtet. Dieses Verhalten ist durch eine Fließkurve (Umdrehungsgeschwindigkeit-Drehmoment), bei welcher der fallende Ast (abnehmende Umdrehungsgeschwindigkeit) auf der *rechten* Seite der ansteigenden Kurve (zunehmende Umdrehungsgeschwindigkeit) liegt, ausgezeichnet. Die umkehrbaren Umdrehungsgeschwindigkeit-Drehmomentkurven wurden bei Pasten, die für ungefähr 45 Minuten hydratisieren konnten, gefunden. Die meisten Kurven gehörten der thixotropischen Art an, sodaß die meisten Pasten ein thixotropisches Fließbenehmen zeigen, und die anderen als Ausnahme von der Regel betrachtet werden können. Thixotropie kann durch eine Fließkurve, bei welcher der fallende Ast auf der *linken* Seite der steigenden Kurve liegt, erkannt werden.

Es wird vorgeschlagen, die Thixotropie als das Kennzeichen des Hydrogels, welches durch die Hydratation des Kalziumsilikats im Zement entsteht, anzusehen. Es wird angenommen, daß diese Gele aus Teilchen gebildet werden, welche Platten oder Fasern sind, und die sich nur an einigen Punkten berühren. Dieser Aufbau aus ausgeflockten Teilchen ergibt ein loses, dreidimensionales Gitter, welches aus festen Körpern, die von einer Flüssigkeit durchdrungen werden, besteht. Erstarrung wird dann einsetzen, wenn sich genügend Gel für die Erhöhung der Fließgrenze und der Viskositäten der Pasten in dem charakteristischen Grad gebildet hat. Eine Verdampfung des Wassers und chemische Reaktionen liefern zu dieser Erstarrung ihren Beitrag.

Es wurde gefunden, daß Trikalziumaluminate die "Festigkeit" oder die Konsistenz der Pasten erhöhen. Die Zuwachsgeschwindigkeiten der Fließkoeffizienten wurden durch eine Erhöhung der Hydratationstemperatur, des Alkaligehalts und des Betrags des ersten Mischens des Zementes mit Wasser vergrößert.

Introduction

Although a knowledge of the flow properties of portland cement pastes is essential to the proper use of concrete and to an understanding of its physicochemical nature, relatively little quantitative information on this subject has been reported. The present study was initiated in order to provide such information. In this paper there is described an investigation of the properties of these pastes in the first few hours of hydration.

Portland cement pastes are made by mixing water and cement in various ratios. The usual ratios by weight of water to cement, w/c, are between 0.3 and 0.7.

Cement is a material which is made up primarily of the following crystalline components sintered together into particles [1][1]: tricalcium silicate ($3CaO{\cdot}SiO_2$), dicalcium silicate ($2CaO{\cdot}SiO_2$), tricalcium aluminate ($3CaO{\cdot}Al_2O_3$), and tetracalcium aluminoferrite ($4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$). To this mixture, gypsum ($CaSO_4{\cdot}2H_2O$) is added.

Pastes are defined by Alexander and Johnson [2] according to the concentration by volume of solid particles in a liquid and by the flow properties. Usually the concentration in pastes is greater than 10 percent by volume. The systems exhibit elastic behavior and are plastic insofar as they show yield values. It is necessary to treat pastes as two-phase systems which are frequently thermodynamically unstable. Pastes are not discontinuously different from gels, since both states are characterized by intimate contact of the solid particles. Perhaps it is possible to distinguish between them by the particle size of the suspended particles. Gels are by definition made up of particles with colloidal dimensions and pastes normally contain particles in the micron range.

Engineers and workmen who make concrete structures are concerned with the flow properties of fresh concrete. Fresh concrete must flow sufficiently for proper placement.

In addition to these practical uses to which a knowledge of the rheology of the system may be put, there are many other matters that the flow properties can help to explain or control. The setting and hardening of concrete are caused by physical and chemical processes which produce a new material. Set concrete no more resembles the cement from which it was made than cement resembles limestone and clay from which it was made. If we are to understand what is meant by setting, which is manifested by a change in the flow properties of the material, then we must study

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[1] Figures in brackets indicate the literature references at the end of this paper.

the flow properties by the best scientific methods. It is because of the ease with which fresh concrete may be placed, and because of the mechanical properties of set concrete, that this material is so useful. The rates at which setting and hardening of concrete proceed affect seriously our ability to handle the material, and they affect the strength of the final product. To control the setting process, it will be necessary to understand: (1) the fundamental chemical processes proceeding in cement pastes, (2) the nature of the colloidal products formed, and (3) the forces exerted between hydrate particles.

The chemical reactions which proceed in concrete by reactions of cement and water lead to many hydrated products. The nature of these products is still being investigated. Perhaps the most important components of cement are $3CaO{\cdot}SiO_2$ and β-$2CaO{\cdot}SiO_2$, which make up more than 70 percent of the material. When $3CaO{\cdot}SiO_2$ reacts with water, a hydrated calcium silicate and calcium hydroxide are formed. Similar hydrates are formed from β-$2CaO{\cdot}SiO_2$ [3]. The other components of cement react to form a variety of products [1].

The nature of the set hydrated cement has been examined for many years by Powers and his colleagues [4–6]. According to the results of their research it appears that on hydration of portland cement the surface of the solids increases from about 0.2 m^2/g to over 200 m^2/g. This shows that on hydration of micron-size portland cement, a colloidal material is formed. The colloidal product exhibits the properties of a gel. Measurements reported by Powers [6] demonstrate that the gel particles are separated by about 20 to 40 A. The gel would naturally consist mainly of hydrated calcium silicates since over 70 percent of the cement is composed of tri- and dicalcium silicates. Very little has been reported about the contributions of the other components to the gel structure.

A great deal of work has been performed to investigate the rheological problems mentioned here by methods which are semiquantitative [1]. Only a little attention will be given to this literature although the information provided by this research has materially benefited the field of cement technology [7]. In the present report only research based on modern theories of rheology and of colloid chemistry will be mentioned.

Reiner [8] has discussed the rheology of concrete. Apparently relatively few investigators were concerned with fresh pastes. Powers and Wiler [4] in an early paper outlined very well the problems involved in such a study, and proceeded to show the thixotropic nature of concrete at some stages of hydration.

Later Forslind [9] and L'Hermite [10] initiated investigations. More recently Dellyes [11], Papadakis [12], and Tattersall [13, 14] conducted research on pastes in coaxial cylinder viscometers essentially according to the methods outlined by Green [15].

In Green's method a coaxial cylinder rotational viscometer with variable speeds is employed. If a material is a Newtonian, a straight line relationship will be obtained for the plot of speed of rotation, Ω, against the torque, T. For Newtonians, the intercept on the torque axis will be at zero; however, for Bingham bodies and plastic materials the curve will intersect the torque axis at a value proportional to the yield stress, which is the minimum stress necessary to cause flow. The plastic viscosity, U, of the material in this procedure is inversely proportional to the slope of the linear portion of the rpm-torque plots.

The Green method for measurement calls for increasing the speed of rotation and then decreasing it in a prescribed manner. The corresponding torques measured in this way form an *upcurve* and a *downcurve* in a plot of speed of rotation against torque. If the material is thixotropic, the upcurve does not coincide with the downcurve; thus a hysteresis loop is formed. In this case the upcurve is concave towards the speed of rotation axis and the downcurve is in many cases a straight line, to the *left* of the upcurve. For standard conditions of operation, the area of the hysteresis loop, A, is related to the amount of breakdown of the thixotropic structure, and two successive cycles of this kind would define, according to Green, a quantitative parameter—"the coefficient of thixotropic breakdown".

For convenience in characterizing materials which are not Newtonians, but for which the downcurve portion of the flow curve is approximately linear, numerical values of yield stresses, f, and plastic viscosities, U, are evaluated from the linear portion of the rpm-torque curve using the Reiner-Riwlin equations [16, 17]. Strictly speaking, however, the lower portions of these curves do not conform to Bingham bodies with the calculated parameters.

Dellyes [11] and later Papadakis [12] did an excellent job of characterizing pastes of cements according to the rheological system of Green. Dellyes reported finding both thixotropy and a behavior which he defines as "antithixotropy" in some pastes. In antithixotropy, the descending curve falls to the *right* of the ascending curve—the opposite of the result for thixotropy. The nature of antithixotropy is unusual but may resemble the general behavior of concentrated pastes [18–20]. Many inorganic pastes show an increased resistance to flow with increased shearing stress. To some of these pastes the term "dilatant" is applied.

These authors reported the presence of the various types of rheological behavior present in fresh pastes. In addition, they demonstrated the influence of water-cement ratios on the rheological coefficients. Tattersall attempted to develop a quantitative picture for thixotropic breakdown.

Much work remains to be done to incorporate the knowledge of the rheological behavior of this system into the pattern now being developed for the physics and chemistry of the changes which occur during the hydration of cement. Also, much research is necessary before it will be possible to incorporate the empirical findings into the theories of Freundlich, Kruyt [21], and Verwey and Overbeek [22] for the behavior of gels.

Forslind [9] has developed a theory which is contrary to the current approach to gels, which explains the rheological properties of hydrogels on the basis of the water structure. According to this author, water behaves as if a structure existed in the water in contact with high-surface-area silicates. This structure, he believes, causes the observed properties. However, many other scientists [22] feel that it is the interaction of the solid particles which is the controlling factor. In the present paper the latter approach was adopted.

A number of difficulties are encountered in rheological studies on portland cement gels and pastes which limit the methods and the range of variables that can be examined.

(1) The rheological properties of the cement pastes are time dependent, antithixotropic, and thixotropic, and as such present the usual difficulties [17]. The structures of these materials change as they are disturbed. Therefore, in order to completely characterize the materials, it would be necessary to measure the flow properties at each stage of the structural transformations.

(2) The first item is even more serious, if the cement paste is hydrating during the study.

(3) At the beginning, rather large particles of cement are present. Therefore, sedimentation becomes a problem at high water-cement ratios.

(4) The large particle size of cement also prevents the use of cylinders with very small clearances in the coaxial cylinder viscometer and also the use of cone-plate viscometers.

Experimental

Materials

Pastes of a variety of commercially prepared portland cements were examined in order to observe the rheological behaviors and to try to correlate the differences in flow behavior with the variations in chemical composition. In table 1 the computed compound compositions and surface areas are listed. These cements were specially prepared and have been examined by many techniques in this laboratory.

The sample of alite was obtained from Dr. D. L. Kantro and Mr. C. H. Weise of this laboratory and the procedure for the preparation is described elsewhere [24]. This sample contains 0.75 percent free CaO, 0.88 percent Al_2O_3, and exhibits a surface area of 1,800 cm²/g. The surface areas were determined by the Wagner turbidimetric method [25].

Preparation of Pastes

Standard procedures for the mixing of cement and water have been developed in order to obtain reproducible results. Some of the problems involved have been discussed by Powers [26].

In a typical procedure, 750 g of paste were mixed in a 1–3–2 min cycle of mix-rest-mix in a Waring Blendor under vacuum. Samples were mixed under vacuum in order to avoid the entrainment of air. The effect of air on the flow properties of pastes has been studied [27]. The cement powder was added gradually to the water with only a small amount of stirring. This step was followed by a vigorous mixing period. A normal procedure involved: (1) adding the cements to water with mild agitation, (2) 1 min of vigorous agitation and (3) 3 min of rest, followed by (4) 2 min of vigorous agitation. The effects of variations in this procedure will be described.

The temperature of the paste after the mixing procedure will be referred to as the final temperature; it normally was 25±2 °C. In some special experiments this final temperature was varied by adjusting the initial temperature of the water, or by the addition of ice.

The rheological measurements were made usually at 25 °C (with water jacket) after various periods of hydration t_h. Usually the samples were hydrated at a room temperature of approxi-

TABLE 1. *The computed compound compositions*

Composition, percent	A 15366 (*C* 2.2.7) Type I normal (clinker)	B 15367 (*C* 16.2.2) no gypsum	C 15698 (*C* 12.2.3) Type I normal	D 15669 (*C* 14.2.2) Type IV low heat	E 15622 A (*C* 13.2.3) Type II moderate heat	F 19648 (*C* 15.2.2) zero C_3A
C_3S	44.8	45.4	45.3	33.0	49.2	66.0
C_2S	26.9	28.5	28.6	54.2	28.5	14.7
C_3S/C_2S	1.67	1.59	1.58	0.61	1.73	4.5
C_4AF	6.7	6.8	7.6	5.8	12.8	10.15 (3.16% C_2F)
CaA	13.6	14.3	9.8	2.3	4.4	0.0
$CaSO_4$	3.3	0.7	3.0	3.1	2.7	4.30
MgO	2.5	2.63	3.4	1.72	1.44	0.60
Free CaO	0.93	0.98	0.08	0.15	0.49	0.58
Total alkali (Na_2O+K_2O)	0.33	0.33	1.57	0.27	0.22	0.12
Surface area, cm²/g (Wagner turbidimeter)	2,260	1,500	2,250	2,280	2,200	2,640

mately 25 °C. However, in a series of experiments the pastes were allowed to stand at temperatures between 20 and 35 °C in a constant temperature bath to examine the effects of the temperature of hydration on the rates of changes of rheological properties.

Apparatus

Viscometer—General

Various rotational viscometers have been used for the investigation of the rheology of portland cement pastes, but most of them resemble closely the viscometer developed by Green [15]. In this study the Haake Rotovisco instrument designed by Heinz was employed [23]. The instrument was calibrated with oils of known viscosities.

With a concentric cylinder viscometer, the angular velocity of the bob, Ω, in rpm, and the torque, T, in dyne-cm, are measured. In the Rotovisco instrument, the bob of radius r_0 and length h may be rotated at various angular velocities, Ω, in a sample contained in a stationary cup of radius R_0. A substance of viscosity η is inserted in the annular space between the bob and cup. Because of the viscosity of the material, a torque, T, is required to maintain each velocity.

The torque developed causes a spring attached to the bob to wind up. The displacement of the spring is converted by an electrical device to a reading on a meter. The combination of motors and gears makes it possible to obtain the following bob speeds: 3, 6, 9, 18, 27, 54, 81, 162, 243, and 486 rpm at a line frequency of 50 c/s. At the line frequency of 60 c/s used in the present study the speeds are increased by a factor of 6/5.

In the Rotovisco apparatus the cup is 2.102 cm in radius, and the bob used has a radius of 1.999 cm. The length of the bob is 6.0 cm. To reduce the end effect at the bottom of the bob, a recess is provided to entrap an air cushion. A water jacket fits over the cup, and water at a constant temperature is passed through it. The temperature of the water in the jacket is referred to as the temperature of the measurement.

The equation for the flow curve of a plastic Bingham body is

$$(\tau - f) = U\dot{\gamma} \tag{1}$$

where τ is the shearing stress, $\dot{\gamma}$ is the rate of shear, f is the yield value or yield stress, and U is the plastic viscosity.

Reiner and Riwlin [16] derived the relationship for the flow of a Bingham body in a rotational viscometer.

$$\Omega = \frac{T}{4\pi U h}\left(\frac{1}{r_0^2} - \frac{1}{R_0^2}\right) - \frac{f}{U}\ln\frac{R_0}{r_0} \tag{2}$$

when the total torque is sufficient to exert a shearing stress that exceeds f at the inner surface of the cup of radius R_0.

Usually the velocity of the bob, in revolutions per minute (rpm), is measured versus the deflection S of the meter and a plot of these quantities forms the flow curve. From the slopes and intercepts and the calibration constants of the instrument, the values of f, U, and A are calculated.

Results

Results of a Typical Fresh Cement Paste and Definition of Terms

Figure 1 is a schematic plot of the results on a Type I cement (A), and will be used to point out their characteristic features. Table 2 summarizes a set of actual data. Curves A, B, and C are plots of rpm against torque. They were obtained for identical samples at successively longer times of hydration. In each one of these sections, results of two successive cycles are drawn in: (1) denoting the first cycle and (2) the second. The second

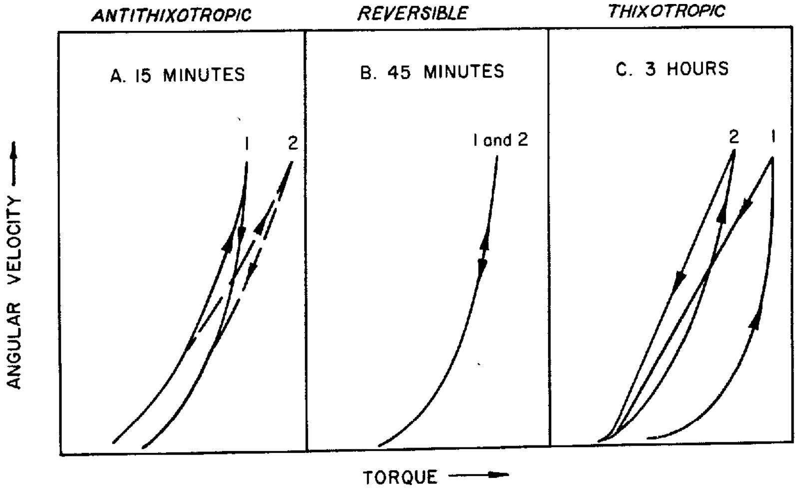

FIGURE 1. *Three types of flow behavior for fresh portland cement pastes.*
The times given are for the periods of hydration. The numbers on the curves show the order in which the curves were made.

cycle represents a flow curve obtained immediately after the first cycle is completed.

In curve A, the downcurve in each cycle is to the right of the upcurve, and the second cycle is to the *right* of the first one, indicating an increase in viscosity. Exactly the reverse holds in C. However, both are similar in that the area of the hysteresis loop, A, is smaller in the second cycle than in the first one. The curve shown in B is *reversible:* i.e., the upcurves and downcurves in both the first and second cycle coincide.

For convenience in communication, these characteristics of rheological behavior are assigned names on a *strictly operational* basis. The curves shown in C are examples of thixotropy [15].

The fact that successive cycles in C decrease the area of the loop and move it to the left tends to show that, at best, the process of spontaneous buildup of a thixotropic structure is very slow. Some comparative measure of the *amount* or *extent* of thixotropic breakdown can be derived from the area of the hysteresis loop, A, obtained under specific conditions.

TABLE 2. *Results of an experiment with a typical type I portland cement paste*

(Cement A (Sample *C* 2.2.10); w/c=0.5; final temperature 24 °C; hydrated in a water bath at 25.0±0.2 °C)

Time of hydration	Temp. of sample	First cycle			Second cycle	
		Yield Value f	Plastic Viscosity U	Area of hysteresis loop A	Yield value f	Plastic viscosity U
	°C	*dynes/cm²*	*cp*	*arbitrary units*	*dynes/cm²*	*cp*
15 min	25.0	445	24	−25	440	26
45 min	25.4	560	25	−12	560	25
2 hr	25.8	990	54	600	900	51
3 hr	26.0	1,340	93	>730	1,170	68

The behavior shown in A is less common. Dellyes [11] referred to this behavior as "antithixotropy" since it shows a contrasting behavior to "thixotropy". A measure of its extent can also be given by the area of the hysteresis loop. In order to unify the description, the areas of the hysteresis loops are *defined* as *negative* if the downcurve is to the *right* of the upcurve, and are *defined* as *positive* if the downcurve is to the *left* of the upcurve. It is thus possible to describe the extent of antithixotropy and thixotropy in terms of the areas of the loops.

Both antithixotropy and thixotropy have been observed in quite a number of cases in our work, but the reversible case in between was found only occasionally. Its presence between the two extremes might, however, be expected.

It should be pointed out that the use made in this paper of the actual values of A is only as a rough comparative measure of the availability of breakable structure in the system.

Small changes in the conditions of handling the pastes on insertion into the viscometer were found to cause relatively large changes in the loop areas, A, particularly after 3 hr of hydration. At this time the degree of thixotropic behavior was much greater than that at earlier periods. The values of A reported indicate trends very well.

Because of the relatively rapid physicochemical changes proceeding in the pastes, it was initially felt desirable to make the measurements as rapidly as possible. Further investigation demonstrated that the changes occurred at a much slower rate than was initially expected.

In general, the data show that the results are reasonably reproducible if the methods for handling the samples are the same.

The Effect of Cement Concentration

A Type I cement (A, table 1) with a surface area of 2,260 cm²/g was used. The range of water-cement ratios by weight was 0.4 to 0.8. In this series of measurements the whole batch was kept after preparation in a plastic container at room temperature. Samples were drawn from it for rheological measurements at 15 min, 45 min, and 2 hr of hydration. The measurements were made in the Rotovisco without the water jacket.

The results are shown in table 3. The volume percent of solids was calculated assuming the density of the cement to be 3.2 g/cm³, and that of water to be 1.0. The values of the parameters U, f, and A at the same time of hydration may be seen to increase rapidly with increase in concentrations of solids.

TABLE 3. *Rheological parameters of portland cement pastes of various water-cement ratios at different times of hydration*

Designation of sample	w/c	Volume fraction of cement	Final temperature	Time of hydration	First cycle			Second cycle	
					f	U	A	f	U
			°C		*dynes/cm²*	*cp*		*dynes/cm²*	*cp*
C 1.1.2	0.4	0.439	23	15 min	810	39	0	------	----
				40 min	970	52	15	970	48
				2 hr	------	------	Very large	1280	79
C 5.1.1	.45	.410	21	15 min	390	22	18	390	26
				45 min	405	26	22	390	26
				2 hr	810	100	530	820	70
C 2.1.2	.5	.384	16	8 min	250	16	−9	260	17
				30 min	250	16	−10	268	15
				2 hr	340	42	133	340	32
C 4.1.1	.6	.342	20.5	15 min	90	12	−3.2	100	12
C 3.1.2	.7	.307	19.5	15 min	64	8.5	−6	71	8.5
				45 min	52	7.4	0	52	7.4
				2 hr	77	12	29	77	10.3
C 7.2.2	.8	.280	17	15 min	16	5.8	0	16	6.1

Figures 2 and 3 are plots of the plastic viscosity U/U_0 and yield stress f/f_0 in the first cycle against time of hydration. U_0 and f_0 are the values of the plastic viscosity and yield stress after 15 min of hydration. From these figures it may be seen that the *rate of development* of the consistency increases rapidly with increase in the concentration of solids.

The rapid increase in the area of the hysteresis loop, A, at 2 hr hydration time with increase in concentration of solids is evident from the data in table 3.

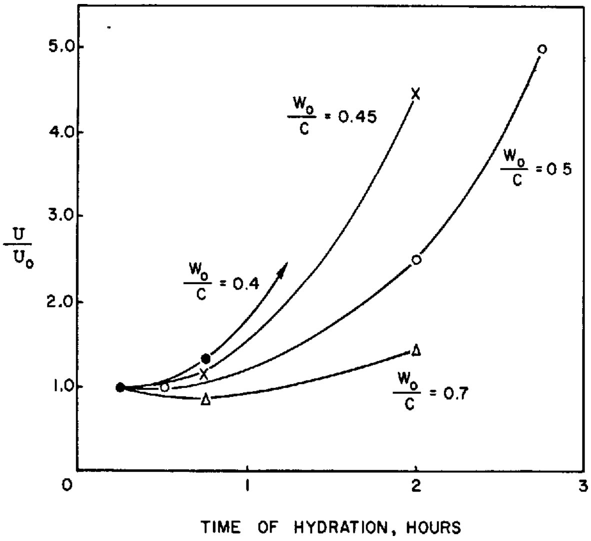

FIGURE 2. *Plot of plastic viscosity against time of hydration for various water-cement ratios.*

U_o is the plastic viscosity of the various samples after 15 min of hydration.

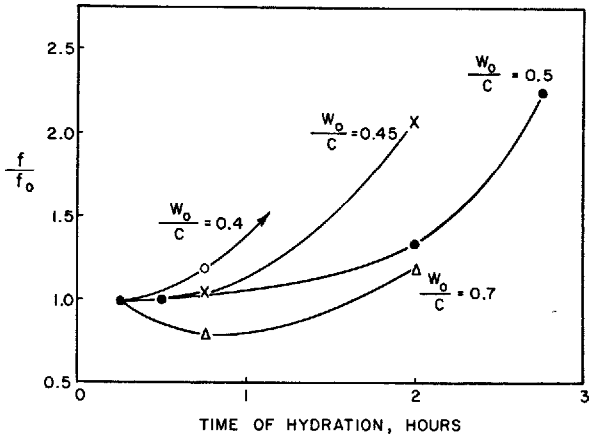

FIGURE 3. *Plot of yield values against time of hydration for various water-cement ratios.*

f_o is the yield value for the various samples after 15 min of hydration.

Effect of the Temperature of Hydration

The development of the rheological properties is presumably related to the chemical reactions proceeding in the pastes. Chemical reactions would be expected to increase in rate with temperature. The relationship between the rate of development of the rheological properties and the rate of the chemical reactions is not known. The details of the chemical reactions at these early stages are not entirely clear either. Nevertheless, it is of interest to examine the development of the rheological properties at various temperatures of hydration. A type I cement, A, was examined. Four preparations were made for hydration at 20, 25, 30, and 35 °C. The temperatures of the samples before measurement are listed in column 4 of table 4, which summarizes the results. It may be noted that the sample temperatures deviated from the temperature of the bath in which they were immersed. These deviations were due to the time it took for the samples, which had a final temperature of 25 °C after mixing, to reach the temperature of the bath and also to the heat released during the chemical reactions.

The results do not apparently exhibit, in general, very large effects on the plastic viscosities, *U*, yield stresses, *f*, and the areas of the loops, *A*. The yield values at 15 min hydration time did not show appreciable differences between 20 and 35 °C hydration temperatures, but after 2 hr of hydration an increase in yield stress of 890 to 1,340 dynes/cm² was noted when the hydration temperature rose from 20 to 35 °C. A similar trend of increases in plastic viscosities may be seen in table 4. A plastic viscosity of 48 cp after 2 hr of hydration at 20 °C may be compared to the 157 cp found after hydration for the same period of time at 35 °C. A similar rate of increase in the extent of thixotropic behavior may be found. The value of *A* after 2 hr of hydration at 35 °C is over 1,150 compared to the 320 measured on a sample hydrated for the same period at 20 °C.

A *small* increase in the rate of development of the rheological coefficients with temperature would be consistent with the theory that after the initial mixing of cement and water the reaction rate is diffusion controlled. Obviously more information on the dependence of rates of the chemical reactions on temperature is necessary before these data can be fully understood.

TABLE 4. *Effect of temperature of hydration*

Designation of sample	Temperature of hydration	Time of hydration	Temp of sample before measurement	*f*	*U*	*A*
	°C	t_h	*°C*	*dynes/cm²*	*cp*	
C 2.2.12	20.0	15 min	23.5	460	24	−19.3
		45 min	20.8	560	23	−28.8
		2 hr	20.8	890	48	320
		3 hr	20.7	1340	101	>666
C 2.2.10	25.0	15 min	25.0	445	24	−24.5
		45 min	25.4	560	25	−11.9
		2 hr	25.8	990	54	600
		3 hr	26 0	1340	93	>730
C 2.2.13	30.0	15 min	28.8	500	25	−26.8
		45 min	30.5	600	32	33.2
		2 hr	30.8	1240	150	630
		3 hr	31.6	Too high to measure.		
C 2.2.9	35.0	15 min	34.0	480	33	−56.3
		45 min	35.7	680	35	30.7
		2 hr	36.5	1340	157	>1150
		3 hr	----------	Too high to measure.		

Effect of Surface Areas of Cements

An increase in surface areas of the cements would be expected to increase the rate of hydration. To explore the effects of this variable, a Type I cement of composition A (table 1) with surface areas of 2,260 cm²/g (15,366) and approximately 1,700 cm²/g (15,365) were made into pastes with w/c ratios of 0.5 and 0.45. The results are summarized in table 5.

The higher surface area cements, for *both* w/c ratios, seemed in general, to exhibit higher yield stresses, plastic viscosities, and extents of thixotropy than the samples with the lower surface areas.

The greater activity of the higher surface area cement is demonstrated in the development of heat in the pastes. At w/c=0.5 the final temperatures were 26.5 and 25.3 °C for the 1,700 cm²/g and the 2,260 cm²/g samples, respectively. Upon hydration the temperatures of the 1,700 cm²/g samples were 26.8, 26.8, 26.8, and 27.1 °C at 15 min, 45 min, 2 hr, and 3 hr of hydration, respectively. The corresponding temperatures of the 2,260 cm²/g samples were 26.0, 26.2, 26.8, and 28.2 °C, respectively. The more rapid rise in the temperature of the higher surface area materials as compared to that of the lower surface area materials is evident from these values.

TABLE 5. *Effect of specific surface of cements on the rheological properties of the pastes made therefrom*

	Time of hydration t_h	2,260 cm²/g (*C*2.2.7)			1,700 cm²/g (*C*6.2.1)		
		f	*U*	*A*	*f*	*U*	*A*
		dynes/cm²	*cp*		*dynes/cm²*	*cp*	
w/c=0.5	15 min	260	23	−10.6	200	19	0
	45 min	290	31	0	220	28	0
	2 hr	510	39	290	340	38	10.6
	3 hr	850	195	>800	500	58	176
		2,260 cm²/g (*C*5.2.2)			1,700 cm²/g (*C*11.2.1)		
w/c=0.45	15 min	770	47	−14	------	------	------
	45 min	1,060	53	5.2	540	56	10
	2 hr	([a])	([a])	([a])	860	68	40.8
	3 hr	([a])	([a])	([a])	([a])	([a])	([a])

[a] Too high to measure.

The Rheological Properties of Various Cements

In most of this work on the rheology of fresh portland cement pastes, a single Type I cement (A, table 1) was used. The purpose of the series of experiments reported in this section was mainly to determine whether the rheological behavior that has been observed was typical of the specific cement used or was characteristic of fresh portland cement pastes, in general. In addition to that, it was desirable to get some information about the effects of chemical composition of the cements on the rheological behavior of the fresh pastes. For this purpose samples of cement (table 1) of Types I (A), II (E), and IV (D) were examined at w/c=0.5, as well as a sample of low gypsum content (B), one of high alkali content (C), and one of alite.

Samples were prepared in a Waring Blendor under vacuum, using a 1–3–2 min of mix-rest-mix procedure. The final temperatures were maintained at 25±2 °C, except for the cases of low gypsum content and of alite, in which cases the temperatures were 20 and 33 °C, respectively. The hydration took place in closed plastic containers at room temperature and the rheological measurements were made on the undisturbed samples at 15 min, 45 min, 2 hr, and 3 hr after preparation.

The compositions of the cements are shown in table 1, and the results of the rheological measurements are listed in table 6. In general, the data show that the samples all develop some thixotropy, but certain variations in the details of the flow are evident.

TABLE 6. *Rheological properties of various cements*
(w/c=0.5)

Time of hydration t_h	*f* *dynes/cm²*	*U* *cp*	*A*	*f* *dynes/cm²*	*U* *cp*	*A*
	A 15366 (*C*2.2.7) Type I Normal			B 15367 (*C*16.2.2) No Gypsum		
15 min	260	23	−10	630	110	1,290
45 min	290	31	0	540	93	1,130
2 hr	510	39	290	780	140	>950
3 hr	850	195	>780	430	120	1,300
	C 15698 (*C*12.2.3) Type I Normal			D 15669 (*C*14.2.2) Type IV Low Heat		
15 min	270	29	0	120	15	−5
45 min	330	28	−36	130	17	9.7
2 hr	840	56	145	140	19	32
3 hr	2,110	110	>530	200	31	145
	E 15622A (*C*13.2.3) Type II Moderate Heat			F 19648 (*C*15.2.2) Zero C_3A		
15 min	100	15	5.1	100	23	47
45 min	110	17	15.0	140	28	86
2 hr	160	24	88.0	190	34	110
3 hr	280	53	>220	230	45	154
	G (*C*17.1.1) Alite (C_3S)					
15 min	16	16	16			
45 min	48	26	86			
2 hr	160	80	620			
3 hr	160	120	810			

Tricalcium aluminate, tricalcium silicate, the calcium sulfates, and alkali have been reported to contribute a great deal to the properties of fresh pastes. The effects of each of these constituents will be examined.

Figures 4–6 show, respectively, the changes in yield stress, *f*, plastic viscosity *U*, and the extent of thixotropy or antithixotropy, *A*, as a function of the calculated calcium aluminate content.

In figure 4 the yield values for cements A, D, E, and F may be seen to rise with the aluminate content (above about 4 percent C_3A content) for the 15-min, 45-min, 2-hr, and 3-hr hydration periods. The letters representing the cements appear above their respective positions on the curves. The Type I, high alkali cement C, exhibited the same general increase with time, but the *f* values were much higher than those shown in the curves. Cement B exhibited *f* values (table 6) which were not in accord with the general trend of increasing with time of hydration.

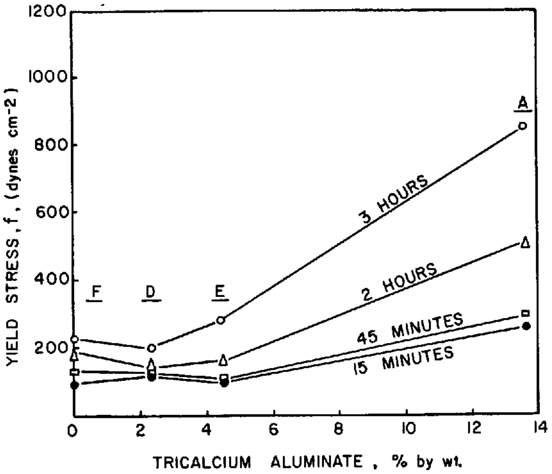

FIGURE 4. *Yield stress, f, as a function of tricalcium aluminate content of the cement.*

A, D, E, F designate the cement used (table 1).

In general, figure 5 shows an increase of plastic viscosity with tricalcium aluminate content (above about 4 percent C_3A content) and hydration time. It may be noted, however, that both cement F and alite, which contain small amounts of tricalcium aluminate, deviate somewhat from the general trend. These cements, however, contain large proportions of tricalcium silicate. Cement B, with a low gypsum content, exhibits plastic viscosities which do not change markedly with hydration time but show substantially higher plastic viscosities.

Figure 6 demonstrates that cements A, D, E, and F show an increase in extent of thixotropy with increase in tricalcium aluminate content after 2 hr of hydration. On the other hand, alite with only 0.88 percent Al_2O_3 shows a much more rapid increase in extent of thixotropy with time of hydration. Cement B, which contains only 0.7 percent $CaSO_4$, demonstrated the most rapid development of thixotropy even after 15 min of hydration (table 6).

General trends of *f*, *U*, and *A* values with the calculated tricalcium silicate contents were not observed. This might be expected since the silicate contents of the cements are high and other components may affect the properties to larger extents than the variations in silicate content.

The effect of the other constituents on the extent of thixotropy is, however, less clear. The alite and the high tricalcium aluminate sample A both develop large extents of thixotropy while samples with intermediate contents of tricalcium aluminate develop much less of it. Obviously, there may be large differences in the nature of

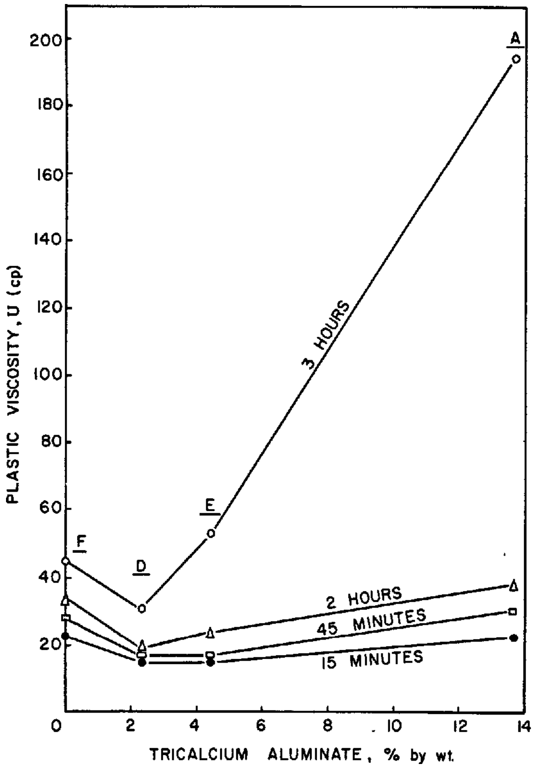

FIGURE 5. *Plastic viscosity, U, as a function of tricalcium aluminate content of the cement.*

A, D, E, F designate the cement used (table 1).

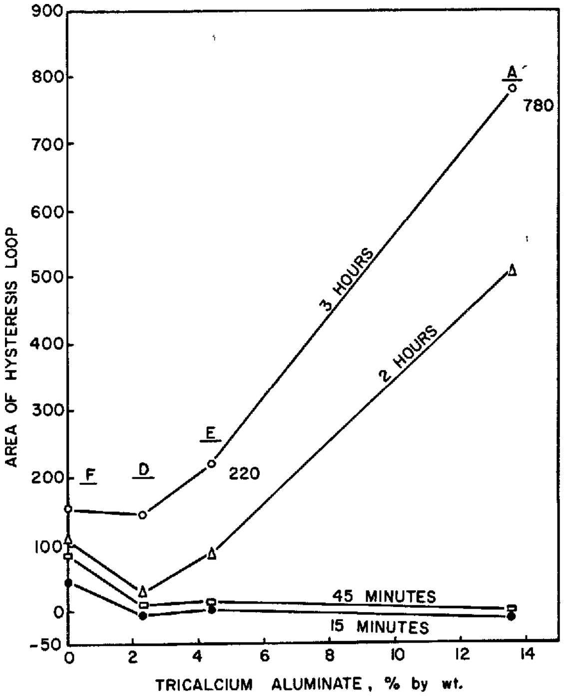

FIGURE 6. *Extent of thixotropy as a function of tricalcium aluminate content of the cement.*

A, D, E, F designate the cement used (table 1).

thixotropy between these two extremes, which cannot be detected by comparing values of A alone.

It has been apparent in the experimental work that the influence of the minor components is marked. Their influence on the rates of chemical reactions, on the nature of the products, and on the electrolyte concentrations in solution would be expected. It may be assumed that the ions in solution influence strongly the interactions of both the hydrate and cement particles.

Cements A and B were made from the same clinker except that no gypsum was added to B, which therefore is simply clinker. The behavior of cement B on mixing differed substantially from those of the other cements. Within the 3-min rest period it stiffened considerably. The subsequent mixing was not efficient for this reason. The paste of cement B may be seen in table 6 to exhibit thixotropic properties after 15 min of hydration, but the relatively high yield values, and plastic viscosities did not change appreciably over 3 hr of hydration time. This behavior was in contrast to that of the paste of cement A which developed from an antithixotropic material to a thixotropic one during the 3 hr of hydration and the f and U values increased with hydration time. The behavior of cement B with no added gypsum is probably characteristic of what is referred to as "flash" set [7].

It is also possible to compare the behavior of cement F with that of alite. Alite and cement F contain no tricalcium aluminate but the latter contains 4.3 percent $CaSO_4$, whereas in alite there is no sulfate. Both F and alite pastes developed thixotropic behavior with no indication of antithixotropy. The extent of thixotropy in the paste of alite was greater than for paste F. Although the yield values of paste F were greater than those for the alite paste after 45 min hydration, the reverse is true for the plastic viscosities.

Pastes made from cements A and C differ mainly in their alkali and free CaO contents. The free CaO contents are 0.93 and 0.08 percent for cements A and C. On the other hand, cements A and C contain 0.33 and 1.57 percent total alkali, respectively. The difference in the tricalcium aluminate contents, i.e., 13.6 percent for A and 9.8 percent for C, would not be expected to cause much difference in properties (figs. 4, 5, and 6). An examination of the rheological behaviors of pastes A and C does show (table 6) substantial differences.

The Effects of Mixing Conditions

The changes in the characteristics of portland cement pastes in the first few hours of hydration may be expected to be rather sensitive to the conditions of mixing of the ingredients. In most of the work the 1–3–2 min of mix-rest-mix procedure in a Waring Blendor under vacuum was used. The purpose of the experiments reported in this section was to obtain some information about the effects of mixing on the rheological properties of the fresh paste.

In the present series of experiments the Waring Blendor under vacuum was still used, but variations were made in the time of mixing, procedure of mixing, and final temperature after mixing, and there was some variation in the temperature of hydration. All samples were prepared with w/c=0.5. Cement A was used. The rheological measurements were made on the undisturbed samples at 15 min, 45 min, 2 hr, and 3 hr after preparation.

The following experiments were performed.

(1) *1–3–2 min mix-rest-mix.* A normal run was made, with 1–3–2 min mix-rest-mix, controlling the final temperature to 25±2 °C. The samples were kept in a water bath at 25.0±0.2 °C until viscometric measurements were made.

(2) *Time of mixing.* Four separate preparations were made with 1, 3, 6, and 10 min of continuous mixing. The final temperatures were 25 °C. The samples were kept undisturbed in the room until rheological measurements were made.

(3) *Final temperature.* Three batches were made by 3 min continuous mixing, allowing the final temperature to attain values of 15.8, 23.2, and 34.5 °C. The samples were subsequently kept in a water bath at 25.0±0.2 °C until the measurements were performed.

Table 7 summarizes the results obtained when a 1–3–2 mixing schedule was compared with a 3 min continuous mixing period. It is worth while noting that the values of A for the cases of antithixotropy ($A<0$) are rather *small* relative to the values of A for the cases of thixotropy ($A>0$).

The values of the plastic viscosities are not significantly different from each other. However, comparing the values of A and f in both runs, one notes significant differences. In experiment 1 the values of f are *higher* and those of A *lower* than the corresponding ones in experiment 2.

The results did not show any appreciable effect of the final temperature after mixing although the differences between the final temperatures after mixing were rather large, 15–35 °C.

TABLE 7. *Comparison of effects of variation in mixing conditions*

Time of hydration t_h	Expt. 1 (C2.2.10) 1–3–2 mixing			Expt. 2 (C2.4.6), 3 min mixing		
	f	U	A	f	U	A
	dynes/cm²	*cp*		*dynes/cm²*	*cp*	
15 min	450	24	−25	310	25	−9
45 min	560	25	−12	350	29	19
2 hr	990	54	600	650	58	650
3 hr	1340	93	730	860	90	880

From all our experiments with cement pastes, the natural trend (within the first 3 hr at least) has been for the system to increase in thixotropy with time of hydration, as well as in "strength", as measured by the increasing value of the yield stresses f. From the data it appears as if the omission of the 3-min rest period in experiment 2 *enhanced* the development of thixotropy and *retarded* the development of "strength".

Table 8 summarizes the results for the four preparations in which the time of continuous mixing was varied from 1 to 10 min.

It is apparent from the table that the plastic viscosities tend to increase with an increase in the mixing time, and so do the yield stresses. From the values of A at 15 min of hydration, it is obvious that thixotropy does have a tendency to develop rather early, but is broken down by further mixing. This is also consistent with the relative values of A at 15 min of hydration shown in table 7. They are -9 for 3 min of continuous mixing and -25 for the 1–3–2 mixing schedule. The thixotropy developed during the 3 min of rest has been efficiently broken down by the subsequent 2 min of mixing, allowing more antithixotropic behavior to appear.

Table 8. *The effect of time of continuous mixing on the rheological behavior of fresh cement paste*

Time of hydration t_h	Sample *C*2.3.3 1-min mix			Sample *C*2.4.5 3-min mix			Sample *C*2.5.7 6-min mix			Sample *C*2.6.3 10-min mix		
	f	U	A	f	U	A	f	U	A	f	U	A
	dynes/cm²	*cp*		*dynes/cm²*	*cp*		*dynes/cm²*	*cp*		*dynes/cm²*	*cp*	
15 min	220	21	25	400	24	−6	490	29	−19	520	47	−66
45 min	210	24	21	460	25	0	570	34	0	680	38	~4
2 hr	310	39	192	730	53	550	670	42	130	1,490	86	~700
3 hr	480	84	620	940	59	~840	1,720	111	>750	1,950	119	>670

Discussion

Much additional research will be necessary on the rheology of fresh pastes before all the factors which control the flow properties will be understood. Nevertheless, an attempt will be made here to correlate as much information as possible into a picture of the physicochemical nature of the pastes. In order to do this many assumptions must be made.

At the present time, it is believed by many research workers [1] in this field that portland cement hydrates by solution and diffusion mechanisms. When portland cement is mixed with water, it appears that the solution immediately becomes supersaturated with respect to hydrated silicates and aluminates and calcium hydroxide. From this supersaturated solution the products of hydration precipitate as a gel around the unhydrated particles. After these initial solution reactions, further hydration proceeds by diffusion through the gel. These hypotheses are supported by several pieces of evidence.

One is that the solution phase immediately after mixing cement with water is saturated with respect to hydrated calcium silicate and supersaturated with respect to calcium hydroxide [31]. Another piece of evidence in support of the above theory of hydration was obtained from sedimentation studies. Powers [26] has reported that the sedimentation rate of cement in water does not change over the first hour of hydration. This behavior indicates that the particle sizes and numbers do not change appreciably in the early stages of hydration. Therefore, it is possible to conclude that the hydration in the early stages causes a gel layer to form around the cement particles without appreciable change in the size or number of active particles.

The major components (table 1) of portland cement are tricalcium silicate, dicalcium silicate, and tricalcium aluminate. The effect of the tetracalcium aluminoferrite on the flow properties is not well understood [7]. In order of rate of hydration [32], tricalcium aluminate is most rapidly hydrated, tricalcium silicate is next, and dicalcium silicate hydrates relatively slowly. In cements to which gypsum has been added, some hemihydrate of calcium sulfate is usually formed in the process of grinding the clinker with gypsum [33]. Varying amounts of alkali are found in portland cement. In the literature [7], many effects have been attributed to alkali.

It is reasonable to assume that the principal products of hydration of cement up to 3 hr are formed by the reaction of tricalcium silicate and aluminate. The hydration of calcium sulfate hemihydrate also proceeds rapidly. In order to have some quantitative notion about the chemical changes that have proceeded in the first 3 hr of hydration, it is worth while estimating the degree of hydration of these components. According to the data obtained in the present study and those derived from the literature [34], it appears that about 5 percent of portland cement hydrates in 3 hr. This estimate is based on the degree of hydration of the principal components. Thermobalance results in our laboratory show that about 6.5 percent of alite hydrates in 3 hr. Since about 45 percent of the cement is alite (A, table 1) then this would amount to about 3 percent hydration of the cement. According to Copeland, Kantro, and Verbeck [34] about 10–20 percent of the tricalcium aluminate hydrates in about 2 hr. If we assume that 15 percent hydration occurs in 3 hr, and we know that about 13.6 percent of the cement (A, table 1) is tricalcium aluminate, then this corresponds to an additional 2 percent hydration of the cement. Ershov [32] reported that considerable hydration of the aluminate occurs.

From a separate study of the composition of the aqueous phases in contact with portland cement it appears that the aqueous phase does not change appreciably with time. Apparently in the case of normal Type I cements the pH values and calcium ion concentrations remain relatively constant over the first few hours of hydration. The pH in this period of hydration was approximately constant at 12.8. However, the calcium ion concentration increased from 0.031 to 0.033 M, which may very well be within experimental error.

Since tri- and dicalcium silicate make up 70–80 percent of portland cement, it is not unexpected that the mechanical strength of set hydrated cement should be due almost entirely to the contribution made by them. Therefore, the nature of the contributions made by these components will be reviewed first. Certain conclusions which have been drawn on the basis of research on pure tricalcium silicate or alite, or dicalcium silicate or belite *may* not be valid for the hydration of alite and belite in portland cement. Nevertheless, until this information is available on the cement system, we shall use the available information on the pure components. The hydration of tricalcium silicate leads to products [3] which are in the form of plates and needlelike crystals. Some authors believe the fibers or needlelike crystals are formed by rolling up of the plates. Let us assume for simplicity that these particles are either fibers or plates [35].

At this point in the discussion it would be convenient to propose a structure for the calcium silicate hydrogel which forms on hydration of the silicates. The hydration of alite leads to a product which is thixotropic at all stages (table 6). According to current theory [22] thixotropic gels are made up of particles which touch at certain points only. For example, van Olphen [36] has proposed that bentonite gels form contact points between the negative charges on the surfaces of the plates and the positively charged edges. Such a structure would be like that shown in figure 7. The negatively charged surfaces may be there because of the presence of silanol groups, SiOH, which ionize in alkaline solution to SiO^- species. The positive charges van Olphen proposed are due to unsatisfied Al^{+++} charges at the edges of the plates. Bentonite gels are relatively strong structures at low concentrations of solids because of this network arrangement of the particles and the strong and numerous bonds [37] between the particles.

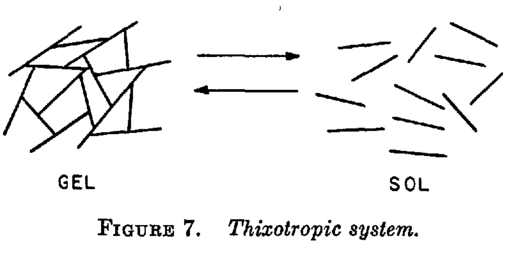

Figure 7. *Thixotropic system.*

It is possible to assume that a similar structure exists in hydrated cement except that large particles of unreacted material, calcium hydroxide, etc., are dispersed in the gel. According to the sedimentation studies of Powers [26] the gel is apparently densest around the cement particles.

The forces between the particles in the pastes are van der Waals and electrostatic forces. Zhuravlev and Tikhonov [38] and Reshetnikov [39] have reported that the solid hydrate particles in portland cement pastes exhibit a positive surface charge. By change in pH and ionic strength of the aqueous media in contact with solid surfaces, it has been found possible by Kruyt and his coworkers [21] to change the forces of attraction and repulsion between particles in thixotropic gels. The detailed nature of the forces between hydrate particles is not known.

To exhibit thixotropic properties, the forces between the particles must be sufficiently strong to hold the system together with a relatively low concentration of solute particles, but the forces must not be so strong that a small shearing stress will not break the bonds and cause a sol to form (fig. 7). The gel will reform when the sol is allowed to stand for a sufficiently long time. It must be pointed out, however, that after a portland cement paste, which has been hydrated to some extent, is agitated, the gel does not recover its original behavior. It has been reported [40] that strong agitation of a partially hydrated concrete mixture leads to a weak product.

Tricalcium silicate, portland cement, and mixtures of calcium oxide and pozzolanic materials, made up primarily of silica, hydrate to produce hard, strong products. On the basis of present information it is reasonable to assume that the hydrated silicates in these products exhibit the same properties.

The processes of setting and hardening probably consist of two factors. First, when sufficient calcium silicate hydrogel forms, the system exhibits large yield values and plastic viscosities. A study of calcium silicate hydrogels [41] shows that the yield values and plastic viscosities rise rapidly in the range of concentrations above 5 percent.

Reiner [8], in a review of the rheology of concrete, points out that the reduction of water content by evaporation and chemical reaction increases considerably the concentration of solids. Also, according to Powers and Brownyard [5], much of the free water is adsorbed on the large surface of the hydrate particles.

Whether or not chemical bonds form between the thixotropic gel particles (fig. 7) during setting is not clear. Such bonds could form through calcium ions or by condensation of silanol groups, SiOH. Copeland [34] has found that although it is difficult to disperse portland cement pastes even by ultrasonic techniques, tri- and dicalcium silicate pastes may be dispersed. Perhaps these results indicate that the bonds are stronger in cement pastes than in silicate pastes because there are chemical bonds in cement paste gels.

Cement F with no tricalcium aluminate shows no antithixotropic behavior and only relatively small degrees of thixotropy compared to alite or Type I cement pastes (A and C). The rapid rise of thixotropy within 15 min and the extent of thixotropic behavior (where *A* is approximately 1,300) shown by cement B which contains only 0.7 percent calcium sulfate seem to indicate that the hydration of the silicates and of the aluminates both lead to a higher degree of thixotropic behavior. Whether or not the hydrated aluminates alone form thixotropic structures is not known yet. It is reasonable to assume that cement B to which no gypsum was added undergoes "flash" set to some extent. This kind of set apparently leads to high yield values, >540 dynes/cm^2, plastic viscosities, >93 cp and extents of thixotropy of 1,130 even after 45 min of hydration.

When pure tricalcium aluminate reacts with water an immediate set results. This is commonly referred to as "flash" set. The introduction of gypsum into cement prevents the formation of "flash" set by forming, instead of the aluminate hydrate, a sulfoaluminate when the sulfate content is high.

It is perhaps reasonable to assume that the increase in yield values, plastic viscosities, and thixotropic development with tricalcium aluminate content in cements may be attributable to the formation of cross links in the silicate gels by the needle crystals of ettringite. It has been reported [7] that tricalcium aluminate increases the strength of set hydrated cement in the early stages. Budnikov [45] attributes the increase in strength to the sulfoaluminate crystals. If the tricalcium aluminate hydrates rapidly then it is also possible to attribute the increase in rheological coefficients to a removal of water (which would, of course, increase the solids content) and to the formation of a considerable amount of colloidal aluminates.

The presence of gypsum leads to two effects in cements: (1) formation of sulfoaluminates and prevention of "flash" set, and (2) development of "false" set because of dehydration of gypsum to calcium sulfate hemihydrate when ground with clinker. "False" set is sometimes called "plaster set" and apparently proceeds by hydration of the hemihydrate to gypsum. According to some authors [7], the sulfates apparently do not affect the rate of hydration of the silicates, but Bernal, Jeffery, and Taylor [42] have proposed that gypsum prevents the formation of an aluminate gel layer on the surface of the alite. According to these authors the gel layer slows the rate of hydration. Although the details of "false" set will be examined in the future, several observations may be made on the basis of the results obtained in the present study.

False set may easily be broken up by sufficient mixing. Powers [26] has reported that the presence of "false" set influences the behavior of pastes and should be destroyed in order to obtain reproducible results. This is the reason that the mixing procedure followed in the present study was employed. The experiments on mixing procedures indicate that "false" set enhances the degree of thixotropic behavior. Nevertheless, when increasing times of mixing are used or a rest period between mixing is employed, the thixotropic structure is destroyed. This is also manifested by the appearance of antithixotropy which apparently is exhibited only in the absence of a large degree of thixotropic behavior.

The effect of alkali in cement on setting has been discussed by Steinour [7]. Alkalies in clinker have been reported by Schmidt [43] to cause the development of quick set. Alkalies in clinker have been found by Lerch [44] to accelerate the formation of sulfoaluminate and even to accelerate the hydration of the tricalcium aluminate. Cements high in alkali are reported to require higher gypsum additions.

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Discussion

A. J. Gaskin

The rheological behavior of cement pastes is influenced by so many factors that it is probably misplaced optimism to expect that clear isolation of any mechanism involved can be reached at this stage.

Ish-Shalom and Greenberg show that pastes exhibit antithixotropy at an early age if C_3A is present, and later develop thixotropic characteristics. The authors propose only the most general explanation of the main trend, attributing the thixotropy to the generation of hydration products capable of effecting cross linkages of a mechanical or possibly chemical nature, between particles.

There can be no doubt that the relative amount and nature of the colloidal hydrates will be the main factors controlling the rheology of pastes in a general sense. It may be useful, however, to give more specific consideration to certain minor factors at this juncture, in particular rheological effects possibly associated with the granular unhydrated cement particles, such as antithixotropy, and the influence of degree of flocculation on yield values and thixotropy

Antithixotropy

One possible view of "antithixotropy" is that it represents persistence of the type of grain arrangement responsible for the appearance of dilatancy, an effect common to most granular systems with an interstitial Newtonian liquid phase. The phenomenon originates in the flow mechanism described by Endersby [1] [1] as "granular structural resistance," whereby particles temporarily lock together in bridging arrays when forced into contact with one another during shear.

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[1] Figures in brackets indicate the literature references at the end of this paper.

The intensity of the transient resistance offered by the formation of any array depends on such factors as the liquid/solids ratio, the shape of the particles, the particle size distribution, the degree of interparticle adhesion or surface friction, and the viscosity of the liquid.

If the particles are not well wetted by the liquid, or if interparticle frictional effects are reduced by adsorbed lubricating layers, the effect is weakened. Conversely, when particles are strongly cross linked or aggregated into flocs of high stability, the effect degenerates into "structural viscosity" as the relaxation time for breakdown of arrays becomes very long.

The terms "dilatancy," "false-body," and to some extent "shear-hardening" as applied to suspensions, refer to effects produced by the granular structural resistance which opposes deformation of such systems.

Classical "Osborne-Reynolds dilatancy," in which the dilation of the overall volume of the locked arrays of granules is observable during shearing, is an extreme instance of the general phenomenon, only discernible when the liquid/solids ratio is near the critical minimum required to just saturate a close-packed system of grains. Actual "close-packing" of grains is not required, the only essential being the formation of an extensive skeleton of locked arrays of particles which will hold together long enough to permit the liquid phase to flow into the internal shear cracks developed between domains of particles, and so result in drying out of the surface.

Cement pastes, ceramic oxide casting slips, and similar systems, usually have a higher liquid/solids ratio than that required for the appearance of "drying-out" on deformation, but nevertheless exhibit the more basic features of dilatancy. Surface drying is not apparent for two reasons, first, the relaxation time for destruction of arrays shortens as the liquid content of the system increases, and second, slight transient changes in the total volume of the particle arrays are not easy to detect when the surface layer of the system as a whole contains extra liquid.

There can be no fundamental objection, therefore, to the extension of the term "dilatant" to serve as a general reference to the increase in viscosity which commonly accompanies an increase in the rate of shear of granular suspensions, when it is desired to relate such a viscosity increment to the "granular structural viscosity" mechanism. Persistence of dilatant effects as shear rates are reduced then leads to the feature termed "antithixotropy".

In the broad sense dilatancy is a feature of granular systems, as distinct from colloids, and should therefore be a dominant characteristic of cement pastes and suspensions at the time of mixing, when the material can hardly be considered to be "colloidal" in any sense of the word.

Pastes show progressive change from "granular" to "colloidal" behavior as hydration products of truly colloidal type are generated within the system.

The extent to which a paste will show dilatant characteristics will depend on the ease of formation of locked arrays of particles during shear, and the extent of antithixotropy should then be governed by the persistence of such arrays, once formed, at lower rates of shear.

At first a cement paste will contain free granules and water only, and should show strongly dilatant characteristics, arrays forming readily but decaying rapidly as shear rates are reduced. The presence of the first colloidal hydrates will reduce dilatancy by restricting the mobility of the water films between the grains, but this effect, together with the growth of hydrate films on the grains, should increase the persistence of arrays (relaxation time) so leading to the appearance of antithixotropic features.

A simpler model which demonstrates the effects of increasing the relaxation time in such systems is a starch-water paste in which glycerol is progressively substituted for water, so reducing the mobility of the liquid phase [2].

A ceramic analog is found in the addition of increasing amounts of colloidal clay to a "false-bodied" granular mixture, whereby dilatant effects are suppressed in intensity but prolonged in time. If more clay is added the mass retains some "shear-hardening" characteristics which persist indefinitely even when the shear rate is reduced almost to zero.

Flocculation

In cement pastes the factor which generally appears to obscure the simple picture of a dilatant system being modified by colloidal hydration products is the degree of flocculation of both the cement particles and the hydrates.

The breakdown of floc structure on application of shear is the opposite effect, rheologically, to the formation of arrays in dilatancy. The period of recovery of structure following reduction or cessation of shearing, if long enough, results in thixotropy, and is the converse of the period of relaxation of locked arrays produced in the shearing of dilatant systems.

Initial dilatant features of pastes, such as antithixotropy, are therefore supplanted as hydration proceeds by flocculation effects either characterized by short recovery times, leading to increased yield values, or longer recovery times, giving thixotropy.

The results of Ish-Shalom and Greenberg may thus be considered as showing that normal cements containing C_3A are not strongly flocculated at periods of hydration between 15 and 45 min, but thereafter flocculation completely dominates any effects of the dilatant type. Without C_3A, pastes are well flocculated even at 15 min, and the extent to which yield values and thixotropic effects develop at later ages depends only on the proportion of colloidal material resulting from hydration.

The mechanical and chemical cross-linking factors mentioned by the authors are no doubt responsible for some of the interparticle attraction responsible for flocculation, but the impression given by the data is that some type of electrostatic flocculation is a major factor.

Recovery times appear to be short, for example, and no severe reductions in yield value or thixotropy are shown in "second cycle" data.

If the usual electrostatic considerations should therefore be applied to the cement paste system, an interesting position arises. The hydration products are known to be positively charged, and should therefore be flocculated by anions in the liquid phase, unless it is proposed that charge reversal is occurring at some critical solution concentration during the hydration process, by secondary adsorption of anions. Since this reversal is most improbable, an original reversal having occurred at a very early stage already by adsorption of calcium ions, it seems likely that the paste components remain stable, with positive charge, throughout the period under consideration, the stabilizing ions being calcium and any other cations in the solution phase.

Flocculating ions must then be either hydroxyl, or the more effective divalent anionic components of the solution, mainly sulfate ions.

The degree of flocculation will then be determined by the balance existing at any stage between positive dispersing ions such as calcium and the alkalies, and flocculating anions such as sulfate and hydroxyl.

The function of gypsum and its dehydration products may then be to supply calcium in soluble form, as far as the dispersing action of these components is concerned, although the reason for gypsum addition is primarily the need to avert the formation of hydrates of C_3A.

Once the conversion of C_3A into a sulfoaluminate phase has been accomplished, it may therefore be deduced that the sulfate ion in solution is unwelcome, as it will give rise to a high degree of flocculation, increasing the yield value and plastic viscosity of the paste and hence resulting in an unnecessarily high water requirement for standard consistency.

Reduction of sulfate concentration through extensive sulfoaluminate formation may be expected to cause a reduction in the intensity of flocculation. It would be interesting to know whether the relative delay in the appearance of thixotropy in pastes containing C_3A is connected with such a mechanism.

Again, if sulfate is replaced by a less potent flocculating ion, as in the addition of barium chloride after the initial mixing period, reduction of paste consistency should follow, rather than thickening. Conversely, addition of extra sulfate without concurrent addition of an efficient stabilizing cation, as in the addition of ammonium sulfate for example, should cause further thickening of pastes not already fully flocculated. Trivalent anions, though difficult to retain in solution in pastes, should also promote flocculation, as for instance in the addition of ammonium phosphate.

The whole question of the stiffening or dispersing effects of additions of soluble inorganic salts to pastes should, theoretically, be a matter of anionic flocculation and cationic dispersion.

The picture for organic additives is complicated by the introduction of effects due to orientation of large molecular groups during adsorption on the solid phase resulting in special types of peptization or flocculation. In some instances the stabilizing action of a cationic group can still be observed, however, as in the adsorption of cetyl-trimethyl ammonium bromide, reported by Bruere [3] to be a dispersant of cement once the first oriented layer is adsorbed and covered by a second layer in which the molecules present positive polar groups to the surrounding solution.

In practice the flocculating effects of added anions may be obscured by precipitation, or by concurrent adsorption of highly polarizable cations, but if these factors are taken into account the results seem to be in accord with the theoretical predictions which follow from the model proposed above.

In our laboratory no striking exceptions to the proposition have yet been found. If calcium adsorbed on the particles of a paste, or in the interstitial solution, is stripped out as a precipitate, flocculation becomes very intense if no other suitably adsorbed cation is introduced.

If sulfate is removed and no substitute strongly flocculating anion is introduced, the paste reverts toward the deflocculated state. The ultimate state of all pastes is of course determined by the progress of hydrolysis of the primary clinker compounds, liberating calcium as the stabilizing cation and hydroxyl as the dominant counter-ion.

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Closure

Moshe Ish-Shalom and S. A. Greenberg

Dr. Gaskin in his discussion of our paper has presented a model for the hydrating cement system to explain the flow behaviors observed. In the early stages of hydration he presumes that a paste consists of free particles in water and that as hydration proceeds the colloidal products coat the unreacted particles and flocculation occurs. The "antithixotropic" flow behavior found in fresh pastes after 15 min of hydration (fig. 1, curve A), he attributes to a system of portland cement particles dispersed in water and he states that this system should be dilatant. He has suggested also that the thixotropic properties develop in pastes as the "degree of flocculation" increases with hydration. It is of interest to compare the model proposed by Dr. Gaskin with the experimental evidence.

The authors of this article have avoided giving a detailed explanation for the flow behaviors of fresh pastes for two reasons:

1. The terminology and definitions that are used to describe the flow behaviors of relatively simple aqueous dispersions, which are stress-dependent, have not been standardized. Therefore, there is a great deal of confusion on both the colloid chemistry and rheology of dilatant and thixotropic systems in particular. The situation has also been complicated by the variety of methods used to measure the flow properties of dispersions.
2. The various physicochemical factors, which influence the flow properties of fresh pastes, are not well understood. Dr. Gaskin in the first sentence of his discussion says substantially the same thing.

A committee on communication problems in industrial rheology has been formed to establish authoritative definitions and a standard terminology for the stress-dependent flow phenomena of dispersions. This committee is sponsored by several divisions of the American Chemical Society, by the Society of Rheology, and by the American Society for Testing Materials. Up to this time the committee has issued only one article on recommended terminology [1].[1] Three basic quantities, according to the committee, are measured: (1) shear stress (S), (2) shear rate (D), and (3) time. Therefore, they recommend that the ratio S/D should be described as a function of D in each of the three broad areas of flow behavior. A constant S/D ratio is characteristic of a Newtonian system. A material which shows a decrease in the ratio S/D with increase in D is referred to as shear thinning. An increase in S/D with increase in D is given the name shear thickening. It is clear that to some investigators shear thinning and shear thickening refer to thixotropic and dilatant [2] flow behaviors, respectively.

The paper under discussion was written before the recommended terminology was available. Therefore, this terminology was not incorporated in the paper. However, in the future we shall employ these recommended terms in reporting data wherever possible. Nevertheless colloid chemists will use the words dilatant and thixotropic and they therefore must be defined. The term antithixotropic has been used by Dellyes [3] to describe the behavior of very fresh pastes (fig. 1, curve A).

The classical experiments demonstrating dilatant behavior were conducted by Reynolds [4] on sand-water mixtures. Reynolds found that an applied stress on this system caused the volume occupied by the sand to expand or dilate. Reynolds also observed an increase in rigidity of the sand-water system when the system was distorted. Working with quartz-water and starch-water systems, Freundlich and Roder [5, 6] observed an increase of "viscosity" with rate of shear. To these systems they also gave the name dilatant. On the basis of these and related experiments, it is now common [2] to ascribe the name dilatant to systems which are Newtonian at low rates of shear and are shear thickening at higher rates of shear. After an examination of the reported dilatant inorganic systems, Metzner and Whitlock [2] concluded that our information on these systems is based on a few quantitative studies and that much more research is necessary before we shall understand this behavior better.

The authors of this article would be reluctant to apply the name dilatant to cement-water systems on the basis of commonly accepted usage of the word. Curve A in figure 1 of our paper shows no indication of a Newtonian behavior except perhaps at very low rates of shear. Dilatant systems show flow curves which are concave toward the torque axis. This is not the case with cement pastes. The ratio S/D increases with *time* in this case. Antithixotropy is perhaps *related* to dilatancy but more research will be required before we understand this relationship.

Dr. Gaskin states that "At first a cement paste will contain free granules and water only, and should show strongly dilatant characteristics." Dr. Gaskin apparently defines dilatant systems as those which build up a structural array as they are sheared. We shall not argue with Dr. Gaskin's definition of dilatant behavior or his model for it, but we cannot agree that fresh cement pastes are a dispersion of free granules. Powers [7] has reported sedimentation data which demonstrate that cement-water systems are flocculated. Also with the relatively high concentration of calcium ions in the aqueous phases in pastes, flocculation would be expected [8].

In addition to cement granules in water, several investigators [9] have reported that immediately on mixing cement and water several hydration products appear. False set [10] caused by the formation of gypsum occurs only a few minutes after cement is mixed with water. In addition, hydrated calcium silicates and aluminates, calcium hydroxide, and ettringite are formed at early stages. All these species interact by physical and probably chemical bonds. Dr. Gaskin shows his awareness of this problem in the first sentence of his discussion yet he tends to ignore it in the model he proposes.

Peterfi and Freundlich [5] originally defined thixotropy as an isothermal, reversible sol-gel transformation. Freundlich later extended the definition of gel to include particles greater than 1μ in size. This behavior is attributed to the attracting and repelling forces between the particles. The application of the word thixotropic to cement pastes is not entirely consistent with the definition because the transformation is not com-

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[1] Figures in brackets indicate the literature references at the end of this paper.

pletely reversible. Our experiments indicate at this time that only the hydrated calcium silicates form a reasonably reversible system. Many of the hydration products lead to shear-thinning behaviors, but information on their ability to completely recover their original consistency when allowed to stand will require additional research. The irreversibility in cement pastes is probably due to chemical bonds or crystalline intergrowths of the various species, which when once broken will not reform. False setting cements are an example of this behavior. False setting concretes may frequently when agitated become workable. Thus the bonds between the recrystallized gypsum particles when broken do not reform.

Apparently Dr. Gaskin misinterpreted our discussion of the bonds between the particles in fresh pastes and especially the hydrated calcium silicate particles. We believe the solids are held together primarily by attractive van der Waals forces, and we brought up the possibility of chemical bonds or crystalline intergrowths between the various species in fresh pastes. It appears that hydrated calcium silicate gels, where the particles are held together by van der Waals forces, exhibit strongly bonded structures. Dr. Gaskin refers to the word flocculation in a way quite different from the meaning we give it. We use the word to mean the reverse of dispersion or deflocculation [11]. Flocculation occurs when the attractive van der Waals forces between the particles in the paste or suspension exceed the electrostatic repulsive forces. This terminology follows that of Verwey and Overbeek [12] which obviously differs somewhat from that of Dr. Gaskin.

The assumption by Dr. Gaskin that calcium is a dispersing ion in cement pastes is not in accord with the evidence [11]. We have stated already that the evidence demonstrates that pastes form flocculated systems. Stein [13] has reported that calcium ions may reverse the negative charge of hydrated calcium silicates and thus reduce the zeta potential. These effects would lead to flocculation by calcium ions. Similarly Powers has shown [11] that calcium ions flocculate silica dispersions. No evidence has been offered to show that calcium ions by increasing the positive zeta potential can stabilize a silicate or silica sol.

In conclusion it may be said that a detailed understanding of the rheology of cement pastes will require a better knowledge of the rheology and chemistry of the colloidal and macroscopic particles in cement pastes. Research on the component systems, combinations of these systems, and on cement pastes is in progress in our laboratory.

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SESSION VI. DESTRUCTIVE PROCESSES IN CONCRETE

Paper VI-1. Chemical Reactions Involving Aggregate*

Per Bredsdorff, G. M. Idorn, Alice Kjaer, Niels Munk Plum, and Ervin Poulsen

Synopsis

This paper comprises a review of the literature concerning chemical reactions in concrete involving aggregates, with emphasis on reactions leading to deterioration because these reactions have been particularly studied as problems of concrete durability.

The first and second sections deal with different inorganic and organic impurities—or contaminations, or constituents—of aggregates. There follows a brief account of studies on the aggregate bond strength related to chemical reactions in the contact phase and a description of a rather particular case of deterioration in harbor works in Portugal. Next, a detailed review of available papers on alkali-aggregate reactions is given. The complex character of this subject is demonstrated by the discussions in different passages. The last section contains comments on some so-far unidentified so-called cement-aggregate reactions in Canada and the U.S.A.

Résumé

Cet exposé passe en revue la littérature qui traite des réactions chimiques dans le béton comprenant les agrégats, en concentrant sur les réactions qui provoquent la détérioration, parce que ces réactions ont été étudiées particulièrement sous forme de problèmes de la durabilité du béton.

Les première et deuxième sections traitent des différentes impuretés organiques et inorganiques—soit contaminations, soit constituants—des agrégats. Ces sections sont suivies d'un bref compte-rendu des études sur la résistance de la liaison ciment-agrégat relatives aux réactions chimiques dans la phase de contact, et la description d'un cas assez particulier de détérioration dans des travaux portuaires au Portugal. Puis, on fait une revue détaillée des exposés disponibles sur les réactions alcali-agrégats. Les discussions en différents passages démontrent le caractère complexe de ce suject. La dernière section contient des commentaires sur certaines réactions, au Canada et aux Etas-Unis, appelées réactions entre le ciment et l'agrégat et jusqu'à présent non-identifiées.

Zusammenfassung

Dieser Vortrag beschäftigt sich mit der Literatur der chemischen Reaktionen, die sich im Beton ereignen, an denen Zuschlagstoffe teilnehmen, und Nachdruck ist auf solche Reaktionen gelegt, die zu einer Zerstörung führen, weil doch solche Reaktionen besonders studiert worden sind als Probleme der Dauerhaftigkeit des Betons.

Das erste und zweite Kapitel beschäftigen sich mit den verschiedenen anorganischen und organischen Verunreinigungen oder Bestandteilen der Zuschlagstoffe. Danach werden die Untersuchungen über die Bindungsstärke der Zuschlagstoffe in ihrer Beziehung zu den chemischen Reaktionen in der Kontaktphase kurz besprochen, und ein besonderer Fall der Zerstorung einer Hafenkonstruktion in einem portugiesischen Hafen wird erörtert. Danach wird die vorhandene Literatur über Alkaliaggregatereaktionen besprochen. Wie kompliziert dieses Gebiet wirklich ist, ist an Hand einer Besprechung verschiedener Literaturstellen dargelegt. Das letzte Kapitel enthält Bemerkungen über einige Zementzuschlagstoff Reaktionen, die in Kanada und den Vereinigten Staaten aufgefunden und niemals näher identifiziert worden sind.

Introduction

Very different types and circumstances of reactions were in mind when the compilation of papers for the present report commenced. However, the majority of papers available dealt with alkali-aggregate reactions which apparently represent the most pronounced menace to concrete durability in rather extensive areas. It has appeared that pertinent problems in the field of alkali-aggregate reactions are still unsolved, and some questions may even be considered as unapproached, at least as judged from published works.

In many respects, therefore, the report is rather incomplete in the sense of forming a synthesis on the basis of hitherto reported investigations of the different aspects of the reactions. Moreover, the paper is mostly qualitative, because it so far has not been possible to interpret the available data adequately in quantitative models. One major problem, which in the opinion of the writers is not clarified sufficiently, is the fundamental nature of the chemical reactions between alkalies and reactive aggregates and the nature of their mechanical effects. Problems regarding a proper realization and evaluation of empirical tests is another field where still much research will be needed, and the

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Danish National Institute of Building Research, Copenhagen, Denmark. (Co-author Idorn is now at Aalborg Portland-Cement-Fabrik, Copenhagen.)

"unidentified cement-aggregate reactions" is one more important question to which the clue might be hidden in the solution of the former two problems.

On the whole, the report may have developed into too much of an attempt at presenting that which is not known today about alkali-aggregate reactions, rather than being a mere compilation of existing data. It is hoped that the viewpoints brought forward in this treatment may be found useful with respect to further research. The writers also hope that the unavoidable imperfection of the paper will be eliminated by supplementary contributions from other authors.

Inorganic Impurities in Aggregates

Oxidation, hydration, and carbonation of oxide minerals in aggregates have repeatedly been said to cause troubles in concrete.

E. G. Swenson and V. Chaly [1] [1] reported that magnesia as an impurity in aggregates may occasion damage by carbonation, due to a considerable volume increase and to a higher solubility of $MgCO_3$ than of the original periclase. R. F. Blanks and H. L. Kennedy [2] mentioned a concrete canal lining in California, in which pop-outs developed, because magnesia and lime in the aggregate expanded by hydration and carbonation.

Pyrite and marcasite may also expand by oxidation and hydration. They may further cause disintegration by being the sources of a development of free sulfuric acid and sulfates, which may dissolve the binding constituents of the cement paste and precipitate vulnerable substances as gypsum and ettringite. T. Hagerman and H. Roosaar [3] recommended about one percent as the upper limit for the content of the easily oxidizable sulfide minerals, especially iron pyrite.

I. Moum and I. Th. Rosenqvist [4] reported severe concrete deterioration in the Oslo region, caused by alum shales containing small amounts of pyrite and pyrrhotite. The latter mineral, easily weathered, produces an unusual kind of sulfate attack when concrete is placed in or near rock foundations of alum shales. Severe and rapid deterioration of this type has been a rather common occurrence in foundations, tunnel linings, sewers, etc., in and around the town of Oslo for a number of years. The critical limit of the content of pyrrhotite in the shale seems to be as low as about 0.01 percent, when normal portland cement is used. In recent years sulfate resistant cement with low C_3A-content has been recognized as a reliable safeguard.

In some cases, where alum shales by accident or for economic reasons have been used in the aggregates, seams of ettringite have been observed to develop as reaction rims in the adjacent paste around the alum-shale pebbles. This reaction has caused cracking and disruption, probably initiated by swelling and partial dissolution of such pebbles.

Alum shales similar to those of the Oslo region are mentioned to occur also in other countries. A detailed account of the Norwegian problems is given [5] by R. Bastiansen, I. Moum, and I. Th. Rosenqvist.

G. M. Idorn [6] reported a case of comprehensive development of pop-outs in lightweight concrete blocks made with cinder slags as aggregates and used for the inner walls in multistory flats. Petrographic examination of thin sections of the damaged concrete suggested that swelling of slag particles, presumably due to delayed reaction of pyrites in the slag, led to the development of the pop-outs. The damage was observed on plastered walls only and continued to occur during the following 10 yr on bathroom walls (humid) as well as on walls of living rooms (dry). Evidence of delayed hydration of hard-burned lime (CaO) as a deleterious factor was looked for, but was not found.

Sulfate reactions in concrete may in some regions be due to the presence of gypsum in the aggregates. The effects may be expansion, cracking, and further disintegration by alteration of the hydrous calcium aluminate and silicate with additional development of calcium aluminosulfate, etc. R. F. Blanks and H. L. Kennedy [2] suggest that the upper limit for the content of gypsum in coarse aggregate should be less than 0.25 percent by weight.

Zeolitic minerals and some clays of the montmorillonite types are subject to base exchange by which calcium ions from the cement paste are adsorbed, replacing sodium and potassium ions in the said minerals. These changes may affect potential alkali-aggregate reactions as mentioned later. However, setting and hardening of the paste may also be affected, and efflorescences may develop on surfaces. R. F. Blanks and H. L. Kennedy in their book [2] mentioned that concretes with such efflorescence and cases of deterioration in southern California were ascribed to a base exchange in zeolites.

R. E. Grim [7] mentioned that if the soil around concrete members, basements, pillars, etc., contains montmorillonite clays, a base exchange may take place between sodium from the mineral and calcium from the hardened cement paste. Grim stressed the possibility of tremendous effects on structural stability by such an exchange. A further treatment of this subject, however, is not within the scope of the present paper.

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[1] Figures in brackets indicate the literature references at the end of this paper.

Organic Impurities in Aggregates

Different organic impurities and contaminations in aggregates are reported chemically active in concrete.

M. F. MacNaughton and J. N. Herbich, for instance [8], mentioned some rather peculiar cases of accidental air-entraining in concrete due to the presence of some organic substance in the aggregate. The substance was not detected by standard testing of the aggregates, but it was possible to isolate a nonvolatile brown crystalline solid, which possessed foaming properties when used in concrete mixtures. The air entrainment could amount to about 7 or 8 percent, but was unstable and not controllable. Aggregates of this type are said to occur frequently in Ontario, particularly in the area covered by the Laurentian shield.

Abnormal hydration of cement paste due to certain organic impurities of aggregates and sometimes causing serious decrease of strength and durability have been investigated and discussed for many years. For instance, E. G. Swenson and V. Chaly [1] characterized the following organic impurities as deleterious: soil, humus, wood particles, bark, coal, lignite, and other vegetable and animal products. The standard colorimetric test was, by the authors mentioned, regarded as effective in detection of harmful quantities of the substances, although the presence of coal or lignite could cause anomalous results.

Other authors have, according to recent research, questioned the validity of the colorimetric test.

F. S. Fulton [9] mentioned that much trouble with South African concrete structures had been traced to contamination of aggregates by sugar and that the colorimetric test had been useless.

T. Karttunen and T. Sneck [10] prepared a literature summary concerning the influence of humic sand on the strength of concrete. They found that when the quantity of organic impurities in sands is to be estimated by the colorimetric NaOH test, it is common practice not to take into account the chemical nature of the impurities. The test, therefore, is not considered reliable. Investigations of reported cases regarding the influence of humic compounds on durability suggest a marked decrease of durability now and then, whereas other authors have not observed any influence at all. Attempts to neutralize humic compounds in sands are reported in some cases to have improved the quality of the concrete, while other authors have not found any effects of such measures. Karttunen and Sneck suggested that the cement composition might be a factor influencing the effects of humic compounds. They mentioned that Forsén had observed humic substances to act as accelerators in the presence of alkalies.

Cement-Aggregate Bond Strength

Later in the present paper is mentioned a case where improvement of the bond between chert aggregate and cement paste in a concrete was believed to be due to mild alkali-aggregate reaction. K. M. Alexander [11] discussed the possibility of a similar type of reaction in a study of bond strength. In the case of an opaline aggregate, stronger bonds than with inert aggregates developed in 7 days (with low-alkali cement), whereas reactive volcanic rocks did not develop significantly better bond than inert aggregates in the same period. Incidentally, the bond strength was found to depend upon a considerable amount of other physical and mechanical factors. J. Farran [12] claimed that flint (from northern France) gave a bad bond strength. The same result was attained with mica minerals, whereas quartz performed better, and calcite and dolomite were found to adhere excellently to cement paste. The author suggested that some rearrangements of the lattice in the contact phase between aggregates and paste developed a particular type of "epitaxy". This phenomenon is generally known among metallurgists. According to C. Zwikker [13], "epitaxy" means that electrolytically deposited metals tend to adapt themselves to the lattice of the metal base, a result of the surface electrical field, and hence exhibit stresses. Farran suggested that such epitaxy would cause better adhesion in concrete with limestone or dolomite than with other rock types and also would cause pneumatically applied mortar to adhere better to limestone rocks and dolomites than to various other metamorphic and igneous rocks.

The Port Leixões Case

An extensive investigation of maritime works in Portugal, reported by M. Rocha, A. Coutinho, and A. Beja Neves [14] suggested certain chemical reactions between cement and aggregate to be a disintegrative factor. Nine harbors along the Atlantic coast were inspected, and the behavior of concrete and joint mortar in ashlar work was recorded. Chemical analyses were carried out for determining the alterations of cement paste. Rough estimates of the rock compositions of aggregates were also made, and the original mix compositions were calculated with a view to a comparison with records from manufacturing.

Rapid deterioration was found to occur in the north region only and had particularly progressed in the works of Port Leixões. All the cements applied were of national brands complying with the standard specification, but it appeared that the concrete showed durability and decay as well. Nor was the cement content found to be related to the deterioration, as in much of the bad concrete 300 or more kilos of cement per cubic meter had been used. Unsuitable grading of sand was mentioned as a possible contributory factor in causing poor workability of the fresh concrete and high permeability of the hardened concrete, thus facilitating soaking by sea water and concentration of salts by evaporation.

The severe deterioration was believed to be primarily due to certain chemical reactions between the cement and constituents of the aggregates, though under additional influence of the presence of sea water. This hypothesis was found sustained by the observation in Port Leixões, inasmuch as white exudations developed in joint mortar before it had been exposed to sea water. Likewise, some 90-ton blocks for a submarine breakwater showed cracking and exudations of a white substance through the cracks already during storage before placement in the water. However, a chemical analysis of samples of the exuded substance on some of the blocks that had been stored immersed in sea water for 1 yr proved the substance to contain only a minor amount of silica, and a negligible amount of alkalies, see table 1.

Also, in a jetty at Port de Peniche severely deteriorated blocks were found showing a pattern of deep, wide cracks. Chemical analyses of cement paste of such blocks proved the paste to be chemically unaltered and sound, and the appearance of the cracks suggested internal expansive reactions rather than superficial chemical attacks from sea water.

The fine aggregates in question consisted of about 85 percent of quartz, 14 percent of feldspar, and 1 percent of accessory mineral. Sometimes the feldspar was somewhat disintegrated. Coarse aggregates consisted of granite, occasionally with kaolinized feldspar.

TABLE 1. *Chemical analysis of white substance exuded through cracks in concrete blocks for a submarine breakwater in Port Leixões*

From [14]

Component	Percent
CaO	7.5
SiO_2	1.1
Al_2O_3	9.9
Fe_2O_3	3.0
MgO	27.2
SO_3	1.0
Loss at 105 °C	18.0
Loss at 500 °C	42.7
Loss on ignition	48.6

In the paper the deterioration seems ascribed to some reactivity of these rocks. The comprehensive analytical work presented seems in its entirety to offer further information about the action of sea water on readily attackable cement paste in porous mortars and concrete. Figures 1 and 2 are reproductions of two series of analyses, showing the compositions of the cement paste in deteriorated samples taken from different heights within the reach of tide and waves. The composition of the original cement is also tabulated.

The most pronounced alterations can be seen to have occurred in the range from about +0.50 to +3.00 m, where a marked decrease in CaO corresponds to an increase in MgO. Also an increase of the SO_3 content seems significant. Presumably the cause of the changes is leaching combined with precipitation of $Mg(OH)_2$ and possibly also of calciumaluminosulfate or maybe even gypsum, and the compilation of the data should be considered of interest to anyone dealing with such troublesome work as diagnosing disintegrated concrete.

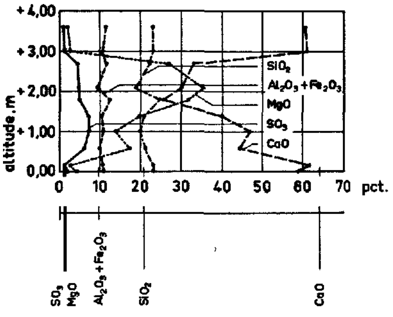


FIGURE 1. *Chemical analyses of cement in mortar, affected by sea water.*

Pier wall (mur d'arcades), Port Lexiões, Portugal. Alteration of cement comprises augmentation of MgO and SO_3 and a very marked decrease of CaO. From [14].

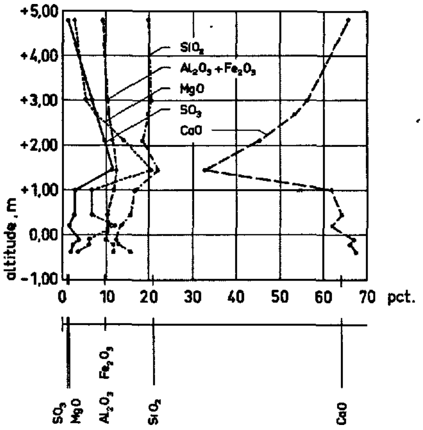


FIGURE 2. *Chemical analyses of cement in mortar, affected by sea water.*

Pier wall (mur continu), Port Leixões, Portugal. Alteration of cement comprises augmentation of MgO and a very marked decrease of CaO. From [14].

Alkali-Aggregate Reactions

Aggregate particles that contain or consist of silica in an amorphous or low-crystalline phase are, in concrete, attacked by alkalies and lime from the liquid phase of the cement paste. Rocks and minerals in aggregates of this type are designated alkali-reactive, and the processes are designated alkali-aggregate reactions. By these reactions is produced a solid, viscous, or liquid silica gel, holding alkali ions and calcium ions in the random network of silica molecules. By imbibition of water, the gel may either swell almost without limit, being therefore referred to as being of the *unlimited-swelling type*, or may not swell to any appreciable extent, therefore being referred to as the *limited-swelling type*.

The reactions may affect the mechanical properties of the concrete to a remarkable extent. The partial or total alteration to a gel of certain mineral components of aggregate particles represents a weakening of the physical structure of the particles and therefore also of the strength of any cross section of a concrete member containing such particles. If only limited-swelling gel is produced by the reactions, this weakening may be the only direct effect on the qualities of the concrete.

If unlimited-swell gel is produced, pressure develops, directed from the reacting particle against the ambient cement paste. This pressure may exceed the tensile strength of the mineral structure and the paste, consequently causing microfracture. Such disruption may be recognized and registered as expansion of a mortar bar, a concrete bar, or even of a structural member.

Homogeneously distributed microfracturing in a concrete mass may sometimes result in gross expansion of a structural member without any noticeable accompanying cracking, especially if reactions affect the fine fractions of aggregates only, and provided that expansions are not impeded by the static conditions.

Heterogeneously distributed microfracturing may result in overall cracking of the concrete mass, on surfaces frequently taking the character of the so-called *map-cracking* or *pattern-cracking*.

The swelling of gel in reacting aggregate particles situated in or close below a surface may cause a cone of adjacent, overlying material to fall off, forming what is commonly known as a *pop-out*. Swelling gel deposited in a void in the cement paste may likewise develop a pop-out if situated sufficiently near a surface. Exudations of gel through pores and cracks to jelly-like beads on surfaces are, besides pop-outs and cracks, a frequent evidence that alkali-aggregate reactions are going on in the concrete.

Affected structures should be considered less resistant to deleterious effects of concurrent weathering. Reacting or reacted siliceous aggregate particles that are more or less impregnated by gel may be less resistant to freezing and thawing than before reacting. Cracking may facilitate the corrosion of reinforcement and the leaching of the cement paste, and as a whole may gradually open the internal concrete structure to damaging agencies of ambient air, ground, and water. Secondary cracking, corroded reinforcement, and exudations of calcium carbonate therefore are common additional evidences of deterioration where alkali-aggregate reactions take place in exposed structures.

Reported Deterioration and Researches

U.S.A. Structural failures attributed to alkali-aggregate reaction have been reported from several states in the United States since about 1940; see figure 3, here reproduced from [15]. It is seen that after about 20 yr of research, alkali-aggregate reactions have been found to be a severe cause of deterioration over wide areas. In some of the cases freezing and thawing as well as sea-water attack is out of question, and it has been rather easy to assert that another preponderant agency of deterioration was in action. The map also shows that some major rivers apparently are "roads of infection". It seems natural that alkali-reactive minerals and rocks eroded from soils or rock formations along the upper reaches may instigate troubles along the river sides. It may, however, also be a factor that the structures in question comprise important constructions such as dams and bridges which probably will be under steady surveillance and maintenance so that deterioration is observed at an early age. Besides, an accelerating factor may be that many structures along rivers may partially or totally be exposed to a rather humid atmosphere.

Several papers by American colleagues, long since classics in any bibliography on alkali-aggregate reactions, are to be attended to later on. It appears that numerous research organizations, laboratories, and individuals have been involved in nearly every phase of the problem. Although it is impossible to mention all of them in the present paper, it seems, however, proper to list the following: State Division of Highways, California; Bureau of Reclamation, Denver, Colorado; Portland Cement Association, Chicago; Army Corps of Engineers, Waterway Experiment Station, Vicksburg; Highway Research Board, National Academy of Sciences; National Research Council; the ASTM, Committee C–9, and many others.

In recent years also, cement-aggregate reactions other than those entirely dependent on the alkalies of the cement seem to have been recognized and to have been the subject of investigation. This will be considered later.

Canada. Two cases of deterioration involving alkali-aggregate reactions have been investigated by the Division of Building Research, National Research Council, Ottawa; see, e.g., E. G. Swenson [16].

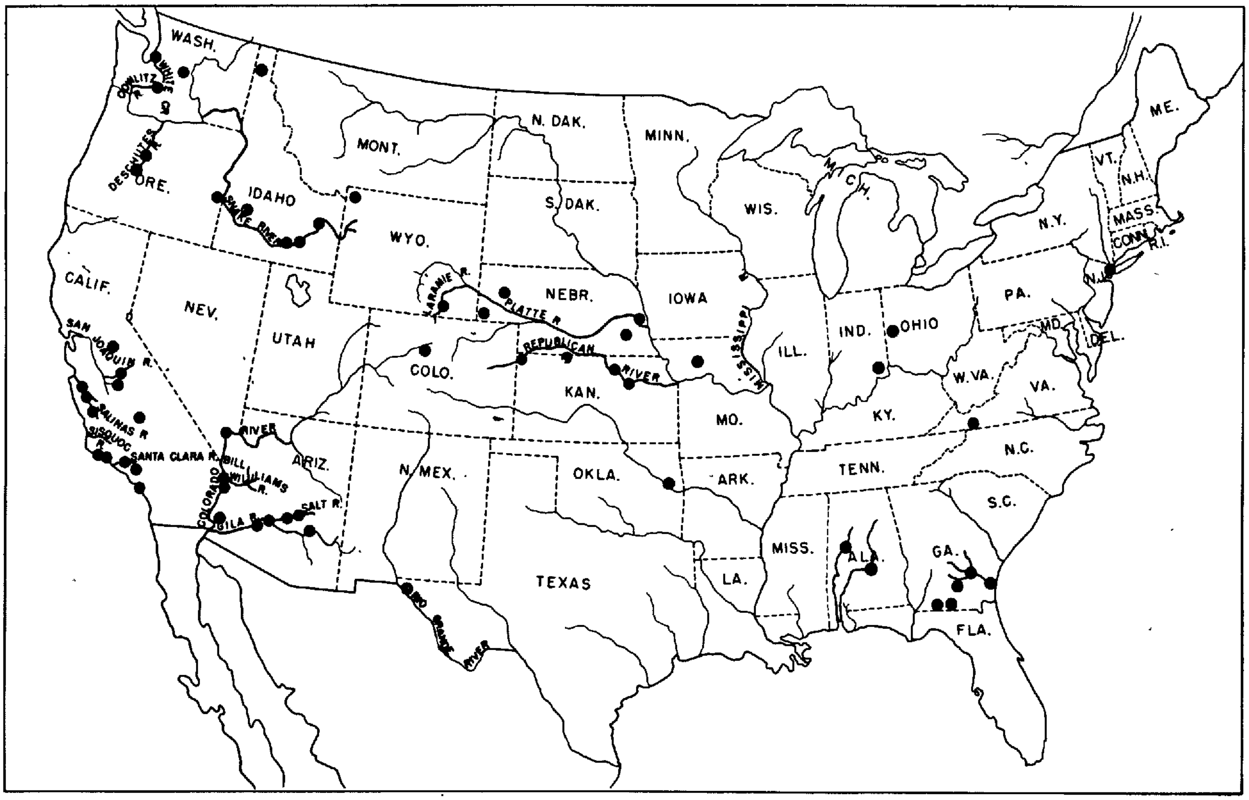


FIGURE 3. *Location of structures in the United States known to be affected by, and rivers known to carry, deleteriously reactive aggregate* [15].

One case comprised two sections of the deck of a bridge in eastern Canada. Troubles caused by expansion of the concrete had already been met with about 7 yr after its construction, and at the time of investigation at 25 yr, deterioration was everywhere severe. In one section almost half of the coarse aggregates were found to be phyllites, chalcedonic sandstones, and other alkali-reactive aggregates, and the concrete showed extensive evidence of alkali-aggregate reaction. In the other section only minor amounts of alkali-reactive materials (less than 1 percent) occurred in the aggregates, and evidences of alkali-aggregate reactions were not found in the concrete in spite of its considerable expansion. It was concluded that a not fully understood type of cement-aggregate reaction was going on.

The other case was encountered at Kingston, Ontario, and comprised several structures, all made with the only available local coarse aggregate which was a dolomitic limestone. Investigations showed that the troubles were due to some chemical reactions between the cement and the limestone and that the alkalies of the cement were a factor. The reactions were, however, not of the ordinary alkali-aggregate type, as siliceous mineral components were absent.

Ethiopia. S. W. Stephensen has [17] reported an alleged case of alkali-aggregate reaction in Deri Dawa, Ethiopia. A two-story, reinforced-concrete framework was found cracked to a much higher extent than could be explained by lacking reinforcement, etc. No deterioration occurred until 4 yr later, but damage then followed quickly. The aggregate was reported to contain alkali-reactive minerals. Similar deterioration was found in some other structures in the same town.

India. Cases of deterioration of field concrete due to alkali-aggregate reactions have so far not come to the knowledge of the writers. Research undertaken in recent years, e.g., by P. J. Jagus and N. S. Bawa [18] and H. L. Uppal and M. Singh [19], has shown that alkali-reactive aggregates of different types are not uncommon in India.

It is, according to B. S. Sathya Narayanswami [20], considered important at this early stage of development of the utilization of concrete to become aware of the risk of deleterious reactions that might occur in future construction. Research seems predominantly conducted by the Concrete Association of India, the Central Road Research Institute, and the National Institute of Engineering, Mysore.

Australia. No cases of structural deterioration due to alkali-aggregate reactions have so far come to the knowledge of the writers. However, in the field of research, extensive work has been carried out by A. R. Alderman, A. J. Gaskin, R. H. Jones, and H. E. Vivian, with regard to both studies of the mechanism and testing methods, in particular the mortar-bar test. Several papers have been issued by the Council for Scientific and Industrial Research since 1947 [21].

Great Britain. So far no cases of structural failure have been reported from Great Britain where damage has been due to alkali-aggregate reactions. However, the Building Research Station has carried out an extensive work now described by F. E. Jones [22, 23] and by F. E. Jones and R. D. Tarleton [24, 25, 26] in order to investigate English cement and aggregates and possible interactions of any combinations of these in mortar and cements. In short it has been found that, as a rule, cements high in alkalies are applied and that alkali-reactive aggregates do occur and often are used in some parts of England but may generally be considered not to be "expansively reactive". The research carried out also provides extensive critical data on different testing methods and procedures elaborated upon for recommended testing. Some details of the contents in the papers mentioned are to be referred to later on. Additional investigations carried out by F. E. Jones on Danish reactive aggregates, etc., are reported in [27] and a survey of durability of British reinforced concrete in buildings is given in [28].

Holland. A rather peculiar case of cracking phenomena in concrete is attributed by the late R. A. J. Bosschardt [29] to alkali-aggregate reactions. At a factory for precast concrete products some slabs were found to develop cracking when they, after some weeks' curing with subsequent drying in the factory, were exposed as stock to moist weather in free air. The cracks appeared as starlike formations on the surfaces of the slabs and were explained as developed over expanding aggregate particles. The aggregates originated from the Rhine and were found to contain siliceous rocks such as cherts and flint.

Sweden. Investigations conducted by a representative Committee on Deleterious Aggregates in Concrete have shown that deterioration of the concrete in a dam in northern Sweden was at least partly due to alkali-aggregate reactions and that some carboniferous phyllites were the alkali-reactive part of the aggregates. Quartzites and sparagmites from other aggregate sources were also found to be alkali-reactive by some of the ordinary accepted tests.

These rocks, however, in some respects did not at all show evidences of the general type of alkali-aggregate reaction. Physical factors have been suggested to play a part, but also the possibility of other cement-aggregate reactions is under investigation.

Norway. Investigations, undertaken by the Norwegian Geologic Research Institute, concerning alkali-reactivity of certain phyllites in Norwegian aggregates are said to be in progress. Results have so far not been reported.

Denmark. The first observation of field failure attributed to alkali-aggregate reactions is referred to by P. Nerenst [30]. Thereupon, in 1952–53, preliminary investigations were undertaken by the Danish National Institute of Building Research with the assistance of the F. L. Smidth Laboratories under the direction of Th. Heilmann. The work carried out demonstrated that alkali-aggregate reactions occurred in concrete all over the country. Cases of severe and rapid deterioration were found at different places, chiefly however, in coastal areas. Ordinary aggregates containing types of flint were found to be highly alkali-reactive.

These preliminary results in 1954 led to the establishment of a representative Danish Committee on Alkali Reactions in Concrete by the Danish National Institute of Building Research and the Academy of Technical Sciences (ATV).

Detection of Alkali-Aggregate Reactions

It is well known that Th. E. Stanton in 1940 for the first time stated that chemical reactions between alkalies from the cement and siliceous rocks in the aggregates were a cause of deterioration of concrete structures.

The first matter thoroughly investigated concerned a pavement in Bradley, California, which in 1938, only a little more than a year after its construction, failed by excessive expansion and cracking. Severe and rapid deterioration of concrete structures had, however, for several years been a problem in California. A bridge built in 1919–20 had shown marked deterioration already in 1923. The concrete walls of a school built in 1931 were severely cracked in 1934. This was also the case with seawalls, etc. C. W. Beardsley, C. M. Wakeman, and P. S. Wright mention [31] that a viaduct in Los Angeles constructed in 1931 was in distress in 1940. With regard to many of these structures, preliminary and rather intensive investigations had been made. Stanton says [32] about the results thereof:

"In general, the number of opinions expressed equaled the number of reports made. The causes of failure advanced by the different investigators were: the sand; unsound cement; excess water; extreme variations in temperature; faulty curing; faulty concrete design; variable coefficient of expansion between different parts (including reinforcing steel); electrolysis; overstressing of under-design; and rusting of anchor bolts, reinforcing steel, iron pipes, washers, etc."

Stanton also says that:

"The solution of the problem was complicated by the fact that, although without exception cracking of the nature described was noted only when local fine aggregate had been used, there were numerous instances where the apparently same local aggregate performed in an entirely normal and satisfactory manner."

In the Bradley pavement two different local sands had been used in alternate sections, and distress occurred in the sections only with one of the sands (Oro Fino). However, in structures made with low-alkali cements this specific sand had caused no deterioration. The sand was found to consist of 90–95 percent of chemically inactive rock types and minerals, comprising granites, feldspars, etc., and about 5–10 percent of siliceous rocks comprising opaline limestones, opaline shales, and some cherts reported to contain opal and chalcedony.

By means of mortar-bar experiments and petrographic examinations it was proved that the siliceous rocks were the reactive components, and by further studies, including elaboration of testing methods, Stanton very soon arrived at the following conclusions:

1. Deterioration was due to some siliceous rocks in the aggregate reacting with alkalies in the cement. Alkali-silica gel was produced by the reaction.
2. The mortar-bar test made it possible to reproduce the reactions and their mechanical disruptive effects—expansion and cracking—and thus to predict the behavior of the particular aggregates.
3. Decisive factors for the reactions were:

Alkali-content of the cement. No deleterious reactions would occur with cements low in alkalies, i.e., less than 0.60 percent of equivalent Na_2O.

The amount of reactive materials in the aggregate. Expansion would increase with increasing amounts of reactive material up to a certain point (the "pessimum" proportion) whereafter expansion would decrease with still increasing amounts.

The particle size of reactive materials in the aggregates. Fine grinding of a reactive material would cause decrease of expansion. However, coarse reactive aggregates might also cause little or no expansion compared with the same material in the sand fractions.

Surveys of Structural Failures

Intensive investigations of structures and aggregates were carried out all over the United States of America during the years following Stanton's inventory studies [33]. Table 2 represents a rough summary of a survey compiled by F. E. Jones [22] from different American reports.

The deterioration referred to in this table comprised map-cracking, spalling, off-setting, etc., and in some cases even considerable structural expansions have been measured.

Aggregates from the structures were also investigated and the following common rock types found to be suspiciously reactive: opaline and chalcedonic cherts and shales, siliceous limestones and dolomites, andesites, rhyolites, glassy acid volcanics, and phyllites. In many cases mortar-bar tests with these aggregates and high-alkali cements duplicated the cracking and expansion in the structures.

TABLE 2. *Survey of U.S.A. structures reported deteriorated because of alkali-aggregate reactions*

The table is prepared on the basis of [22]

Structures		Year of construction	Severe deterioration noted	Age
Type	State			
				yr
Dams	Calif.	1938	1940	2
	Calif.	1937–1938	1940–1941	2–4
	Oreg.	1932	1943	11
	Idaho	1925	1940	15
	Ark., Nebr.	------------	------------	8
Bridges	Kans.	1934	1942	8
Roads	Calif.[a]	1927	1932	5
	Wash.	1930–1931	1939	8–9
	Nebr.	1931	1932	1
	Calif.	1932	1941	9
Buildings	Va.	1912	1922, 1929	10, 17
	Kans.	1938	1940, 1942	2, 4
	Idaho	1934	1942	8

[a] From [33].

In all of the cases where the alkali content of the cement is reported, the content is stated to have been higher than 0.6 percent, and in some of them up to 1.44 percent, equivalent Na_2O, while a considerable number of comparable structures, cast with low-alkali cements, are reported to have shown excellent durability.

Recently a renewed, extensive survey of structural failures in the United States Army has been reported by the Highway Research Board [31] on the basis of a questionnaire which was circulated in 1953. A concentration of the data is given in table 3. Reported cases both of alkali-aggregate reaction and cement-aggregate reaction are represented, and also represented are the ages of the structures in question at which deterioration has been discernible. It should be mentioned that negative replies were obtained from 19 States as to the occurrence of field failures due to the men-

TABLE 3. *Survey of structural failures due to alkali-aggregate reactions and unidentified cement-aggregate reactions in the U.S.A.*

Compiled from a survey reported in [31] by the Highway Research Board

State	Records of occurring		Age of structure
	Alkali-aggregate reactions	Cement-aggregate reactions	
			yr
Ala.	+	+	4–8
Ariz.	+		2
Calif.	+		1–5
Fla.	+		–
Ga.	+		6
Idaho	+	+	2
Ind.		+	12–20
Kans.		+	7
Ky.		+	–
Miss.	?	?	3–10
Nebr.	+	+	5
N.J.		+	4
Oreg.	+	+	5–10
R.I.		?	1
Tenn.		?	5
Utah	+	+	2
Va.	+		–

tioned agencies. Twelve States apparently did not reply to the questionnaire.

Very interesting statements appear in the comments to this survey. B. Tremper [34] mentions that as regards the western United States, three States reported failures ascribed to the cement-aggregate reaction. In Arizona, the alkali content of the cements has been limited to below 0.60 percent for the last 10 yrs, and troubles have so far not been encountered in structures from this period. In California, low-alkali cements are mentioned as the sole corrective measure since about 1943. Although in many cases highly reactive aggregates have been used as judged from comprehensive field surveys, results have been quite satisfactory.

C. W. Beardsley, C. M. Wakeman, and P. S. Wright [35] report for the Los Angeles area: Many examples of alkali-aggregate reaction occur. Restrictions for the use of potentially reactive aggregates and low-alkali cements are generally prescribed.

W. E. Gibson [36] reports for the central United States: Only two States that replied observed alkali-aggregate reaction, and two others observed cement-aggregate reactions. These reactions were particularly severe in Kimball, Nebraska, and in St. Francis, Kansas, in some cases where low-alkali cements were used. (See further in a later section.)

D. O. Woolf [37] reports for the eastern United States: Besides clear-cut cases of alkali-aggregate reaction, failures due to unsound cement, i.e., extremely high magnesia content, are also mentioned. With reactive aggregates the specification of low-alkali cement has proved a promising safeguard. However, joint cracking is observed in recent structures prepared with low-alkali cement.

In Denmark extensive field inspections have been reported from 1914, 1924 to 1927, 1952, 1954, and 1955, respectively. The first three concerned concrete of coastal structures. The fourth is a general survey inspection, a preparation for a detailed investigation.

The 1914 survey was carried out by A. Poulsen, covering concrete in coastal and maritime structures on the west coast of Jutland dating back to 1870. Much concrete made with ordinary portland cement was found to disintegrate rapidly after showing white exudations and cracking. The deterioration was attributed to the action of the sulfates in the sea water. Poulsen in 1910 invented a pozzolanic cement manufactured by grinding a Danish diatomaceous earth, "moler", together with ordinary portland cement.

On the basis of big-scale field experience and laboratory experimental work, Poulsen claimed that the use of pozzolanic cements increased the durability by inhibiting the suggested deleterious effect of calcium aluminosulfate.

In the years 1924 to 1927 a renewed field inspection of the West Coast concrete was carried out by I. K. Danø, who found wide variations of durability for both concrete with ordinary portland cement and concrete with moler cement. As a rule, however, ordinary portland cement was found to be less satisfactory. With the use of this cement, map-cracking and white exudations were typical evidences of deterioration, while surface scaling and early abrasion was attributed to the moler cement.

Both investigations are dealt with by G. M. Idorn [38] together with a renewed inspection carried out by this author in 1952. The latter inspection also covered a great deal of the concrete recorded in the two previous investigations, proving for it a considerable lifetime, i.e., a good durability. As a whole, this survey inspection corroborated the results of the previous investigations. However, the moler cement could not, to such an extent as earlier stated, be considered a sufficient protective measure against the rapid disintegration that was found to be a common phenomenon. Further studies confirmed the suggestion that the primary cause of deterioration was alkali-aggregate reaction. It appears from these studies that A. Poulsen in 1910, by inventing the pozzolanic moler cement, actually did find a a corrective measure against alkali-aggregate reactions, though he believed he was fighting the action of sulfates.

A survey inspection of Danish structures was carried out by G. M. Idorn in 1954–55 on behalf of the Danish Committee on Alkali Reactions in Concrete. The condition of some 400 structures was briefly surveyed and recorded during visits, and they were classified in six groups ranging from quite undamaged (0) to progressed, overall deterioration (5). Also the typical evidences of distress (cracking, pop-outs, gel exudations, etc.), if any, were recorded. The inspections included a good many railroad over- and under-passes; bridges across rivers, sounds, and inlets; harbor structures, etc., while pavements and buildings were little represented.

Table 4 summarizes the recorded behavior of the structures, except as to ages of the concrete. However, since few structures were older than about 25 yr, a considerable number were quite new, and as a few old ones had been subject to a general repair prior to the inspection, the classification seems to indicate that durability of structures of the categories concerned might be a prolific field of research.

Table 4. *Classification of conditions of selected concrete structures in Denmark based on survey inspections 1954–1955*

Extent of deterioration	Classification	
	Number	Percent
0	112	26
1	130	30
2	62	15
3	61	14
4	48	11
5	18	4
Total	431	100

The recorded structural behavior was also plotted against the exposure conditions, very roughly characterized as:

1. Inland location, not directly exposed to water (e.g., railroad over- and underpasses, etc.)
2. Inland location, exposed to water (e.g., bridges across streams, etc.)
3. Coastal conditions, exposed to sea water (e.g., bridges across sounds and inlets, piers, groins, etc.)

Table 5. *Classification of conditions of 431 selected concrete structures in Denmark based on survey inspections 1954–1955*

Behavior of structure plotted against exposure conditions, divided in the categories: Inland, no water; Inland, water; Coastal

Extent of deterioration	Classification			Total [a]
	Inland, no water	Inland water	Coastal	
	%	%	%	%
0	23	35	17	26
1	31	37	7	30
2	15	12	20	15
3	14	12	17	14
4	14	3	17	11
5	3	1	22	4
Total	100	100	100	100
Distribution according to classification	62	28	10	100

[a] From table 4.

Table 5 shows the analysis of the data. It appears that the two inland exposures seem to be of like severity (maybe because the climate in Denmark is rather humid), and they seem to be of less severity than coastal exposures. This difference may, however, not necessarily be due to the action of salts delivering alkalies or sulfates to the disintegrative reactions. The mere physical factors might also cause a more rapid weathering at the coast than in the inland areas.

Field evidences of disintegration leading to detailed studies undertaken in 1955 have been discussed by G. M. Idorn [39] and elsewhere. A list of the structures dealt with is presented in table 6. According to this survey and those previously presented, it appears that alkali-aggregate reactions may often result in an extremely progessive deterioration which necessitates extensive repairs much earlier than required by ordinary weathering.

The Danish surveys tend to show that coastal exposure may be an accelerating factor by weathering as such and by alkali-aggregate reactions in particular. These problems seem to be a promising field for further research.

At the Danish inspections, the observer was puzzled by the fact that amongst a number of quite unaffected concrete structures examples of typical and severe deterioration, obviously involving alkali-aggregate reactions, often were located within the same area. In this connection it seems relevant to point out that it was then a well-known fact that the alkali content of Danish cements varied comparatively little, and also that a difference in exposure, in cases where deteriorated as well as sound structures were mingled, was improbable.

Table 6. *Survey of structures dealt with by the detailed investigation 1955, conducted by the Danish Committee on Alkali Reactions in Concrete*

See G. M. Idorn [39]

Structure		Exposure		Year of construction	Severe deterioration recorded	Age
Type	Part of country	Coastal	Inland			
Bridge	Jutland	X		1939	1951	12
Do	do	X		1938	1951	13
Underpass	do		X	1942	1954	12
Do	do		X	1920	1954	[a] (34)
Pier	Funen	X		About 1930	1954	[a] 24
Sea wall	Sealand	X		1943-1947	1952	9-5
Building	Jutland		X	1947	1954	7
Do	Sealand		X	1951	1954	3
Basement	do		X	1953	1954	1
Do	do		X	1951	1954	[b] (3)

[a] Probably severely affected much earlier.

[b] Alkali-aggregate reactions not proved a decisive factor.

The American and the Danish surveys seem to disagree in that in the United States of America deleterious alkali-aggregate reactions in pavements are common and in buildings not unusual, while in Denmark pavements have so far not been reported in distress and buildings only exceptionally.

The mortar-bar test (see below) is widely accepted as an accelerated imitation of the reactions that may be expected in a concrete structure. However, the above-reported rates of deterioration seem to show that the test in many cases is not much accelerated. In other words, considering it a scale-model test, the time factor may be nearly without reduction.

Examination, Testing, and Inspection Methods

From the above it appears that the necessity of *examination* of cements and aggregates, of *testing* of these materials combined in mortars or concrete, and of a comparative *inspection* of concrete structures and concrete samples was early experienced. Table 7 is an attempt to outline the different categories of research gradually applied to these problems, introduced, elaborated, or abandoned during the first 10–15 yrs of work.

The division chosen is intended to reflect the principle that firstly it should be examined whether the components of concrete—cement, water, aggregates—contain the reactants of alkali-aggregate reactions. In this way a potential, chemically based reactivity could be either confirmed or found not existing. Every possible mechanical effect, however, representing the deleteriousness of the reactions, could not be predicted from the chemical conditions alone. Testing of potentially reactive materials, therefore, suggested concurrent measurements of mechanical effects, i.e., expansion resulting from internal disruption of mortar and

TABLE 7. *Survey of methods applied in research on alkali-aggregate reactions*

Category of treatment	Object of treatment	Method	Specification
Examination	Cement	Determination of alkali-content	Ordinary chemical analysis or flame-photometry.
	Water	Determination of alkali-content	Chemical analysis.
	Aggregates	Description of geological characteristics.	
		Petrographic analysis	Determination of rock composition and of mineral composition of rocks.
		Float separation with heavy liquids	Possible aid for petrographic analysis.
		Fluorescence examination	Recording of presence of opaline silica.
		Etching test	Recording of chemical reactivity to alkalies.
		Gel pat test	Recording of chemical reactivity to alkalies (development of alkali-silica gel).
		Quick-chemical test	Recording of chemical reactivity to alkalies (determination of solubility in alkaline solution).
Testing	Mortar (cement plus fine aggregates plus water).	Mortar-bar test	Determination of mechanical effects of reactions.
		Measurements of: Expansion Tensile strength Modulus of elasticity	
		Observation of: Warping Cracking Gel exudations Internal disruption	
	Concrete (cement plus fine and coarse aggregates plus water).	Concrete-bar test	Determination of mechanical effects of reactions.
		Measurements of: Expansion Tensile strength Modulus of elasticity	
		Observation of: Warping Cracking Pop-outs Gel-exudations Internal structural disruption	Investigation of origin of mechanical effects.
		Glass-jar test	Recording of enlargements.
Inspection	Concrete structures	Field inspection	Recording of field service, symptoms of deterioration, cost of maintenance, etc.
		Supplementary laboratory investigation	Examination of concrete samples.

concrete. The application of these tests for prediction of structural behavior subsequently necessitated an ascertainment of reliable model laws, which have been studied by comparative inspections and investigations of concrete structures and test specimens. Laboratory examination, chiefly by petrographic methods, has proved to be a necessary part of such studies.

Cements

An alkali content of 0.6 percent of equivalent Na_2O was at an early stage accepted in the United States of America as an upper limit for cement used in combination with reactive aggregates. Cements considered to meet this requirement were generally termed low-alkali cement.

The fixation of the above-mentioned critical limit naturally focused attention on the previously neglected subject of the alkali contents of different brands of cement. It appeared that not only was there a wide variation in alkali contents between different brands but also that the same brand might exhibit great variations during a longer period. Examples from the literature are given below.

Analyses of about 60 American cements are given by A. D. Conrow [40]. The absolute maximum found was about 1.2 percent equivalent Na_2O and the minimum about 0.2 percent.

A. R. Alderman, A. J. Gaskin, R. H. Jones, and H. E. Vivian in 1947 [41] reported alkali contents of 16 different Australian cements showing a range from 0.12 percent to 1.09 percent equivalent Na_2O. These determinations were part of preparatory investigations on alkali-aggregate reactions.

F. E. Jones [23] compiled data on British cement from routine analyses carried out since 1928 by the Building Research Station. These data have been utilized for the graphs, figure 4, for the brands A, B, C, D (ordinary portland cement) and E, F, G, H (rapid-hardening portland cement).

The cumulative-frequency polygons for the distribution of the equivalent Na_2O (percent) are shown, and from these, as regards the brands A, B, and E, may be read:

1. The percent of analyses falling below 0.6 percent of equivalent Na_2O.
2. The mean value of equivalent Na_2O percent.
3. The approximate standard deviation.

E. V. Meyer [42] gives the determinations of alkali content in ordinary portland cement produced by one of the factories in Denmark during the years 1949–1956. A treatment of these data shows that the mean for the whole period was 0.70 percent of equivalent Na_2O, with a slight decreasing tendency for the last few years. The standard deviation is found to be 0.09 percent of equivalent Na_2O and the coefficient of variation is 13 percent. It also appears that about 15 percent of the production has had a monthly mean less than 0.60 percent of equivalent Na_2O. It is mentioned too that variations are smaller over more limited periods. Eight tests on one day are for instance reported to give a mean of 0.70 percent of equivalent Na_2O, with a standard deviation of 0.02 to 0.04 percent of equivalent Na_2O and a coefficient of variation of about 5 percent.

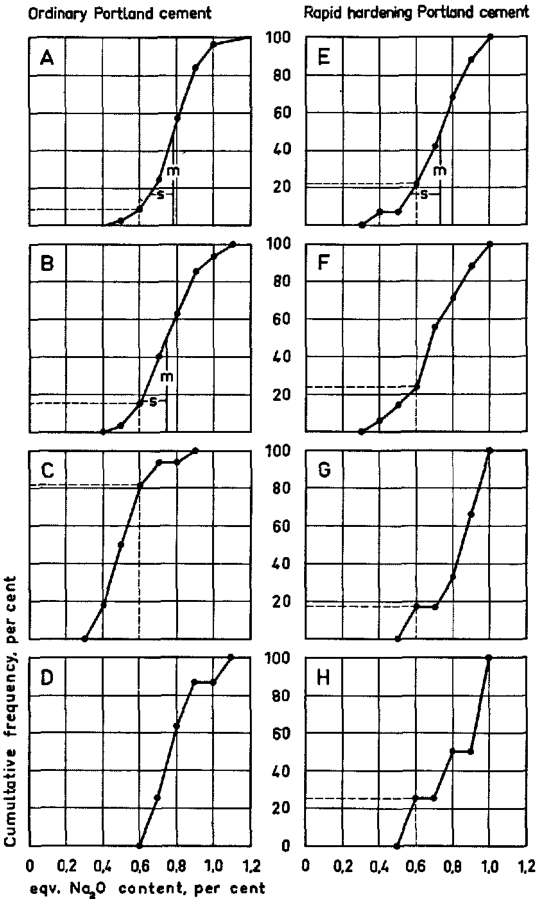


FIGURE 4. *Cumulative frequency polygons of equivalent* Na_2O *content of 8 British cements.*

The graphs are compiled from F. E. Jones [23].

For the 96 Danish analyses, results of monthly equivalent Na_2O contents during the years 1949–56, the cumulated frequency curve is outlined on probability paper in figure 5.

P. J. Jagus and N. S. Bawa [18] reported analyses of alkalies in 26 Indian cements. As the examination was preparatory, only one sample from each cement factory was analyzed. Results showed a minimum and maximum total equivalent Na_2O of 0.15 and 0.99 percent, respectively. Eleven out of 26 cements had total equivalent Na_2O higher than 0.60 percent.

From other countries the alkali contents of national brands of cement have been reported only exceptionally, and most of the available data ought to be supplemented before a critical treatment seems motivated.

The above examples suggest that many cements have average alkali contents considerably above the critical limit of 0.6 percent of equivalent Na_2O. The great variations observed within the same brand suggest the suspicion that some cements, considered to be of the low-alkali type, occasionally may have alkali contents above the critical limit. This view was put forward by W. C. Hanna in 1948 during the discussion of a paper by Stanton [43].

By suitable arrangements it may be possible for the producer or consumer of low-alkali cement to control the alkali content in such a way that the critical value of 0.6 percent is not exceeded. However, the validity of the 0.6-percent limit as a general safeguard could be questioned on the basis of observations made by various authors. Th. E. Stanton already in 1943 [44] mentioned that "in any adversely reactive combination there is a markedly greater expansion of a 1:2 mortar than a 1:3 and usually a greater expansion of a 1:1 than a 1:2. However, with some highly

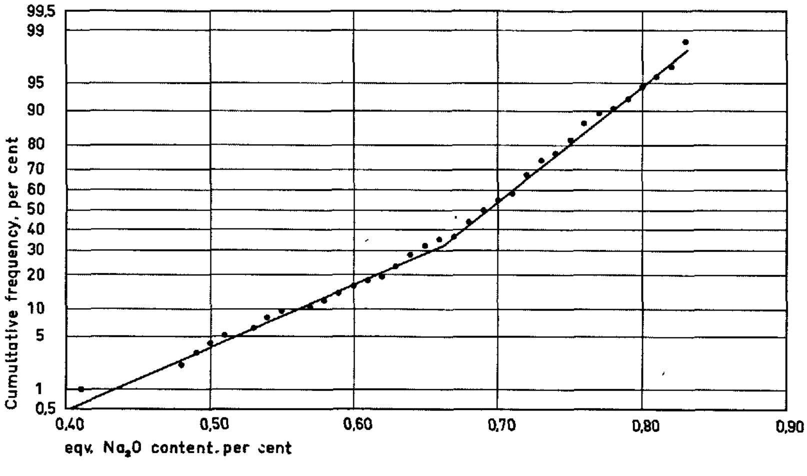


FIGURE 5. *Fractile diagram of 96 monthly averages of equivalent* Na_2O *content of Danish portland cement for the years 1949–56.*

The averages are plotted on normal probability paper, and it will be observed that they exhibit a marked deviation from the normal distribution.

reactive combinations the ultimate expansion appears greater with the 1:2 than the 1:1 mix". It is also mentioned that a low-alkali cement may "become quite active in mortars of equal proportions of cement and reactive fine aggregate". Consequently Stanton draws the conclusion not to use cement contents higher than 1:2 for routine testing.

Also D. McConnell, R. C. Mielenz, W. Y. Holland, and K. T. Greene [45] emphasize both the alkali content of the cement and the cement content of the concrete or mortar. They state, however, that "so far no deterioration of field concrete due to cement-aggregate reactions is known to have occurred where low-alkali cements were used".

A. D. Conrow, in the discussion of a paper by W. C. Hanna [46] in 1947, reported destructive expansion in mortar bars prepared with cements as low as 0.09 percent of equivalent Na_2O, and accordingly questioned the validity of low-alkali cements as a preventive measure.

D. O. Woolf in 1948 [47] mentions that "apparently the controlling factor is not the total amount of alkali in the cement, but is the availability of the alkali for the chemical reaction". The *concept of availability is discussed in the present* paper in the section on mechanism of reaction.

In 1952 D. O. Woolf [48] reported the analysis of a number of mortar-bar tests made with crushed opal as the reactive component of aggregates and cements ranging from 0.22 percent to 0.99 percent of equivalent Na_2O. This investigation proved that: "Low-alkali cement used with aggregate containing a small amount of reactive material may result in objectionable expansion, while the same cement with aggregate containing a relatively large amount of reactive material may have little if any reaction". Appreciable expansion was found with cements of as little as 0.22 percent of equivalent Na_2O, when sufficently small amounts of reactive aggregates were used. Woolf mentions that similar results were reported in 1951 by C. E. S. Davis [49].

Ervin Poulsen [50] presented a statistical analysis of Woolf's test results. From this paper the mapping of expansion levels corresponding to different combinations of the percent of reactive materials in aggregate and the percent of equivalent Na_2O in cement is reproduced in figure 6. Attention should be paid to the fact that the iso-expansion curves in figure 6 are the outcome of fitting an analytical expression to Woolf's data, and the fitting is not altogether satisfactory. It will be observed that the magnitude of the expansion depends not only on the absolute value of percent equivalent Na_2O, but also on the ratio between percent equivalent Na_2O and percent reactive materials.

In view of the observations reviewed above, it may be concluded that a lowering of the limit for the alkali content of low-alkali cements will reduce the risk of dangerous expansion when reactive materials are used.

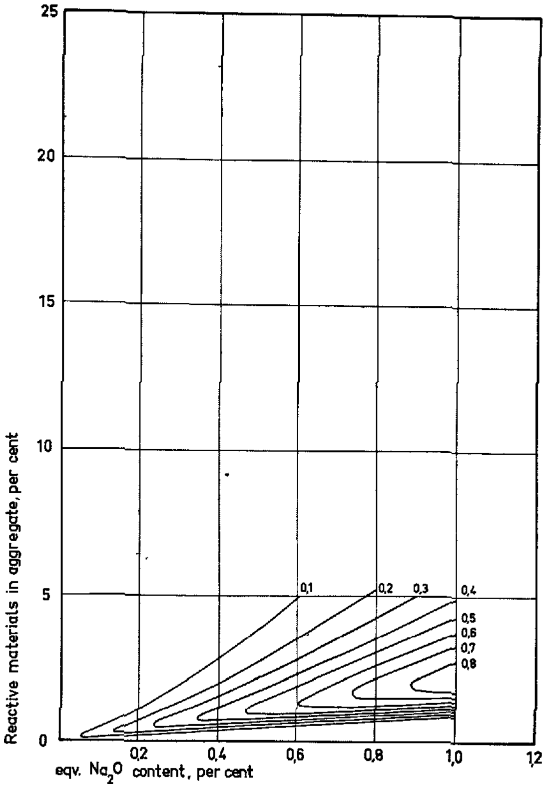


FIGURE 6. *Expansion of mortar-bars in relation to reactive material and alkali content of cement (data from D. O. Woolf).*

Each solid curve shows combinations of reactive material and alkali which give equal expansion measured in percent. Reproduced from [50].

It should be added that in cases where alkalies may be contained in the mixing water, the aggregate *or the surroundings of the concrete, special* precautions, besides the use of low-alkali cements, are called for.

Water

Only limited attention has originally been paid to the fact that mixing water in the case of sea water or alkaline ground water could be a possible supplementary source of alkalies in concrete.

O. J. Porter mentioned in 1942 [33] the possibility of reactions with low-alkali cements, "where the soil, water, or aggregate contains water-soluble salts of sodium or potassium". In the same paper L. C. Meder reported that addition of slight amounts of NaCl to mortar bars cast with reactive aggregates and low-alkali cements caused excessive expansions.

R. F. Blanks and H. S. Meissner in 1946 [51] and H. E. Vivian in 1950 [52] reported mortar-bar studies proving that addition of alkalies—as NaOH—might cause an increase of expansion dependent, however, on the amount of reactive aggregate, etc., i.e., in aggreement with a statement of D. O. Woolf [48] as regards the alkali-opal ratio *being a controlling factor.*

G. M. Idorn [53] tabulated the potential supply of alkalies to concrete by using as mixing water either sea water, brackish water, or salt ground water (of recorded Danish types). The calculations appear in table 8.

So far such results have not caused any prescriptions of analyses of mixing water, nor of avoidance of contaminated water, nor special care in placing concrete in alkali soils or sea water.

Table 8. *Supply to concrete of alkalies from mixing water, when different water types and different w/c ratios are used.*

Type of water	Sodium milligrams/liter	Supply to alkalies in cement Na_2O, percent by weight		
		w/c=0.5	w/c=0.7	w/c=1.0
Sea water	12,000	0.8	1.1	1.6
Brackish water	4,000	0.3	0.4	0.5
Salt ground water	250-1,500	max. 0.15	max. 0.15	max. 0.20

Aggregates

Earlier, it is mentioned that Stanton in 1940 found opal, opaline shale, and some cherts to be alkali-reactive. Already in 1940 the alkali reactivity of some andesitic rocks was set forth by H. S. Meissner [54] and by B. Tremper [55].

These identifications of the alkali-reactive constituents of the aggregates suggested that the actual reactive substances were those consisting of silica in either an amorphous (opal, volcanic glass) or a low-crystalline phase (cherts).

Opal, which may be characterized as a solidified, water-containing gel, occurs in various manners. It may be found as a distinct mineral, e.g., in basaltic lava or in shale, etc., or as a coating substance on pebbles of sedimentary rock deposits. It is then hard, though it is porous and of a low specific weight. It also occurs as an interstitial material in limestone formations, sometimes together with flint and cherts. In these conditions opal may form part of extremely light, porous rocks which over widespread areas are common in moraines and in beach and river deposits.

Volcanic glass may be considered an undercooled melt which, in order to be alkali reactive, must be rich in silica and may accordingly occur as interstitial substance in acid volcanic rocks. Also basic lavas may be found alkali reactive, when partly crystallized, because the remaining glass will be more acid than original glass prior to crystallization. Thus basalts also may sometimes be potentially alkali reactive, and reactivity has recently been confirmed by some tests according to the quick chemical method carried out in Denmark on basalts from Greenland. Both opal and glass are metastable under normal geological conditions compared with the regularly crystallized phase of silica in quartz. Therefore, incipient crystallization—devitrification—may be found in glasses. Likewise, during geological ages crystallization tends to proceed in opaline silica in limestone, etc., thus developing cryptocrystalline phases appearing as flint or chalcedony. Similar tendencies of crystallization may be met with in opal occurring in vacuoles or veins in basalts.

This classification of alkali-reactive minerals is believed to cover the majority of reactive silica materials in concrete aggregates, and only some exceptions need particular comments.

The minerals tridymite and cristobalite, which are crystalline modifications of silica, have been reported alkali reactive, see, e.g., F. E. Jones [22]. T. M. Kelly, L. Schumann, and F. B. Hornibrook [56] reported expansion of mortar bars where only tridymite (from silica bricks) could be the reactive component. However, both minerals are rare and of little importance in concrete aggregates, but they are of interest in the system of silica minerals, both being metastable phases of crystalline silica at ordinary temperatures. Their reactivity may therefore be regarded as related to the metastability.

Sandstones and quartzites have been claimed reactive by some authors. In sandstones the binding matrix may be amorphous or cryptocrystalline silica and therefore reactive. Orthoquartzites are quartzose sandstones with sedimentary megacrystalline quartz as the binding matrix. Metaquartzites originate from metamorphosis of such sandstones and also contain only megacrystalline quartz. Reactivity of these rocks is not a priori to be expected.

B. Mather, however, in 1951 [57] reported exudations of gel in highly fractured quartzite pebbles in deteriorated concrete, and L. S. Brown in 1955 [58] mentioned a quartzitelike aggregate, reported as strained quartz, to have caused distress.

P. J. Jagus and N. S. Bawa [18] reported significant expansions of mortar bars with quartzite as the reactive constituent of aggregate.

Having discussed quartzite and strained quartz, we are approaching the perfect order of crystallization of silica represented by pure, megacrystalline quartz which, however, is considered quite inert in the general sense of alkali reactivity and is, therefore, used as blind material in standard tests of suspicious aggregates.

Regarding an artificial silica material, we have in Pyrex-brand glass an undercooled, rather pure silica melt, i.e., an amorphous phase which inevitably is alkali reactive and therefore is commonly used as a standard reactive material for the purpose of comparison.

A survey of the described family of silica minerals is given in table 9. Also mentioned in this table are those common rocks that contain silica and may occur in concrete aggregates, causing these to be alkali reactive. Fortunately, it has repeatedly been found that the widespread minerals of the silicate group are not reactive. This fact and the inertness of quartz places all the igneous and most of the metamorphic rock types among the alkali-inactive aggregates.

TABLE 9. *Silica minerals and rocks*

Reactive substance	Physical structure	Chemical formula	Rock types
Opal	Amorphous	$SiO_2 \cdot nH_2O$	Concretions in basalts and other lavas. Opaline limestones. Opaline cherts. Opaline shales. Different coated rocks.
Silica glass	Amorphous	SiO_2 [a]	Rhyolitic, andesitic and other acid lavas and their tuffs, containing glass matrix. Synthetic glass (Pyrex glass).
Chalcedony	Crypto- to micro-crystalline.	SiO_2	Siliceous limestones. Flints. Cherts. Sandstones, with chalcedonic matrix.
Cristobalite tridymite.	Crystalline	SiO_2	Ceramics.
Quartz [b]	Crystalline	SiO_2	Quartzites. Sands. Sandstones. Igneous and metamorphic, acid rocks.

[a] With minor contaminations of other oxides etc.
[b] Reactive in some quartzites and when strained, microfractured, etc.

A possible, though questionable, exception is one or more of the mica minerals. R. W. Carlson in a contribution to a discussion of [33] mentioned that 5 percent of muscovite mica in a sand caused excessive expansion of mortar bars with high-alkali cement. This quite unique statement may possibly be supported by some evidences of reactivity of phyllites which can be characterized as a metamorphic, mica-rich, argillaceous shale.

R. J. Holden already in 1935 attributed deterioration at Buck Hydroelectric Plant, Virginia, to a chemical reaction between cement and phyllites in the coarse aggregate. The reaction was later found to be alkali-aggregate reaction and the reactive mineral constituent was assumed to be a "hydromica", see, e.g., D. McConnell, R. C. Mielenz, W. Y. Holland, and K. T. Greene [45]. E. G. Swenson [16] referred to a case of alkali-aggregate reaction in a bridge in Canada and mentioned phyllites as the reactive rock in coarse aggregate, without discussing the reactivity of the components of the phyllite.

Recent observations pertaining to cases of deterioration in Sweden (see T. Hagerman [59], indicate deleterious reactivity of phyllites also without so far having disclosed the reactive constituents. In the opinion of the writers these may be microcrystalline quartz present in the rock just as well as hydromica. Likewise, the above case mentioned by Carlson may possibly cover processes other than the alkali-aggregate reaction, maybe even purely physical processes. Hence, alkali reactivity probably still should be considered limited to the different phases of silica minerals with regular megascopic crystallized quartz as the only safe exception.

Some minerals of the zeolite and montmorillonite groups are capable of releasing alkalies by cation exchange. Zeolites may be found in vacuoles in basaltic rocks (which also may contain some volcanic glass and opal), and montmorillonite occurring in some clays may be met with as a contamination of aggregates. Actual examples of deleterious alkali-aggregate reaction dependent on alkalies from these sources are not known to the writers.

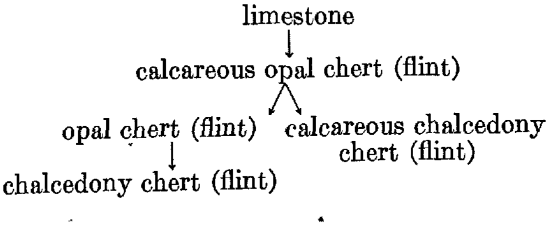
There seem to be widely different opinions with regard to the mineralogical composition and structure of flint and chert types and with regard to the cause of alkali reactivity of chalcedony. J. D. H. Donnay [60] found, by means of specific-weight determinations, that chalcedony is a low modification of quartz containing interstitial opal. B. Mather [61, 62] basing his investigation on optical measurements, agreed with this conclusion and suggested that the potential reactivity of chalcedony is due to the content of interstitial opal. In agreement with these authors is ASTM designation C 294–56 T, which states: "It (chalcedony) is now generally believed to be composed of a submicroscopic mixture of fibrous quartz with a smaller but variable amount of opal".

H. G. Midgley opposed the above hypothesis on the composition of chalcedony. By petrography, X-ray photogrammetry, and measurements of specific surface it was found that chalcedony consists of a network of microcrystalline quartz with numerous micropores, but does not contain any opal. C. R. Pelto [64] mentions that this "quartz-with-holes theory" may explain many unsolved problems regarding chalcedony, but not, for instance, the solubility and the chemical reactivity of the mineral.

In Denmark, the problems concerning the composition, structure, and properties of flint have been taken into consideration during the investigations conducted by the Danish Committee on Alkali Reactions in Concrete. Research work on the geology and petrography of flint has been carried out by A. Berthelsen [65], H. Gry and B. Søndergaard [66], and F. E. Jones and H. G. Midgley [27]. X-ray photogrammetry and diffractometry on Danish flint types were carried out by A. Tovborg Jensen, C. J. Wøhlk, K. Drenck, and E. Krogh Andersen [67].

The designation "flint" is used in Denmark for all types of sedimentary silica concretions that originate from cretaceous limestone and chalk formations. This flint is believed to have been formed when water percolation caused a concentration of the silica from sponge spicules, etc., deposited together with the limestone.

According to the petrographic descriptions the Danish flint consists mainly of calcite, opal, and chalcedony. The morphology and the relative frequency of the minerals suggest the following phases of development according to H. Gry and B. Søndergaard [66]:



all of which frequently do occur in Danish concrete aggregates.

The X-ray diffractometry investigation proved that chalcedony consists of α-quartz with a particle size of about 400 A, and that the opal consists of cryptocrystalline silica which, among others, contains 2-d-cristobalite. This investigation also offered results of quantitative measurements of the mineral composition, showing that the white, porous flint types may consist of some 90 percent of cryptocrystalline silica while the dense flint types generally consist of α-quartz entirely.

It appears from the above description of alkali-reactive minerals and rocks that the determination of their presence or absence in a certain aggregate or in a potential source of aggregates sometimes might be a very easy problem to solve for anyone familiar with the geological conditions of the area concerned, i.e., the origin of the aggregates in question.

Provided such surveys, however, prove or indicate the presence of alkali-reactive constituents, actual investigations of the materials will be needed.

As the foremost among methods, petrographic examination must be mentioned. In the first place, the disclosure of alkali-aggregate reactions gradually has attached to this method of examination the importance it deserves also in many other aspects of concrete technology. In the second place, it is the only practical means by which a detailed qualitative and quantitative knowledge of the nature of any aggregate may be obtained, thus representing a basis for the evaluation of results of other tests, examinations, and researches. Detailed descriptions of procedures for petrographic examination have been given in numerous papers, see, e.g., B. Mather [61], R. C. Mielenz and L. P. Witte [68], R. C. Mielenz [31], ASTM Designation: C 295–54, and in addition hereto various mineralogical handbooks, etc. E. Poulsen has [69] described the development of a technique for the preparation of samples for microscopic examination and of statistical methods for evaluation of the results of the observations made.

Originally, petrographic methods were used as a means of finding those types of rocks that might be the source of reactivity in an aggregate causing distress in concrete. As previously mentioned, petrography has now been applied for both quantitative and qualitative determination of the contents of rocks and minerals known as alkali reactive, in unknown or suspected aggregate. A few other methods, merely concerning a qualitative estimation of alkali reactivity of either aggregate samples or selected rocks or minerals, have survived the first year's intensive research applying different, already known principles and methods also for the studies of alkali reactivity. These are the gel pat test and the quick chemical test.

Gel pat test

This test was first described by Th. E. Stanton, O. J. Porter, L. C. Meder, and A. Nicol [33] and has later been elaborated by F. E. Jones and R. D. Tarleton [70]. Suitable pieces of an aggregate under investigation are embedded in a circular pat of neat cement paste with a ground face of each particle exposed at the surface of the pat. After curing, the pat is immersed in an alkaline solution and the exposed faces of the particles examined at intervals for exudations of gel. On some reactive rocks gel may develop very rapidly, on others more slowly. By the procedure recommended and described in detail in [70], importance is attached to the first 7 days of observation. However, a period of 28 days' observation is mentioned as useful in order to obtain a safe distinction between inactive and reactive materials. In the same paper some tests with British aggregates are referred to, by which the pats were removed from the alkaline solution after a 28-day period and then further observed during moist curing. The only British aggregate that showed gel exudation after 28 days in an alkaline solution was said to be a sandstone.

Quick chemical test

Familiar to everyone in the concrete research field is the problem of the practical builder who sometimes has to prove a certain quality of materials in the moment he is to commence concreting, and rarely at such an early stage that for instance, the 1-yr mortar-bar test or even a 28-day gel pat test is applicable. These circumstances have early inspired researchers to develop rapid methods for testing suspected aggregates. In table 7 is mentioned the later abandoned fluorescence and etching tests besides petrographic examination. The latter of course is reliable, provided that a skilled and well-trained petrographer with adequate equipment is at hand. In that case even a detailed petrographic analysis may be a question of only a few hours' work, and the costs will be accordingly small. However, as records of petrographic analysis do not directly express the reactivity of the examined materials and as untested rocks still remain to be tested, the exigency of a really rapid test of the alkali reactivity of aggregates still exists. As such a test the rapid or quick chemical test has been elaborated.

In [71] R. C. Mielenz, K. T. Greene, and E. J. Benton report their development of a method for a rapid chemical test. Today, more than 12 yr later, this article includes the essentials of what has appeared concerning the quick chemical method.

The aggregate was treated with an alkaline solution in order to determine:

1. The effect of the solution upon the aggregate and
2. The effect of the aggregate upon the solution.

Various alkaline solutions have been used, and amongst them those containing sodium hydroxide only are generally most destructive.

Re 1: The destruction was measured as weight loss and as degree of etch on polished surfaces. Unfortunately, only little correlation between the two processes and the mortar-bar tests was found.

Re 2: The changes in the solution have been determined as concentration of substances in solution, particularly silica, and changes in alkalinity. Measurements of silica dissolved prove that dissolution of silica is not quite correlated to deleteriousness. The reduction in alkalinity of the solution, which is effected by different aggregates, is widely variable. It would appear that this reduction to some extent is a measure of the efficiency with which the potency of the solution is utilized during the reaction. Since the alkali content of portland cement rarely exceeds 1.50 percent, the efficiency with which these alkalies liberate silica from the aggregate probably is a significant control of deleteriousness. Seventy-one different aggregates were ground to the fixed fineness of 0.15–0.30 mm, and a powdered material was also used.

In short, the procedure may be described as follows: 25 g of the crushed material was weighed and poured into a container of stainless steel. Upon addition of a solution of 25 ml 1*N* NaOH the container was closed airtight and placed in a thermostat for 24 hr at a constant temperature of 80 °C (the tests were tripled). Afterwards the content was filtered and in the filtrate *Sc*=dissolved SiO_2 as mM/l and *Rc*=reduction in alkalinity as mM/l were measured.

Since the ratio of released silica to alkalinity reduction appears to be significant, the factor *Sc* is plotted against *Rc* in a system of coordinates. On this basis the innocuous materials can be separated from the deleterious materials by a line whose locus approximates $Sc/Rc=1$, see figure 7.

The authors' working hypothesis is that the deleterious materials are characterized by their more effective utilization of the alkalies in the liberation of silica than the innocuous materials. For that reason $Sc:Rc$ is less than 1 for innocuous materials and usually greater than 1 for deleterious materials. In order to certify the theory, comparisons with mortar-bar tests are made.

The mortar bars are produced by high-alkali cement (1.38 percent of equivalent alkali) and reactive aggregate combined in various proportions with crushed quartz.

The authors believe that the phenomenon of the pessimum proportion might represent the operation of two opposing characteristics of cement-aggregate reactions, namely: The tendency to increased expansion of the mortar as progressively more reactive particles are made available for attack, and the tendency to decrease in the silica-producing reaction as the available alkalies are more and more used up. From the continuation is quoted:

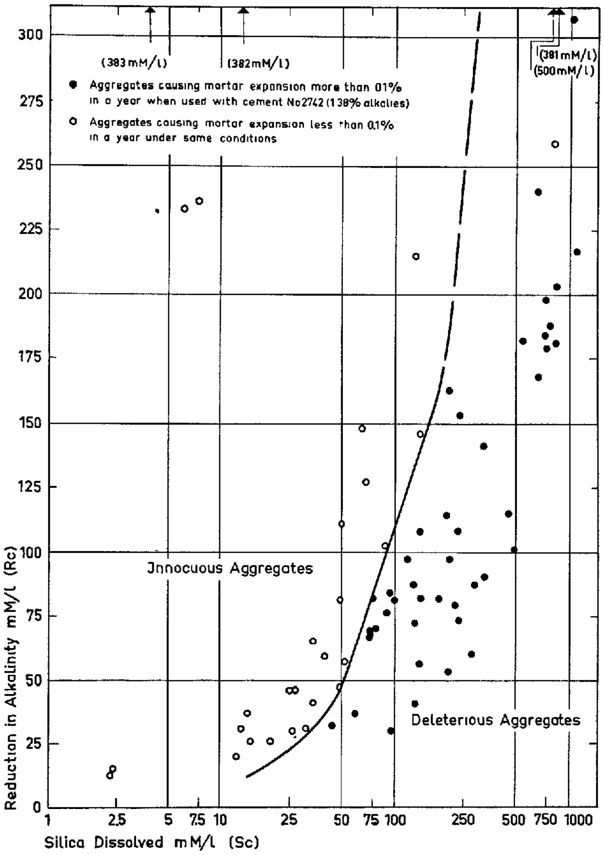


FIGURE 7. *Results of chemical test applied to American aggregates* [71].

"If these deductions are correct, then the pessimum proportion should be low for those aggregate materials which considerably reduce the alkalinity of the solution during the chemical test, and it should be large if the reduction in alkalinity is small".

By examining the 22 out of 71 aggregates the theories were found to be in accordance, see figure 8.

In [68] R. C. Mielenz and L. P. Witte summarize the five known test methods of identifying reactive concrete aggregates:

1. Petrographic analysis.
2. Quick chemical test.
3. Mortar-bar test.
4. Concrete-bar test.
5. Examination of concrete structures.

In the discussions the authors pointed out (see figure 9) that the areas for deleterious materials can be separated into two parts, of which the upper part includes materials which may be innocuous when constituting the entirety of an aggregate. The bordering line should be in accordance with a pessimum proportion of 20 percent.

Deleterious materials whose pessimum proportion is more than 20 percent (the lower part of the area) typically cause significant mortar-bar

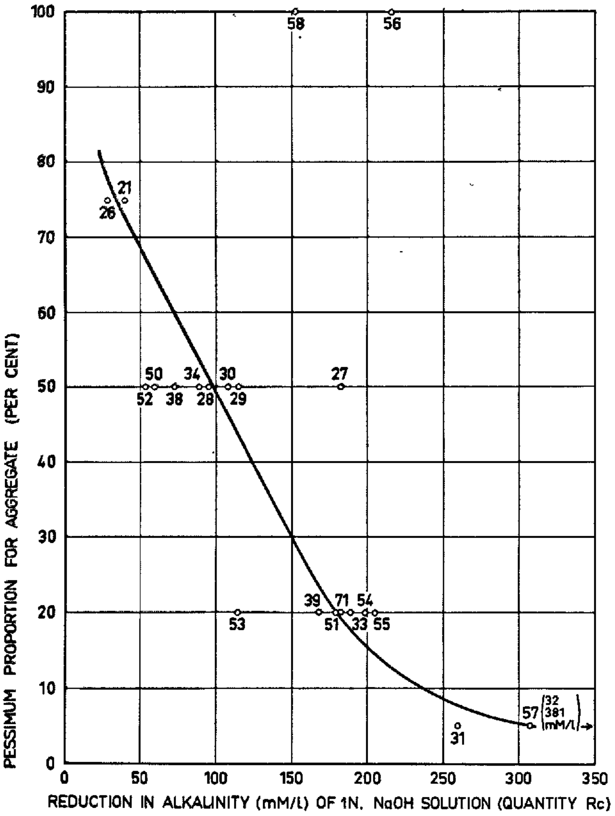


FIGURE 8. *Reduction in alkalinity in the chemical test as related to the pessimum proportion* [71].

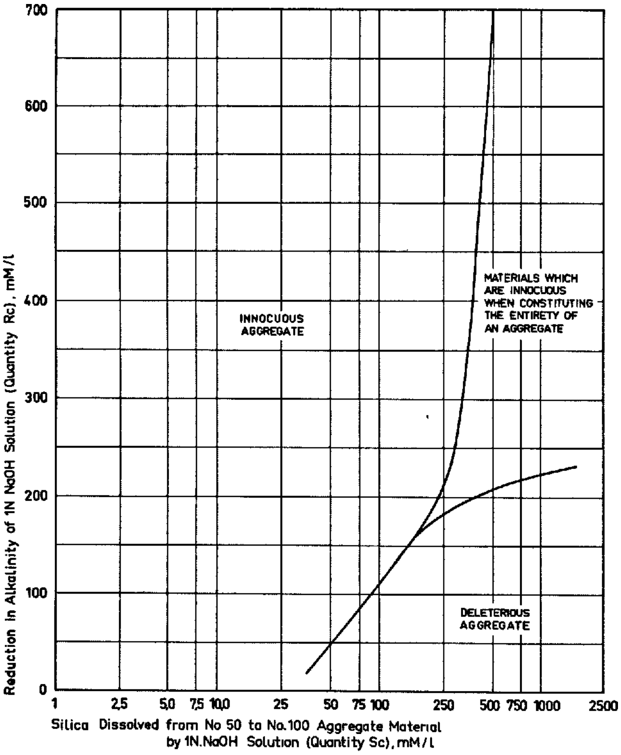


FIGURE 9. *Modified boundary lines* [68].

expansion when they constitute the entirety of the aggregate.

The quick chemical method has been worked out as a tentative standard method [72], ASTM Designation: C 289–57T, issued 1952, revised 1954 and 1957. The method is based on the work of R. C. Mielenz, K. T. Greene, and E. J. Benton [71], and the procedure is mainly the same as used by the authors.

The use of the *Rc* and *Sc* values for interpretation of the potential reactivity of aggregates is not, however, given in the standard, but in the specification for concrete aggregates, ASTM Designation: C 33–57 as:

1. If *Rc* exceeds 70 mM/liter the aggregate is considered potentially reactive if *Sc* is greater than *Rc*.
2. If *Rc* is less than 70 mM/liter the aggregate is considered potentially reactive if Sc is greater than $35+\frac{Rc}{2}$.

The boundary line between innocuous and deleterious aggregates is drawn in accordance herewith.

F. E. Jones and R. D. Tarleton [70] conclude that the rapid chemical test is a useful acceptance test. Thus, following the ASTM method of test, aggregates with *Sc*/*Rc* ratios of less than 1.5 can be accepted as safe. Aggregates with higher ratios will not necessarily be troublesome, and further examination by means of the expansion-bar test is required.

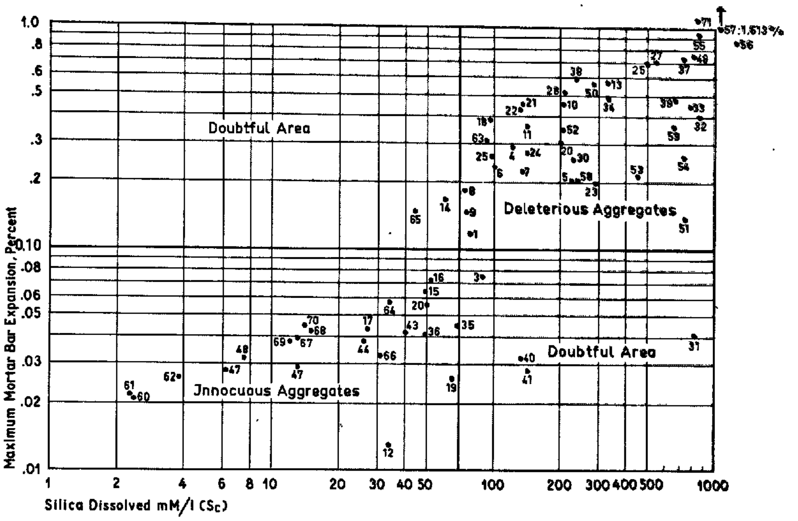
K. E. Haulund Christensen [73] thoroughly reviews the chemical test and, contrary to several other investigators who found the chemical test, mortar-bar test, and practice to be congruous, found inconsistency in 22 percent of the cases where Danish aggregates had been investigated. The author suggests a "Modified Chemical Test" which might improve the consistency. Thus the dividing curve is substituted by the line *Sc*=70 mM/liter, which makes the reactivity independent of the reduction in alkalinity. Consequently, the testing procedure becomes more simple, and the possibility of systematic errors is diminished. In figure 10, R. C. Mielenz's, K. T. Greene's, and E. J. Benton's data [71] are applied by plotting dissolved silica against expansion of mortar-bars.

R. C. Mielenz and E. J. Benton [74] carried out an analysis of the chemical test, ASTM Designation: C 289–54T, and arrive at the following conclusions:

1. The test is a useful means by which to evaluate potential deleterious reactivity of aggregates with cement alkalies. Its rapidity (2 days) is especially of credit.
2. The reproducibility of the method is acceptable.
3. When certain aggregate components, as, e.g., magnesium and iron carbonates (dolomite, magnesite, and siderite) or serpentine are present, the result may be a minor increase of the reduction in alkalinity and an increase of the concentration of

FIGURE 10. *"Modified chemical test."*

Dissolved silica (Sc) in relation to maximum mortar-bar expansion [73].



silica. A similar effect may be caused by calcite and may instigate an erroneous indication if the potential reactivity is marginal.

4. Because of this influence of certain minerals the evaluation of the chemical test should be supplemented by a petrographic analysis.

5. No changes in the standard procedure are suggested. It is recommended to investigate the influence of whether Rc is determined from the changes in the concentration of sodium and potassium or rather from the reduction of the titratable hydroxyl ion concentration.

B. Chaiken and W. J. Halstead [75] write upon the assumption that mortar-bar tests generally reflect the reaction in the actual structure. The mortar-bar tests were started before the ASTM standard method was developed. In these tests, bars with reactive aggregate in pessimum proportions seem not to have been included. Medium alkali cement (equivelent Na_2O percent 0.73–0.90) was used, and expansions <0.08 percent were considered indicative of nonreactive materials, expansions $\geqq 0.1$ percent as indicative of reactive aggregates, while expansions of 0.08 or 0.09 percent were regarded as questionable.

In the graphical presentation of the results of the chemical test an adjustment of the main boundary line is proposed. The deviation from the ASTM line might be explained by the fact that Mielenz and others obtained their results with a cement of a higher equivalent alkali content and used other limits for indication of reactive and doubtful aggregates.

The modified diagram is shown in figure 11. The diagram is divided into four parts. The area including the innocuous materials is separated by the line $Rc=60$ mM/liter, and the area including the deleterious materials is separated by a line similar to the boundary line shown in figure 9. On the bais of the available data, area B should be clearly indicative of safe aggregates. Chemical results appearing in this area should be reliable and no further tests are required. Materials falling in area A are generally safe but a petrographic analysis to disclose the possible presence of interfering minerals might be useful.

Area D contains reactive aggregates which are capable of producing excessive expansions in mortar bars. No further test would be necessary.

Aggregates in area C are classified as "highly reactive". The pessimum proportion is most

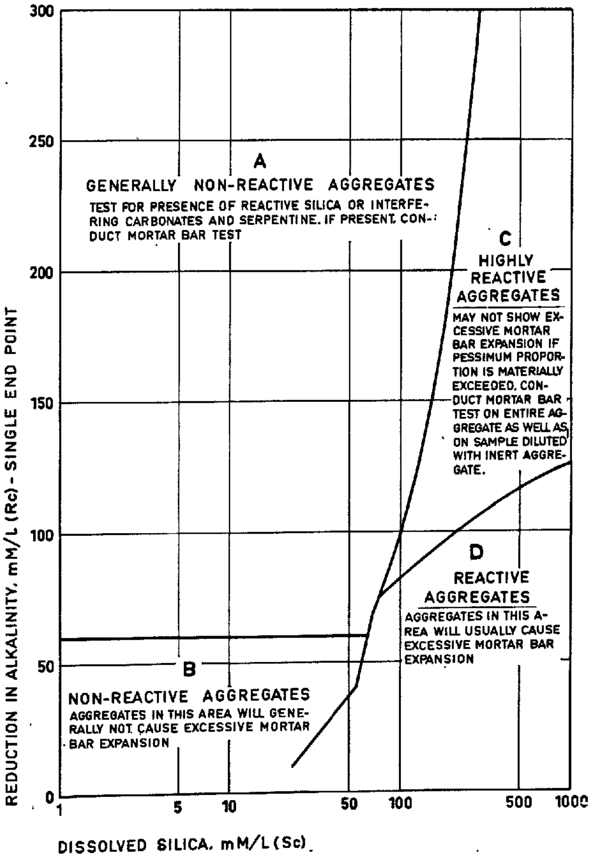


FIGURE 11. *Evaluation of results of chemical test for potential reactivity of aggregates* [75].

commonly about 20 percent for those situated in the lower parts of the area and less for those situated in the higher parts. Some are innocuous when constituting the entirety of the aggregate. If such aggregates are to be applied, mortar-bar tests with the aggregate in dilutions of 5, 10, 20, and greater percentages of inert materials as well as in its entirety, must be carried out solicitously.

In the summary of the above-mentioned paper the authors remark as follows:

"Nevertheless, the present criteria shown (in fig. 11) should broaden the usefulness of the quick chemical test and, in many cases eliminate the need for supplementing the chemical test with a long-term mortar-bar test program or tedious petrographic analysis."

The above review of literature on the quick chemical test leads to the conclusion that it is a helpful guide to determining the potential reactivity of aggregates. The test is of a qualitative character and does not indicate the size of the expansions that are to be expected in mortar bars or in structural concrete. The chemical test reveals chemical properties of an aggregate, viz., its ability for dissolving silica and reducing alkalinity.

It may be possible to apply the chemical test to a greater extent if the tracing of a relationship between the location of an aggregate in the *Sc*—*Rc* diagram and its pessimum proportion could be furthered.

Mortar-Bar Test

The methods of examination of concrete materials treated above are seen to enable a judgment of the potential risk that an aggregate will be alkali reactive. They even enable a judgment of whether an aggregate may be susceptible to intensive and rapid reaction or only to superficial and slow reaction. In other words, it is possible by means of the examination to characterize an aggregate as either "highly" or "slightly" reactive. This judgment may be based upon evaluation of petrographic data giving type, amount, and physical properties of reactive constituents in the aggregate, and also on solubility in alkaline solutions, clarified by means of the mentioned chemical tests. However, these approaches neither reflect the mechanism of alkali-aggregate reaction in mortar or concrete, nor imitate the mechanical effects which are the real evidence of the reaction and the cause of distress in structural concrete. Therefore, the necessity is obvious of testing combinations of cement, water, and susceptible aggregates as mortar and concrete.

This viewpoint is supported by regarding the generally applied terminology as characterization of alkali-reactive aggregates or of the reactions themselves. Reactive aggregates are generally differentiated as either "innocuous," "non-expansively reactive," etc., or "deleteriously reactive," "expansively reactive," etc. Similarly the reactions may be classified as either "harmless," "safe," "non-expansive," etc., or "harmful," "deleterious," "expansive." Most of these terms clearly refer to mechanical effects, either purely qualitative, as "deleterious," or quantitative, as "expansively reactive," and seem derived from observations and measurements of phenomena in the testing of mortar bars.

Development of the Method and Survey of Procedures

Before going into further discussion of the mortar-bar test method it seems appropriate to recall that the original investigation made by Stanton concerned the alkali reactivity of the sand fraction of the aggregates only (see [33]). Although reactivity of coarse aggregates was reported not much later than the findings by Stanton; see, e.g., R. F. Blanks in the discussion to [32] where chemical alteration of 6-in andesitic cobbles is mentioned, the already applied mortar-bar test proved advantageous in so many respects that coarse aggregates since then mostly have been tested and studied after crushing down to sand sizes. This practice has no doubt facilitated the examination and the tests, but this advantage seems in some cases to have been reduced by the disadvantage of a confused interpretation of the test results.

The very first experiments with mortar bars, referred to by Stanton [33], apparently only concerned observations of cracking and gel exudations. Expansion measurements have later on proved to be the probably most reliable means of standard testing of aggregate reactivity and a most valuable aid to studies of the reactions in research.

Furthermore, studies by means of mortar-bar tests have utilized measurements of tensile strength, bending strength and compressive strength; of dynamic modulus of elasticity; etc. Different procedures have been developed at different laboratories with respect to dimensions of bars, mix proportions and preparation methods, storage conditions concerning maintenance of suitable humidity and temperature, and various other technical details.

The more important discrepancies appear from the survey of procedures as given in table 10.

Design of Mortar-Bar Tests for Expansive Reactions

By now the percentage expansion of mortar-bar specimens after a suitable period of storage seems to be a generally accepted routine criterion on which the judgement of cement-aggregate combinations for concrete work is based. This scope of the mortar-bar test is aptly expressed in the first paragraph of ASTM Designation: C 227–52T:

"Scope

"1. This method of test is intended to determine the potential expansive alkali reactivity of cement-aggregate combinations by measuring the expansion developed by the combinations in mortar-bars under prescribed conditions of test".

A survey of elaborated procedures is given in table 10, and it appears that most procedures directly or indirectly fix such expansion-controlling factors

Table 10. *Survey of procedures of mortar-bar tests as applied by different authors*

	ASTM (USA) Standard	BRS (Great Britain) Research	CSIRO (Australia) Research	DNIBR/FLS (Denmark) Research
Dimensions (effective length).	1·1·10 in. (10 in.).	1·1·10 in. (10 in.).	1·1·11¼ (10 in.).	25·25·125 mm (105 mm).
Number of specimens per combination.	4 (2 from each of 2 batches).	at least 2 (a)	2	2
Grading of aggregate.	Fine: requirements of project specifications. Coarse: crushed and recombined in 5 fractions, sieve No. 4–No. 100 (20 percent each).	Crushed if necessary; recombined in 5 fractions, 3/16-in–100 (B.S. sieves) (19 percent each, washed and dried)+5 percent passing 100.	Natural gravel used without further treatment (or crushed if undesirable large particles contained). For crushed stones 18–52 B.S.S. mesh fraction used alone.	Fine: Sieved and recombined in 5 fractions 4⅛ mm mesh (20 percent each). Coarse: Crushed and recombined in 5 fractions as above.
Mix proportions.	Cement: Aggregate = 1:2.25; flow=105–120.	Cement: Aggregate=1:2 (a) w/c to obtain moist surface; min. alkali content in mix: 1.2 percent.	Cement: Aggregate=1:2 w/o=0.4–0.5 to obtain constant consistency.	Cement: Aggregate=1:2; flow=100 (w/c ~ 5).
Molding.	Double or (preferably) single molds, thinly covered with mineral oil and outside sealed with a paraffin mixture.	Single molds without grease or oil (b).	Double or single molds thinly covered with mineral oil.	18 bars in one mold greased with oil and outside sealed with paraffin wax (c).
Placing and compaction.	Placed in two layers and compacted with tamper of medium hard rubber or impregnated oak.	Placed in thin layers and hand tamped with a square-nosed rod.	Placed in three layers each being carefully pressed down.	Placed in two layers and compacted by means of a tamper.
Storage.	Bars vertical over water and at 37.8 °C±1.7. Readings at 23 °C±1.7. Inverted position after readings.	Bars vertical over water and at 20 °C±0.5. Inverted position after readings.	Bars vertical over water and at room temperature (yearly mean 58.5 °F=15 °C.	Bars vertical at 100 percent R.H. and at 38 °C. Inverted position after readings.
Records.	Expansion: Excessive when average exp.>0.05 at 3 months and average exp.>0.10 at 6 months. (d)	Expansion: Aggregate expansively reactive when exp.>0.05 percent in 6 months or exp.>0.1 percent in 12 months. Weight changes checked at readings. (e) Visual inspection of wet surfaces, gel deposits, cracks, etc.	Expansion: Dangerous when exp.>0.1 percent in 24 months. Visual inspection of damp spots, gel deposits, cracking, etc. (f)	Expansion: Potentially harmful when max. exp.>0.1 percent at 24 months. Visual inspection of damp spots, gel deposits, cracks, etc. (g)
References.	[72], p. 514-21, [44], [71], [82] and others.	[25], [70].	[21].	[73], [80], [81], [83].
Notes.	(d) The ASTM designation says nothing on criteria. The above information is found in [70].	(a) The specifications are partly from the "Recommended procedure for expansion bar test" [70], p. 44. (b) The amount of mortar mixed just filled molds. (e) In special series recordings bending strength were made, the expansion only recorded until the bending tests were effected.	(f) In special series the effect of expansion on tensile strength has been investigated.	(c) Since 1957 this method is considered obsolete, and only single molds are used. (g) After 24 months the flexural strength and compressive strength are determined.

as mix proportions and—to some extent—grading. Originally these factors appear to have been fixed at levels which were considered to be conducive to maximum expansion of mortar bars made of susceptible aggregates, when used in combination with cements of known alkali content. The expression "potential expansive alkali reactivity" in the passage quoted above may be a reflection of this view.

However, on the background of experiments made with systematically varied mix proportions and experiments measuring the influence of particle-size distribution, it may be questioned whether the rules adhered to by the mentioned procedures always allow us to observe the potential expansive alkali reactivity of the aggregates represented in the mortar bars.

The cement-aggregate ratio, for instance, is fixed at 0.5 or 0.44, whereas in concrete work this ratio may be lower. The influence of the cement-aggregate ratio on the expansion of mortar bars is not too well known, but it is imaginable that a lowering of this ratio in some cases may coincide with a movement towards pessimum proportion and thus induce a rise in expansion.

Most procedures fix the water-cement ratio indirectly in the neighborhood of 0.5 through requirements of flow. As mentioned later the water content of the cement paste is a factor influencing the mechanism of reaction, and as w/c in actual concrete work may be far from 0.5 one should be cautious in making general inferences based on a fixed water-cement ratio. Experimental work by H. E. Vivian [21] indicates that expansion of mortar bars (made with a uniform cement-aggregate ratio of 0.5) decreases rapidly when the water-cement ratio is lowered below the standard level of 0.4 to 0.5. It is, however, not known whether this result may be generalized as a law of nature.

From a practical point of view the most irrelevant requirement in the procedures is the rule that coarse aggregates should be crushed, sieved, and recombined to a linear grading curve. To this rule the ASTM standard has added:

"Note.—Coarse aggregate crushed to sand size may give accentuated expansion, owing to the increased surface exposed upon crushing the aggregate. Therefore, if coarse aggregate tested by this method produces an excessive amount of expansion, the material shall not be classed as objectionably reactive with alkali unless tests of concrete specimens confirm the findings of the tests of the mortar".

The note does not consider the opposite (and more perverse) possibility that coarse aggregates crushed down may cause small (safe) reaction, whereas concrete specimens with aggregates in the original particle size may produce dangerous expansion.

The standards for mortar-bar tests do not lay down rules as to which combinations of aggregates and types of cement are to be tested; the decision in this matter must be taken by the experimenter with a view to the purpose of the test series.

The purpose may be more or less specific. In section 4 of the ASTM standard cited previously it is stated that fine aggregates shall be tested in a grading meeting the specifications of the project.

In the design of such tests with the specific purpose of testing fine aggregates for a definite project, it should be remembered that deposits of gravel may exhibit great variations both as regards grading and the percentage of reactive aggregates within each fraction. Some information about this variability may be obtained by taking several independent samples from the deposit, sieving them, and making petrographic analyses fraction by fraction for each sample. As an example it should be mentioned that the percentage by weight of reactive materials (flint) in the fine aggregates from a Danish deposit varies between 12 percent and 30 percent (see B. Søndergaard [76]).

Under such conditions it may be very misleading to make all tests from one sample of fine aggregate, even if it is made representative of average conditions at the deposit by pooling a great many samples.

The variations in the deposit should be represented by a corresponding variation from bar to bar in the composition and grading of the aggregate. This recommendation springs from the fact that a slight change in the percentage of reactive materials may cause a move from safe to dangerous expansion, as illustrated in figure 12.

When the fine aggregate in a deposit is known to contain expansive reactive materials it may be questioned whether the mortar-bar tests for fine aggregates should be limited to the grading specified by the project.

From a survey of Danish deposits of gravel made by B. Søndergaard [76], it has turned out that on an average there is a very marked increase in percentage reactive aggregate with rising particle size of aggregates. By the mortar-bar test it may possibly be demonstrated in some cases that by excluding one or some fractions from the fine aggregates, the alkali reaction will take place without causing dangerous expansion.

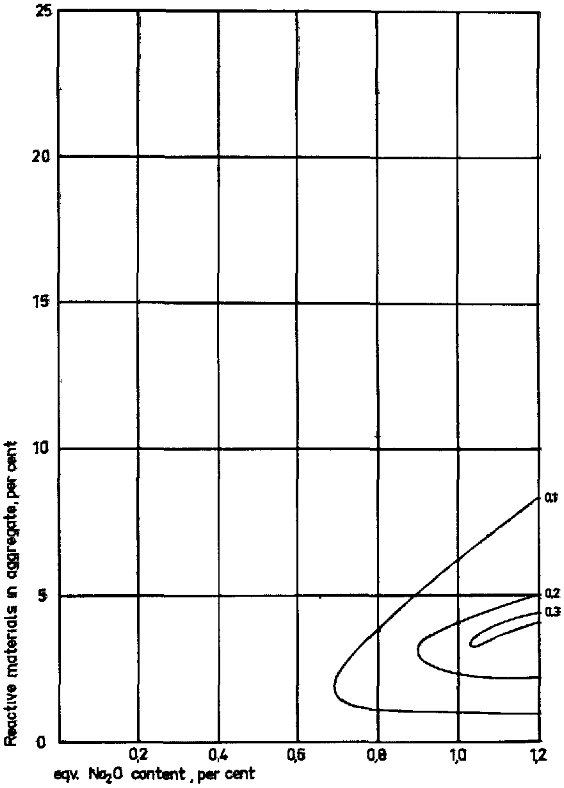


FIGURE 12a. *Expansion surfaces for five grain sizes of the same reactive aggregate (porous flint).*

The surfaces are indicated by iso-expansion curves, plotted as function of equivalent Na$_2$O, percent, and reactive materials in aggregate, percent.

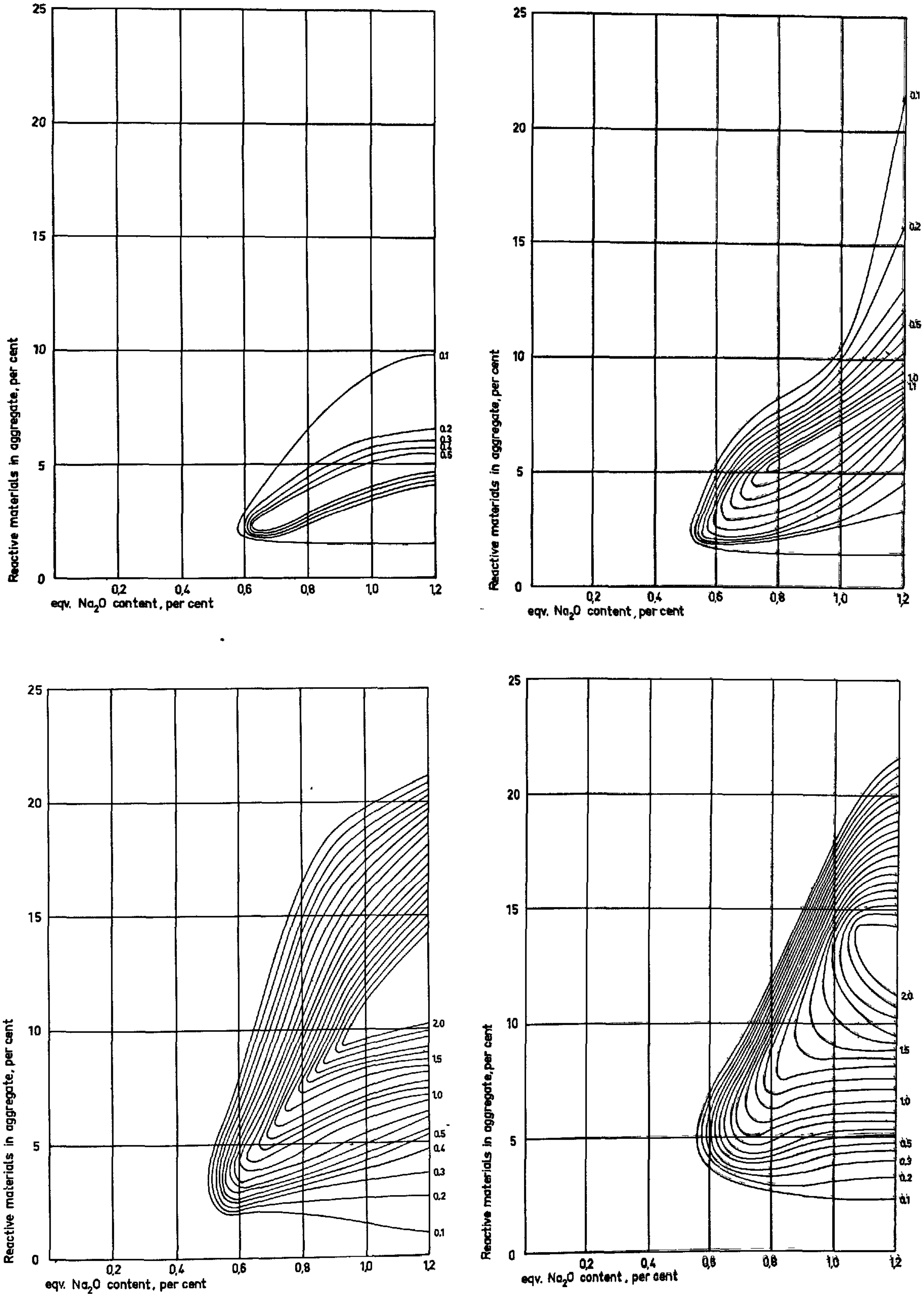
By changing the grading specifications in accordance with such results it may be possible to use fine aggregate from a deposit in the vicinity of an actual project, a solution which may be preferable from cost considerations. In this connection it should be remembered that specifications of grading may be varied within a very great range without damage to the concrete quality, if only the energy of compaction is changed correspondingly.

Evaluation of the Mortar-Bar Test

Contemplating the immense amount of data now available for studies of the still unsolved principal problems of alkali-aggregate reactions it may be profitable briefly to consider the possible findings which may result from the mortar-bar test. In table 11 the theoretical possibilities of the occurrences are presented and numbered.

TABLE 11. *Combinations of possible results of the mortar-bar test*

Aggregates classified according to petrographic or chemical analyses	Aggregates classified according to results of mortar-bar tests	
	Innocuous	Deleterious
Inactive	1	2
Reactive	3	4



FIGURES 12b,c,d,e. *Expansion surfaces for five grain sizes of the same reactive aggregate (porous flint).*
The surfaces are indicated by iso-expansion curves, plotted as function of equivalent Na$_2$O, percent, and reactive materials in aggregate, percent.

auch bei hohem

d. h. bei einem Gehalt von 25 % des reaktiven
Materials in den Zuschlägen ist ein treibender

The combinations No. 1 and No. 4 serve as background for the applicability of the test and do not need any particular direct comment. The combinations No. 2 and No. 3 represent complications in the sense of the test as a standardized method for testing susceptible aggregates. In table 12 are recorded possible explanations of their occurrences. Some of these explanations have been treated in the above discussion on the design of the mortar-bar test.

Although the first of the combinations in table 12 may be considered most exceptional, some attention should be paid to certain cement–aggregate reactions not definitely recognized as alkali-aggregate reactions. Expansive reactions in the cement paste alone most probably should not be considered possible, as long as the quality of the cement is subject to adequate supervision.

Table 12. *Complications to the mortar-bar test*

Combination	Explanation of occurrence
No. 2	1. Unidentified cement-aggregate reactions
	2. Expansive reactions in the cement paste only
	3. Unknown reason
No. 3	4. High porosity of cement paste
	5. High strength of cement paste
	6. Low alkali content of cement
	7. Few particles of reactive aggregate
	8. Non-expansively reactive rock types
	8.1 Highly porous
	8.2 Insignificantly attackable
	9. "Safe" reactions, i.e., production of sufficient amounts of non-swelling gels
	10. Insufficient duration of storage
	11. Unknown reasons

Combination No. 3, the occurrence of reactive aggregates that do not show expansion when tested according to standard procedures, is the most troublesome, because it may happen with any reactive aggregate and frequently does. Therefore, in practice it may lead to an acceptance of aggregates that should be avoided. Such test results may also cause confusion in research if not properly analyzed. The possible explanations listed as points 4–11 in table 12 comprise some of a physical character (4 and 5), some of a physico-chemical character (6–9), the time factor (10), and other possible but unknown reasons (11).

The influence of the mentioned physical factors, (4 and 5), has been investigated in particular by Vivian [77, 78], and by F. E. Jones [24, 25]. Vivian found that nonexpansive reactions in highly porous mortars may occur because of a sufficient space in the voids for the reacting particles and for the gel produced. However, a lack of sufficient free water seems also to be a possible influencing factor. The question of too few reactive particles (7) and the problem of whether reactions are "safe" or not is discussed elsewhere, and the possibility of meeting more or less readily reacting types of aggregates has been discussed earlier. Attention must be paid to the fact that very detailed analyses of results may be necessary in order to distinguish between "safe" reactions and "non-expansively reactive rock types". It is apparent that much work still remains to be done in this field.

The duration of storage is an important factor to consider when a known or a susceptible aggregate does not show any expansion in mortar bars. The practical application of the mortar-bar test inevitably suggests as limited a time as possible, i.e., as accelerated a test as feasible. Structural experience as well as many investigations by means of mortar and concrete bars suggest that expansion may develop with more or less delay under certain conditions, e.g., when low-alkali cements are used. Therefore, it is not possible as a rule to rely upon proportionality between time and expansion, and there may be a long time to wait for the first significant expansion to develop. Much work remains to be done before "no expansion" during a limited storage time may safely be interpreted as no expansion at all.

The influencing factor "unknown reason" (11) is mentioned, because in this field one may expect to meet so-far-undetected factors involved in the reactions and their mechanical effects.

Finally, the writers would emphasize that although the expansion proper has been given much attention as the quantitative result of the mortar-bar test, visual inspection of the appearance of the mortar bars should not be neglected. It appears from table 10 that recordings of damp spots, gel exudations, cracking, etc., are commonly prescribed as part of the useful observations which are obtainable from the mortar-bar test.

In T. E. Stanton's original paper [32] the formation of liquid drops accompanied by gel deposits was reported and suggested as indicative of reactivity.

A. R. Alderman, A. J. Gaskin, R. K. Jones, and H. E. Vivian [21] have reported detailed recordings of observed surface phenomena. The development of spots and random cracking has further been used as one of the means of studying the effect of alkali movement in hardened mortar. In this way the possibility of the migration of alkali through the mortar and the presence of the solution derived from excess mixing water as a continuous liquid medium throughout the mortar was clearly demonstrated.

Later J. K. McGowan and H. E. Vivian studied the correlation between crack development and expansion [79] and found a very good although not perfect correlation between expansion calculated from the mean number and width of cracks and expansion measured directly (correlation coefficient=0.92). It was shown that the expansion of mortar bars, which H. E. Vivian [21] observed to be preceded by the development of cracks and a loss of tensile strength, can be regarded as essentially due to the widening of cracks.

F. E. Jones and R. D. Tarleton [24] discussed the significance of various surface observations made on test bars, and arrived at the conclusion that such observations might be instructive as to reactivity of the aggregate.

As the writers also, in a more qualitative way, have outlined some applications of these principles [80, 81], it seems justified to consider the observations made by visual inspection an important part of the evaluation of the mortar-bar test. The more so, as these observations concern phenomena produced by or reflecting those internal processes, the result of which in the mortar-bar test is nominally measured as expansions.

Concrete-Bar Tests

As previously mentioned, Stanton first observed deterioration in the Bradley pavement in sections made with reactive sand. Later on, however, he also recognized a delayed expansion and cracking, where the reactive constituents were present in the coarse aggregates only (see [32], p. 110 of the discussion). Concurrent laboratory experiments showed that large specimens (6- by 12-in cylinders and 6 by 6 by 34-in beams) with reactive coarse aggregates expanded significantly between 1 yr and 18 months, independently of whether the exposure was dry, humid, or wet. On the other hand, 2 by 2 by 10-in bars (minus ¾-in aggregates) failed to expand when stored in water, whereas they expanded considerably in sealed containers (humid storage).

B. Tremper [84] reported experiments with mortar bars and concrete bars from the Washington area. Some mortar bars showed typical alkali-aggregate reactions when tested according to the standard mortar-bar procedure (sealed containers, constantly at 70 °F). Certain other aggregates did not expand except when concurrently with the standard storage they were exposed to cycles of freezing and thawing combined with wetting, reflecting conditions by local examples of structural failure. Similar results were found in concrete bars (4 by 4 by 20 in) cured in a dry room at 70 °F and thereafter exposed to freezing and thawing combined with leaching. Measurements of the dynamic modulus of elasticity were used for expressing the "durability factor". The conclusions of the experiments do not seem quite clear with respect to the characteristics of the alkali reactivity of the aggregates, whereas it is emphasized that high-alkali cement considerably lowered the resistance of mortar and concrete to freezing and thawing.

R. F. Blanks and H. Meissner [51] reported experiments with 3 by 3 by 15-in concrete bars, some of which had expanded 1.24 percent after 15 months in humid, sealed storage. It appeared that large open cracks, developed on the surfaces, extended only a short distance into the concrete, corresponding to what had been observed in structures. In the conclusions of this investigation it is recommended that coarse aggregates be tested by using the mortar-bar test after having been crushed down to sand sizes. In the discussion to [46] A. D. Conrow reported expansions obtained on concrete bars made with even exceptionally low alkali contents. The storage comprised:

1. Water curing at 70 °F,
2. Water curing at 160 °F and thereafter
3. Drying in an oven at 160 °F.

This rather extraordinary exposure was primarily intended to accelerate hydration in the cement paste to such an extent that expansive reactions were not veiled or eliminated by plastic deformations, but necessarily caused measurable expansion and disruption.

R. C. Mielenz and L. P. Witte [68] mentioned that attempts to develop a suitable procedure for moist-stored concrete-bar tests had been largely unsuccessful insofar as no dependable correlation with the mortar-bar test had been established. Meanwhile, natural weathering (wetting and drying, heating and cooling, i.e., purely physical factors) was found an important factor for development of disintegration in experimental concrete specimens. Subsequently a laboratory procedure was outlined, comprising exposure to cycles of wetting and drying of concrete bars. Bars 3 by 3 by 15 in were used. Wetting took place at 70 °F, drying at 130 °F, one cycle lasting one day. This procedure was very similar to the methods described by C. H. Scholer and W. E. Gibson [85]. Data from their experiments were found to indicate that expansion of more than 0.07 percent in 310 cycles or less should be regarded as reflecting structural failure in a similar exposure. It was also found—particularly with "sand and gravel aggregates" from Kimball, Nebraska—that excessive expansion and cracking occurred even with concrete made with low-alkali cement. It was herefrom concluded that "although alkali-aggregate reaction may contribute to the expansion developed during the test, the cement-aggregate incompatibility being evaluated is essentially independent of this reaction." This conclusion may be considered a confirmation of the results arrived at by Scholer by similar investigations of the Kansas sand-gravel aggregates, see [33], and by Scholer and Gibson in the above-mentioned paper on further investigations of the Kaw River aggregates. These aggregates were again investigated by W. Lerch [86]. From this paper it appears that they contained about 95 percent of quartz and feldspar, and about 5 percent of limestone and chert and occasionally opaline silica, volcanic glass, and other rock fragments. The quick chemical test proved the aggregate to be alkali reactive. Scholer's wetting and drying exposure was used on concrete bars, 3 by 3 by 11¼ in, cast with cements with the alkali contents ranging from 0.17 to 1.05 percent equivalent Na_2O. The deleterious reactions were found to produce alkali-silica gel, and by examination also reacted aggregate particles (opal) were observed. However, no relationship could be established between the alkali content of the cement and the expansion of the bars, and therefore it was also in this case concluded that some cement-aggregate reaction other than alkali-aggregate reaction might be a factor, and the alkali-aggregate reaction only contributory to the deterioration.

At this place the writers feel inclined to mention that in view of present-day theories on alkali-aggregate reactions, it is not obvious that these should be excluded as the primary cause of expansion and deterioration in the three papers treated above. Hence, the hypothetical "cement-aggregate reaction" in these cases may possibly be considered a result of inadequate means of investigation. This remark also pertains to similar investigations reported by C. H. Scholer and G. M. Smith [87], with the reservation that the reported inhibitive effect on the expansion of a certain amount of crushed limestone added to the coarse aggregate cannot immediately be explained merely by assuming the alkali-aggregate reaction to be the primary factor.

Th. B. Kennedy and K. Mather [88] presented a thorough study of correlation between accelerated laboratory freezing and thawing tests on concrete bars and weathering of concrete specimens of the same composition by natural, severe exposure on Treat Island, Maine. A discussion of this paper is not considered to be within the scope of the present report, because its main topic is purely physically determined disintegration. However, the paper should be mentioned as outstanding with respect to its treatment of the fundamental difficulties in transferring laboratory results to field concrete tests and vice versa. It is also of interest that the authors found evidences of beneficial effects of "mild" alkali-aggregate reaction, believed to have caused a measurable improvement of bond between slightly reacted chert pebbles in the coarse aggregate and ambient cement paste. This observation seems so far unique in the literature.

E. Trudsø [89] described freezing and thawing tests with 4 by 4 by 24-in concrete bars. Measurements were made by the resonant frequency method, and different Danish aggregates were tested in both lean and richer mixes. Supplementary visual inspections were made of evidences of deterioration, referred to as pop-outs, off-scaling, and map-cracking. It appeared that pop-outs developed over coarse aggregate particles of porous rock types (limestone and white, light cherts). Off-scaling was traced to the cement paste or mortar, and was the predominant effect in the lean mixture. The causal relation was less apparent for cracks. The porous, light cherts might have caused pop-outs (by enlargement) as a result of alkali-aggregate reaction in the bars as well as freezing and thawing, or maybe as a concurrent effect of both agencies. This may be the case too as regards the map-cracking. This remains to be further investigated by petrographic examination, etc. In principle, however, the attention paid to the visual phenomena is important, forming part of the necessary bridge from standardized mortar bars under defined exposure to field concrete that is subject to a complexity of disintegrating agencies.

C. E. S. Davis [90] presents a comparative study of the expansion of mortar and concrete. Mortar bars were used in the sizes 1 by 1 by 11¼ in and 2 by 2 by 11¼ in. The latter size was used also for concrete. Alkali-aggregate reactions were obtained by including 2.5 or 5.0 percent of opaline rock in the sand fraction, and in some cases also in the coarse fraction (½–3/16 in). Alkali contents of the cement comprised 0.18, 0.81, and 1.18 percent equivalent Na_2O, respectively. The paper contains a great many interesting observations and comments, among which are:

1. Bars with inactive aggregates did not expand, while all bars with opal cracked and expanded, the more so the higher the alkali content of the cement. Rates of expansion were greatest at first and slowed down after a few months' time. Rates depended on the season, being greatest in summer.

2. A certain absolute minimum alkali content of the cement (0.4 percent equivalent Na_2O) was necessary to obtain expansion in mortar bars. Increase of the amount of opal in aggregates necessitated a greater alkali content. Concrete bars needed more alkali for expansion than did mortar bars.

3. Larger mortar bars began to expand slightly later than smaller ones, but after 3 months' time their rate of expansion was the greatest. The large bars developed the widest cracks by expansion.

4. Concrete bars with inert coarse aggregate cracked and expanded later than mortars. The relationship with respect to the time factor was found expressed by the equation:

$$T=\frac{t^2}{11}$$

in which T=time of significant expansion of a concrete bar, t=time of significant expansion of a mortar bar made up of the mortar part of the concrete.

5. Expansion develops as a result of internal cracking, which again is caused by the swelling of reacted particles. Measurable expansions demand that cracks cross the line joining the inserts in the ends of a bar. Therefore, the size of a bar, particularly of the cross section, is a factor in the ultimate expansion, the delay before, and the rate of an expansion.

6. Coarse, inert aggregate particles form a delaying or preventive barrier against expansion in the mortar section. Oriented rods cause cracking to take place parallel to the longitudinal direction of the rods. Reinforcement should be expected to give this effect in structural concrete. Rods decrease expansion, as does coarse inert aggregate. Coarse, reactive aggregate particles ease or increase expansion, particularly with small amounts of alkalies. Concrete made with cement with as little as 0.4 percent equivalent Na_2O may expand within a few years, if the aggregates contain small amounts of coarse opaline particles.

7. The time factor in the empirical relationship for expansion of mortar and concrete, respectively, can be established so that mortar-bar tests any-

where may be reliable for the prediction of the behavior of comparable concrete with any reactive aggregate.

Inspection of Structures

Many examples of deterioration of field concrete due to alkali-aggregate reactions have probably been diagnosed merely by means of examination and testing of the used aggregates and cements in connection with more or less rough field inspections. Other cases have been reported where supplementary minute examinations of the deteriorated concrete have been carried out, particularly by applying petrographic methods for the studies of the macrostructure and the microstructure of the concrete. Outstanding examples of such investigations have been reported by, for instance, D. McConnell, R. C. Mielenz, W. Y. Holland, and K. T. Greene [45], R. C. Mielenz and L. P. Witte [68], B. Mather [57], K. Mather [91], and L. S. Brown [58].

There is but little doubt that in many cases only such examinations can furnish the proof that deleterious alkali-aggregate reactions have either taken place in the concrete or have not contributed to observed deterioration, thus confirming or eliminating hypotheses that might have been established on the basis of tests and examinations as previously discussed.

The petrographic examination of concrete structures and concrete samples, etc., is also treated by G. M. Idorn [92]. An even more extensive report on recent investigations in Denmark by the same author is given in [93]. It is emphasized that these papers deal particularly with description and interpretation of phenomena of deterioration in existing concrete (or mortar) and do not, at least directly, represent means of correlation between the above-described tests of susceptible materials and the future behavior of structures made with the materials in question. This problem comprises studies of e.g., model laws, characterization of exposures, microclimates, etc., and represents another rather unapproached field, probably rather because the difficulties are great than on account of overlooking its importance.

Figure 13, quoted from G. M. Idorn [94], may be referred to as an example. There serves as the basis for the presentation of the figure the fact that the expansion of mortar bars, stored under idealized exposure conditions, is a generally used measure of deterioration, both by sulfate attack in sea water and by alkali-aggregate reactions.

However, the aggressive reactants in sulfate reactions originate from the ambient medium, and the deterioration will progress inward from the surface of the bar, while alkali-aggregate reactions are internal reactions of the original concrete constituents. Hence, the applied measures actually cover quite different phenomena of reactions. Severe sulfate attack on a great concrete member under natural exposure must be expected to result in expansion and disruption of a surface layer that ultimately may spall off. The mortar bars regarded as "models" would then be models of the surface layer only, whereas the total volume of the member would be decreasing. It is otherwise in the case of harmful alkali-aggregate reactions in a great concrete member. Enlargements of the whole mass take place, reflecting expansions in any section of the member, and the mortar bars may be considered a rather direct "model" of the true situation, at least qualitatively.

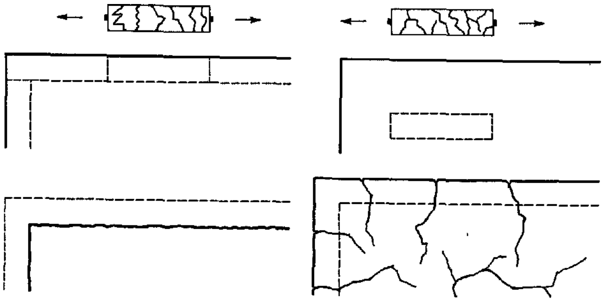


FIGURE 13. *Causes of weathering and mechanical effects in tests on mortar prisms and in concrete under natural conditions.*

Sulfate attack (left) and harmful alkali reactions (right). From [94].

These remarks are intended to point out that the possibilities for erroneous interpretation of the results of experimental work are considerable if due regard is not paid to both the mechanisms of the investigated reactions and the practical conditions that are believed to be imitated by the experiments.

Mechanism of Reactions

W. C. Hansen [95] ascribed the expansive reactions to pressure developed by osmosis, suggesting that the hardened cement paste around a reacting particle acts as a semipermeable membrane. H. E. Vivian [96] claimed this hypothesis to be improbable and explained the expansive pressure to develop as water is imbibed in the still rigid gel. D. McConnell, R. C. Mielenz, W. Y. Holland, and K. T. Greene [45] reported experiments actually proving that cement paste may act as semipermeable membrane for a sodium silicate (waterglass). Pressures more than 550 p.s.i. were obtained within 4 days. W. H. Parsons and H. Insley [97] claimed that pressure causing cracking develops in pores that are filled by liquid gel from reacting aggregate particles and that the pore walls form the necessary semipermeable membrane. McConnell, Mielenz, Holland, and Greene [45] opposed the latter hypothesis and claimed that pressure is primarily exerted by the gel in the reacting aggregate particles and that cracking caused by expansion takes place early during the softening of the gel.

T. C. Powers and H. H. Steinour in 1955 [98] discussed the chemical reactions and the way in which they caused expansion.

The body-building structural arrangements in silica minerals are due to links between the silica molecules. These may be imagined as tetrahedra with a silicon ion (of 4 valences) in the centre, and four oxygen ions (of 2 valences) each in a corner of the tetrahedron. Each oxygen ion is common to two tetrahedra, the charge thus being satisfied. The crystalline silica minerals are characterized by strictly defined, oriented-pattern arrangements of the tetrahedra. The noncrystalline silica minerals are characterized by a random network of tetrahedra with numerous, irregular spaces between the molecules or groups of molecules.

In an aqueous medium the surface of a silica particle will be slightly acid. Each silica tetrahedron at the boundary holds one oxygen ion with an unsatisfied negative charge, and the corresponding silicon ion similarly holds one positive charge. Hydrolysis, therefore, takes, place, H^+ joining with the available oxygen ion and OH^- going to the positive silicon ion. In this way a surface layer of hydroxyl groups is produced. The H^+ ions are bound less firmly than are the OH^- groups, and therefore the surface of any silica particle in aqueous surroundings will be slightly acid. This acid character is negligible in crystalline silica in which the specific surface is very low. In microcrystalline to cryptocrystalline silica, and most extreme in the case of noncrystalline colloidal silica minerals, the hydration will be more and more pronounced due to the greater specific surface containing considerable amounts of unsatisfied ionic charges.

If the ambient medium is a strongly alkaline solution, not only will surface hydration take place, but also the internal silicon-oxygen-silicon bonds will be severed, and accordingly the substance may be peptized. Orderly crystallized silica, as quartz, is under normal conditions not attackable in this way.

Referring to experiments by Kalousek, Vivian, and van der Burgh, a hypothesis on how the above reactions may proceed in concrete was also outlined, i.e., when attackable silica particles are placed in a cement paste holding a caustic solution with both calcium and sodium (potassium considered equivalent sodium) as the available cations.

It was found that in the boundary layer of a reacting silica particle a lime-alkali-silica complex is produced, and that this layer can prevent further diffusion of calcium ions to the still unattacked interior parts of the particle where the reactions proceed by further imbibition of sodium and water, producing an alkali-silica gel without lime.

Hence, the surrounding layer of lime-alkali-silica complex acts as a semipermeable membrane, and the diffusion through this causes osmotic pressure to develop.

Reference was also made to the clay minerals of the montmorillonite type that expand by taking up water in the lattice. If water is prevented from entering by applying just sufficient pressure to the solid substance, the counteracting pressure may be considered osmotic pressure developed without the presence of a semipermeable membrane.

It was further stated that the alkali-silica gels imbibing water are of the so-called unlimited-swelling type, due to the peptizing effects of alkali hydroxides, while the lime-alkali-silica gels and also lime-silica gels (cement gel) are nonswelling or only limited swelling.

The presented explanation of the chemical reactions and of the mechanism of expansion due to the reactions seems to agree with the suggestion by W. C. Hansen and others that hydraulic pressure of osmotic origin develops, maintained by the walls of reacting particles acting as semipermeable membranes. However, it also seems to cover the opinion of Vivian and others that no semipermeable membrane need be involved, the expansion being due to swelling of the solids only.

It was furthermore mentioned that when alkali-silica gel exudes from reacting particles into nearby cracks or voids, osmotic pressure may develop in such deposits by further diffusion, the cement paste itself acting as a semipermeable membrane.

A concurrent paper by the same authors [99] further discussed the conditions determining whether the reactions lead to expansions or not, in which latter case they are designated nonexpansive or safe.

Reviewing older experimental data, the authors found that the quantity and the particle size (i.e., total boundary area) of the reactive constituents in aggregates are factors, and that each combination of these characteristics determines a safe concentration of alkalies in the cement paste.

The hypothesis was put forward that the lime-alkali-silica gel initially formed in the boundary of a reacting particle adsorbs lime and alkali from the ambient paste. The relative amounts of adsorbed lime and alkali are controlled by the alkali content of the solution in the cement paste. By diffusion, adsorbed lime and alkali move through the reacted layer to attack the silica in the interior of the particle. Lime can diffuse fast enough through the layer to secure continued production of the nonswelling gel if the ratio of adsorbed lime to adsorbed alkali in the external layer is kept high enough. The alkali concentration of the cement paste, therefore, must be low. If the ratio of adsorbed lime to adsorbed alkali in the outer layer of the nonswelling gel is not kept high, lime cannot reach the reaction site sufficiently fast, and a pure alkali-silica gel is produced, which swells by imbibition of water and causes cracking and concurrent expansion of the surrounding paste.

Even in a safe reaction some of the initially reacted alkali is released and thus made available for deeper reaction in the silica until the whole particle is altered to a lime-silica-alkali complex. In such a safe reaction some silica must diffuse out of the particle and react with lime and alkali outside, i.e., in the paste.

The authors found this hypothesis to some extent supported by investigated, available data, and concluded that with cements of up to about 0.6 percent of equivalent Na_2O the alkali concentration appears to be low enough to secure safe initial reactions. The continued reactions can be safe only when the quantity of reactive silica is at minimum or more than a certain amount, depending on the alkali concentration and the fineness of the reacting particles. With high-alkali cements safe reactions will occur only if the reactive silica presents sufficient surface area. If the silica particles are relatively uniform and not of extreme fineness, the required ratio of silica to alkali for securing safe reactions is much higher than for low-alkali cements.

The effectiveness of pozzolanic additions for prevention of harmful reactions is due to their large specific surface which provides an almost initial decrease of alkali concentration, so that the reactions must proceed in the safe phase.

In mortar bars, as well as in concrete, reactions can be expansive even with low-alkali cements when the aggregates do not meet the requirements above stated.

It was mentioned in the paper that these circumstances may be present in the wetting and drying test developed by Conrow (further treated later in this report). Similarly these considerations should be remembered as regards the sometimes stated "lacking correlation between alkali content of cements and expansions of mortar bars or concrete bars in standard tests".

Ervin Poulsen [50] further treated the established analytical relationships, using the experimental data presented by D. O. Woolf [48].

G. Verbeck and Ch. Gramlich [100] by means of an osmotic-cell technique investigated the theory of osmotic pressure by formation of alkali-silica gels of the viscous and the solution type. The influence of various factors on the magnitude of the pressure was studied. The results implied among others that "there should exist some intermediate water-cement ratio of the paste at which a maximum rate of expansion or ultimate expansion should be observed as a function of this variable alone and that the observed expansions would be less for either lower or higher water-cement ratios".—In other words, in alkali-aggregate reactions there may also exist "pessimum proportions" as regards the water content of the cement paste.

In general, the results of these studies seem to corroborate the hypothesis put forward by Powers and Steinour.

K. E. Haulund Christensen [73] concluded from a discussion that: "It is reasonable to suppose that the prerequisite of a safe reaction consists not only in a sufficiently great diffusion velocity for Ca^{2+} towards the reaction zone, but also in the degree to which the gel is capable of retaining a sufficiently high concentration of SiO_3^{2-} in the pores."

R. G. Pike and D. Hubbard [101] reported experiments by an interferometric technique, suggested to confirm the inhibitive effect of calcium hydroxide on alkali-aggregate reactions.

The rate of attack on opal of sodium hydroxide plus calcium hydroxide was found to be about ⅕ the rate of attack of sodium hydroxide alone. It was also found that the magnitude of the *p*H of the attacking solution is a determinative factor of the reactions, and it was suggested that the ionic charge of aggregates and cement, respectively, may be of influence. These observations, no doubt, ought to be given much attention in future research on the nature of the reactions.

R. G. Pike [102] reported some very interesting measurements with a special pressure cell, showing that alkali-aggregate reactions in cement pastes and mortars may develop pressures in excess of 2,000 psi. The paste or mortar was packed in a small steel tube around which was wrapped a strain gauge which served as the measuring device. The high pressures were obtained in about 140 days when a high-alkali cement was used and 4 g of opal (No. 16 to 20, U.S.-sieves) was embedded in the paste.

The late R. A. J. Bosschart and R. Wyatt [103] presented an interesting account of the nature of the chemical aspects of alkali-aggregate reactions, emphasizing the structures of partly microcrystalline quartz modifications and the role of OH^- ions in the destruction of reactive aggregate particles.

From the above review of research on the mechanism of alkali-aggregate reactions it appears that so far very few have dealt with the relative reactivity of different types of siliceous aggregates, or presented the relationships between the molecular structure of the silica minerals and their behavior under attack by alkalies. Neither has the influence of the particle size of coarse aggregates on the mechanisms and on the effects of reactions been particularly studied.

These two factors: (1) type and structure of reactive minerals and (2) behavior of coarse size aggregates, therefore, ought to be considered prominent objects of attention in further basic investigations of the nature of alkali-aggregate reactions. The not yet clarified influence of the water content of the cement paste and of variations in water contents should also be borne in mind. All these matters are of obvious importance as regards the behavior of field concrete under natural exposure.

Unidentified Cement-Aggregate Reactions

According to previous passages in this paper several authors in the United States of America have reported certain deleterious cement-aggregate reactions, considered to differ from the ordinary alkali-aggregate reactions. The nature of these peculiar processes has so far not been clearly described. The deleterious structural effects of both types of deterioration seem to be quite alike, consisting in expansions, map-cracking, and popouts. This similarity indicates that fundamentally the mechanism of the reactions should be the same, i.e., developing chemical alteration of aggregate particles, which lead to enlargements causing pressure and eventual structural disruption.

Summarizing the major papers on cement-aggregate reactions it seems justifiable to divide them roughly into two groups.

To the first group belong those reactions that are believed not to be traditional alkali-aggregate reactions, mainly because no correlation has been found between alkali content of the cement and expansion of mortar-bar or concrete-bar specimens and because the standard mortar-bar test has failed to reveal expansive reactivity of aggregates that have performed badly in field concrete.

The second group of cement-aggregate reactions comprises those that are believed not to be alkali-aggregate reactions because no alkali-reactive rocks at all, or only negligible amounts thereof, have been found by petrographic examination of the aggregates, and because alkali-silica gels and reaction rims on aggregate pebbles have not been met with by petrographic examination of affected concrete. Moreover, the standard tests for alkali reactivity have failed to give positive indications.

The most concentrated occurrences of unidentified cement-aggregate reactions of the first group seem so far to have been recognized in Kansas, Nebraska, and Wyoming, U.S.A., and to concern concrete with certain "sand-gravel" aggregates from beds of some of the major rivers. In other passages of this report references to the investigations of the troubles met with in these areas are made several times, when comparisons to alkali-aggregate reactions have made it natural to do so. Some concise comments, however, on the investigations by A. D. Conrow, reported in [40], seem here in place also because these studies have formed the basis of a standard procedure for evaluation of reactivity of aggregates by a concrete-bar test, ASTM Designation: 342–55T.

The sand-gravel aggregates concerned were deficient in coarse aggregates, and much of the concrete in pavements, bridges, etc., therefore, had been cast with a somewhat high cement content. The tests were interpreted as showing that expansion in the concrete was not related to the alkali content of the cement and that low-alkali cements did not assure against damage. The studies did not comprise petrographic examination of aggregates, but these are designated "siliceous". In some tests coarse limestone fractions were added. This addition was found to decrease the expansion of concrete bars. The observed expansion of the sand-limestone concrete was found to be due to the siliceous sand component.

It was considered a strong possibility—though not directly supported by observations—that the potential release of calcium hydroxide by hydration of the cement and the rate of this release might be an accelerating factor.

The test procedure, elaborated after a great number of experiments had been made, comprised after 28 days water curing at standard temperature:

1. Seven days storage in water at 130 °F.
2. Cooling and storage in water at standard temperature for 20–24 hr.
3. Seven days drying at 130 °F.
4. Indefinite storage in water at standard temperature.

Adequate measurements of length and of fundamental vibration frequency by the sonic method for Young's modulus of elasticity are to be made at intervals during the above storage.

W. Lerch in a recent paper [104] has reported further studies of the problem. In this work the sand-gravel aggregates are characterized as predominantly siliceous, being essentially composed of granite, feldspar, and quartz. "They contain smaller quantities of sandstone, rhyolites, andesites, siliceous limestone, and chert. The relative quantities of these various constituents vary somewhat along different rivers and from different locations along the same river. So far as deleterious reactivity with cement alkalies is concerned, these aggregates range from innocuous to slightly deleterious, depending upon their content of rhyolite, andesite, chalcedonic or opaline cherts, and siliceous limestone. An examination of concretes made with these aggregates usually reveals the presence of some alkali silicate gel or other evidence of alkali-aggregate reaction".

Concerning the nature of the reactions the following is stated in the same paper:

"The deterioration of the sand-gravel aggregate concretes involves a chemical or physical phenomenon that is not yet clearly defined. Although the alkali content of the cement appears to contribute to the deterioration of the sand-gravel aggregate concretes, this development cannot be ascribed completely to alkali-aggregate reaction of the type described by Stanton. Mortar-bar tests made with the sand-gravel aggregates in combination with cements of different alkali contents do not develop expansion related to the alkali content of the cements. Furthermore, the use of low-alkali cements does not inhibit the deterioration of the sand-gravel aggregate concretes as it does in concretes with truly alkali-reactive aggregates".

For many reasons the writers do not feel inclined to comment on the statements referred to. The *locus in quo* is far away, and more papers offering the wanted information and adequate explanations of the problems may be on the way and may throw light on the unsolved problems, even before the present report is published. It seems right, however, to point out a few facts already apparent from the published data.

A. D. Conrow mentioned that the sand-gravel concretes often had been cast with a somewhat high cement content. Sometimes, however, this may have eliminated the assumed effect of using low-alkali cements.

It was also stated that no relationship could be established between the alkali content of cement and expansion of mortar bars and concrete bars. However, it appears that by the tests and experiments, the types, amounts, and grain-size distribution of reacting particles in the aggregates have not been determined, let alone selected. Referring also to the above statement by W. Lerch concerning the origin and composition of the aggregates, it seems rather possible that unregistered and not recognized variations in the composition of the concrete, including amounts of available alkalies and characteristics of reactive constituents of aggregates, etc., so far have prevented the lacking correlations to be disclosed. Expansion with low-alkali cements (and even without high cement contents) are even now known to be a possibility where only minor amounts of certain reactive constituents are present. In some cases these "minor amounts" have been less than one percent by weight of the total aggregates, dependent on grain-sizes, types, etc.

It seems also striking that, according to W. Lerch, alkali-silica gel may be expected to develop during the reactions.

In the opinion of the writers these circumstances tend to raise an argument for more elaborate studies to be presented before any major difference between the described processes and the traditional alkali-aggregate reaction is so definitely stated that the particular designation is motivated. Differences appearing from the empirical testing methods only, should, a priori, be considered just as well to reflect incapability of the testing methods as different processes of reaction.

Two reports on cement-aggregate reactions in Canada have been prepared by E. G. Swenson. One of the cases, treated in [16] presumably may be considered as covered by the above remarks on the American cases; the other seems somewhat different as it appears from the treatment in [105]. The deterioration, which as regards the mechanical effects, was quite similar to the result of alkali-aggregate reactions, was found related to a coarse argillaceous dolomitic limestone aggregate. The absence of alkali-silica gel and reaction rims, and the fact that reactivity of the aggregates failed to be revealed by the ASTM standard tests, made it necessary to investigate other possible factors. The Conrow test, ASTM Method C 342–55 T, did not give sufficient further information, although expansions were obtained with some sands under investigation. Exposure tests with concrete beams, however, involving wetting and drying and freezing and thawing, indicated that abnormal expansion occurred preferably under the influence of moisture and temperature. It was also indicated that expansion due to the coarse limestone aggregates was sharply influenced by the alkali content of the cement. No doubt future papers on this matter will receive much attention.

For obvious reasons the writers prefer to finish the present passage without a general evaluation of the presented data, but rather to quote some remarks by B. Mather in the discussion to the above-treated paper by A. D. Conrow:

"Mr. Conrow implies that the phenomena observed are limited, at least as far as is at present known, to concrete made with certain natural siliceous aggregates from the Central Great Plains region of the United States. He concludes that there is a strong possibility that the abnormal expansion is related in some way to the amount and rate of development of calcium hydroxide during cement hydration, and that the alkalies (soda and potassa) act as catalysts. He finds that the abnormal expansion can be prevented or much decreased by the use of a proper amount of suitable pozzolan. He seems to suggest that possibly the principal function of the pozzolan is the obvious one of using up the calcium hydroxide. Since he states that it has been quite definitely demonstrated that the abnormal expansion is not consistently related to the alkali content of the cement, he appears to imply that the phenomena involved are significantly different from what now might be called the 'classical' alkali-aggregate reaction.

"Mr. Conrow suggests that if the calcium hydroxide is responsible for the expansion, the carbonation of the hydroxide might be expected to prevent or inhibit the expansion. In this connection reference may be made to the experiments by Gaskin, who investigated the possibility of preventing alkali-aggregate reaction by carbonating the sodium and potassium hydroxides by exposure to carbon dioxide. His results led him to conclude that the presence of an excess of carbon dioxide prevented the expansion, apparently by the formation of relatively impermeable protective shells of calcite around particles of reactive aggregate.

"It has been observed in this laboratory that all samples of concrete or mortar that have undergone alkali-aggregate reaction, and that have been subjected to microscope examination are characterized by materially reduced quantities of crystalline calcium hydroxide. The presumption that the alkali-aggregate reactions themselves are responsible for this apparent consumption of calcium hydroxide is therefore suggested. It has been indicated that the pozzolanic reaction which consumes calcium hydroxide prevents or inhibits the deleterious effects of the alkali-aggregate reaction. If it may be further assumed that the presence of crystalline calcium hydroxide is necessary to the progress of the alkali-aggregate reaction, then the interesting possibility, which Mr. Conrow has mentioned, is suggested: that the mere consumption of calcium hydroxide by reaction with a pozzolan is sufficient to explain the beneficial effects of pozzolans in preventing abnormal expansion.

"Mr. Conrow indicates that additional study is needed. The writer would like to propose several items, the study of which might be expected to shed light on these and related problems:

"1. Thorough petrographic examination of the aggregates that are involved, with particular reference to differences between them and apparently similar materials that do not behave similarly and to differences between the aggregates before and after they have been used in specimens that have undergone abnormal expansion.

"2. Microscopic examination of the concrete at various stages in the development of the expansion to determine if detectable changes occur progressively in the aggregate particles, the hydration products of the cement, or in the cement-aggregate texture.

"3. Subjection of other cement-aggregate combinations to the test exposure to determine if similar results may be obtained."

The extensive work of the Danish Committee on Alkali Reactions in Concrete under the joint auspices of the Academy of Technical Sciences and the Danish National Institute of Building Research is the background for the present general report.

The preparation of the report has been made by a team of senior members of the committee staff, officially under the authority of Niels Munk Plum. It is, however, only fair to stress that by far the greater part of the work has been done by G. M. Idorn.

It stems from the very nature of a compilatory work that we have been forced to present only very brief and probably often rather inadequate summaries of the opinions and findings of the various authors, and we beg to apologize for all imperfections.

It is a special pleasure to thank Mr. Jørn Jessing, who has carried the editorial responsibilities and Mr. Gunnar Larsen from the Geological Survey of Denmark for the contribution on investigations of flint and cherts, etc.

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Discussion

Tor Hagerman

The Swedish Committee on Aggregates was set up for the purpose of assessing the suitability of various types of rocks as aggregates in concrete. The investigations conducted by the Committee have been carried on since 1954. The object of these investigations is to find out whether and to what extent harmful effects of a chemical nature have been produced by natural gravel materials as well as by crushed stone.

In particular, the Committee is dealing with two subjects, first, the types of damage caused by the presence of pyritic minerals in the aggregate, and second, the types of damage due to reactions between alkalies and silica.

Investigations of Types of Damage Caused by Pyritic Minerals

These investigations were started immediately after the formation of the Swedish Committee on Aggregates. They were urgent because large-scale construction projects were in process of execution in regions where such cases of damage had previously been observed. Aggregates which had varying contents of pyritic minerals (magnetic pyrites, i.e., pyrrhotite, and pyrites) as well as rocks which were completely free from such minerals were used in making concrete beams, which were stored in different ways, indoors as well as outdoors. Even after a short time (8 months), those beams which had been tested at a rate accelerated by heat treatment showed unmistakable signs of deterioration in the form of swellings and deflections around strongly expanding portions situated in the interior, frequently in conjunction with rusting. These observations were made in the cases where the aggregates had relatively high pyrite contents, which ranged from about 15 to 20 percent. Subsequently, all beams were stored outdoors, and then—after about 5 yr—it was found that, irrespective of the method of previous storage, many of those beams which contained pyrite had totally disintegrated. On the other hand, the comparison test specimens, made with granite aggregate which was practically free from pyrite, did not exhibit any signs of defects.

Investigations of Types of Damage Due to Reactions Between Alkalies and Silica in Swedish Aggregates

These investigations were made, first, by means of petrographic examination, and second, by the aid of chemical determination in accordance with ASTM designation C 289–54 T and as mortar-bar expansion tests in conformity with ASTM Designation C 227–52 T.

The investigations (about 40 in all) dealt with gravel and rocks. They were largely carried out on aggregate materials belonging to the Caledonian series, which originated from mountainous regions of Sweden.

Some investigations made in Denmark have thoroughly clarified the types of damage, the expansion effects, etc., due to flint concretions, or the like, which are found in chalk deposits. Such chalk flint from Scania, in south Sweden, has also distinctly shown harmful expansion in the investigations under consideration. It may be mentioned as an example that an admixture of 5 percent of flint added to a granitic material resulted in an expansion of slightly over 0.3 percent after 12 months. The alkali content of the cement was 1.2 percent of equivalent Na_2O.

It is suspected that some types of gravel from mountainous regions can likewise cause harmful effects. These gravel types can contain, among other things, quartzite, sparagmite, and phyllite.

Field observations have revealed some cases of damage to concrete in which the reactions between alkalies and silica were regarded as a possible cause of damage. Up to now, however, it has not been possible to verify this assumption.

Chemical examination of aggregate materials has in several cases indicated that the amount of silica (S_c) dissolved out of quartzites and similar rocks is so great that the occurrence of harmful expansion is to be expected. It is true that manifest expansion of bars made with such aggregate has been observed in some cases where the cement had a high alkali content, but no reliable signs of an alkali reaction were to be detected.

The bars made with aggregates which were obtained from rock types belonging to the Caledonian series did not exhibit any cracks or any formation of an alkali-silica gel. Thus, it has not yet been found out what caused the expansion referred to above. It is known that expansion phenomena whose causes have not been elucidated had also been met with in Canada. Unfortunately, the available data on the types of rocks used in Canada are not sufficient to permit any conclusions by analogy as to the observations made in Canada and in Sweden.

Discussion

W. C. Hansen

The authors of the paper "Chemical Reactions Involving Aggregate" make the following statement: "One major problem, which in the opinion of the writers is not clarified sufficiently, is the fundamental nature of the chemical reactions between alkalies and reactive aggregates and the nature of their mechanical effects." The following is an attempt to offer a solution to this problem.

In my 1944 paper [1],[1] I stated "Since the alkali silicates must form in the space originally occupied by the silica from which they formed, and since these silicates must occupy a greater volume than that occupied by the silica alone, they would tend to exert pressure against the confining paste which would be augmented by the hydrostatic pressure."

In 1947, Vivian [2] stated "A series of changes in the properties of the opal particles can be observed as they react and absorb water. Initially, opal particles are hard but, as they react with alkalies, they soften gradually and swell and eventually become jelly-like." He also states "Expansion continues as long as the reaction product can absorb water and retain the property of rigidity characteristic of a gel. Since the gel exerts both hydrostatic and directional pressures, the reaction product not only expands in the plane of the crack through the mortar but also at right angles to it."

L. S. Brown [3] states "As observed in the variety of instances illustrated, damage by alkali-aggregate reaction appears to be effected by direct enlargement of the affected aggregate unit."

These statements lead to the conclusion that the investigators visualized solid opal reacting as a solid with OH^-, Na^+, and K^+ ions and H_2O molecules to form a solid reaction product. Jeffery [4] called this type of reaction a solid-state reaction.

Studies with glasses support the concept of this solid-state reaction. Marboe and Weyl [5] state the following regarding cesium glass: "If such a glass is stored in a desiccator over $CaCl_2$, it is exposed to an atmosphere which has a finite but a very low partial pressure of H_2O. Each H_2O molecule hitting the surface of the glass must be given sufficient time to migrate into the interior in the form of OH^- ions. If the H_2O concentration in the atmosphere is higher, hydrated alkali silicates are formed. Within three to four months, a cesium disilicate glass took up approximately 15 percent water and changed into a plastic translucent hydrate."

In 1955, Gaskin, Jones, and Vivian [6] placed opal and quartz-containing aggregates in a cement paste containing radioactive sodium. The hardened pastes were ground to expose the aggregate particles, and the surfaces were autoradiographed. They found a considerable accumulation of sodium throughout the opal particles after storage at room temperature for only one week.

McConnell, Mielenz, Holland, and Greene [7] found the following reactive components in aggregates: opal, chalcedony, volcanic glass, devitrified glass, and tridymite. Vivian [8] found that tetramethyl ammonium hydroxide as well as NaOH and KOH reacted with opal and produced expansion in mortar bars. In this paper, the discussion will be limited to opal and NaOH, but it should be understood that what is said regarding opal and NaOH applies in a general way to other reactive materials and other relatively strong alkalies.

It seems that the work in this field clearly shows that OH^- and Na^+ ions migrate into opal and form solid alkali silicates. As these products imbibe water and tend to become jellylike, one may question whether or not they should be classed as solids. However, the pieces of opal have been transformed from hard solids to jelly-like bodies without having formed what is usually visualized as a solution.

In my paper, I suggested that the hardened cement paste might act as a semipermeable membrane to permit concentrated solutions of alkali silicates to form and exert hydrostatic pressure. Vivian and Brown were of the opinion that the solid state reaction cracked the concrete before such solutions were formed. According to Vivian, the concrete would be cracked sufficiently to permit the product to flow away from the site of the opal grain when the product became less rigid than the rigidity normally associated with a gel.

It is well known that the various forms of silica, quartz, opal, etc., are not generally attacked by acids and solutions of neutral salts but are attacked by alkaline solutions. This fact, of course, leads to the conclusion that OH^- ions are the units which attack the silica. As these ions penetrate the lattice of the silica, positive ions must accompany them to maintain electrical neutrality. From the standpoint of mass action, it is obvious that the rate of attack will vary with the concentration of the OH^- ions in the liquid surrounding the particle of silica. The work by Vivian with radioactive sodium indicates that Na^+ and OH^- ions migrate some distance into a grain of opal embedded in a hardened cement paste before the opal is changed to any marked degree.

Terms such as alkalic silica gel, alkali-silica complex, lime-alkali-silica complex, and silica gel have been used in referring to reaction prod-

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[1] Figures in brackets indicate the literature references at the end of this paper.

ucts formed by opal in cement pastes. It seems unquestionable that opal cannot produce any expansion in cement pastes until the SiO_2 groups of the opal have been converted to SiO_3 groups. It is conceivable that some particles of SiO_2 may be more or less suspended in the reaction products, but they would have no ability to produce expansions, and, accordingly, one need not attempt to use language which would include such particles. Since there must be a chemical reaction between the opal, OH^- ions, and certain cations to form the SiO_3 groups which are associated with the silicates, it seems desirable to refer to these reaction products as silicates.

Let us review briefly some of our knowledge of alkali silicates. Suppose 140 g of crystalline $Na_2SiO_3 \cdot H_2O$ is placed in a beaker in a desiccator over pure water. The crystals will take up water to form a jellylike mass which will become less and less viscous until it resembles water containing a little sediment. What happens is that the sodium silicate goes into solution and hydrolyzes to form relatively insoluble hydrated silica or silicic acid and a dilute solution of NaOH.

The 140 g of $Na_2SiO_3 \cdot H_2O$ contained the equivalent of 80 g of NaOH. If we substitute 80 g of pellets of NaOH for the crystals of $Na_2SiO_3 \cdot H_2O$, the pellets will take up water to form a similar jellylike mass which will become less and less viscous until it resembles water. In this case, there will be no sediment in the beaker. In each case, we have prepared a dilute solution of NaOH. By using large containers and sufficient water, one can prepare infinitely dilute solutions of NaOH from these two compounds, and these could give rise to large hydrostatic pressures.

Suppose we placed either a quantity of crystalline $3CaO \cdot 2SiO_2 \cdot 3H_2O$ or of $Ca(OH)_2$ in the beaker. It would take very careful measurements to observe the imbibition of water by either of these products whereas the imbibition of water by the $Na_2SiO_3 \cdot H_2O$ and NaOH would be readily observed. The $3CaO \cdot 2SiO_2 \cdot 3H_2O$ would eventually hydrolyze into hydrated SiO_2 and an infinitely dilute solution of $Ca(OH)_2$, and the $Ca(OH)_2$ would eventually form an infinitely dilute solution. However, the rates of these reactions are extremely slow because of the relatively insoluble natures of $3CaO \cdot 2SiO_2 \cdot 3H_2O$ and $Ca(OH)_2$.

In the terms used by Powers and Steinour [9], the crystalline $Na_2SiO_3 \cdot H_2O$ would be classed as an unlimited swelling gel and the crystalline $3CaO \cdot 2SiO_2 \cdot 3H_2O$ as a limited swelling gel. According to Webster, a gel is a jellylike material formed by the coagulation of a colloidal liquid. If one accepts this definition of a gel, it may be inaccurate to refer to the reaction products of opal with alkali and calcium hydroxides as gels. Since the behaviors of the alkali and calcium silicates are so readily explained on the basis of solubilities, there appears to be no reason for thinking of them in terms of gels.

From the experiments described above, one sees that approximately equal hydrostatic pressures would be produced by 80 g of NaOH and by 140 g of $Na_2SiO_3 \cdot H_2O$. One can, therefore, arrive at the conclusion that the expansion produced by the alkali-aggregate reaction in a hardened cement paste is produced by the NaOH and that the aggregate plays a secondary role. On this basis, it may be concluded that the role of the aggregate is to concentrate the alkali into a few spots and change it into a form in which it can exert pressure by a reaction with water. How can NaOH and SiO_2 develop pressures in a hardened cement paste? They can react as follows:

$$Na^+ + OH^- + SiO_2 = NaHSiO_3 \quad (1)$$

$$Na^+ + OH^- + NaHSiO_3 = Na_2SiO_3 \cdot xH_2O \quad (2)$$

$$Na_2SiO_3 + \text{Water} = Na_2SiO_3 \cdot xH_2O \quad (3)$$

$$Na_2SiO_3 + SiO_2 + \text{Water} = Na_2H_2(SiO_3)_2 \cdot xH_2O \quad (4)$$

$$Na_2SiO_3 + nSiO_2 + \text{Water} = Na_2H_{2n}(SiO_3)_{n+1} \cdot xH_2O \quad (5)$$

One can visualize that, in reaction (1), an OH^- and an Na^+ ion penetrate the lattice of the grain of opal. As additional ions penetrate, they may form water molecules and molecules of Na_2SiO_3 which can imbibe water molecules from the hardened paste. As the $Na_2SiO_3 \cdot xH_2O$ imbibes more and more water, Na^+ and OH^- ions will be released to react with additional SiO_2 to produce a product such as $Na_2H_{2n}(SiO_3)_{n+1}$. The reaction indicated by eq (5) might be capable of continuing until an infinite amount of SiO_2 is converted to $Na_2H_{2n}(SiO_3)_{n+1}$ or until each silicate molecule contains only a trace of Na^+. However, the rate of this reaction will become too slow to be of concern to the cement technologist when some finite amount of SiO_2 has reacted. This amount, of course, will vary with the alkali content of the specimen under study.

It is well to digress here to point out that the liquid phase of the cement paste contains Ca^{2+} as well as Na^+ ions. Hence, as the Na^+ ions are migrating into the grain of opal, Ca^{2+} ions will accompany them. However, because of the low solubility of $Ca(OH)_2$ in solutions of NaOH, the number of Ca^{2+} ions available for migration into the opal is very small compared to the number of the Na^+ ions. However, the Ca^{2+} ions that do migrate into the grain of opal will produce an insoluble calcium silicate which will occupy more volume than that of the opal from which it was formed. In other words, any cation that migrates into the grain of opal will cause an expansion regardless of the solubility of the product. Attention was recently called to this fact [10].

According to Vail [11], crystalline compounds of the compositions $Na_2SiO_3 \cdot 2H_2O$, $Na_2SiO_3 \cdot 6H_2O$ and $Na_2SiO_3 \cdot 9H_2O$ are known. Hence, highly hydrated metasilicates could be produced by the reaction of eq (2). The densities of these compounds are, respectively, 1.749, 1.807, and 1.646.

When 1 mole of SiO_2 reacts to form 1 mole of $Na_2SiO_3 \cdot 9H_2O$, 60.1 g of SiO_2 with a density of 2.3 yields 284 g of silicate with a density of 1.65; that is, 26.1 cc of SiO_2 forms 172 cc of silicate.

This reaction can be expressed in terms of dimensional change by taking the cube roots of 26.1 and 172, which are 2.9 and 5.6, respectively. Hence, if a particle of opal could be transformed (without any of it going into solution) into solid $Na_2SiO_3 \cdot 9H_2O$, the dimensions of the particle would be approximately doubled. The results of this calculation certainly lend support to the conclusion of Vivian and Brown that the concrete is cracked before the sodium silicate becomes fluid. However, one must remember that hardened cement paste can yield to pressure without cracking and that reactive particles may vary markedly in size. A small particle may have to undergo a greater percentage enlargement than a larger one before the paste ceases to yield to it. Hence, it may be that, in some cases, the alkali silicate develops a fairly high degree of fluidity before the paste cracks.

Vivian [12a] performed an experiment in which 18–52 mesh opal was used in a mortar made with a cement containing alkalies equivalent to 0.98 percent. At the age of 224 days, the expansions were approximately as follows:

Ratio Opal/ Na_2O	Expansion
	Percent
2	0.6
5	1.3
10	1.6
20	1.2
40	.6
60	.2
80	.0

It is well known that SiO_3 ions in silicic acid are highly polymerized and that the degree of polymerization can be decreased by additions of alkali hydroxides. The extent to which the hardened cement paste can confine the alkali silicate to the reaction site will depend upon the degree to which the SiO_3 ions are depolymerized when the alkali silicate assumes the properties of a liquid. Verbeck and Gramlich [13] have shown that sodium silicate can diffuse through hardened cement pastes having water-cement ratios of 0.55 and above.

Hence, it seems that, in specimens with the same water-cement ratio, the expansions will be controlled by one of two factors. When the specimen contains a small amount of opal with respect to Na_2O, all of the opal will be converted to a silicate with a composition in the range Na_2SiO_3 and $Na_2H_{2n}(SiO_3)_{n+1}$. When n is either zero or a small number, the volume change probably ends when the silicate reaches a certain fluidity. The specimen may or may not have developed cracks before this fluidity was reached. When n is a larger number, the silicate may never become fluid because of the lack of NaOH. That is, this product can be visualized as largely hydrated silica.

When the specimen contains a large amount of opal with respect to the Na_2O content, opal will react until the silicate has the composition $Na_2H_{2n}(SiO_3)_{n+1}$ in which n is a relatively large number. This product will be a solid that cannot imbibe water and cannot generate NaOH for reaction with the unreacted opal. To be correct, one should say that the rates of imbibition of water and of splitting off NaOH have become too low to be significant in the expansion of the specimen. Gel exudations from concrete have been analyzed by a number of investigators, and, according to Vivian [12b], the $Na_2O:SiO_2$ ratios have ranged from 1:2 to 1:16.

Vivian obtained maximum expansion at a ratio of $1Na_2O$ to $10SiO_2$. In accordance with eq (5), the composition of this product would be $Na_2H_{18}(SiO_3)_{10} \cdot xH_2O$ or $Na_2SiO_3 \cdot yH_2O + H_{18}(SiO_3)_9 \cdot yH_2O$. The ratio of Na_2O to SiO_2 by weight is 60 to 620. This is approximately 10 percent of Na_2O by weight of silica. It seems reasonable to believe that reaction (5) might convert all of the SiO_2 to SiO_3 in this product at a fairly rapid rate.

A high expansion was obtained at a ratio of $1Na_2O$ to $20SiO_2$. The product might have had the composition $Na_2SiO_3 \cdot yH_2O + H_{38}(SiO_3)_{19} \cdot yH_2O$. In this, the ratio of Na_2O to SiO_2 is 60 to 1240. This is approximately 5 percent Na_2O by weight of SiO_2.

The rate of reaction (5) is controlled by the rate at which water can reach the reaction site. It seems entirely possible that, where the specimens are exposed only to water vapor, the rate of this reaction would become very low because of the slowness with which water could reach the reaction site.

Suppose, for the sake of argument, that the reaction stops when the molecular ratio of $SiO_2:Na_2O$ is greater than 20:1, that the composition of the reaction product is $Na_2H_{38}(SiO_3)_{20}$ and that the volume of the reaction product is equal to the sum of the volumes of the reactants. We then have

$$\begin{array}{l} 2NaOH + 20SiO_2 + 18H_2O = Na_2H_{38}(SiO_3)_{20}. \\ \quad 36.6 \; + \; 522 \; + \; 324 \; = \quad 882.6 \end{array}$$

The cube roots of 522 and 883 are approximately 8.0 and 9.9. The dimensional changes of any particle are then about 24 percent; whereas, for the production of $Na_2SiO_3 \cdot 9H_2O$, they are about 100 percent. In the case of $Na_2H_{38}(SiO_3)_{20}$, it was assumed that its volume equalled the sum of the volumes of the reactants. Actually, its volume would be somewhat less than this, and, accordingly, the dimensional changes would be less than 24 percent.

The expansion per particle when the ratio of $SiO_2:Na_2O$ is 80:1 would then be approximately as follows:

$$\begin{array}{l} 2NaOH + 80SiO_2 + 18H_2O = Na_2H_{38}(SiO_3)_{20} + 60SiO_2 \\ \quad 36.6 \; + \; 2088 \; + \; 324 \; = \quad 883.6 \quad + \; 1566 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad = 2448.6. \end{array}$$

The cube roots of 2088 and 2449 are approximately 12.7 and 13.5. In this case, the dimensional expansion of an opal particle is only 6 percent.

When the opal to Na_2O ratio exceeds 20:1 (such as 40:1), one half of the particle would expand linearly about 24 percent, but the other half would not expand at all. Hence, the overall expansion of the particle would only be about 12 percent. One can explain easily that, for a given amount of Na_2O, the expansions would increase with increasing amounts of opal up to some maximum because of the increase in the amount of alkali silicate produced. However, one might expect the expansions to remain at this maximum as the quantity of opal reached and exceeded some value at which the rate of reaction (5) became very low.

The point that must be remembered in order to understand results such as those obtained by Vivian is that we are dealing with a solid-state reaction. As pointed out in the introduction, Vivian described how opal particles change from solids to jellylike particles. I [14] observed the same behavior for particles of commercial "silica-gel" when used as an aggregate. These observations seem to demonstrate unquestionably that grains of opal, except possibly extremely fine grains, do not form fluid alkali silicates until long after the cement paste has hardened.

The reaction of Na^+ and OH^- ions with opal must begin almost as soon as the concrete is made. Since this is a solid-state reaction, the grains of opal expand during the period when the cement paste is plastic as well as later. For some time after the paste becomes rigid, the paste is able to yield to the pressure exerted by the opal reaction. All the expansions of the opal particles that occur during this period and periods preceding setting do not result in any expansion of the concrete specimen. The amount of reaction of opal with alkali that occurs during these periods increases with increases in the surface area of the opal particles.

As the ratio of SiO_2 to Na_2O increases, the ability to imbibe water shown by the product produced as the Na^+ and OH^- ions migrate into the grain of opal decreases until the rate of imbibition becomes insignificant from the standpoint of the expansion of concrete. One can visualize that these particles of opal that have partially reacted with NaOH will take up Ca^{2+} ions and molecules of water at very slow rates for long periods of time and might, accordingly, tend to produce expansions at extremely slow rates.

Powers and Steinour [9] attempted to explain what they called safe alkali-aggregate reactions such as shown by Vivian when the Na_2O:SiO_2 ratio was 1:80 on the basis of approximately half of the SiO_2 escaping from the reaction site and being converted to calcium silicate. Their explanation ignores the experimental evidence presented by Vivian as to the manner in which opal reacts in mortar bars.

Very finely divided opal has been suggested as a pozzolanic material for preventing expansion when reactive aggregates are used with high-alkali cements. It seems that an extremely fine opal might react with the alkali hydroxide so rapidly that it would be converted to a calcium silicate with the release of the alkali hydroxide while the cement paste was still plastic. In that event, the alkali hydroxide would be available to react with the aggregate, and the pozzolanic material would be ineffective in preventing expansion. It appears, therefore, that the most effective pozzolans may not necessarily be the finest.

McCoy and Caldwell [15] suggested that it might be possible to inhibit the reaction of opal with NaOH by adding certain compounds to the cement. They found that lithium salts were effective in decreasing the expansion in certain mortars. However, in general, the additions of lithium salts did not eliminate expansion. For example, the following percentage expansions at 12 weeks were obtained with 1:2 Ottawa sand mortar with 0 and 2.5 percent of opal: No opal—0.036; no inhibitor—0.812; 0.5 percent of Li_2CO_3—0.505; and 1.0 percent of Li_2CO_3—0.073.

It appears from limited information in the literature that lithium forms relatively insoluble and only slightly hydrated silicates. For example, according to Mellor [16], Vesterberg prepared $Li_2SiO_3 \cdot H_2O$ by treating a solution of sodium metasilicate with solutions of lithium salts. The addition of lithium ions to a mortar containing opal would, therefore, tend to convert the opal into a product that would have little, if any, tendency to imbibe water.

In a recent paper [10], I suggested that lithium and barium salts would decrease the expansion caused by the alkali-aggregate reaction by converting the opal to insoluble silicates.

Since the rate of alkali-aggregate reaction is a function of the OH^- ion concentration, any salt that would not decrease this concentration should not influence the rate. Hence, since LiOH and $Ba(OH)_2$ are relatively soluble, their ions could be expected to migrate into the grains of opal along with the Na^+. The relatively insoluble $Ca(OH)_2$ would furnish a few ions to migrate along with the other ions. Hence, as pointed out earlier, one can visualize that a small amount of insoluble calcium silicate is produced as soluble sodium silicate is being produced. In the case of Li^+ and Ba^{2+} ions, relatively large amounts of insoluble lithium and barium silicates should be produced as the sodium silicate is being produced. Since they are insoluble salts, they should replace the Na^+ ions in the silicates so that, if sufficient amounts of either Li^+ or Ba^{2+} ions were present to react with all of the opal, there would be no sodium silicate in the reaction product, and the Na^+ ions would be free to migrate back into the cement paste.

If the Li and Ba silicates formed after the cement paste became rigid and formed in the space occupied by the opal, they should cause some expansion. However, being insoluble salts, they would not have the power of sodium silicate to imbibe water and produce hydrostatic pressures.

According to Mellor [16, p. 361], LeChatelier obtained a reaction between colloidal silica and a solution of $Ba(OH)_2$. He prepared $BaSiO_3{\cdot}6H_2O$ by allowing Ba^{2+} ions to diffuse into a solution of sodium metasilicate.

Two questions that have been discussed by several investigators are as follows:

(1.) Is the hardened cement paste impermeable to silicate ions and molecules or do calcium-alkali-silicate membranes form?

(2.) What part does hydrostatic pressure play in developing expansions?

Since Vivian has shown that the grain of opal expands more or less as a solid and produces expansion before the product becomes fluid enough to have any possibility of diffusing from the reaction site, the answers to these questions are not particularly relevant to an understanding of the chemical reactions involved when alkali reacts with opal in a cement paste.

In my discussion [14] of Brown's paper, I argued that grains of opal that appeared to be solids might, in reality, be extremely viscous liquids and, accordingly, be exerting hydrostatic pressure. Regardless of when the reaction product passes from the solid to the liquid state and regardless of whether or not a calcium-alkali-silicate membrane is produced, the fundamental nature of the alkali aggregate is illustrated in eq (1) to (5). It seems that, from Vivian's work, there can be no question that part of the expansion is produced while the grain of opal is solid and that a large amount of expansion can occur before the silicate molecules will be depolymerized sufficiently to migrate from the reaction site. In the case of large amounts of opal, the silicate molecules probably never become depolymerized to this extent.

It seems that some investigators and writers have failed to realize that Vivian was stating a fact when he said "Initially, opal particles are hard but, as they react with alkalies, they soften gradually and swell and eventually become jelly-like." For example, it seems that Powers and Steinour could not have proposed a hypothesis for a "safe reaction" which required the migration of relatively large amounts of silica from the reaction site if they had recognized that expansion occurred while the opal was either a solid or a highly viscous liquid.

I do not wish to give the impression from this discussion that no problems remain in the field of chemical reactions between aggregates and components of the cement. However, I do feel that the fundamental nature of the alkali-aggregate reaction is understood.

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Discussion

T. C. Powers

Although the review of our hypothesis (Powers and Steinour, 1955) on the alkali-aggregate reaction in the paper on "Chemical Reactions Involving Aggregate" was quite satisfactory, it seems advisable to present more explicitly some aspects of the hypotheses that are involved in Dr. Hansen's discussion [supra]. Dr. Hansen refers to the second of our two papers, but it is in the first paper, which was issued together with the second as PCA Research Department Bulletin No. 55, that we gave the results of our study of the questions dealt with by Dr. Hansen. Perhaps this accounts for the unfortunate misunderstanding reflected in the following quotations from Dr. Hansen's discussion.

Near the close of his discussion, Dr. Hansen said, "It seems that some investigators and writers have failed to realize that Vivian was stating a fact when he said, 'Initially opal particles are hard, but as they react with alkalies, they soften gradually and swell and eventually become jelly-like. For example, it seems that Powers and Steinour could not have proposed a hypothesis for a "safe reaction" which required the migration of relatively large amounts of silica from the reaction site if they had recognized that expansion occurred while the opal was either a solid or a highly viscous liquid.' " In an earlier passage he said, with respect to our explanation of a safe alkali-aggregate reaction (one that does not cause expansion), "Their explanation ignores the experimental evidence presented by Vivian as to the manner in which opal reacts in mortar bars."

Since our hypothesis was derived mostly from data published by Vivian and his collaborators it can hardly be said with justice that Vivian's data were ignored. What we did conclude, in a summary of several pages of discussion of the mechanism of expansion in our first paper, is given by the following quotation (pages 511–12).

"We can conclude that swelling pressure able to cause concrete to dilate significantly beyond its original dimensions can be produced only by the gel of the unlimited-swelling type—the alkali-silica complex. If the alkali-silica complex is fluid, and if it is confined, pressure may be generated as described by Hansen, that is, it may be hydraulic (osmotic).[1] If the complex is solid, that is, still a solid reaction rim, pressure may be generated by the swelling of the rim, even though cracks or cavities are present that would relieve hydraulic pressure. If the reaction rim, though solid, is plastic, semi-hydraulic pressure could develop, the pressure being hydraulic to the degree that it is equal in all directions. The fundamental cause of swelling is the same in all cases—the entry of water into a region where the effect of a solute or of adsorption reduces its free energy.

"The foregoing explanation of the mechanism of producing swelling through cement-aggregate reaction is in agreement with some features of explanations previously advanced. It involves the same mechanism proposed by Hansen: the swelling is due to imbibition of water, as Hansen supposed, but it is not necessarily the result of hydraulic pressure maintained by a semi-permeable membrane. . . . Vivian, whose explanation is nearly the same as ours, concluded that no semi-permeable membrane is involved—that the expansion is due to swelling of solids only. We, on the other hand believe that Vivian's conclusion was influenced by his observations on small laboratory specimens. When cracks occur in such specimens, soft or fluid gels may exude to the surface without producing further swelling. In mass concrete, however, isolated cracks may fill with alkali-silicate solution, and therefore the soft gel or solution in such cracks may develop osmotic pressure, the concrete itself functioning as a semi-permeable membrane. However, all such swelling is likely to be of less consequence than that which will have occurred earlier, that is, the swelling that produces the cracks that later become osmotic pressure cells. Hence, we agree with Vivian that solid swelling is probably the primary cause of damage."

Finally, in the general summary of the first paper the following statement appears:

"Expansion is produced when the alkali-silica complex imbibes water. The initial, most damaging expansion probably occurs while the reaction product is still solid, though expansion may occur after the product becomes plastic or fluid, if the initially formed cracks have no outlets. The force is that of a swelling pressure or osmotic pressure (hydraulic), the two being fundamentally alike."

In our development of an explanation for an expansive reaction we made no attempt to give the stoichiometry of the reaction product because we could find no evidence that the stoichiometry of the product was determinable from data at hand, or was an important factor. The important point seemed to be that the products would have a relatively high solubility in water, whether or not enough water was present to form an actual solution in the ordinary sense. On page 509 of the first paper we said,

"Whether water is held in a liquid solution, a solid solution,[2] or a 'surface solution' [i.e., by adsorption,] an energy potential does exist between that water and free water, provided that the solution is not infinitely dilute or that the gel is not already water saturated. When equilibrium does not exist, the same kind of change will take place in each case—that is, free water will begin to enter the solution or the gel, thus diminishing the initial free energy potential.

"Hence to know that water will have a tendency to enter a given region we need only to establish that the water already in that region exhibits less free energy than the water outside; the particular mechanism by which the energy potential is created is a secondary matter. Conversely, when water is observed to move spontaneously from one region to another, we know that for some reason an energy potential exists."

It is thus seen to be a fact that we recognized experimental evidence showing that when an expansive reaction occurs, expansion usually occurs while the reaction product is in the solid, or a quasi-solid state. It is *not* true that we postulated that such a reaction would involve diffusion of the silicate away from the reaction site, but it seemed to Dr. Hansen that we did so, apparently because he admits for consideration neither the possibility of a reaction product

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[1] This refers to Dr. Hansen's original hypothesis, which he now seems to have abandoned.

[2] Or, in view of the ideas expressed in Dr. Hansen's present discussion, we might add, "held by solid-state reaction."

different from any of those given in his five equations, nor the possibility of a reaction process that involves opal in a mature specimen and yet requires no expansion. He did not discuss the evidence presented in our papers that such a product and such a process does exist; instead he asserted that ". . . any cation that migrates into the grain of opal will cause an expansion regardless of the solubility of the product." Yet, the unique aspect of our hypothesis is the presentation of evidence contrary to this assertion, the description of a reaction process that requires no expansion, and the defining of conditions necessary for this process. I shall now present further evidence supporting the hypothesis, but first let us examine alternative explanations.

Explaining why pulverized opal caused no expansion, Vivian said, "It is assumed that the volume increase of −300 mesh particles is smaller than the volume of pore space in the hydrated cement contiguous to the particle surfaces." (However, in the same place he spoke also of ". . . other reactions akin to that of pozzolanas.") Hansen says all reactions occurring in an opal particle are expansive whether they involve lime or not, but "When the specimen contains a large amount of opal with respect to Na_2O content, opal will react until the silicate has the composition $Na_2H_{2n}(SiO_3)_{n+1}$ in which n is a relatively large number. This product will be a solid that cannot imbibe water and cannot generate NaOH for reaction with unreacted opal." In other words, the reaction stops, at least virtually, after enough reaction has occurred to raise n of the product to a sufficiently high value. He suggests that this value might be 20, and he calculates that when the total silica is 80 times the amount of alkali, the opal particles could not expand more than 6 percent before the reaction stopped. How this 6 percent expansion occurs without a corresponding expansion of the specimen is indicated by the statement, ". . . the grains of opal would expand during the period when the cement paste is plastic as well as later. For some time after the paste became rigid, the paste would be able to yield to the pressure exerted by the opal reaction. All the expansions that occurred during this period, and periods preceding setting, would not result in any expansion of the concrete specimen. The amount of reaction of opal with alkali that would occur during these periods would increase with increase in the surface area of the opal particles."

Vivian's supposition that the paste is able to absorb the expansion of small particles runs counter to what was revealed later about the size of pore spaces in hardened paste, if the absorption is supposed to involve pores; if it is supposed to to be a mechanical yielding, it runs counter to mechanical considerations, as will be shown later. We find evidence to support Hansen's view that a significant amount of an expansive reaction may occur before time of set, but the supposition that some expansion of opal particles after set could occur without dilating the specimen also is contrary to mechanical principles. We find no evidence to support the supposition that the reaction stops, even virtually, when the expansion stops. Experimental evidence that reaction continues will be given further on. Also, we find no experimental support for the statement made with reference to the calcium ion, that ". . . any cation that migrates into the opal will cause an expansion . . .". Evidence that this is not true has already appeared and more will be given below. I find no experimental evidence that an impervious reaction product unable to imbibe water is ever formed.

There is, however, an area of agreement common to Hansen's theory and ours that can be seen in figure 1. This curve gives the number of days required to reach about 90 percent of ultimate expansion, as a function of the opal content of the mortar. The data are from the same source as the data quoted by Hansen (see table in his discussion). The opal is in the form of −18+52 mesh particles; the alkali content of the cement is equivalent to 0.98 percent Na_2O. The graph is based on the expansive effect of reactions occurring after the first 20 hr. For the present purpose, we are mainly interested in the decrease in expansion period as opal contents rise higher than 2 percent of the volume of the mortar bar.

According to Hansen's hypothesis, expansion occurs until the ratio of silica to alkali reaches an upper limit beyond which the reaction virtually stops, the product having become impervious. Part of the reaction occurred while the mortar was plastic, and part afterward, the latter part being that which produces expansion. Or, since the reference length was that at about the age of 20 hr, we can say that part of the expansion occurred before the first measurement of length, and the rest afterward, the latter part being that represented in figure 1. The length of time during which expansion was observed was therefore determined by the fraction of the total reaction remaining to be completed after the initial length reading. This fraction depends on the total area of the opal particles presented to the alkali solution, the area in this case being directly proportional to the opal content of the specimen.

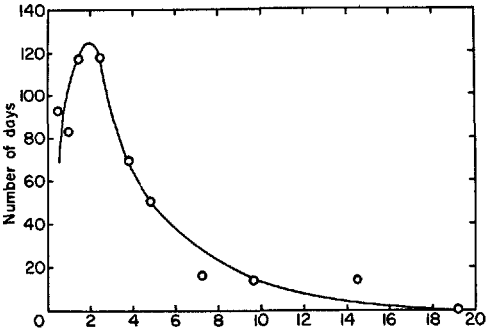

FIGURE 1. *Time required to reach 90 percent of ultimate expansion.*

Data from same source as in table 2.

At some sufficiently high surface area, all the reaction could be completed before the first length measurement. Evidently, this condition was found when the opal content reached about 20 percent of the volume of the bar.

Our hypothesis agrees with this interpretation to some degree. It recognizes that the reactions occurring before the paste sets play a highly important role, but beyond that ours differs radically from Hansen's. So far as the data of figure 1 are concerned, there is no obvious reason for preferring our hypothesis. The reason appears when such data as those shown in figure 2 are considered. This is a plot of expansion of mortar bars against elapsed time after molding, the time being expressed on a square-root scale as a convenient means of compressing the scale. Seven sets of mortar bars are represented, each containing the same amount of opal, namely 20 percent of the aggregate or 9.6 percent of the specimen; but each set of bars contained a different size of opal particle. The main point of interest is brought out by the data given in table 1 derived from figure 2. For each size of particle there was a period during which no expansion occurred. For the largest particle, the period was 12 days, for the −200 +300 mesh particles it was 115 days, and for the pulverized opal, −300 mesh, the period was apparently indefinitely long. Other data show that only when the ratio of opal surface area to alkali is low does the experimenter find expansion already under way at the time of the initial measurement. A successful hypothesis must take into account the various lengths of time that may elapse before expansion first begins.

TABLE 1. *Periods of nonexpansive reaction*

Opal content: 20 percent of aggregate; 9.6 percent of mortar

Alkali content of cement: Na_2O, 0.45 percent; K_2O, 0.81 percent

Data from: H. E. Vivian, Studies in cement-aggregate reaction *XIX* Australian J. Appl. Sci., 2, 488-494 (1951), table 4.

Sieve-size of opal BSS mesh	Period of nonexpansive reaction, days
−7+18	12
−18+52	12
−52+100	25
−100+150	80
−150+200	105
−200+300	115
−300	Indefinite

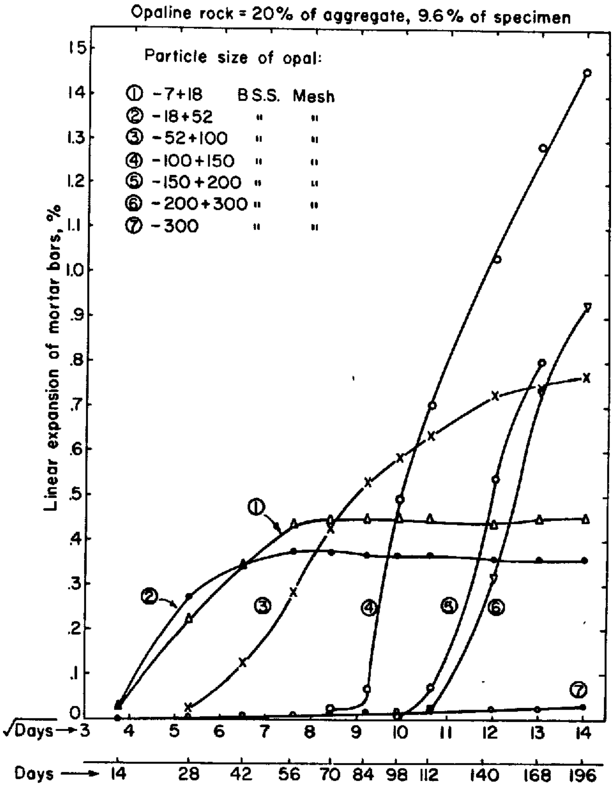

FIGURE 2. *Nonexpansive and expansive periods as functions of particle size.*

Data from source given in table 1.

We can hardly conclude, with figure 2 before us, that a period of no expansion is necessarily a period of no reaction. Curve 2 of figure 2, representing coarse particles of opal, shows that expansion was going on during the period of no expansion by finer particles, curves 4, 5, and 6; yet it isn't conceivable that fine particles could remain inert while coarse particles of the same material, and initially in the same environment, reacted and expanded. There seems to be no way to explain the various periods of no expansion in terms of Hansen's five chemical reactions, and the formation of an impervious, high-silica product, without adopting fantastic assumptions to the effect that a once impervious product later becomes pervious, and that this event is later the smaller the opal particle.

The periods of no expansion discussed above are what we called periods of safe reaction. The nature of the safe reaction becomes clear when one takes into account, as we did, the effect of the initial reaction on the composition of the liquid phase in the mortar bar, using Kalousek's data. One finds that the alkali content may become so depleted by the initial superficial reaction with opal particles that the ratio of adsorbed calcium to adsorbed alkali quickly rises to a level that gives a lime-alkali-silica complex that is pervious but cannot expand. Presumably, when the initial alkali concentration is high, the first reactions with silica produce an expansive product; but if the silica surface area is high enough, the layer of this product is very thin, and as the alkali concentration falls, calcium ion concentration rises, and the thin layer is converted to a nonswelling calcium-alkali-silica complex, all before the first time the length of the specimen is measured. The lime-bearing product may then continue to be formed, even in a well-hardened specimen, as long as the calcium ion concentration outside the opal particle remains high enough. For example, during the 115 days of nonexpansive reaction, the −200+300 mesh particles probably acquired a slowly ingrowing layer of nonexpansive reaction product.[3] We believe that the process is the same (although the *reaction* is not the same) as that by which water attacks cement particles and produces an ingrowing layer of hydrated cement, and at the same time causes no expansion. This process requires the outward transport of about half the product of reaction. Thus, it was in connection with this *safe* reaction that we postulated the outward diffusion of silica. The expansive reaction is expansive precisely because such a transfer of matter cannot take place before destructive expansion occurs. I have discussed the mechanics of this process, as it occurs in the hydration of cement, in a recent paper. (Journal of the PCA Research and Development Laboratories, Jan. 1961). The process is possible when the reaction product is a dense, limited-swelling, gel. It is not possible if the product is an unlimited-swelling gel, or if the product is noncolloidal.[4] The factors governing the conditions for the safe reaction, and the duration of the safe period, are fully discussed in our second paper.

Hansen expressed the view that the reaction of lime with sodium silicate releases *all* the alkali and thus may restore conditions for a high-alkali reaction, but Kalousek's data shows that this need not be so, and the behavior of bars as seen in figure 1 indicates that it is not so in this case; and the probable reason is that the reaction product has a very high specific surface area. Kalousek's data enabled us to deal quantitatively with the fraction of alkali released by the calcium reaction, and the fraction retained by the product of the reaction, presumably by adsorption. There need be no fear about using extremely fine opal powders, or other pozzolanic powders. The finer the powder, the less of it required, up to the point where the initial reaction consumes all the material.

Bennet and Vivian (1955) demonstrated that when enough pulverized opal was used, coarse particles could be present also without undergoing expansive reactions. This shows that we are not concerned with particle size per se, but with the control of the environment of reactive particles.

It may be that some persons will be inclined to explain figure 2 in terms of an assumption that some of the expansion of small particles is somehow "absorbed" by the matrix. Since this is a recurrent argument, it seems appropriate to deal with it here. The following analysis is probably not as rigorous as it might be, but it seems to be adequate for the present application

Consider a hollow sphere of concrete, this shape being chosen for simplicity. The radius of the outside surface is b, and that of the inside surface is a. The question is, how much will each surface be displaced radially when a pressure, p, is applied to the inside surface.

Assume that the material has virtually no tensile strength, and therefore develops radial cracks between segments of unstressed material when dilation occurs. Under this condition, the changes of radial length are equal, and therefore,

$$\frac{\Delta b}{b}=\alpha_1\frac{\Delta a}{a} \qquad (1)$$

where $\alpha_1=a/b$, and Δb and Δa the changes of the two radii.

Now assume that the sphere offers elastic resistance to dilation. Using established formulas of mechanics, Pickett (1956) gave the following general expression for radial displacement, δ, of any point in the sphere at the distance r from the center.

$$\delta=\frac{pa^3}{Er^2}\left[\left(\frac{1-\mu}{2}\right)\left(\frac{b^3+2r^3}{b^3-a^3}\right)+\mu\left(\frac{b^3-r^3}{b^3-a^3}\right)\right] \qquad (2)$$

E is Young's modulus and μ is Poisson's ratio of the concrete.

Letting $r=b$ and solving for δ gives the displacement of the outside surface, Δb, i.e.,

$$\frac{\Delta b}{b}=\frac{3p}{E}\left(\frac{a}{b}\right)^3\left[\left(\frac{1-\mu}{2}\right)\frac{1}{1-\left(\frac{a}{b}\right)^3}\right]. \qquad (3)$$

Similarly, from $r=a$, the displacement of the inner surface, Δa, is obtained;

$$\frac{\Delta a}{a}=\frac{p}{E}\left(\frac{1-\mu}{2}\right)\left[\frac{1+2\left(\frac{a}{b}\right)^3}{1-\left(\frac{a}{b}\right)^3}\right]+\mu. \qquad (4)$$

Letting $a/b=n$, and dividing eq (3) by eq (4) gives

$$\frac{\Delta b}{b}=\alpha_2\frac{\Delta a}{a} \qquad (5)$$

where

$$\alpha_2=\frac{3n^3\left(\frac{1-\mu}{2}\right)\left(\frac{1}{1-n^3}\right)}{\frac{1-\mu}{2}\left(\frac{1+2n^3}{1-n^3}\right)+\mu}=\frac{3}{\frac{1}{n^3}(1+k)+(2-k)} \qquad (6)$$

where $k=2\mu/(1-\mu)$.

Each opal particle in a mortar bar may be regarded as occupying a cavity, the radius of the cavity being the same as that of the particle. If v is the total volume of all the opal particles in the bar, and the particles are spherical and all the same size, the number of particles, N, is

$$N=\frac{v}{\frac{4}{3}\pi a^3}. \qquad (7)$$

The amount of mortar per opal particle is V/N

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[3] The product might grow inward not only from the outer surface of a particle, but also from the boundaries of the pores of permeable opal particles. Such pores are probably very large as compared with pores in cement paste.

[4] Although cement-gel particles are somewhat crystalline, as may be also the particles of the Kalousek complexes, they are also colloidal.

where V is the volume of the bar, and thus the bar can be considered as being composed of N cubes of edge length $2b$ such that

$$8\,N\,b^3=V. \tag{8}$$

From (7) and (8),

$$\left(\frac{a}{b}\right)^3=\frac{3v}{V}\cdot\frac{2}{\pi}=\frac{6g}{\pi}=n^3 \qquad |0<g<0.523| \tag{9}$$

where g is the volume of opal per unit volume of the mortar bar. The maximum value of g, 0.523, is fixed by the chosen model.

Equation (1) can now be stated in terms of g; i.e.,

$$\frac{\Delta b}{b}=n\frac{\Delta a}{a}=\left(\frac{6g}{\pi}\right)^{\frac{1}{3}}\frac{\Delta a}{a} \tag{10}$$

and

$$\alpha_1=1.24g^{\frac{1}{3}}. \tag{11}$$

Similarly, eq (6) becomes

$$\alpha_2=\frac{3}{\frac{\pi}{6g}(1+k)+(2-k)}. \tag{12}$$

At this point, we may observe that in eqs (6), (10), (11), and (12), which give the relationship of the unit expansion of a mortar bar to the unit expansion of the opal particles it contains, the size of the particle does not appear; for a given percentage expansion of an opal particle, the effect on the bar depends on the total volume of the opal particles. This mechanical principle, plus the fact that expansion, when it occurs, begins while the particles are solid, shows that arguments based on a special effect of size are not tenable. Actually, as may be seen in figure 1, small particles may produce more expansion than an equal volume of larger particles. Vivian reported that, as might be expected, the smaller the particle the shorter the cracks. Because of this the cracks around small particles do not develop outlets to the exterior through which soft alkali-silica gel can escape until after a relatively high degree of expansion has occurred.

Arguments based on special size effects appear all the weaker when one considers how small an amount of opal can cause expansion, and especially how little expansion is required of the opal particles to produce observable effects when the opal content is upwards of 1 percent. This is considered further in the following paragraphs.

We shall now assume that all the cavities containing opal particles become expanded by pressure associated with the alkali-silica reaction, and that they expand simultaneously. Resistance to expansion is determined by the elastic properties of the mortar as indicated by Poisson's ratio, μ, and by the extent of crack development. If no cracks are produced the normal value of μ would apply, about 1/5. If the mortar deformed plastically, the value of μ would be 1/2, but studies of deformation under sustained stress show μ due to creep and plastic flow to be equal to or less than that due to short time loads. Therefore there is no factual basis for assuming that μ can exceed about 0.2. If cracks become so extensive that all resistance to expansion is lost, eq (11) applies. Therefore, calculations may be based on values of α_1 and α_2, the latter for $\mu=1/5$, or $k=1/2$.

Figure 3 gives plots of α_1 and α_2 vs. the opal contents of the bars, as calculated from eqs (11) and (12). From these functions it is possible to estimate the amount of expansion of the opal particles from the measured expansion of the bar. However, the result can be no better than an estimate, in most cases, because the degree of elastic resistance remaining at any given stage of expansion is not known. At a given opal content the value of α should fall between α_1 and α_2, if cracks are present. Probably, cracks appear at strains exceeding 0.05 percent. Under a normal tensile force, this amount of strain would correspond to a stress of 1,000 psi if the modulus of elasticity is 2 x 10^6 psi. From the measured expansion of the bar, the extent of cracking can be estimated on this basis.

An application to some of the Vivian data already cited is given in table 2. The first 3 columns give the opal-alkali relationships, and the 4th column the total expansion occurring

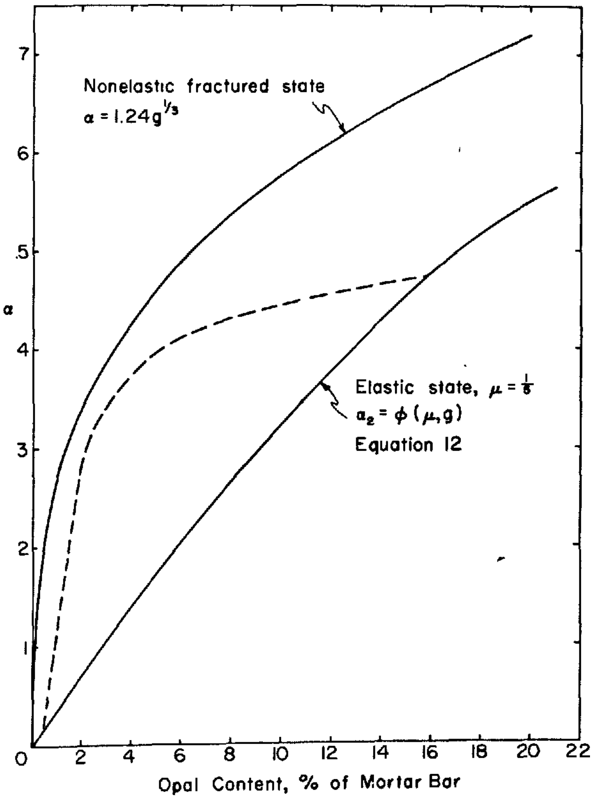

FIGURE 3. *The factor α of eqs (11) and (12) as functions of opal content of mortar bar.*

Table 2. *Calculations of expansion of −18 +52-mesh opal particles in mortar bars made with high-alkali cement*

$$\frac{\Delta a}{a}=\frac{1}{\alpha}\frac{\Delta b}{b}$$

Data from: Studies of cement-aggregate reaction: Bulletin 256 CSIRO Australia, p. 15, table 3.

1	2	3	4	5	6	7	8
Opal/ Na_2O	Opal content		Observed exp. 224th day	α (see text)	$\frac{1}{\alpha}$	$\frac{\Delta a}{a}$	Remarks
	Aggregate	Bar					
	Percent	*Percent*	*Percent*			*Percent*	
0.04	0.02	0.0096	0.0083 [a]	0.000036	28,000	230	Elastic.
.2	.10	.048	.0417 [a]	.0018	5,600	22	Elastic.
2	1.0	.48	.417 [a]	.025	40	17	Partly elastic.
4	2.0	.96	.83 [a]	.10	10	8.3	Partly elastic.
6	3.0	1.44	1.26 [a]	.18	5.6	7.0	Partly elastic.
10	5.0	2.4	1.62	.31	3.2	5.2	Partly elastic.
15	7.5	3.6	1.31	.36	2.8	3.8	Partly elastic.
20	10.0	4.8	1.03	.40	2.5	2.6	Partly elastic.
31	15.0	7.2	0.76	.42	2.4	1.8	Partly elastic.
41	20.0	9.6	0.52	.44	2.3	1.2	Partly elastic.
61	30.0	14.4	0.13	.46	2.2	0.3	Elastic.
82	40.0	19.2	0.00	.54	1.8	0.0	

[a] Values taken from a straight line through the data points. All the rest are results as reported by Vivian.

during 224 days of moist storage at room temperature. From the latter data, it was estimated that no cracks occurred in specimens containing less than 0.5 percent opal, also that cracks did not occur when the opal content exceeded 16 percent. At maximum expansion, found at an opal content of 2.4 percent the tensile strength was probably not over 15 percent of normal (Vivian, 1947), and therefore the value of α must have come close to α_1 at that value of g. The broken-line curve in figure 3 was drawn on the basis of these considerations as a reasonable guess of the locus of α vs. g for these particular data, and the values in table 2 are from this curve, except for the items marked "elastic", for which α_2 values were used.

The values in column 6 show the factor by which the unit linear expansion of the bar must be multiplied to obtain the unit linear expansion of an opal particle. For very small amounts of opal, less than 0.05 percent, this factor was found to be large, indicating that much of the expansion of the particles could be "absorbed" by elastic compression of the matrix. But for amounts of opal upwards of ½ percent, the factors are not large, partly because of cracks.

Column 7 shows the calculated linear increase of the opal particles corresponding to the measured increase in length of bar given in column 4. At peak expansion (1.6 percent), the estimated expansion of the opal particles is about 5 percent. If the expansion could have taken place elastically (no cracks) the particle expansion would have been about 11 percent. With 9.6 percent opal in the bar, the observed 0.52 percent expansion of the bar could be produced by only a 1.2 percent expansion of the particles, and with 19.2 percent opal there could have been virtually no expansion without measurable expansion of the bar.

Although it is obvious that various other sets of figures could have been arrived at by the general procedure followed above, it is also clear that any other set would tell the same story as to the magnitude of particles swelling.

These considerations also have significance with respect to Hansen's concepts of the expansive reaction. Referring to the bar containing 4.8 percent opal (SiO_2:Na_2O: :20:1), he says, "Suppose . . . the composition of the reaction product is $Na_2H_{38}\ (SiO_3)_{20}$ and that the volume of the hydration products is equal to the sum of the reactants." He then shows that, "The dimensional changes of any particle are then about 24 percent." It should be observed that this calculation includes only the water of constitution of the solid crystalline product, the $x\ H_2O$ of his eq (5) not being included. The calculation therefore gives the least possible space the product could occupy before any additional water was taken into the site of the opal particle.

The prediction of a 24 percent linear increase of each cavity containing opal may be compared with the corresponding data in table 2, showing that the opal particles need expand only about 2.6 percent to account for the 1.03 percent expansion of the bar. It thus appears that the stoichiometries of the sodium silicates produced in the expansive reactions cannot be obtained directly from the total alkali and total reactive silica in the mortar bar.

There is much experimental evidence to support our conclusion that the alkali-aggregate reaction can produce either an expansive or a nonexpansive product, and that which of the two products will be produced depends upon the relative amounts of alkali and lime in the solutions outside the opal particles and on factors that control the rates of diffusion of water and ions.

Discussion

R. G. Pike, Donald Hubbard, and E. S. Newman

This paper on the chemical reactions involving aggregate has been very instructive, and we are particularly interested in the latter portion of the paper dealing with the alkali-aggregate reaction—specifically those remarks suggesting that calcium hydroxide may play an important role in the mechanism of alkali-aggregate expansion.

The importance of the role of calcium in the alkali-aggregate reaction is suggested by recent work in this laboratory on synthetic aggregates composed of binary silicate glasses. A paper has been submitted for publication (as Bull. 275) to the Highway Research Board in which the results of this work can be interpreted as an indication that the presence of a certain (unknown) concentration of calcium ions in solution is necessary to help in the formation of a semipermeable osmotic membrane about the individual aggregate grains before disruptive expansion can proceed.

In this investigation mortar bars were made and tested in accordance with ASTM Specification 227–52T, Tentative Method of Test for Potential Alkali Reactivity of Cement Aggregate Combinations, in which various glasses (reactive aggregates) replaced 6 percent of the nonreactive graded Ottawa sand.

One series of these glasses varied in composition from 50 percent Na_2O: 50 percent SiO_2 to 0 percent Na_2O: 100 percent SiO_2.

Figure 1 illustrates the expansions obtained with mortar bars made with these glasses using high-alumina cement and "pressure calcined" gypsum plaster. Since neither the cement nor the plaster contains any detectable alkali, these curves show that the soda-silica glass can supply the alkali necessary for expansion and can, at the same time, act as the reactive aggregate.

Figure 2 illustrates the same effect with a low-alkali (0.29 percent K_2O) portland cement, and it can be seen that the greatest expansion is caused by the glass composed of 15 percent Na_2O: 85 percent SiO_2.

This high expansion may be largely eliminated or greatly retarded by the substitution of pozzolan for part of the cement. This effect is illustrated in figure 3 for bars containing various amounts of pozzolan. In this series the bars containing no pozzolan expanded about 1.4 percent. This potential expansion was reduced to 0.2 percent by the substitution of 4 percent and to 0.02 percent

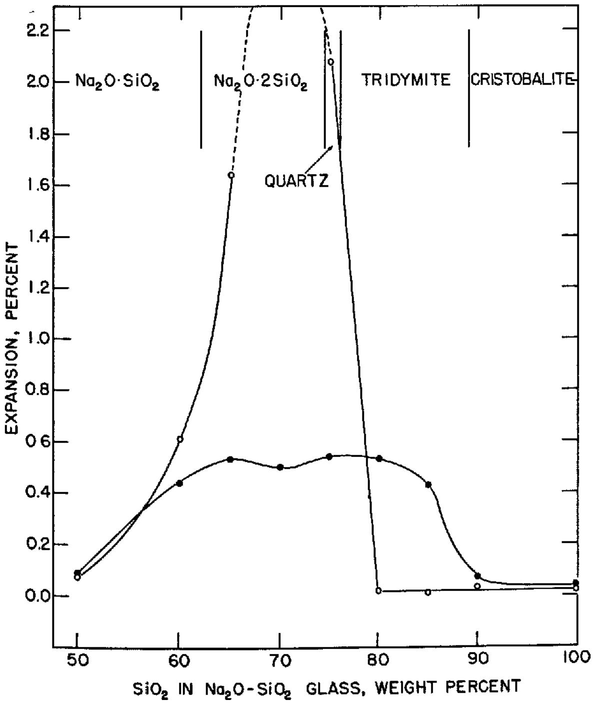

FIGURE 1. *Expansion of mortar bars containing a series of* Na_2O–SiO_2 *glasses.*

Stored over water at 100 °F.
● with high-alumina cement, aged 8 months.
○ with gypsum plaster; aged 2 months.
Also shown are the primary phase regions for the system Na_2O–SiO_2.

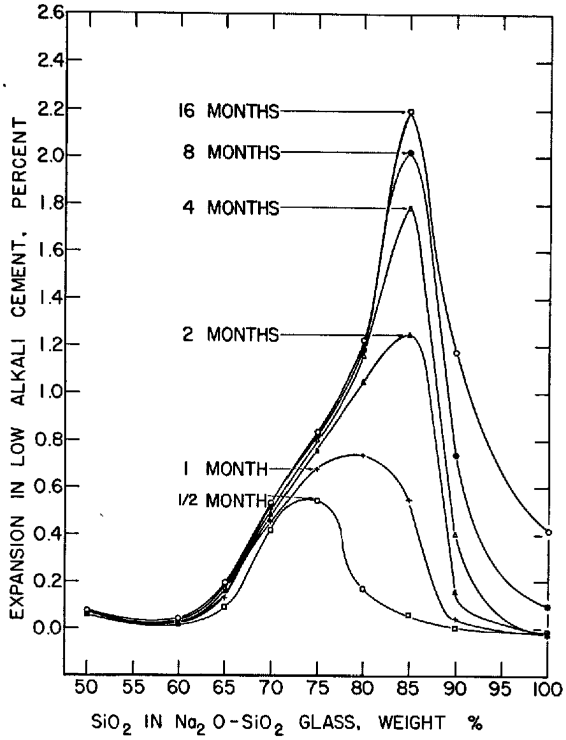

FIGURE 2. *Expansion of mortar bars containing a series of* Na_2O–SiO_2 *glasses in a low-alkali cement at various ages.*

Stored over water at 100 °F.

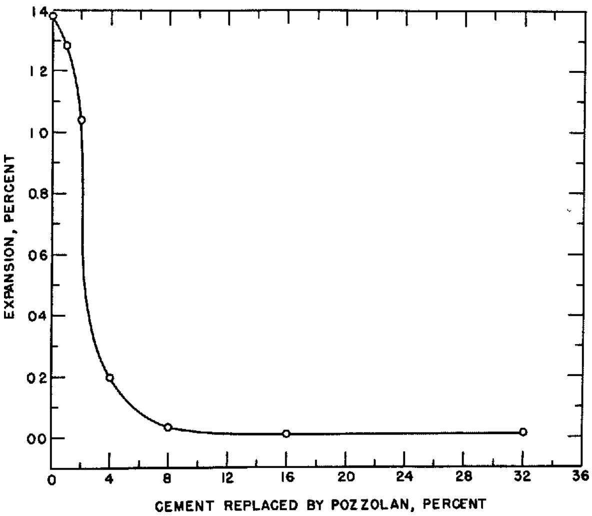

FIGURE 3. *Reduced expansion of mortar bars containing a 15-percent* Na_2O:*85-percent* SiO^2 *glass caused by partial replacement of the low-alkali cement with pozzolan (opal passing #325 sieve).*

Bars stored over water 4 months at 100 °F.

by the substitution of 16 and 32 percent of the cement by pozzolan.

It would appear from these results that the remarks of Conrow [1] and Mather [2] quoted by the authors are very apropos. The fact that there is less than one percent of total alkali in the mortar bar while about five times this much pozzolan is required to reduce the expansion to a low value suggests that direct reaction of the pozzolan with the alkali is not the only factor in reducing expansion.

The mechanism by which this pozzolan-calcium hydroxide reaction reduces expansion is not known, but we may speculate (since pozzolans are by definition materials which react with calcium hydroxide to form insoluble silicates and aluminates) that the reduced expansion is concerned with this traditional pozzolanic activity.

Kalousek [3] has suggested that precipitation of a soda-lime-silica gel about the reactive grain to form with the cement a semipermeable membrane is necessary for the harmful expansive reaction to occur. If such a membrane is necessary, any reaction which would tend to reduce the concentration of calcium ion in solution to a point where the membrane would not form should decrease expansion. Conversely, addition of materials which tend to increase the calcium ion concentration might be expected to increase expansion. Various investigators have shown that the addition of very small amounts of different materials can greatly increase or decrease the concentration of calcium ions in the liquid phase of setting portland cement pastes [4, 5, 6]. If the work of McCoy and Caldwell [7] is examined with this fact in mind, it appears that those materials which might be expected to cause an increase in the calcium ion concentration tend to increase expansion, and those which might be expected to cause a decrease in concentration or ionization of calcium tend to reduce expansion.

Some recent work by Lerch [8] on concrete specimens made with sand-gravels of the Kansas-Nebraska area is also of interest in regard to the role of lime in alkali-aggregate expansion. From an examination of his tables numbered 3 and 4 it appears that the cement having the highest percentage of C_3S (64.5 percent) and the lowest C_2S (10.0 percent) (that is, the cement which would be expected to release the most calcium) causes the greatest amount of cracking of the concrete specimens. Conversely, that cement with the lowest percentage of C_3S (25.0 percent) and the highest C_2S (48.0 percent) (that is, the cement which would be expected to release the least calcium) causes the least cracking. For those cements containing more than 0.57 percent of combined alkalies (either in the original cement or as added alkali) and falling between these two extreme values for C_3S and C_2S, there appears to be a fair correlation between the amount of C_3S and the cracking of the concrete.

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Discussion

John Lemish

The discussion presented below concerns the section on "Unidentified Cement-Aggregate Reactions" in which mention is made of concrete deterioration related to argillaceous dolomitic limestone aggregates. A considerable amount of research has been conducted on carbonate aggregate-cement reactions as part of the general study on the suitability of carbonate rocks as concrete aggregate, which inadvertently did not reach the authors in time to be incorporated in their paper. These reactions which occur in response to the alkaline environment of concrete are not typical alkali-aggregate reactions associated with siliceous aggregates such as opaline cherts, volcanic glasses, etc. The reactions are associated with certain carbonate aggregates whose service records indicate that deleterious performance in concrete has occurred. It is my purpose to review briefly carbonate-aggregate research conducted at Iowa State University and present some new data on the problem of carbonate aggregate-cement paste reactions.

Although a considerable amount of material has been published on concrete aggregates, few papers deal specifically with carbonate aggregates. One of the first papers on carbonate aggregate was written by Loughlin [1][1] in 1928. Other work by H. S. Sweet [2], B. Mather, et al. [3], and K. Mather [4] dealt directly with carbonate rocks, emphasizing the petrographic and physical aspects. Within the past 5 yr, however, the recognition that certain carbonate aggregates contribute to distress in concrete because of chemical reaction has led to participation in research by several

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[1] Figures in brackets indicate the literature references at the end of this paper.

other groups in the United States and Canada. Significant contributions have been made by Swenson and Gillot [5] on the Kingston aggregate in Canada, by Hadley and others under the direction of Verbeck at the Portland Cement Association Laboratories, and by Chaiken and Halstead [6] of the Bureau of Public Roads. Their work emphasizes the expansion of carbonate rocks in alkaline environments and especially the the reaction of carbonate minerals or "dedolomitization" with alkalies.

Because of direct correlation of poor service record of certain Iowa highways with the use of coarse carbonate aggregates from certain quarries, studies sponsored by the Iowa State Highway Commission were first begun in 1948 by Dorheim [7], who, by means of expansion tests on concrete bars, concluded that clay in limestone might be indicative of poor performance. Work was continued by Roy, et al. [8], who made a petrographic study of the Mississippian carbonate rocks which included those from LeGrand with a poor service record. Although there was no correlation of petrographic characteristics with service record, they observed that weathered aggregates with increased absorption were associated with distressed concrete.

In 1955 the research was renewed and investigation of Devonian rocks from the Glory quarry which produced rock with a notoriously poor service record led to a publication by Lemish, Rush, and Hiltrop [9] on the physical properties of the aggregates. They concluded that impure carbonate rocks characterized by high residue and clay content were poor aggregates, and they postulated that the pore-size distribution of the rock was important to serviceability. Examination of deteriorated concrete indicated that the softer matrix was carbonated and that impure coarse carbonate aggregates were characterized by reaction shells. Bisque and Lemish [10] also described the chemical properties of carbonate rocks as related to the durability of concrete, and found that reaction shells were silicified and selectively formed on aggregate containing clay, a high percentage of insoluble residue, high magnesium content, and higher amounts of silica. They reported a method of growing reaction shells on these impure carbonate rocks in silica-rich solutions at pH 12 and demonstrated that carbonate rocks reacted chemically in concrete environments.

Further study by Hiltrop and Lemish [11] conducted on the relationship of pore-size distribution and other rock properties to serviceability, led to the conclusion that pore-size distribution alone is not indicative of performance as an aggregate but that the presence of clay and the Ca/Mg ratio were definitely related to serviceability.

Continued study by Bisque and Lemish [12] demonstrated that reaction shells could be experimentally grown on impure aggregates in concrete bars and that shell growth in the instance of Glory aggregate was due to introduction of silica from the cement paste. Shells were also grown rapidly in cement-paste bars by Lemish [13] in an autoclave. Further studies [14] indicated that sodium and potassium were not introduced into the shell and that bars in which shells were grown had no increase in compressive strength accompanied by no excessive expansion. It was postulated by Bisque [15] and demonstrated by Hiltrop [16] by means of silicon tetrachloride and vaporous organic silicone compounds, that silica introduced into the rock could be stabilized or fixed by clay particles.

In recent unpublished research at Iowa State University under the direction of Lemish, Harwood [17] continued the study by measuring compositional variations in aggregate and cement resulting from carbonate aggregate-cement paste reactions. A series of different aggregates cut in the shape of a cube were placed in cement-paste bars of Type I cement (0.52 percent of alkali reported as Na_2O) and were soaked continuously in distilled water at 55 °C for 3 months. Two cubes of reactive Glory aggregate were similarly reacted with cements consisting of alite ($3CaO{\cdot}SiO_2$) and belite ($2CaO{\cdot}SiO_2$), respectively, at a pH 12 environment. Chemical analyses and X-ray studies were made on samples taken at specified intervals across the aggregate into the cement paste. Figure 1 gives the summary of silica behavior for different types of aggregates.

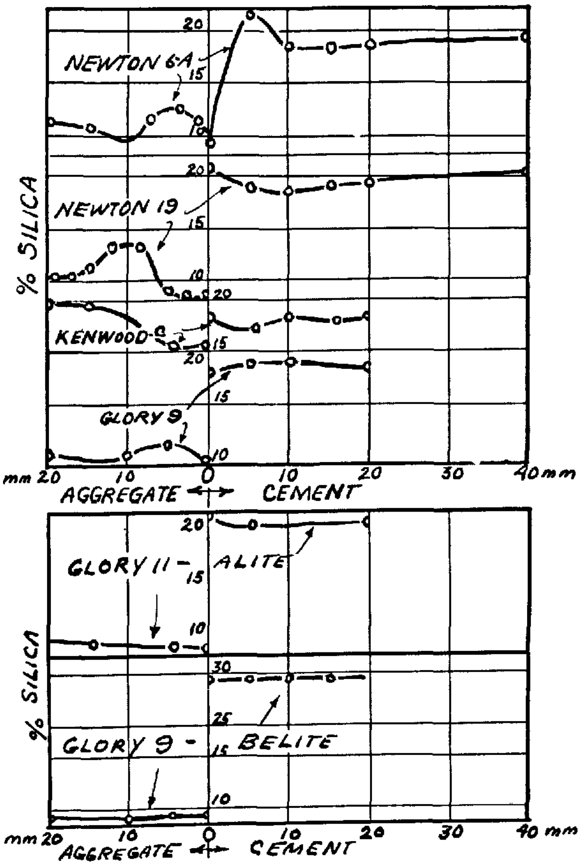

FIGURE 1. *Variation of silica content with distance from aggregate-cement paste interface.*

Silica shows variable behavior. In the case of the Glory aggregates which served as a basis for Bisque's work, silica increases in the reaction shell, and shows a drop in the cement paste. This behavior is also true for the Newton aggregates. Both aggregates can be characterized as dolomitic, lower-to-moderate insoluble residue types. In the Kenwood aggregate, a rock which behaves like the Kingston aggregate and is dolomitic with a high silica-rich residue, the reaction shell decreased in silica content and silica increased in adjacent cement paste. Regardless of how silica varies, a resistant silicified shell of amorphous silica results. In all cases magnesium migrates from the shell zone and some calcium migrates into the shell from the cement.

The cubes of Glory aggregate placed in alite and belite showed a behavior different from that when placed in portland cement. Silica was removed from the same type of aggregate which characteristically gained silica when placed in portland cement bars, indicating that alite and belite are not the source of silica in the shells.

X-ray data of the shell zone indicate quartz and dolomite decrease; calcite increases. In some instances some $Ca(OH)_2$ was found in the shell. In the immediately adjacent cement, the hydrated cement compounds showed a more disordered pattern.

Harwood's data suggest that silica migration is essentially an equilibrium reaction controlled by (1) the relative concentration of available silica in adjacent aggregate and cement, and (2) by the local pH environment. The dolomite-hydroxyl ion reaction (dedolomitization) explains the dolomite decrease and calcite increase in the shell. Some calcite could form through the introduced $Ca(OH)_2$ or Ca ions with CO_3 released during the reaction. Aggregates with low insoluble residue do not extract silica because they lack sites for silica precipitation or fixation and generally would have a good service record.

This latest research indicates that silica appears to move either way, and that all components of a carbonate aggregate are affected by alkali reaction. It emphasizes that several changes occur in the shell zone simultaneously. Shell formation does not mean a definite increase or decrease in silica content; it signifies the formation of amorphous silica.

Interesting as this data is, it must be pointed out that during all of Harwood's experiments it was assumed that the composition of the rocks was uniform and representative. One of the major problems in these studies is the experimental and quantitative controls needed to be positive of the direction of ion migration and compositional changes before and after an experiment. Since most of the quantitative methods of analysis are destructive, the initial composition must be assumed to be uniform and representative of similar materials.

In order to get around some of these experimental difficulties and to study silica behavior more accurately, Hiltrop [18] adapted a refluxing technique to measure silica more representatively. In an attempt to learn the form that the available silica or "silicate" is in and the conditions under which it migrates in and out of rocks, he applied the concept of "reactive" and "nonreactive" silica on the basis of the ammonium molybdate method [19] of silica determination and subsequent hydrofluoric acid treatment. After measuring the amount of silica in solution contributed by an aggregate by the ammonium molybdate method, it was found that HF treatment always increases the soluble silica present, indicating that more complex unavailable species of silicate are present. The immediately available species (probably monomeric silicate) was called molybdate "reactive" silica and the more complex HF-treated silicate, molybdate "nonreactive" silica.

Refluxing different deleterious aggregates in glass vessels at pH 12 produced varying amounts of reactive versus nonreactive silica. Hiltrop found that glass vessels produce 100 percent "reactive" silica in large amount. Cement pastes when refluxed in glass at the same conditions as the rocks produce very small amounts of total silica in solution, a large proportion of which is nonreactive and is accompanied by a coating of a calcium silicate compound on the walls of the reaction vessel.

This promising line of attack is being carried out in silica-free refluxing vessels, and it may show promise as a means of differentiating the potential reactivity of an aggregate in a manner more positive than present testing methods.

Summary

The research at Iowa State University raises more problems than answers. Research to date shows that the cement-aggregate reaction is selective and that dolomitic argillaceous carbonate rocks characterized by relatively high residues react with cement. All the components of the rock react to form a silicified "dedolomitized(?)"[2] shell. Silica can move in or out of an aggregate, and an attempt to study the form of the silica or "silicate" has led to the concept of "molybdate reactive" and "molybdate nonreactive" silicate.

Several problem areas remain where research needs to be done:

1. A need exists for more data on the behavior of Na and K in shell zones.
2. More data is needed on the behavior of silica and the conditions under which it migrates.
3. Data is required on sources of readily available silica in rock and cement.
4. More data on the true nature of carbonate rocks, especially mineralogical composition, texture, structure, and geological relationships.
5. The relation of carbonate aggregate-cement reactions to performance of concrete.

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[2] Magnesium may also come from a high-magnesium calcite.

6. Most important of all, knowledge of how alkali-induced reactions contribute to distress in concrete.

With regard to this last point, present information indicates that (excluding physical damage) distress can be produced by expansion, changes in the concrete or cement matrix, or a combination of both. If alkali reactions occur in the aggregate producing amorphous or some form of soluble silica which in turn may swell or expand because of osmotic processes, one can visualize that it is not the excessive amount of reactive silicate minerals which need be present, but the critical relationship between the size of the pore and the reactive silicate material present. A small amount of silica reacting in a small enough pore could cause enough confinement to produce expansion. This may be why some of our impure carbonate aggregates do not respond to the traditional alkali-reactivity tests which are being used.

One could also visualize that if silica is extracted from the cement, a gradual weakening of the concrete would result. Evidence that concrete in which carbonate aggregate-cement reactions have occurred does not gain strength during curing supports this possibility. Changes brought about in the cement during the reaction might even condition the concrete to later secondary changes which could cause additional expansion or deterioration.

Considerable progress is being made in carbonate-aggregate research, but the greatest gain this work has accomplished to date is the awareness that many types of reaction can and will occur when an aggregate is placed in concrete. The concept of cement-aggregate compatibility is more meaningful.

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Discussion

R. R. Hattiangadi and P. J. Jagus

Alkali-aggregate reactivity is known to have taken by far a very large proportion of the total toll of deterioration of concrete due to cement-aggregate reactions. There are, however, countries like Australia and Great Britain which are noted for complete absence of any notice of this reaction, although they have worked extensively on the very subject. For India, however, it cannot be said with any degree of confidence that there have been no cases of deterioration due to alkali-aggregate reactivity, as there do exist very large deposits of aggregates which are likely to contain potentially reactive minerals. The Deccan trap formations covering as much as 200,000 sq. miles in western India are known to contain reactive silica in the form of chalcedony, agates, zeolites, and glass. Besides, there are also known deposits of highly reactive traps and quartzites in the Kashmir area, and some reactive quartzites in the Delhi region.

Although there have been no cases of deterioration reported due to alkali-aggregate reactivity, it would be unwise to preclude its possibility merely on this consideration, because of the extended period of 8–12 yr. over which it could take place and the chances of its having gone unidentified due to want of scientific investigations.

As regards the part played by the level of alkali in cement, the two-decade-old contention regarding limiting the level at 0.6 percent Na_2O equivalent as a full and adequate safeguard against the possibility of the reactions could be looked upon with some doubt. Research work by Hanna and analysis of his and other data by D. O. Woolf in 1951 has brought out a concept of the alkali-silica ratio as governing the order of expansion more than the individual levels of the alkali and silica. Laboratory tests carried out at the Central Road Research Institute (India) have shown some validity of this statement. It could perhaps mean that the emphasis put exclusively on the level of the alkali may in the past have been overdrawn.

It may be mentioned that the current Indian standard specifications for portland cement do not contain any restrictive clauses regarding the maximum permissible limit for alkali content. However, utilizing the present-day knowledge of the subject, it would seem that potential reactivity could be avoided in areas of highly reactive aggregates by generally avoiding the use of high-alkali cements. In the absence of availability of cement with a sufficiently low alkali content, a recourse to the use of pozzolanic admixtures or pozzolan cements is indicated. With the extensive amount of research work that has been done all over the world on the subject, it cannot be denied that the mechanism of this reaction as understood even today carries a considerable element of hypothesis, if not of speculation. Even the precautionary measures recommended under some of the building codes and specifications on the basis of this work could perhaps be challengeable in respect of the safeguards assured by them.

I would like, therefore, only to emphasize that the authorities enforcing these codes should not have a tendency to run away with the mandates that are suggested in the codes, as research has made it amply clear that no one single variable, namely the level of the alkali or the reactive material, can cause harmful reactions. Due importance must be given to all scientific investigations and research and more particularly in considering the possibility of the reactions in the field to the study of single variables, their combinations, and the probability of any changes which may be brought about in their levels through peculiar environmental conditions before definite steps as safeguards against the dangers of these reactions are decided on.

Discussion

A. de Sousa Coutinho

In the very interesting and very well written report "Chemical Reactions Involving Aggregate", by P. Bredsdorff and co-authors, reference is made to a case of disintegration of mortar and concrete in sea water in the harbor of Leixões, Portugal.

The description of this alteration was obtained through a report presented by myself and co-authors to the XVIIth International Navigation Congress held at Lisbon in 1949.

Since then, a certain amount of research has been carried out in the Laboratório Nacional de Engenharia Civil, in Lisbon, Portugal, on this subject, and we are now in a position to advance a theory on the causes of this disintegration. Experience shows that *disintegration of portland cement mortar occurs when aggregate is composed of granite in which the feldspar component is altered.* As is well known, sodic and potassic feldspar is altered to kaolin by weathering. When this kaolinized feldspar is an aggregate component of a portland cement mortar maintained in sea water, a reaction takes place between the sea water sulfates and the alumina of the altered feldspar. The result of this reaction is the formation of a sulfoaluminate, and as such reaction takes place in a medium saturated with lime, with a *p*H higher than 12—as is the medium furnished by the hydration of portland cement—the formation of an expansive sulfoaluminate is obtained. We are then in the presence of a classical phenomenon of portland cement mortar disintegration in sea water. The formation of ettringite is obtained through reaction between sulfate from sea water, alumina from the aggregate, and calcium hydroxide from the hydrated portland cement.

Experience also shows that the replacement of part of the portland cement in the mortar by a good quality pozzolan is a means for counteracting this type of disintegration. In this case, the pozzolan combines with calcium hydroxide, and a decrease in the alkalinity of the medium of hydrated cement is obtained. Then, when sea water sulfate reacts with alumina from the kaolinized feldspar, formation of ettringite does not occur, as this reaction takes place in an unsaturated solution of calcium hydroxide.

When granite with sound feldspar is used as aggregate in a mortar or concrete exposed to sea water no corrosion occurs. Nevertheless, altered granite is used without any inconvenience in general construction works. Actually, in a certain region of northern Portugal, in which the harbor of Leixões is located, this altered granite is used as a mortar and concrete aggregate without difficulty, provided the concrete will not be exposed to sea water.

Figure 1a shows mortar prisms made with a granitic aggregate in which the feldspar component is kaolinized (São Gens granite), after being exposed to sea water for 2 yr and for 6 months. The mortar is completely destroyed after 2 yr; the first signs of corrosion appear at 6 months.

In figure 1b the same is shown except that the aggregate was a granite with its feldspar component perfectly sound (Madalena granite). No corrosion occurs.

In similar prisms, 30 percent of portland cement was replaced by pozzolan. Figures 2a and b show their appearence after 3-yr conservation in sea

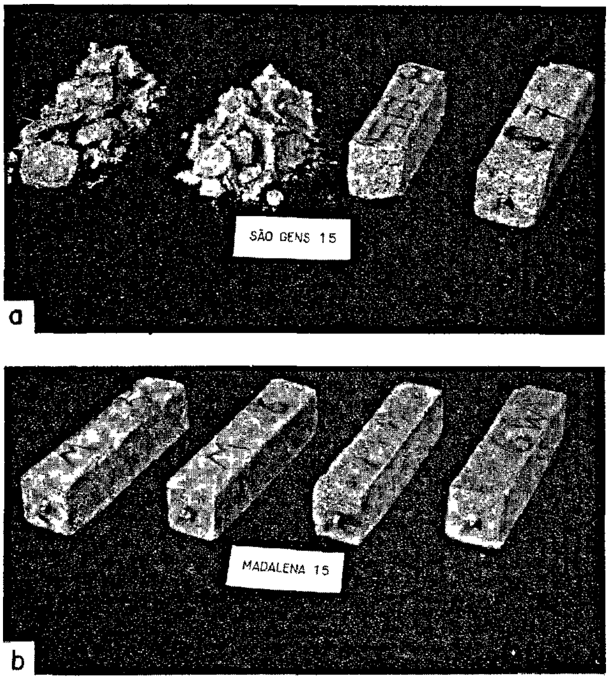

Figure 1. *Portland cement mortar prisms of granitic aggregate maintained in sea water.*

Mix proportions: 1 part portland cement to 5 parts of crushed granite between sieves No. 20 and 40.
a. Mortar prisms with kaolinized feldspar (S. Gens), kept for 2 yr (the two at left) and for 6 months (the two at right) in sea water.
b. Mortar prisms with sound granite (Madalena), kept for 3 yr in sea water.

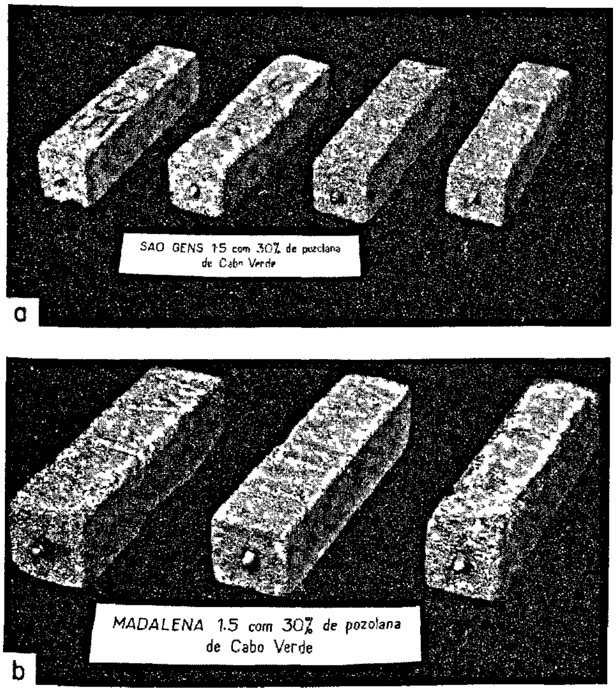

Figure 2. *Portland cement and pozzolan mortar prisms of granitic aggregate maintained in sea water.*

Mix proportions: 0.7 parts portland cement, 0.3 parts natural pozzolan of Cabo Verde to 5 parts of crushed granite between sieves No. 20 and 40.
a. Mortar prisms with kaolinized feldspar (S. Gens), kept for 3 yr in sea water.
b. Mortar prisms with sound granite (Madalena), kept for 3 yr in sea water.

water. As is seen, no disintegration occurs. In figure 3, expansion curves of these prisms are shown. These diagrams confirm the results shown in the photographs.

The study of the causes of this kind of alteration is still in progress in the Laboratório Nacional de Engenharia Civil. We have not yet done much experimental work on the problem but hope to do that in the next years.

Some notes already have been published on this subject, but unfortunately in Portuguese,[1] so the authors of the excellent paper under discussion have not had access to them.

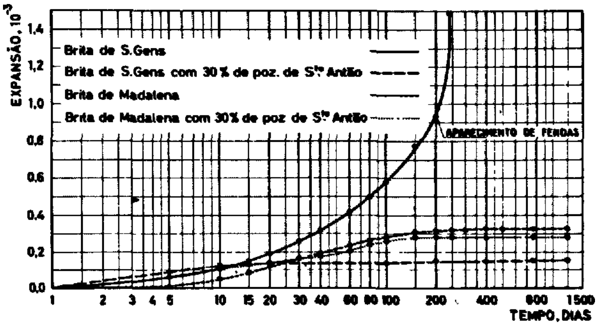

Figure 3. *Curves showing the expansion as function of time for the 4 series of prism tests shown in figures 1 and 2.*

(Ordinate: expansion, 10^{-3}. Abscissa: time, days. Legend gives source of aggregate and amount of pozzolan. Arrow indicates appearance of cracks.)

Discussion

Levi S. Brown

Two practical purposes are served in drawing up such a comprehensive and detailed bibliography and review. Though the paper is essentially self-sufficient, some merit may attach to a further word or two in practical application.

Firstly, when faced with a new problem in concrete malperformance, it is human nature to look first to precedent for guidance to explanation. This paper excellently facilitates the search for precedent. Experience however shows that no two cases ever are identical. Every case must be analyzed and judged on its own merits. That is the way precedent is built up.

This approach, while essential, faces two difficulties. The first is imperfect understanding of mechanical features of chemical reactions. One may perceive chemical products that obviously are secondary, yet perceive no proof that their production has been mechanically damaging. The second is that malperformance usually represents the combined effect of many factors. Usually also some one of these factors opened the way to contributory action of the others, but it can be difficult to perceive which one effected initial damage.

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A second purpose for a review such as this paper is to forestall recurrence of similar trouble in future construction, that is, to provide a basis for preventive measures. For example, the risk of alkali-aggregate deterioration should be diminished by keeping alkalies and reactive aggregates, insofar as they can be recognized, out of the concrete. There will be cases where neither can be avoided, completely.

But experience has shown that the presence of incompatible components in concrete does not of itself lead to deleterious action. Perhaps no concrete has ever been completely at equilibrium, either within itself or with its surroundings. That is, there are conditional features or circumstances, not in themselves sources of energy, which permit or open the way to deleterious action. Thus they may be called permissive features.

There is nothing new about this concept. It simply means that a quality concrete can be expected to endure and continue to serve its designed purpose. Of course, that is another way of saying that proper attention is given to composition of the cement and reactivity of the aggregate. The more common implications, however, are those of adequate cement factor, low water-cement ratio, perfect mixing, proper placing, protection, and curing. The extended variety of inimical agents reviewed in this paper leads to an impression that good concrete, that is, concrete that long endures in performance of its designed function, is the exception rather than the rule. Actually, with assiduous attention to these so-called quality factors, malperformance itself is the exception.

Discussion

R. Wyatt and G. C. A. Schuit

Silica (opal) when contacted with an alkaline solution will depolymerize according to the equations

$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}- + 2\mathrm{OH}^- \longrightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}^- + {}^-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}- + \mathrm{H_2O}$$

$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}- + \mathrm{H_2O} \longrightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH} + \mathrm{HO}-\overset{|}{\underset{|}{\mathrm{Si}}}-$$

This causes a swelling essentially due to the incorporation of water and (earth) alkalies penetrating into the concrete structures from the environment. Thermodynamically this is equivalent to an increase in osmotic pressure. The two explanations, the thermodynamic and the mechanistic, are therefore not necessarily in conflict. In fact, they represent two alternative manners of describing the same phenomenon.

Movement of $\mathrm{Ca^{2+}aq}$, $\mathrm{Na^{+}aq}$, and $\mathrm{OH^-}$ ions into an amorphous structure such as silica (opal) will not be determined in the first place by the size of the hydrated ions because their radii are almost equal, due to the presence of hydration water.

The important point is the chromatographic effect that occurs, since the Ca—O—Si bond is far more stable than the Na—O—Si bond. (Ca silicates are relatively insoluble, while Na silicate is soluble.) Hence, if a mixed solution of $\mathrm{Ca^{2+}}$, $\mathrm{Na^+}$, and $\mathrm{OH^-}$ is allowed to penetrate into a silicate column there will occur ion exchange because of the presence of OH groups on the surface of the silica.

$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH} + \mathrm{Ca^{2+}} + 2\mathrm{OH^-} \rightleftarrows -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}\ldots\mathrm{Ca}\ldots\mathrm{OH} + \mathrm{H_2O}$$

$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH} + \mathrm{Na^+} + \mathrm{OH^-} \rightleftarrows -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}\ldots\mathrm{Na} + \mathrm{H_2O}$$

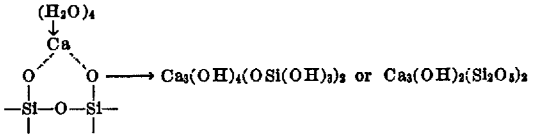
$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}\ldots\mathrm{Ca}\ldots\mathrm{OH} + \mathrm{Na^+} \rightleftarrows -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}\ldots\mathrm{Na} + \mathrm{Ca^{2+}} + \mathrm{OH^-}$$

Since the relative residence time of the $\mathrm{Ca^{2+}}$ ions may be assumed to be much longer than of the $\mathrm{Na^+}$ ions, the outer parts of the silica will be enriched in $\mathrm{Ca^{2+}}$ while $\mathrm{Na^+}$ together with its counter ion $\mathrm{OH^-}$ will be able to move further in.

It is our contention that the first product formed by the penetration of $\mathrm{Ca^{2+}}$, $\mathrm{Na^+}$, and $\mathrm{OH^-}$ into the silica is a surface compound of $\mathrm{Ca^{2+}}$ by replacement of surface protons from the OH groups. As has been stated, this occurs preferentially at the outside of the opal particles.

Parallel to this reaction a second one occurs which is essentially akin to the solution of silica in a basic solution, i.e., breaking of Si—O—Si bonds. This reaction occurs as a consequence of the penetration of (earth) alkali and $\mathrm{OH^-}$ ions into the structure.

A slower but possibly important reaction is the conversion of the surface layer of $\mathrm{Ca^{2+}}$ on hydrated silicate, present at the outside of the silica, into a more crystalline Ca hydrosilicate.



$$\longrightarrow \mathrm{Ca_3(OH)_4(OSi(OH)_3)_2} \text{ or } \mathrm{Ca_3(OH)_2(Si_2O_5)_2}$$

The results of Brunauer et al. strongly suggest that this conversion occurs for Ca compounds, while it has been proven for Mg and Ni silicates by Strese and Hofmann, Feitknecht and Berger, Van Eyk van Voorthuyzen and Franzen (Rec. trav. chim. **70,** 793 (1951)). The reaction readily occurs in some hours at 100 °C. At ambient temperature it is probably much slower but even then may well occur if sufficiently long times of reaction are assumed.

Discussion

G. M. Idorn

Research has aimed at knowledge of the properties of the calcium aluminate sulfates and on their influence on concrete through more than a hundred years. Most of this work has been based on the hypothesis that crystallization accompanied by volume increase of the "cement bacillus" was a major cause of expansion and concurrent disruption of concrete exposed to sulfate solutions, e.g., sea water. Later on, studies of the influence of the calcium aluminate sulfates on the initial setting of portland cement paste also commenced. And most recently, successful efforts both in the USSR and in the United States of America have proved that expansive forces ascribed to the crystallization of calcium aluminate sulfates can be controlled and utilized for prestressing of concrete members instead of external mechanical devices. This development may be said to reflect a remarkable range of opinions on the calcium aluminate sulfates: Once considered a common cause of rapid and severe deterioration, today utilized as a means of manufacturing concrete according to the most advanced constructional principles.

Admittedly a pessimistic view could emphasize that such self-stressed concrete has not yet proved durable, but an optimistic view might rather ask whether also other detrimental agencies upon further research possibly could be tamed and utilized. Today, expectations of a such kind may with some right be stamped as banalities, and one might prefer the more limited question: to what extent still nonrevealed factors are involved in the chemical reactions between aggregate particles and components of cement paste in concrete.

This question comes to the mind of the writer, reconsidering the general report: Chemical Reactions Involving Aggregates, the many interesting contributory papers, and supplementary information collected during recent visits in the United States of America, excellently guided by experienced colleagues.

The contribution by A. de Sousa Coutinho concerning the Port Leixões case, referred to in the general report, ought to receive much attention. The described disintegration of concrete exposed to sea water occurred only when the feldspar in granitic aggregates had been kaolinized (by weathering). Alumina released from the kaolinite was found to react with the sulfates of the sea water and with the calcium hydroxide of the cement paste, forming expansive calcium aluminate sulfates. These findings are of interest in other respects. They bring in mind the early investigation by J. C. Pearson and G. F. Loughlin [1],[1] treating disintegration due to reactivity of altered feldspar but, as far as can be seen now, without the presence of excessive sulfates. Also the severe reactivity of the Norwegian alum shale, referred to in reference [5][2] and of the cinder slags, described in reference [6][2] of the general report, should be considered in this connection. Furthermore, as Mr. Coutinho refers to pozzolanic admixtures as a suitable means of counteracting the described disintegration, attention should also be directed to the investigation by W. Eitel [2]. It is for instance mentioned in this paper that some pozzolans, excellently serving their purpose in concrete in sea water, may create expansive reactions in stronger sulfate solutions, dependent on the alumina present in the pozzolan.

All in all, the above-mentioned studies seem to demonstrate the need of renewed treatments of the lime-alumina-sulfate-water system, aiming at a more accurate description of the potentially expansive combinations of cements, admixtures, and particular rock types in aggregates, and with due regard also to the environmental exposure conditions, the structural qualities of concrete (e.g., permeability), and the constructional principles. The need of low-C_3A cements for concrete in sea water may be considered one subject of such studies, and the further development of self-stressing cements may be another. As a whole it is important to remember that the range of deleterious combinations within the outlined system is only a small part compared with the area of beneficial combinations. However, it should also be borne in mind that with deleterious combinations exceedingly rapid and disastrous deterioration has been experienced in several cases.

The basic description of the alkali-aggregate reactions seems to have been the subject of most discussion, whereas to a regrettable extent the practical aspects have received less attention.

W. C. Hansen claims in his contribution that "the fundamental nature of the alkali-aggregate reactions is understood". Judging from other contributions, however, there seem to remain rather different opinions about this fundamental nature. The writer feels that to some extent the disagreements can be ascribed merely to differences of terminology concerning these rather new fields of colloidal chemical-physical problems. But even with this in mind considerable uncertainty remains.

Little is still known about the relative reactivity of different silica minerals—and this is a question of the chemical nature of the reactions. Neither has the influence of particle size of coarse aggregates been sufficiently studied as a means of disclosing the mechanical nature of the reactions. Furthermore, the necessity of an initial precipitation of a lime-alkali-silica complex in the boundary area of a reacting particle before expansive pressure can develop, is emphasized by some of the authors. But other authors have found that the hardened paste itself can act as a membrane for osmotic pressures, and seem not to agree in the significance of two different types of reaction products.

The possible formation of "reaction rims" in the boundary areas of reacted particles, the composition of such rims, the reasons why and the ways in which they form are problems closely connected with the above-mentioned theories.

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[1] Figures in brackets indicate the literature references at the end of this paper.

[2] References in Paper VI-1.

It appears from earlier papers (see for instance W. C. Hanna, p. 93, in reference [32][2] in the general report) that a reaction rim may be a rather solid outer shell of a reacted particle in which the interior has been more or less dissolved and weakened.

Such observations tend to support the hypothesis that a nonswelling lime-containing complex is the reaction product in the boundary zone surrounding the less stable alkali-silica complex without lime in the interior. However, a different type of reaction rim appears in figure 1, showing a reacted particle of dense, black flint in cement paste. The boundary zone (white in the photograph) in this case merely represents a depth of penetration inward from the surface of a partial dissolution of the silica structure (chalcedonic) of the flint, whereas no sign of reaction can be detected in the interior of the particle. Hence, the gel that flowed through cracks to the surface of this specimen originated from the boundary zone.

Incidentally, one similiarity between the classical alkali-aggregate reactions with siliceous aggregates and the cement-aggregate reactions may prove to be the formation of reaction rims, as excellently demonstrated by R. E. Bisque and John Lemish [3], and discussed by the latter in his present discussion. In the oral discussions of the symposium the writer mentioned that investigations of concrete deterioration ought to utilize field examinations of concrete structures to a much higher extent than hitherto. If such examinations are undertaken by especially trained inspectors having a background in basic research on deterioration, and if modern recording devices and adequate statistical treatment of data are utilized, information which we are lacking today on actual conditions of concrete deterioration could rapidly be collected and interpreted, in many countries where concrete is a prevailing structural material, to the benefit of the many other countries where concrete is going to be a prevailing means of technical development.

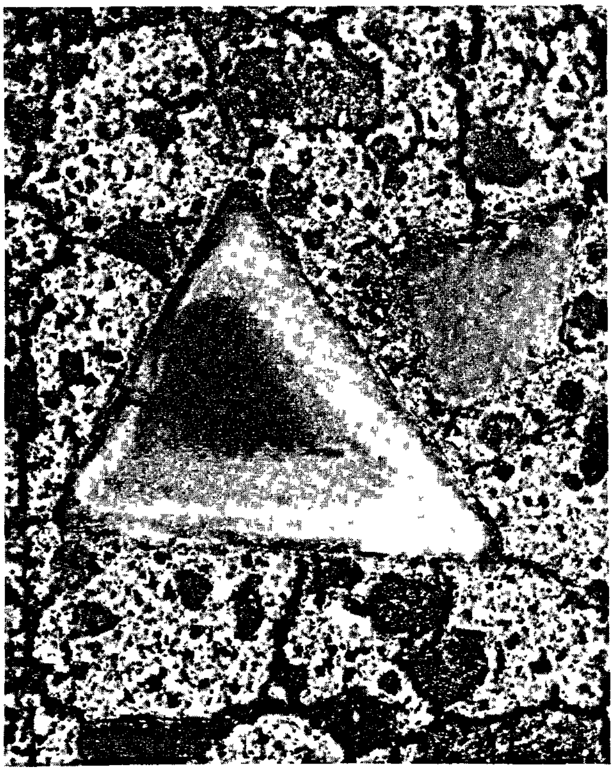

Figure 1. *Triangular particle of dense, black flint in cement paste*

Through some months of alkali-aggregate reactions cracks with gel developed on the outer surface of the cement-paste bar. A thin-section revealed the shown partial dissolution of the boundary zone of the flint. The interior of the particle appears to be unaltered.

The shortest edge of the particle is 4.5 mm true length.

L. S. Brown mentions correctly in his contribution that interpretations of field examinations will always have to face difficulties due to:

1. Incomplete understanding of the mechanical effects of chemical reactions, and
2. The complexity of natural detrimental exposure.

It is, however, the experience of the writer that the significance of the mechanical feature of chemical reactions in concrete is frequently more clearly demonstrated in concrete structures than by selected laboratory experiments designed with consideration to available methods of measurements rather than to the structural conditions. (An illustration of this opinion is briefly outlined in the general report, with reference to figure 13.)

It is also the experience of the writer that the complexity of phenomena of deterioration does not always present insurmountable problems. Several cases can be found of concrete failures that are not at all complex and where accordingly a prevailing type of deterioration can be isolated and studied. Such studies of course facilitate the investigations of more complex cases.

Some observations on the mechanism of alkali-aggregate reactions appeared to the writer during a recent visit to the King City Bridge in California. This structure is referred to by Th. E. Stanton on p. 57 in his paper, reference [32][2] in the general report. It was built in 1919–1920 across the Salinas River west of King City, Monterey County. Within 3 yr after construction, cracking was in evidence in the caps of the piers, and later on the cracks extended into the columns of the piers. In 1940 the cracking apparently had been extensive, see, e.g., figure 1e in the above paper. The condition on November 13, 1960, appears from figures 2 and 3. The bridge is still in use leading the heavy traffic of U.S. 101 over the river, and general repair does not seem to have been undertaken. The following observations may claim some interest:

1. The deterioration seems to have progressed only very little or not at all since 1940. Maybe disruption ceased even much earlier. It was not visible whether all available alkalies have been

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[2] Reference in Paper VI-1.

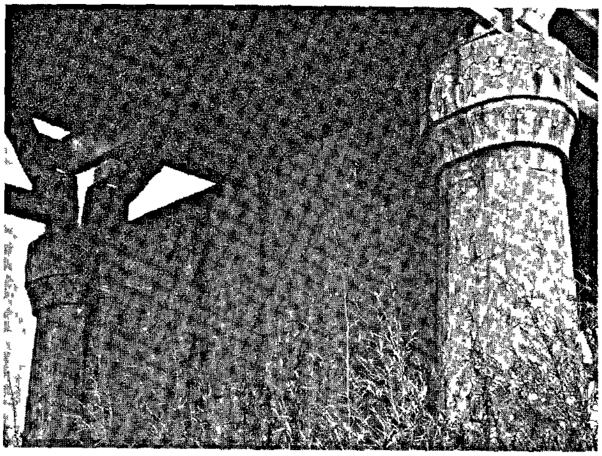

FIGURE 2. *King City Bridge, Monterey County, California.*
Built in 1919 to 1920.
Affected by alkali-aggregate reactions.
Note that deterioration is severe in columns and pier caps, whereas diaphragm wall is undamaged.

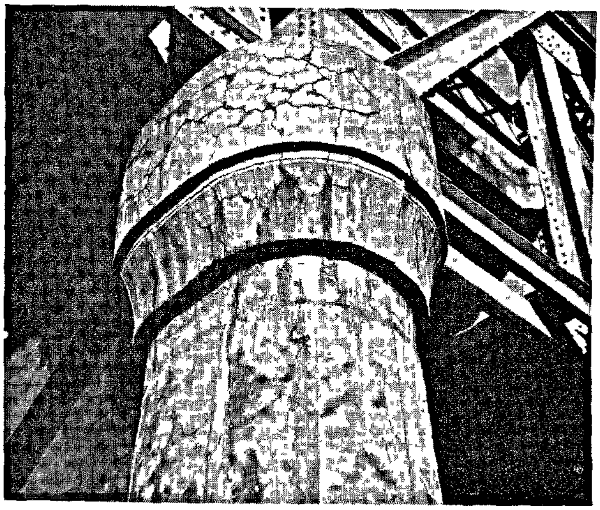

FIGURE 3. *King City Bridge. Pier cap with typical map cracking.*

consumed or all reactive particles have been dissolved, or whether reactions still are continuing, either in a nonexpansive phase, or still expansively, but without further external cracking.

2. Cracking has appeared in the columns and the caps of the piers, but only to a minor extent in the diaphragm walls between the columns. although the concrete composition seems to be the same. This feature is repeatedly met in structural failure caused by alkali-aggregate reactions, i.e., protected parts crack less than exposed areas. The predominant climate conditions are unfortunately not well recorded, and no data are available that could help explain the fact that the north caps and columns are as much affected as are the south ones in this east-west directed bridge.

3. Vertical cracks are seen to prevail downward on the column shafts whereas the caps show extensive pattern-cracking, see figure 3. This feature might be due to differences in either chemical, physical, or mechanical conditions. Laboratory experiments have not always taken all these possibilities into account.

4. Cracking is the prevailing visible evidence of the reactions. Both pop-outs and gel exudations are very infrequent. Could the absence of pop-outs possibly have something to do with the absence of freezing and thawing, and may the lack of gel exudations result from the dryness of the climate, or be related to the season at the date of visit? Obviously these questions need more field examinations as basis for clarification.

5. The climate is apparently very dry, if not arid, but heavy rain had fallen the day before the visit. Is rarely occurring humidity possibly a factor leading to rapid development of the reactions rather than a constantly humid climate or constant aridity? Or may it possibly be that the reactions are only insignificantly influenced by external humidity?

Even more problems could be outlined on the basis of the behavior of the King City Bridge in order to encourage a close correlation between theories and experience in practice. Twenty miles south of King City the San Ardo Bridge, very similar to the above mentioned in construction and size, showed quite the same type and extent of deterioration. Apparently this structure was also a clear-cut case of deleterious alkali-aggregate reactions. But within the next 50 miles at least two similar bridges over the Salinas River are found without evidence of the reactions.

Most authorities consider—as Th. E. Stanton did—the use of respectively high- and low-alkali cements to be the reason for this apparent anomaly. Accordingly, cements with less than 0.6 percent equivalent Na_2O are generally prescribed wherever aggregates known to contain reactive constituents are met, or such aggregates are abandoned.

Repeated field inspections have confirmed that deleterious reactions as a structural problem are effectively counteracted both in these ways and, particularly in dam constructions, by use of pozzolanic admixtures.

More rarely, a choice is at hand between alternate types of aggregates, reactive or definitely nonreactive, or it may be possible sometimes to rely upon improvement of reactive aggregates, e.g., by heavy-medium flotation.

The widespread success in structural practice of these safeguards has established a favorable situation for further research on alkali-aggregate reactions.

The problems have been faced and given attention by comparatively many authorities and individuals. The most urgent demand for solutions has been met by the above mentioned means. The exceptional cases, in which these are going to prove insufficient, will offer excellent possibilities for systematic examination. At the same time, advanced research is to be continued on basic chemico-physical problems of the reactions, as appears from the present series of discussions.

The writer does not consider the now-presented information on the so-called cement-aggregate reactions sufficient to form a general hypothesis on the fundamental nature of this type of deterioration. In fact the presentations by John Lemish and associates, and results reported by H. Hadley at the Portland Cement Association during the Symposium seem to indicate that we ought to consider chemical reactions between components of portland cement paste and of minerals in aggregates in a broader aspect than has usually been done hitherto. The traditional alkali-aggregate reactions might be only one type of mutual reactivity. Other types of such reactivity may be beneficial (and therefore still not recognized). Even the adhesive forces of the contact phase might be studied according to these concepts.

In conclusion, the writer wants to mention certain phenomena referred to by John Lemish in his paper of discussion. Deleterious reactions in dolomitic, argillaceous limestones proved to involve migration of silica ions from the cement paste to the reaction site in the aggregates. If this observation means that silica by internal reactions may be released from the binding constituents of the paste, this would account for a mechanical picture of the deterioration, involving both cracking due to heterogeneous expansion originating from reacting aggregate particles, and crumbling due to partial dissolution and concurrent weakening of the paste. It could possibly also account for loosening of the bonds between aggregates and paste.

Most investigators of structural failures seem to have experienced that by traditional alkali-aggregate reactions the concrete will normally be "sound between the cracks", and figures 2 and 3 of this discussion can be taken as one confirmation of this concept. However, in field concrete (highway pavements) affected by the dolomitic reactivity a general disintegration and weakening both of cement paste and of reacted aggregates have been experienced rather than structural expansion and typical map-cracking.

It seems that proper attention ought to be paid also to this difference by further attempts to enlighten the basic theoretical and practical problems of chemical reactions involving aggregates.

References

[1] J. C. Pearson and G. F. Loughlin, An interesting case of dangerous aggregates, J. Am. Concrete Inst. **19,** 142–155 (1923).

[2] W. Eitel, Recent investigations of the system lime-alumina-calcium sulfate-water and its importance in building research problems, J. Am. Concrete Inst. **53,** 679–698 (1957).

[3] R. E. Bisque and John Lemish, Silicification of carbonate aggregates in concrete, Highway Research Board, Bull. **239,** 41–55 (1960).

Closure

Niels Munk Plum

It is with the greatest interest that we have studied the five contributions to the discussion which was presented at the symposium, and also the four contributions which have later appeared by correspondence.

The well-prepared contributions have altogether thrown so much light on the present knowledge of the subject that the author is left with the satisfying feeling of a most effective symposium, though it leaves little necessity for concluding remarks.

Mr. Lemish has presented such evidence on the subject of unidentified cement-aggregate reactions that it leaves little doubt as to their character being definitely different from the "common" alkali-silica reactions. As minerals similar to those with which Mr. Lemish has been working may be found in other parts of the world, it is hoped that research on this interesting subject will be continued.

Mr. Hattiangadi stresses the nonexistence of a "safe" limit of the alkali content of the cement. This realization is in our opinion very important and strongly supported by the evidence which we have presented in our paper from our Danish tests.

We are grateful for the contribution from Mr. Hagerman as we had only been able to refer to his work very briefly in the general report.

Concerning the contributions from Messrs. Pike, Hubbard, and Newman, Wyatt and Schuit, and Coutinho we feel that they have thrown new light on a number of important questions on which more research certainly is needed, but we find that at this place an extended discussion will not be of much value.

Mr. Brown has made some very interesting remarks on the scope of research on the performance of concrete with which we are quite in accord. We regret if the general report has given the reader the impression that durable concrete is the exception rather than the rule. Even in Denmark where very heavy deterioriation is taking place, by far the greater part of our concrete is performing very well. The reader must, however, excuse the fact that we are more interested in deteriorating concrete and upon second thought he will certainly also understand why.

Finally a vivid discussion has taken place between W. C. Hansen and T. C. Powers, mainly on explanation of phenomena which have previously been described in the literature. We find that the arguments presented by Mr. Powers are very convincing and strongly supported by his evidence, and if a judgment is needed at the moment, we think that we can quite safely leave it to the reader.

Paper VI-2. Frost Action in Concrete *

Poul Nerenst

Synopsis

Considerable progress in knowledge of the different physical properties of concrete has been achieved within the last ten years. Extensive basic research carried out by T. C. Powers and his co-workers at the Portland Cement Association Laboratories in the U.S.A. has also given a much more detailed picture of the various mechanisms of freezing which pertain to hardened concrete.

Freezing of a porous body may cause damage: (1), by macroscopic ice segregation; (2), by microscopic ice formation combined with a drying of cavities with very small dimensions; or (3), by hydraulic pressure generated by the freezing of water in the capillaries.

Freezing may cause rupture of the paste or of the aggregate. The development of air-entraining agents has made it possible to make cement paste which in the hardened state has very high resistance to freezing and thawing. The beneficial effect of the air bubbles may be explained by the hydraulic-pressure theory and the diffusion theory.

The aggregates used in most countries are dense and of high durability to freezing, but difficulties may arise in some countries where porous aggregates are a main part of the available material for concreting. A short review of the theory and of laboratory experiments to determine the freezing resistance of aggregate is given.

Freezing of concrete during the setting period and in the initial stage of hardening may cause serious damage. This problem is of great economic importance to the northern countries, and a number of tests have been performed recently to determine the required prehardening period to avoid damage from freezing at early ages.

Résumé

Des progrès considérables dans la connaissance des différentes propriétés physiques du béton ont été accomplis au cours des dix dernières années. Des travaux de recherche fondamentale extensifs effectués par T.C. Powers et ses confrères aux Laboratoires de la Portland Cement Association aux Etats-Unis, ont également fourni une représentation beaucoup plus détaillée des différents mécanismes de congélation qui on rapport au béton durci.

La congélation d'un corps poreux peut occasionner des dégâts: (1) par ségrégation macroscopique de la glace, (2) par formation de glace microscopique jointe à un séchage de cavités de très petites dimensions, ou (3) par pression hydraulique produite par la congélation de l'eau dans les capillaires.

Le gel peut causer une rupture de la pâte ou de l'agrégat. Le développement d'agents d'entraînement de l'air a rendu possible la fabrication de pâtes de ciment qui présentent à l'état durci une très haute résistance au gel et au dégel. L'influence bénéficielle des bulles d'air peut être expliquée par la théorie de la pression hydraulique et la théorie de diffusion.

Dans la plupart des pays, les agrégats utilisés sont denses et présentent une forte durabilité au gel, mais dans certains pays des difficultés peuvent paraître où les agrégats poreux forment la plupart des matériaux disponibles pour la fabrication du béton. La théorie et des expériences de laboratoire pour déterminer la résistance de l'agrégat à la congélation sont rapidement passées en revue.

La congélation du béton pendant la période de prise et dans le stade initial de durcissement peut causer de sérieux dégâts. Ce problème est d'une grande importance économique pour les pays nordiques, et un certain nombre d'expériences ont récemment été effectuées afin de déterminer la période de prédurcissement nécessaire pour éviter les dommages dus à la congélation pendant les premiers jours de maturation.

Zusammenfassung

In den letzten zehn Jahren wurde viel Neues betreffs der physikalischen Eigenschaften des Betons gelernt. Die Fundamentaluntersuchungen, die T. C. Powers und seine Mitarbeiter in den Laboratorien der Portland Cement Association in den Vereinigten Staaten unternommen haben, haben sehr dazu beigetragen, daß man sich heute ein besseres Bild von den verschiedenen Gefriermechanismen machen kann, die im erhärteten Beton vorkommen können.

Das Gefrieren eines porösen Körpers kann einen Schaden hervorrufen wegen (1) makroskopischer Eisabscheidung, (2) mikroskopischer Eisbildung, die mit einer Austrocknung von sehr kleindimensionierten Löchern Hand in Hand geht, oder (3) hydraulischen Druckes, der durch das Gefrieren des Wassers in den Kapillaren hervorgerufen wird.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the laboratories of Danish Gas Concrete, Inc., Virum, Denmark.

Das Gefrieren kann eine Zerstörung der Masse oder der Zuschlagstoffe hervorrufen. Die Entwicklung der luftzuführenden Mittel hat es möglich gemacht, eine Zementpaste zu erzeugen, die im erhärteten Zustande gegen Einfrieren und Auftauen sehr widerstandfähig ist. Der günstige Einfluß der Luftblasen kann an Hand der Theorie des hydraulischen Druckes und auch mit Hilfe der Diffusionstheorie erklärt werden.

Die Zuschlagstoffe, die in den meisten Ländern verwendet werden, sind dicht und sehr beständig gegen ein Einfrieren, aber in einigen Ländern, in denen überwiegend poröse Zuschlagstoffe für Beton angewandt werden, muß man Schwierigkeiten erwarten. Eine kurze Übersicht über die Theorie und die Laboratoriumserfahrungen der Bestimmung der Einfrierwiderstände der Zuschlagstoffe wird gegeben.

Das Einfrieren des Betons während der Erstarrung und in der ersten Erhärtungsstufe kann einen großen Schaden hervorrufen. Dieses Problem ist wirtschaftlich für die Nördlichen Länder sehr wichtig und eine Reihe von Untersuchungen ist kürzlich angestellt worden, um die nötige Vorhärtungszeit zu bestimmen, sodaß man einer Beschädigung durch ein Einfrieren frisches Betons vorbeugen kann.

Introduction

Deterioration of concrete due to freezing action has been observed in a great number of structures exposed to water and low temperature. The damage caused by freezing has possibly involved higher expenditure to repair than any other destructive force.

Before the second World War an exact knowledge of the factors influencing the resistance of concrete to freezing and thawing were not well known. It was the general idea, however, that strong concrete also would be durable. In the older days when the cost of labor was comparatively lower, and the speed of construction was not as important as today, a number of structures were built with sufficient strength and high durability.

At the 100th anniversary of the use of portland cement in Denmark in 1960, a photograph was shown of a fortress built in the sea east of Copenhagen (fig. 1). The work was begun in 1860 and continued during various periods before 1880. The concrete is today in excellent condition in spite of the exposure to water and freezing-and-thawing cycles.

The ideas of making good concrete are much older than 1918, when Abrams formulated the relation between water-cement ratio and strength. H. L. Childe [1],[1] the managing editor of "Concrete and Constructional Engineering," is to be credited for having quoted a prescription for making good concrete, which was found in a book on concrete written by Henry Reid, a civil engineer, and published in 1868.

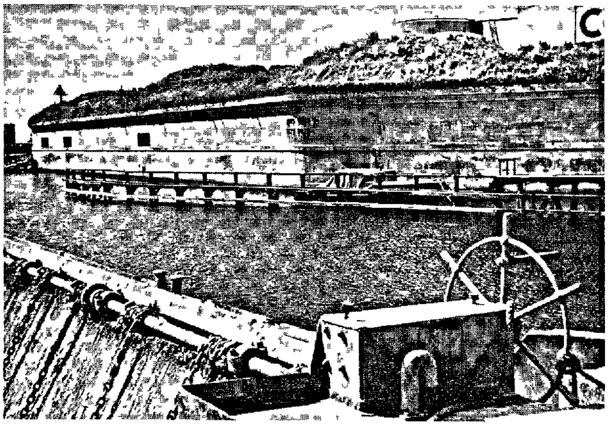

Figure 1. *Concrete structure near Copenhagen of an age of 100 yr.*

(G. M. Idorn)

"The due and thorough incorporation of the cement, sand, shingle or gravel, with the least amount of water, is the ABC of the process of concrete making, and unless this is rigorously attended to much disappointment will be experienced. The whole of the ingredients should be well mixed first in a dry state, and when this is thoroughly done a quantity of water added to render the mixture plastic enough to be put into moulds or placed between the boards used for forming the walls. As a rule the less quantity of water you can use the better. The concrete should be well rammed in as dry a state as is consistent with the proper requirements of the material, for too small a quantity of water would be quite as injurious as an excess; again, that would be materially influenced by the amount of percussion applied by the impingement of the rammer. The rammer should be as heavy as can conveniently be used. Sand, where a choice exists, should be as rough and coarse as possible. A rotten or friable aggregate is to be avoided. The sand must fill up the vacuities in the compound. Where practicable, concrete blocks should be placed for some days or weeks in water. Concrete, when so treated and carefully and thoroughly mixed, will be immensely superior in quality to the ordinary sloppy and roughly-handled mixture commonly called concrete, only in many cases entitled to the name because it contains certain proportions of the necessary ingredients."

In the twenties and the thirties of our century the wet concrete mixes were growing in popularity, foremost in the United States, but also in many countries in Europe, and the freezing resistance of concrete was diminishing. The low durability of concrete roads was growing to be a serious problem, and was presumably one of the reasons for launch-

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[1] Figures in brackets indicate the literature references at the end of this paper.

ing the big research program, "Long-time Study of Cement Performance in Concrete," in 1940 [2]. A few years earlier the beneficial effect upon the freezing resistance resulting from entrained air was discovered in the U.S.A., and much work has since been devoted to research on air-entrained concrete and its properties and manufacture.

The use of air-entrained concrete was only slowly and reluctantly adopted in Europe within the last decade, but even today you may in many quarters in Europe find die-hards, who as yet are not convinced that air-entrainment is an advance of the utmost importance for concrete durability, mostly because they do not want to sacrifice a few percent of the strength in order to get a much higher durability.

The professional and unbiased engineer is ready to adopt a new material or method if all empirical data tell him that good results can be obtained, without knowing the basic and chemical laws involved in obtaining the good results. Portland cement has, for example, been used for several hundred years, although the nature of the hydration products has been the object of vigorous discussions at all symposiums on cement chemistry so far, and it is not to be expected that a final agreement will be reached at this symposium either. The use of air entrainment was adopted in the United States 20 years ago, but a qualitative explanation of the mechanism of freezing air-entrained concrete has been developed within the last decade. Taking into consideration the very complex nature of freezing phenomena, the progress is very notable, and it is mainly due to T.C. Powers and his co-workers at the Portland Cement Association.

The number of reports and studies published on freezing action is so large that it is almost impossible to cover all the aspects of the subject in the present paper in a balanced form. Some excellent reviews by Powers [3] and Möller [4] have been very valuable in the preparation of the present paper, which consequently does not pretend to contain many new points of view.

The first part of the paper deals with the freezing of hardened concrete, where most of the physical properties of the ingredients have definite levels. The different mechanisms of freezing and the effects upon the paste and aggregate are summarized. Only a few references to laboratory tests on concrete are given, because a vast amount of test data is difficult to interpret in the light of the basic knowledge of today, as most of the factors governing frost resistance have not been recorded.

A brief summary of test methods employed in measuring the damage caused by frost action is given.

The last part of the paper deals with freezing of concrete at early ages, which is a much more complicated case than freezing of mature concrete, because almost all of the physical properties of concrete are changing as the hydration is progressing.

Some observations on freezing of aggregate and concrete are related from job sites, and a summary is given of tests carried out to determine the required prehardening time to avoid frost damage.

Freezing of Water in Hardened Concrete

The freezing of water in concrete can give rise to stresses and possibly cause rupture either of the paste or of the aggregates. The disruptive forces are due to the well-known fact that conversion of water into ice is accompanied by an increase of volume of about 9 percent.

The freezing point is 0 °C only for pure water in the normal-stress condition. The water in concrete often contains small amounts of alkalies, which cause a depression of the freezing point, preferably called the melting point to avoid the influence of supercooling.

The melting point of ice is also dependent upon the size of the cavities or pores where the water is situated, as pointed out by Powers and Brownyard in 1947 [5]. For most aggregates having noticeable porosity the size of the pore structure is such that the depression of the melting point is insignificant.

The hardened paste is characterized by a very high porosity combined with pores and interstitial spaces of exceedingly small dimensions. The result is that only part of the water freezes at temperatures just below 0 °C. When the temperature is lowered, increasing amounts of water are converted into ice, but even at −78 °C some of the water in the most narrow spaces within the gel is unfrozen.

In the following considerations it is assumed that the paste has an internal structure (fig. 2) as described by Powers and Helmuth in 1953 [6]. Later observations by Åke Grudemo with the electron microscope have shown that the hydration product consists of slender ribbons and crumpled sheets, so that the idea of the sphericity of the gel particles cannot be maintained. This has,

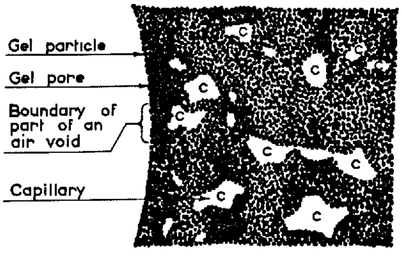

FIGURE 2. *Model of capillaries and gel in hardened portland cement paste.*

(Powers and Helmuth [6])

however, but little influence upon the conception of the way in which water is fixed in the paste. The water molecules are exposed to forces which depend on the distance from the gel particles.

The greater the distance between the gel particals and the water molecules, the more freely is the water moving in the paste and the higher is the resemblance to water in normal-stress condition with regard to water evaporation, melting point, etc.

After presentation of the general ideas pertaining to the mechanisms of freezing, the paste and the aggregate will be treated separately on account of the big difference between the internal structures of the two components.

Theories of the Mechanism of Freezing

Macroscopic Ice Segregation

Taber [7, 8] has explained how frost upheavals occur in soils, due to macroscopic ice segregation. When free water turns into ice in the larger voids and cavities, the capillary water is drawn from the unfrozen soil, and ice lenses are developed. If the possibility of continued capillary suction of water from the ground-water zone exists, the ice lenses will grow, and the result will be frost upheavals (fig. 3). The development of the ice lenses is dependent upon the flow of water through the soil and consequently depends upon the capillary suction and the permeability.

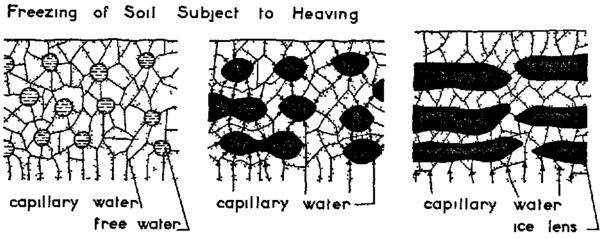

FIGURE 3. *Mechanism of macroscopic ice segregation in soil.*
(Nerenst, Rastrup and Idorn [10])

According to A. Casagrande [9] ice lenses and frost upheaval can be expected in soil of varying grain sizes, if the content of particles below 0.02 mm is higher than 3 percent. In soil of rather uniform grain sizes the content of fine particles may reach 10 percent as shown by the dashed line (fig. 4).

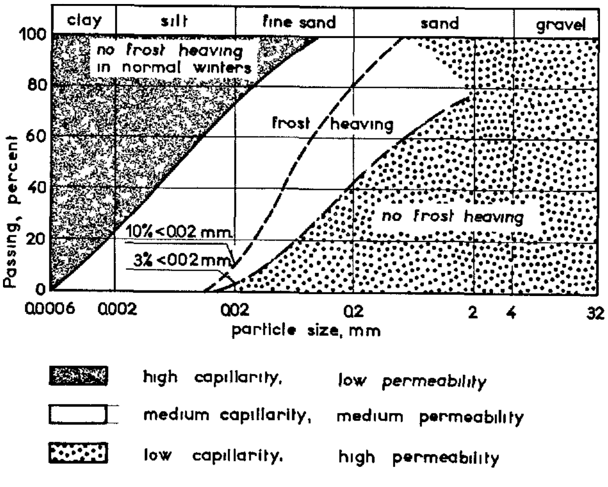

FIGURE 4. *Interrelation between the possibility of frost upheavals and grading of soils.*
(Kögler and Schneidig [9])

Soils with grading curves to the left of the white area will have very high capillarity, but the permeability is so low that no frost heaving will occur in normal winters, as the transport of water from the ground water table is not sufficient to keep the ice lenses growing.

Soils with grading curves to the right of the white area have very high permeability, but the capillarity is too low, so that the water will freeze in place without forming ice lenses.

As pointed out by Nerenst, Rastrup, and Idorn [10] fresh concrete may be considered as an artificial soil, which contains such an amount of fine particles—clay, filler, and unhydrated cement—that the mixture under special conditions is susceptible to the formation of ice lenses according to Casagrande's criterion.

The formation of ice lenses has been used by Collins [11], in Great Britain, as the explanation of the deterioration of low-quality concrete with access to moisture from the surroundings, for instance concrete roads on clay subgrade.

Collins has shown by experiments that cylinders of low-quality concrete frozen from the upper surface show the formation of ice lenses, when the bottom face is in contact with water.

In 1945 Powers [12] presented his paper "A Working Hypothesis for Further Studies of Frost Resistance of Concrete," in which the hydraulic-pressure theory was outlined. Powers stated that the Taber-Collins theory cannot be applied to hardened concrete of average quality, because the growing of the ice lens would be prohibited by the tensile strength of concrete being much higher than the cohesion in soil. He quotes Taber [8], who found that loading of soil often caused it to freeze as a closed system, i.e., a system from which water could not escape and into which water could not enter. Thus Powers at that time thought that ice lenses would not be formed in hardened concrete on a macroscopic scale as in soils, but "it would be reasonable, however, to assume that ice segregation takes place in concrete on a submicroscopic scale. As already pointed out, the hardened paste is considered to be composed largely of a porous gel containing a system of capillaries. If the ice forms only in the capillaries, as seems likely, then we may imagine it to be forming in a container having porous, water-laden walls of gel. Hence, the ice could and probably would receive water from the walls as well as from the more open capillaries. The amount of water available from the gel is very limited; nevertheless some expansive force due to this effect is probable."

It is interesting to note that although Powers at that time emphasized the hydraulic-pressure theory, he still considered it worthwhile to investigate other mechanisms of concrete deterioration due to freezing. Research work was started at the Portland Cement Association Laboratories in the U.S.A., and the result has been the diffusion theory or the theory of microscopic ice segregation, which will be treated in more detail below.

At the RILEM Symposium in Copenhagen, 1956, Powers [13] drew the conclusion that in mature concrete, macroscopic ice segregation will only take place when the water-cement ratio is above 0.9 by weight and under special climatic conditions, while it is likely to take place in any concrete during the early stages of hydration.

Hence, the formation of ice lenses on a macroscopic scale is further treated in a following section, where freezing of fresh and green concrete is discussed.

Microscopic Ice Segregation

The theory of segregation of ice on a microscopic scale within the cavities of the hardened paste has been presented by Powers and Helmuth [6]. G. Pickett [14] has further given a mathematical treatment of the transport of water in cement paste during freezing.

During the research work carried out in the P.C.A. Laboratories in order to verify the hydraulic-pressure theory it was found that it could be experimentally confirmed, but at the same time it was learned that the hydraulic-pressure theory did not account for all the phenomena observed.

Part of the effect of freezing is apparently due to a tendency of microscopic bodies of ice to grow in locations where the water is little influenced by adsorptive forces, i.e., in the capillaries and voids. The ice bodies draw water from the gel by a diffusion process.

Volume change due to freezing was studied on specimens of neat cement paste in the saturated state, some made with and some without entrained air. The length change was recorded in microinches per minute. The temperature was measured with an accuracy of about 0.1 °C. Several hundreds of experiments were made, in which length change, temperature change, and elapsed time were recorded automatically. Typical results of the tests are shown in figure 5.

It is characteristic that cement paste without entrained air dilates as could be expected; and, accepting the hydraulic-pressure theory, it is also understandable that the air bubbles can relieve the stresses from the hydraulic pressure building up in the pores during the freezing, so that the specimens will contract thermally when the temperature is lowered.

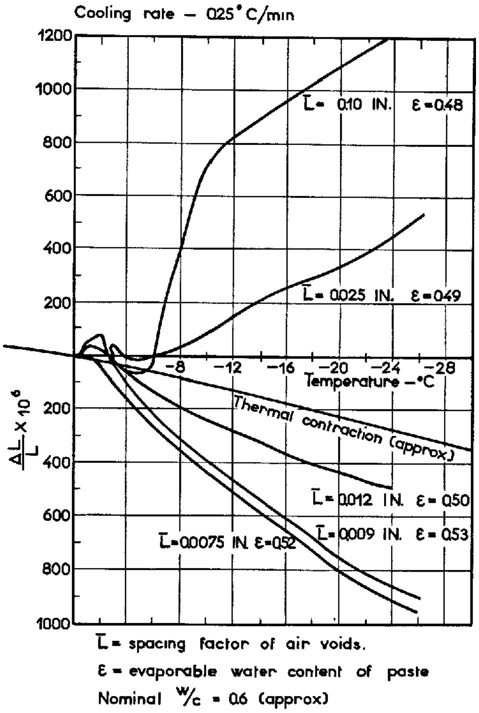

FIGURE 5. *Volume change during cooling of hardened cement paste as influenced by the bubble spacing factor* $\bar{L}$.
(Powers and Helmuth [61])

By closer study it was found, however, that the decrease in length was greater than could be expected from the thermal contraction.

From thermodynamic studies it was concluded that water in the capillaries or on the walls of the air bubbles was forming ice bodies on a microscopic scale, which were able to draw water from the gel by a mechanism similar to that mentioned for macroscopic ice segregation in soils and fresh concrete.

Paste containing sufficient amounts of well-distributed air bubbles will permit this formation of ice without dilating, and as water is drawn from the gel, the overall effect is shrinkage of the specimen, which earlier also was reported by Valore [15].

As the amount of segregating ice depends upon a rather slow diffusion process, the length of the freezing period has an important influence upon the observed changes in length. This is in contrast to the hydraulic pressure, where the rate of cooling is the most important variable of the freezing condition.

The microscopic ice segregation has been further discussed by Powers [13], and it is claimed that this phenomenon will especially apply to mature paste in concrete with rather high cement content, i.e., water-cement ratio below 0.55.

The lower limit of water-cement ratios where this theory is applicable is not determined as yet by experiments. Woods [16] has suggested, that concrete of water-cement ratios below 0.40 would be frost-resistant without air-entrainment. Powers [5] has earlier suggested formulas, from which the amount of freezable water at different temperatures may be computed from the initial water content. From these it was computed that a paste of a water-cement ratio=0.30 would not contain any freezable water at −30 °C after a certain stage of hydration was obtained.

Chapelle [17] has made experiments from which he concluded that the water-cement ratio is the determining factor of freezing resistance, and claims that concrete with a water-cement ratio below 0.45 is damaged only by mechanical stresses due to the alternating temperature. Chapelle does not accept air entrainment as a decisive factor in frost resistance, but emphasizes the influence of the chemical composition of the cement. He states that the presence of pockets of crystals of hydrated lime in the paste without entrained air causes low resistance to freezing.

Hydraulic Pressure

The hydraulic-pressure theory has been developed from concepts earlier used for building materials other than concrete. For clay bricks, it is quite common to correlate the frost resistance with the degree of saturation determined in a standardized way. As water expands about 9 percent when converted into ice, it has been expected that no damage should be caused by freezing a body in which the degree of saturation is below 0.917. This belief is only correct under the assumptions that the water is homogeneously distributed throughout the material and that the water movement caused by the formation of ice does not give rise to stresses.

Whiteside and Sweet [18] applied this concept to concrete, in which the air voids were included when the degree of saturation of the binding matrix—i.e., paste and air voids—was computed. They found, however, that some specimens with a degree of saturation lower than 0.917 deteriorated. Thomas [19] found in 1938 that specimens of rocks at the same degree of saturation dilated differently when the freezing rate changed.

Powers [12] stated that the concept of a critical degree of saturation is not sufficient to explain the behavior of concrete during freezing. This is due to the specific physical properties of the hardened cement paste, which has very high porosity but at the same time a very low permeability. Mature paste with water-cement ratio=0.70 may have a porosity of 50 percent and a permeability of the same order as granite which may have a porosity less than 1 percent [3, 20]. Hence the freezing of nearly saturated paste is accompanied by displacement of water, giving rise to a hydraulic pressure gradient.

On this basis the concept of the critical half-thickness, D_{crit}, is developed.

For thin slabs of paste, D_{crit} is equal to the maximum half-thickness of the body permitting the water to escape through the surfaces without causing damage. Surfaces from which the water may be expelled are termed "escape boundaries."

For air-entrained paste, D_{crit} is equal to the maximum half-distance between the air voids. The walls of the air voids represent a large increase of the escape boundaries.

Assuming that Darcy's law is valid for the flow of water in the hardened paste and expressing that the hydraulic pressure should not exceed the bursting strength of the layer, the following formula is obtained in the notation used by Jessing [21]

$$f(D_{crit})=\frac{KB}{\left(1.09-\frac{1}{s}\right)w_f\frac{dm}{dt}}, \tag{1}$$

where $f(D_{crit})$ (cm^2) may have forms according to the geometrical shape of the paste body or the particle.

K=permeability of material (cm/sec).

B=bursting strength of material (cm head of water).

s=degree of saturation, i.e., amount of freezable water w_f divided by the capacity for freezable water, p.

$w_f\frac{dm}{dt}$=rate of ice formation (cm^3/cm^3 sec).

m=that fraction of water (w_f) which freezes at a given temperature.

It will be seen from eq (1) that the determining factors are the permeability, the strength of the material, the degree of saturation, and the rate of ice formation, which depends upon the rate of cooling.

Hydraulic Pressure in Paste

Structural members of concrete usually are much too thick in comparison with the critical thickness when the paste is saturated and the water-cement ratio has a normal value.

Klieger [22] has found by a comprehensive investigation that non-air-entrained concrete will show great expansion in freezing-and-thawing tests even at water-cement ratios as low as 0.37 by weight. The cooling rate was 11 °C per hour, which is much higher than usually met in the field. During placing of concrete without air-entraining agents air is entrapped in ordinary concrete in irregular cavities and may give some protection at moderate freezing rates, but the amount of air and the distribution of voids is normally not able to give sufficient escape boundaries during the normal freezing procedure employed in the laboratories.

By the use of a suitable air-entraining agent cement paste can obtain a very large number of air voids, which reduces the critical thickness of the layer of paste as each wall of the air bubble may serve as escape boundary. In this way cement paste can attain a resistance to freezing-and-thawing cycles making it almost immune to frost attack.

In earlier papers it has been stated that the spacing between air bubbles should be of the order of 0.01 in. (~250 μ) [23] but lately during a discussion of a RILEM Seminar, 1958, Powers [24] stated that the average distance between air bubbles should be kept as low as 50 μ.

Danielsson [25] has refined the mathematical derivation of the hydraulic-pressure theory and suggested the concept of the frost-protected volume, which in his experiments has given a better correlation with the durability factor than the characteristics of the distribution of air bubbles suggested by Powers.

Hydraulic Pressure in Aggregate

The same concept as outlined in eq (1) pertains to the freezing of rock, i.e., the critical size depends upon the permeability, the strength, the degree of saturation, and the rate of ice formation.

In comparison with mature cement paste, the porosity of aggregate normally used in concrete is usually low, as the apparent specific gravity is only a little lower than the true specific gravity. An exception is the cherts, for instance, used in Denmark and in the southeast of the United States of America, in which the porosity may be as high as 10 percent. Similar porosities may be found for special types of limestone.

The pore system in rocks has usually much larger dimensions than in hardened paste. Hence most of the water freezes at a temperature near the melting point of ice. On the other hand the amount of freezable water in the aggregate is much lower than in paste of average quality.

TABLE 1. *Comparison of permeabilities of rocks and mature pastes (Powers [20])*

Kind of rock	Permeability of rock, $K \times 10^{12}$	Water/cement ratio of mature paste for same K
	cm/sec	
Dense trap	0.345	0.38
Quartz diorite	1.15	.42
Marble	3.34	.48
Marble	80.5	.66
Granite	748	.70
Sandstone	1,720	.71
Granite	2,180	.71

As the pore system in most rocks is formed of capillaries with large diameters, the resistance to water flow is rather low, in comparison to cement paste, when the porosity is taken into consideration as shown in table 1, which was given by Powers in 1956 [20]. Finally, the strength of rocks is high.

From these considerations it follows that most aggregate, when frozen before use in a concrete mix, has a very large critical size in comparison with cement paste. When the aggregate is embedded in concrete the situation is quite different.

Scholer [26], in 1930, had already pointed out that some aggregate is susceptible to frost damage when embedded in concrete even if good results are obtained by freezing tests on the aggregate alone.

Powers [3] explains that the paste is acting as an almost impermeable membrane causing the rock particle to be frozen as a closed container. When the degree of saturation is above a critical limit, which due to mineralogical heterogeneity may be lower than the theoretical value of 0.917, the particle must dilate and give rise to stresses in the surrounding paste.

Determination of Frost Damage

In the following sections test results from experiments with freezing and thawing will be mentioned. In order to give a background for these references a brief survey is given of the methods employed to determine the change in concrete properties as caused by the frost damage.

The discussion is mainly limited to laboratory methods. The first group comprises measurement of the reduction of strength, e.g., compressive and tensile and modulus of rupture. Another group of methods comprises determinations of variations in length or volume of the specimen. The third group comprises determinations of the elastic properties of the concrete by different types of equipment.

Strength Determinations

It is generally accepted that deterioration of concrete caused by a number of freezing-and-thawing cycles is due to the formation of cracks in the hardened cement paste, often combined with reduction of the bond between paste and aggregate. In cases where unsound types of rocks have been used as an aggregate, the stone particles proper may be cracked and deteriorated. Consequently, the reduction of the quality may be revealed in the best way by methods which are sensitive to cracks in the concrete.

The compressive strength is not very sensitive to frost damage, as a large number of minute cracks do not influence the resistance to compression. This situation may be elucidated by considering a concrete cube which has obtained several planes of rupture perpendicular to the direction of load. If we assume rough, interlocking surfaces of the planes of rupture, the cube will have considerable compressive strength almost equal to that of an undamaged specimen, while the tensile strength will be zero. This will be the case even when the planes of rupture are inclined up to a certain angle depending upon the material. Consequently, testing of damaged concrete preferably should be executed in such a way that the tensile strength is a governing factor for the rupture.

While a direct determination of the tensile strength of concrete is not easy to carry out, it is feasible to determine the modulus of rupture. A third-point loading should be preferred, where feasible, as from a statistical point of view it is an advantage that the moment is constant for a great part of the beam length. With loading of the beam in the middle of the span the moment is variable, and rupture will take place where a maximum combination of stress and low resistance exists, which is not necessarily in the middle of the beam.

Variations in Volume and Weight

During the freezing of cement paste or concrete the material is changing in volume not alone during a single cycle of freezing and thawing, but it is also observed that any damage to the concrete will be revealed by residual deformations, whereby the volume of the concrete is increased.

Comparator Measurements

Consequently the progress of deterioration may be followed by measuring the length of concrete specimens at definite intervals by a comparator method, but the length change in itself does not give an estimate of the degree of deterioration. As far as known no definite criteria have been worked out to relate length change with degree of damage, although many laboratories have accepted that a specimen showing an expansion of 0.1 percent represents failure of the concrete. In other laboratories freezing cycles are continued until an expansion of 0.3 to 0.6 percent is obtained [27]. Verbeck and Klieger [28] have recently described an apparatus which automatically records change in length and heat flow, from which the correlation between amount of ice and length may be determined.

Dilatometer Method

The variation in volume of small concrete specimens may be studied by the use of a dilatometer. This method has been used for instance by Powers and Helmuth [6], Valore [15], and Valenta [29], but only specimens of limited size can be used, and the method is consequently more applicable for study of mortar than for laboratory investigations of various concrete mixes.

In connection with the dilatometer method it is important to notice that the measured dilation pertains to the system water–mortar and any growth of an ice layer on the outside of the specimen will be recorded as a dilation of the specimen.

Change of Weight

In earlier studies of the deterioration of concrete specimens exposed to freezing-and-thawing cycles, it has been quite common to estimate damage by determining the change of weight. The results are, however, influenced by disturbing factors. For instance, partly dried specimens will, during the freezing-and-thawing cycles, absorb water and actually increase in weight and may at the same time lose in weight due to spalling. It has also been experienced that concrete specimens have been seriously damaged by freezing and thawing, as measured by the reduction of the dynamic modulus of elasticity, without any weight loss at all. Hence it is concluded that this method should not be used alone.

Elastic Properties

In the last 20 years different apparatus and methods have been developed in the U. S. and Europe to determine the elastic properties of concrete by nondestructive methods, and it is known that the dynamic modulus of elasticity is a rather sensitive and accurate measure of the progressive deterioration of concrete subjected to freezing and thawing cycles.

Resonant-Frequency Method

This method was originally developed in the United States of America and has within the last twenty years been widely accepted. Since 1955 it has been a method of test of the American Society for Testing Materials. From the results obtained it is possible to compute a factor of durability by expressing the measured dynamic modulus of elasticity relative to the initial modulus after a certain number of freezing and thawing cycles.

Wave-Velocity Method

Methods and apparatus for measuring the wave velocity through concrete specimens have been developed in Canada and described by Leslie and Chessman [30]. In Great Britain, Jones has used an apparatus constructed according to similar principles [31] to study the effects of freezing-and-thawing cycles on concrete cubes. In Denmark a condenser chronograph has been developed [32, 33]. Various methods have been developed in France to study the elastic properties of concrete by nondestructive methods [34].

A survey of later developments within this field has been given by Whitehurst and Parker [35], and the merits and drawbacks of the different methods have been discussed by Verbeck [27]. The result of an inquiry to RILEM members has been reported by Jones [36].

It seems that although the resonant-frequency method correlates fairly well with the expansion, some difficulties are encountered in cases where spalling takes place, because the corrections for shape and weight are cumbersome.

The wave-velocity method is not very sensitive to frost damage but may be a suitable indicative method for use in the field.

Visual Observation

This method is among the oldest, and much valuable qualitative information may be gained from observations made with the naked eye by inspections in the field and investigations in the laboratory.

In order to get quantitative measurements, which can be carried out by less-trained personnel, various arbitrary systems of ratings have been chosen, which may serve the purpose by comparisons of different test series. Especially in field inspections, where many different causes of deterioration may be met, the interpretation of observations should be made with great care, and the method calls for an intelligent concrete technologist with broad experience.

The use of petrographic methods in evaluating frost damage is a very promising field for freezing at early ages and for study of aggregate which has expanded and cracked during freezing.

Freezing of Hardened Concrete

In the course of time a tremendous amount of research work has been invested in exposing concrete specimens of varying composition, age, degree of saturation, etc., to artificial freezing-and-thawing conditions with a similar great number of characteristic variables.

It has been common to report the resistance to freezing and thawing of hardened concrete as influenced by cement type, fineness, chemical composition, water-cement ratio, total water content, consistency, grading and amount of sand and stone, maximum particle size, compacting method, curing methods, addition of inert fillers and fly-ash, accelerators, etc.

On the background of the knowledge of today it is to be regretted that all these test data have been the basis for establishing a great number of false correlations or, at best, conclusions which are based upon the appearance of relations between the factors, which only in an indirect and superficial way characterize how the resistance of concrete is affected.

As the test results in most cases are lacking information on the properties of the cement paste, which at present are thought to be of decisive nature, such as air content, void spacing, etc., even for the entrapped air, it is impossible to interpret the older data in the light of the new concepts.

To illustrate this statement reference is made to "Long-Time Study of Cement Performance," chapter 9, where Jackson [37] concludes that the observations from the many field and laboratory studies clearly demonstrate that the chemical composition of portland cement as such has no significant influence upon the resistance to freezing and thawing. This question has been the subject of controversy in America and is still discussed vividly in Europe [17, 38, 39].

The freezing tests in the laboratory have the purpose of obtaining a quick estimate of how concrete would perform when used in actual field structure. In order to obtain the results quickly, the cooling rate has been increased far beyond what can be expected under natural conditions, which may give a distorted picture. The required amounts of air to obtain protection against freezing may by laboratory experiments reach too high values, and some sort of adjustment to actual climatic conditions is recommended. The lacking correlation between laboratory tests and field exposure has, for instance, been studied by Kennedy and Mather [40] and discussed in detail by Powers [3], who suggested a modified procedure of freezing tests, measuring the dilation during cooling at a moderate rate (5 °F (3½ °C) per hour) followed by a period of constant low temperature at −19 °C (0 °F).

The test is carried out between intervals of soaking, each of two weeks duration. When the length of the period of immunity to soaking and freezing has been determined, the specimens may be subjected to successive freezing cycles combined with measurements of the increase of permanent dilation. The suggested procedure should be less expensive than the procedures used at present.

Studies of the methods adopted by the A.S.T.M. in the United States have been carried out by Flack [41] and Arni, Foster, and Clevenger [42]. The characteristics of the freezing procedures used by a number of European laboratories have been reported by Jarrige [43].

Tests on the Freezing Resistance of Aggregate

As it now is possible to produce an air-entrained cement paste which in the mature state is immune to frost action, at least under most natural exposures, more interest is to be placed in the future upon the frost resistance of aggregate, which cannot be improved, if required, in the same easy and economical way as the paste.

The influence of the degree of saturation of chert aggregate upon the freezing resistance of concrete has been studied by Stanton Walker [44], and some of his results are reproduced in figure 6.

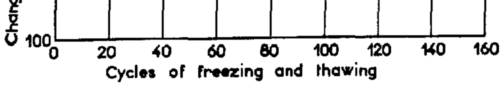

FIGURE 6. *Resistance to freezing cycles as influenced by the degree of saturation of a porous coarse aggregate.*
(Walker [44])

The material with the indication $s=1.0$ (100 percent saturated) was stream wet, and the poor durability obtained shows that porous gravel dug out from rivers or the sea may have initial high water content compared to the same stone material from gravel pits above the ground-water table, as it is difficult to saturate porous material after a drying period.

The frost resistance of stone is especially influenced by the microporosity, i.e., pores of sizes below 5μ. The pore distribution may be determined by measurement of the capillary suction forces by direct suction or by the quantities of water held back during centrifuging.

The sizes of the most narrow capillaries may be determined by measuring the interrelation between the water content and the relative humidity [45].

From these determinations a histogram of the computed pore-size distribution can be prepared, which may be correlated with the resistance to freezing.

Blaine, Hunt, and Tomes [46] have measured the internal surface of stone, bricks, and concrete by low-temperature nitrogen sorption by the Brunauer-Emmett-Teller method [47, 48] and found that stones with high internal surface area have low resistance to freezing. An example of their findings is given in table 2.

TABLE 2. *Surface areas and service records of crushed limestone used in highway concretes [46]*

Limestone No.	Surface area	Reported service records [a]
	m^2/g	
1	0.30	Excellent service record.
2	.78	Good service record.
3	.78	Good service record.
4	1.18	Bad service record, quarry condemned.
5	2.26	Bad service record, quarry condemned.
6	3.63	Bad service record, unsatisfactory perfomrance.

[a] Samples and information on service records supplied by J. E. Gray, National Crushed Stone Assoc.

Measurements on hardened cement paste showed that intentionally entrained air did not cause any significant difference in the measured internal surface area. This result indicates that even if the method is valuable in measuring the microporosity it does not reveal the presence of protective air voids, which also may be found in certain types of dolomite and basalt.

The methods outlined above give more information on the properties of rocks than do determinations of total porosity, which includes both the dangerous microporosity and the beneficial macroporosity.

Wuerpel and Rexford [49] have proposed a flotation procedure using heavy liquids for separation of unsound chert particles. For the materials investigated the unsound materials were particles with a bulk specific gravity below 2.40 after saturation by 5 hours boiling. This limit was based upon field inspection and measurements on particles which had caused "pop-outs."

In Canada and the United States a number of gravel producers have within the last ten years installed equipment for float-sink separation on an industrial scale. The process is called Heavy-Medium Separation, or abbreviated, the H-M-S procedure. Price [50] has made a survey of the H-M-S and other procedures currently used in gravel beneficiation and has reported results which indicate a significant improvement of the treated materials with regard to resistance to freezing. In other cases the improvement has been measured with conventional tests for soundness of aggregate using the crystallization of sodium sulfate or magnesium sulfate; the reliability of these tests has been the subject of active discussion [51].

It is to be expected that the influence of aggregate on frost resistance will be the object of extensive studies in the future, and more detailed information may now be obtained as the influence of the paste may be excluded by the use of adequate amounts of purposefully entrained air.

Freezing of Concrete at Early Ages

Hydraulic Pressure

In the preceding section a survey has been given of the different mechanisms of frost action in mature concrete. It has been shown that the hydraulic-pressure theory has been developed to a very high level of perfection, making it possible to give a satisfying explanation of how the entrained air bubbles are able to protect the paste of hardened concrete against freezing. On the other hand it has also been mentioned that the theory of macroscopic ice segregation seems to be more applicable to concrete in the fresh state.

Based upon studies of T. C. Powers and coworkers and some investigations in Europe, a survey of the change in freezing resistance of concrete during the hardening process will be given.

In 1949 Powers presented a model from which he developed formulas for the hydraulic pressure developed in paste during freezing [23]. At the RILEM Symposium in Copenhagen the author used this theory and model in order to discuss the change of the important factors in this formula during the hardening process, and a brief summary is given below [52].

The basis of this discussion was the following expression for the hydraulic pressure in air-entrained concrete, which is a stage in the development of the general formula, eq (1).

$$P=a\left(1.09-\frac{1}{s}\right)\frac{uR}{K}\left(\frac{L^3}{r_b}+\frac{3L^2}{2}\right)\text{ dynes/cm}^2 \quad (2)$$

where:

a=a factor, depending, among other things, on the viscosity of the water—g/cm sec.
s=saturation coefficient of the cement paste.
u=amount of water, in grams per gram of cement, which freezes when the temperature falls one degree—g/g °C.
R=rate of cooling, °C/sec.
K=permeability, cm^2.
r_b=average radius of air bubbles, cm.
L=spacing factor of air bubbles, cm.

The last part of the equation may be substituted by

$$f(L)=\frac{L^3}{r_b}+\frac{3L^2}{2}. \tag{3}$$

The formula has been derived under the assumption of entrainment of air bubbles, into which water can escape when the concrete freezes. If the hydraulic pressure, P, exceeds the tensile strength, T, of the paste, it will produce rupture. In the following the controlling factors of the formula are discussed.

The degree of saturation, s, of the cement paste has a very great influence on the hydraulic pressure. It will be seen from the formula that $s=0.917$ makes $P=0$, i.e., no hydraulic pressure will develop. The water, in this case, turns into ice within the voids without any movement of water being involved. In practice, evaporation and internal drying—self-desiccation—may, under favorable conditions, reduce the degree of saturation to 0.91 or less and no damage will occur in case of freezing. For degrees of saturation between 0.91 and 1.0 Powers has made a computation under certain assumptions which shows that already at a reduction of the degree of saturation to a value of 0.97 the hydraulic pressure will only be 56 percent of the maximum value. In all these considerations it is assumed that the water is homogeneously distributed throughout the paste, which is seldom the case.

The hydraulic pressure will increase with u, the amount of water freezing per degree drop of temperature. If freezing can be prevented, for example through addition of anti-freeze compounds, protection of the concrete will be attained. The concentration of these compounds generally recommended and used will afford protection only down to a few degrees below 0 °C.

In a discussion of freezing and thawing tests Powers [3] pointed out that supercooling might have a considerable effect upon the rate of ice formation, and mentioned tests carried out by Valore [15] at the National Bureau of Standards several years ago. This effect may be of great importance in investigations carried out in the laboratory, but on the other hand it is suggested by Powers that the same effect is not to be expected in actual structures where an ice layer is formed on the surface. This question is as far as the author knows, not clarified as yet.

The higher the rate of cooling, R, the higher the hydraulic pressure. The rate of cooling can be reduced through insulation of the concrete. The larger the ratio of the volume of the concrete to the area of the exposed surface the less the temperature of the concrete will be influenced by fluctuations of the outside temperature, and a lower rate of cooling will result. Heavy structures are in this respect less liable to damage by frost than are slender structures.

For actual structures the rate of cooling is furthermore determined by the prevailing climatic conditions during winter time. Consequently, the influence of this factor is determined not only by the structure's geographical location, but also from local topographical conditions, wind velocity, radiation to the sky, and so on.

Lower permeability, K, of the concrete involves higher hydraulic pressure. During hydration the permeability is reduced, and the resistance to frost, all other factors unchanged, will not increase with curing time. The permeability depends, moreover, on the qualities of the cement and it will increase with the w/c ratio.

The permeability of hardened portland-cement paste has been studied by Powers and Brownyard [53] and later by Powers, Copeland, Hayes, and Mann [54, 55, 56]. In the latest publications it is stated that the permeability is reduced to one third, approximately, when the temperature is reduced from 27 °C to a little above the freezing point. It was further found that the coefficient of permeability decreases about one order of magnitude a day for the first two to three days of curing at normal temperature.

Air Entrainment

The last part of eq (2) is related to the entrained air and its distribution into tiny bubbles. As already mentioned above, the possibility of relieving the stresses from the hydraulic pressure is dependent upon the distance between the bubbles rather than the amount of entrained air. In most of the theoretical computations carried out by T. C. Powers [23, 57], it is assumed that this spacing factor $\bar{L}$ is equal to 0.01 in. =¼ mm. In the latter reference, tables may be found to determine the air content necessary for different cement contents, water-cement ratios, and values of the specific surface of the voids.

Tensile Strength

The tensile strength of concrete will at lower degrees of hydration mainly be determined by the tensile strength of the paste, T. As already discussed above, internal damage will take place in the concrete if the hydraulic pressure exceeds the tensile strength of the paste. Dividing eq (2) by the tensile strength of concrete and inserting eq (3), we obtain

$$\frac{P}{T}=a\left(1.09-\frac{1}{s}\right)\frac{u\cdot R}{K\cdot T}\phi(L). \qquad (4)$$

If the concrete is exposed to a large number of freezing-and-thawing cycles, the hydraulic pressure should not exceed the fatigue limit of the concrete,

$$F=\beta T \qquad (5)$$

where β is a constant <1.

Hydraulic Pressure as Influenced by the Hardening Process

In eq (4) the following quantities are not influenced by the progress of the hydration, viz, a, which is a constant; R, the rate of cooling; and L, the spacing factor.

The factors following are dependent upon progress of hydration: s, the saturation coefficient; u, the amount of ice formed per degree drop of temperature; K, the permeability; and T, the tensile strength.

For evaluation purposes it may be assumed that in winter concreting in practice it is not always possible to prevent the access of water from melting snow and ice, and consequently the degree of saturation may be equal to 1.0. Hence the maximum hydraulic pressure $P_{\max}$ may be expressed by

$$\frac{P_{\max}}{T}=\gamma\frac{U}{KT}\cdot R\phi(L). \qquad (6)$$

where U is the value of u for saturated paste.

Powers has suggested in one of his papers [23] substituting for the three variable factors the parameter Z, equal to $\frac{K\cdot T}{U}$.

Expressing the left side of eq (6) equal to unity, the requirement for the distribution of the entrained air can be expressed by the following formula

$$\phi(L)_{\max}=\gamma\cdot\frac{Z}{R}. \qquad (7)$$

The author has in a previous paper [52] demonstrated that the factors K, T, and U can be estimated from a single variable, the nonevaporable water w_n. The derivation was based upon Powers and Brownyard's paper "The Physical Properties of Hardened Portland Cement Paste" [58] and the information available at that time [59]. For illustrative purposes figure 7 gives the result of these computations, each of the variables being drawn as a function of the nonevaporable water content, and it is shown that the parameter Z has a maximum corresponding to the highest degree of freezing resistance, when the hydration process has reached a stage where the nonevaporable water content for this specific mix is 0.15 g/g cement.

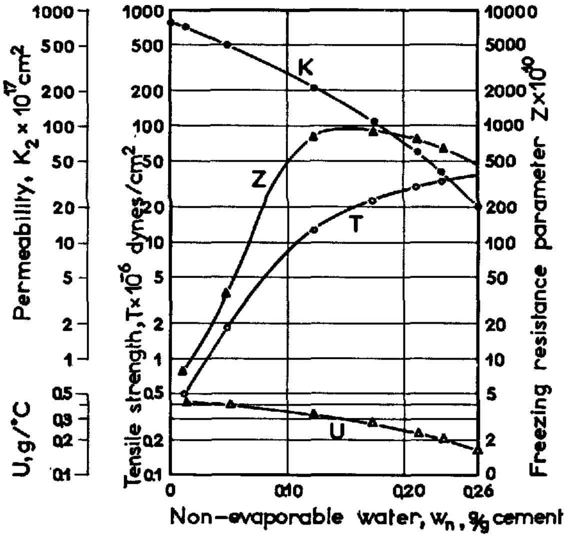

FIGURE 7. *Change of physical properties during hardening of cement paste.*

(Nerenst [52])

Adopting a certain amount of air and specific surface of the voids, it was computed that the Z value should be above 41×10^{-10} in order to obtain resistance to freezing with a specified rate of cooling of 3 °C/hr.

Assuming that damage would be caused by hydraulic pressure only, the necessary degree of hardening could by some further assumptions be converted into a requirement of development of a certain amount of heat of hydration, as a relation exists between the amount of nonevaporable water and the heat of hydration. This has been shown by Powers and Brownyard [60] and been confirmed by experiments carried out by Danielsson [25] in Stockholm.

From experiments Rastrup [61] had determined the relation between heat of hydration and time and temperature for Danish cements. These computations were used in working out recommendations for winter concreting in a Danish publication [10].

The results mentioned above are rather theoretical and based upon a great number of assumptions. Later experiments by Möller [4] to verify the computed prehardening times indicate that they are rather conservative for mixes of low water-cement ratio but seem to be too short for mixes with a water-cement ratio above 0.7 by weight.

The revised prehardening periods appear in table 3 for concrete made with Danish cement, assuming an air content of 4 percent and a cooling rate of 3 °C/hr.

It may be of interest to notice that since these recommendations were published in 1953, not a single case of failure has been reported to the Danish National Institute of Building Research from job sites where these recommendations have been followed.

TABLE 3. *Required prehardening for attainment of resistance to freezing..*

Air content L=4 percent (Nerenst, Idorn, and Rastrup [10])

Danish cement types	Cement content	Required prehardening in hours	
		at 0 °C	at 15 °C
	kg/m³	h_0	h_{15}
Standard portland	300	45	16
	225	49	17
Rapid-hardening portland	300	40	14
	225	43	15
Extra-rapid-hardening portland	300	34	12
	225	37	13

Macroscopic Ice Segregation

In presentation of the various theories which apply to concrete, the theory of macroscopic ice segregation has been mentioned. It is pointed out that this phenomenon is only observed in concrete of low quality or concrete in the first stage of hydration. In a paper presented at the RILEM Symposium in Copenhagen in 1956, Powers [13] mentioned an interesting theory worked out by Winterkorn [62] on the formation of ice lenses in systems with low tensile strength. Application of this suggestion to concrete would indicate that macroscopic ice segregation may be possible within the first two or three days of curing at normal temperature.

In his derivation of this time interval Powers seems not to take the increasing tensile strength of the cement paste into consideration. From soil mechanics it is known by experience that a certain load is able to prevent the formation of ice lenses. If this principle also applies to concrete, essentially shorter curing time should be necessary to prevent the formation of ice lenses.

In the discussion of an earlier report of Powers, Douglas McHenry and H. V. Brewer [12] presented a photograph of concrete showing ice segregation resulting from slow freezing of concrete at the age of 4 hr.

As it is of very great importance to determine the time interval in which macroscopic ice segregation is possible, detailed references are made below to observations made by Bernhardt [63] in Norway and Möller [4] in Sweden.

Bernhardt's Observations

In Bernhardt's [63] investigation Type I portland cement was used at water-cement ratios between 0.4 and 1.2. The concrete was poured at a temperature of +20 °C and placed in the freezer after varying prehardening times. The test specimens were 10-cm cubes, and when the specimens in the freezing series and the blank specimens had obtained the same degree of hydration the compressive strength was determined. After failure the broken specimens were investigated with the naked eye to determine the existence of ice needles.

For all specimens frozen immediately after manufacturing, ice needles were found. When the prehardening time was equal to 4 hr, evidence of the formation of ice needles was found in most cases. After 8 hr this phenomenon was observed in only very few cases. Bernhardt has drawn the conclusion that serious decrease in compressive strength is found only when there is clear evidence of the formation of ice needles. Bernhardt noticed that the ice needles were found mainly on surfaces of the coarse aggregate and suggested that the observed decrease in the compressive strength was caused by the reduction in bond between the aggregate and paste.

Möller's Observations

In Möller's experiments [4] the necessary prehardening time was determined from the modulus of rupture, the change in resonance frequency, and measurements of the dilation during freezing. On the formation of ice needles Möller reports that in four test series all characterized by a cement content of 240 kg/m³ of concrete and made with and without air entrainment and calcium chloride, a pattern of ice needles was found in all specimens with a prehardening time of 4 hr or less. After 8 hr the ice needles were found in one of the four mixes, which was characterized by having no addition of air-entraining agent or calcium chloride.

Whenever ice needles were found, the modulus of rupture and the modulus of elasticity were considerably decreased (10–15 percent). For four series of specimens with a cement content of 300 kg/m³ and water-cement ratio about 0.5, ice needles were found in specimens with a prehardening time of 4 hr at +20 °C or less.

Möller used two different procedures of freezing. In the first case the specimens were stored for a prolonged period in a freezing room at a temperature of −10 to −15 °C. In the second case the specimens were placed in a freezing room giving one cycle per day between −5.5 °C and +5.5 °C. In the latter case the temperature drop of the concrete is milder and smaller than in the first case and consequently the degree of the hydration when freezing starts will be a little higher for the specimens exposed to the cyclic treatment. It is interesting to notice that with the high cement content ice needles were found only in the specimens placed at low temperature. It is normally assumed that the formation of ice needles is favored by slow freezing, and it is difficult to explain the observed differences between the two cooling conditions. Möller reports the initial and final set of the cements employed as shown in table 4.

It may be seen that the formation of ice needles is possible after initial set but not later than the final set. It is readily admitted that the method of observation may have been too crude to obtain an exact fixing of the time necessary to prevent ice needles. Furthermore the absence of ice needles is no assurance that the concrete has not

Table 4. *Initial and final set for Swedish cements*

(Möller [4])

Cement brand	Setting time in hours and minutes	
	Initial set	Final set
G	3-35	9-10
N	2-50	7-30

The values refer to the use of the Vicat standard needle.

been damaged by the freezing, as emphasized by Möller.

Nerenst's Observations

A few observations made by the author in the field may be pertinent to this discussion of the formation of macroscopic segregation of ice.

In the top layer of a gravel pit it was observed about 10 years ago that on stones of the size 10–20 mm, layers of ice had been developed in thicknesses of up to 10 mm. The direction of growth was almost horizontal, i.e., perpendicular to the surface. It was also found that this formation only took place on aggregate with a porous texture. The particles were not investigated in detail, but they were of the type of lime-containing opal which has been causing a lot of trouble in Denmark on account of its reactivity with alkalies. The porosity might have been of the order of 10 percent by volume.

It is suggested that the process which had taken place was that during freezing a small amount of water was on the surface of the particles or perhaps reached the surface when the stone started to freeze. Once a layer of ice had been formed, it had the capability of extracting unfrozen water, as described for instance by Powers and Helmuth [6]. In the thin layer of water at the boundary between the ice and the particle it is suggested that the water is exposed to forces of adhesion which lower the freezing point. As long as the freezing rate is sufficiently low the freezing zone may be on the surface of the particle and water may be drawn from the capillary cavities in the particle passing through the boundary zone and converted into ice with the result that the ice lenses grow in thickness. The water is supplied from the particles proper and possibly from other grains behind the particles in question. It is to be noticed that similar observations could not be made on dense stone particles, for instance of granite, dense flint, etc.

In the second case a concrete floor had been placed in springtime without taking any special precautions, consequently the concrete temperature at placing may have been about +4–5 °C. The rate of hydration is rather low at this temperature, and when the air-temperature during the night dropped below the freezing point the surface of the floor was damaged in a peculiar way.

In the affected area a number of blisters were observed. By closer examination it was found that below each of these small blisters or mounds was a stone. These stones consisted of various proportions of lime and badly crystallized silica in the range from amorphous (opal) to cryptocrystalline structure (chert). By closer examination the author found that a very thin layer of mortar was lifted from the surface of the stone by individual ice lenses formed in the contact layer between paste and stone (fig. 8). In none of the cases were the stones damaged by the freezing. The thickness of the layer was 7–8 mm and as none of the stones had dimensions greater than 30 mm, it may be concluded that the water used for forming the ice lens was drawn not only from the particle proper but also from the surrounding mortar.

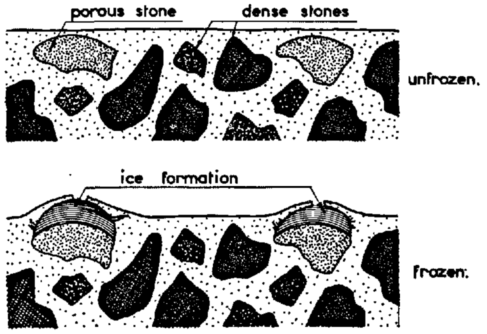

Figure 8. *Macroscopic ice segregation above porous stones in concrete floor frozen at an early age.*

These observations may be difficult to obtain by laboratory experiments as this special type of ice lens may only be developed under certain freezing conditions and in combination with a certain porosity and structure of the stone and degree of hydration of the surrounding paste.

Sandford's Observations

Some recently reported experiments in Sweden carried out by Sandford [64] on clay bricks are illustrative to the discussion of ice in porous materials. In order to get a better reproduction of the natural exposure of bricks to freezing action, each stone was separated from the other specimens by a separating layer of wet mineral wool.

The assembled framework was placed as the door to the freezing room, so that only one end was exposed to the cold air, and the other end to the room at a normal temperature.

When the air temperature of the freezing room was −5 °C, the freezing zone was situated only a few millimeters below the surface. After a certain period it was found that a body of ice was growing from the exposed cold surface and attaining a length up to 10 cm (fig. 9). This phenomenon was observed only on bricks with high resistance to freezing.

It was found very difficult to regulate the location of the freezing zone, and when freezing took place at greater depth than a few millimeters no protruding ice was observed. Application to the

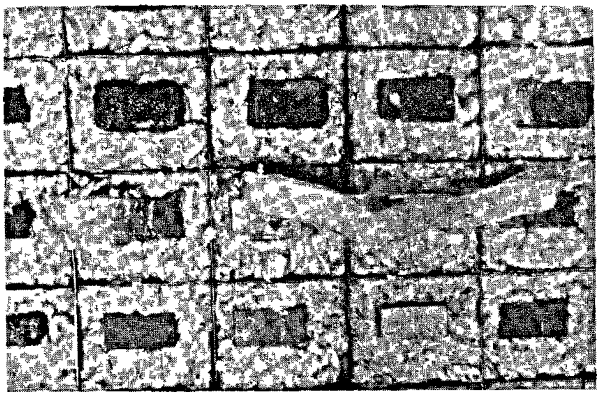

Figure 9. *Ice lenses formed on clay bricks during slow one-dimensional cooling.*

(Sandford [64])

exposed surface of a paint with low bonding strength had the effect that the membrane was displaced by the protruding ice. Application of a thin layer with high bonding strength prevented the formation of ice on the outside, and rupture took place even in bricks which normally had a very high resistance to freezing. From this test Sandford concluded that bricks should not be treated with an oil paint, and we may have a demonstration of how the cement paste increases the risk of frost damage in saturated porous aggregate.

Some Danish Observations

It seems that the boundary layer between aggregate and paste is a locus for favorable conditions for the formation of ice needles up to a certain degree of hydration of the surrounding paste.

Danish concrete aggregate may contain various amounts of porous limestone and chert. The orgin and mineralogic properties have been studied and described by Søndergaard [65] in connection with the comprehensive investigation of alkali-aggregate reactions in Denmark. The permeability of these stones is not known and the following remarks are consequently of speculative nature.

The author observed ten years ago a concrete canal for a distant heating system. The maximum size of the aggregate was about 50 mm, and the cement content about 250 kg/m^3. The concrete was exposed to freezing after a prehardening period equivalent to 4–5 hr at 20°. As will appear from figure 10 the concrete was heavily damaged. The failure was mainly due to destruction of the bond between the porous aggregate and the paste.

The conclusion was drawn that in the very early ages of hydration this special material is able to extract water from the paste into the stone particle, from which water is supplied to the formation of ice coatings or ice needles in the boundary layer nearest to the freezing zone.

At later stages of hydration the permeability of the surrounding paste is decreased, and possibly also water is drawn from the particles to the paste during the self-desiccation period because, as

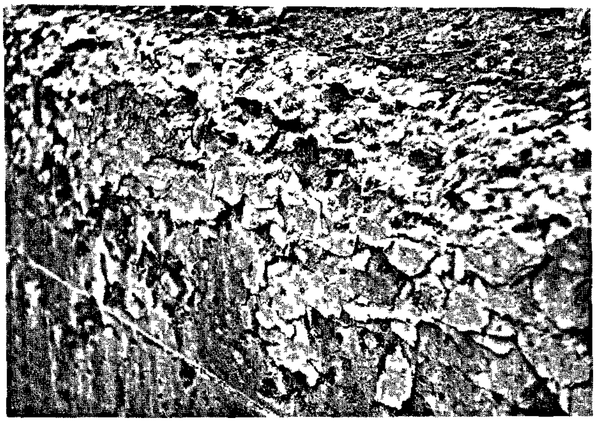

Figure 10. *Frost damage to green concrete containing porous aggregate.*

pointed out by Powers [3], the pores in hardened portland cement paste are much smaller than the pores of most rocks.

This was confirmed at this job site because application of correct winter concreting methods which ensured a higher degree of hydration of the concrete before exposure to freezing gave a concrete with excellent appearance.

It may be mentioned that large amounts of aggregate with high contents of porous stone are used every winter with good results. Only under very severe exposures where the cement paste and later also the stones in the matured concrete are water saturated, the stone may be damaged by freezing causing the well-known pop-outs.

In January this winter the author studied a case where a great number of pop-outs were observed on the underside of a concrete deck above a cellar. Artificial heat was first supplied at an age of the concrete of 2 months because the contractor intended to apply a cement washing on the deck. No pop-outs were observed before the heating started and in the beginning it was difficult to explain where the additional moisture was supplied from, as the upper surface still was covered with snow, which by the way was an indication that the freezing zone was situated at some depth below the surface.

A closer study of the underside of the concrete revealed that water drops were condensing on the cold concrete, and it was assumed that the use of kerosene in the burners was one source of moisture as approximately one liter of water is created by the burning of one liter of kerosene. As the heating sources were moved several times during the work, it was concluded that the freezing zone may have been moving up and down in the concrete, which had been saturated to a critical degree during the heating periods.

The formation of ice lenses in the contact layer between paste and aggregate is shown in figure 11. The specimen is from a large concrete block with unknown time-temperature history before the freezing.

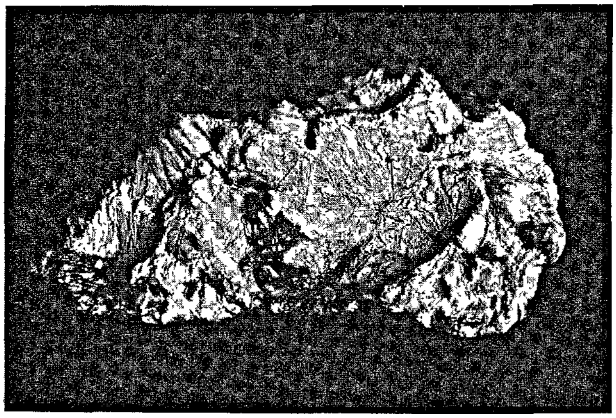

FIGURE 11. *Traces of ice needles in concrete with unknown time-temperature history.*

(Nerenst, Rastrup, and Idorn [10])

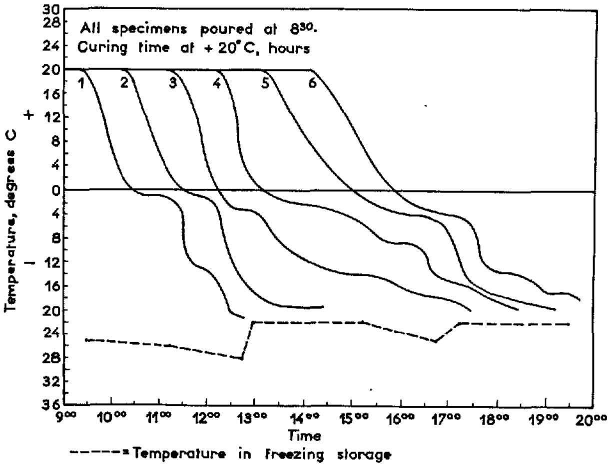

FIGURE 12. *Cooling curves of concrete beams with varying prehardening periods*

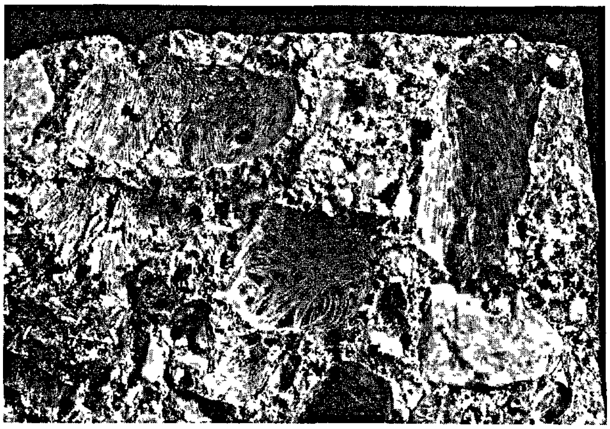

FIGURE 13. *Traces of ice needles in concrete frozen after 4 hr prehardening at +20 °C.*

(Curve 4, fig. 12)

The author has just started a few tests on the formation of ice needles in concrete at early ages. The concrete is cast at a temperature of +20 °C and placed in a commercial freezing storage of low temperature after varying prehardening intervals as shown in figure 12.

The temperatures are measured in the center of beams 10×10×60 cm in steel molds. The cooling curves are somewhat distorted because of heat of hydration, inaccuracies of measurement, and possibly changes in cooling conditions as the storage room has an intermittently working blower.

As an example of observations is shown figure 13, which corresponds to a piece of the beam, which had 4 hr prehardening.

To the author's knowledge, so far very little has been done in the laboratory to study how the direction of frost penetration and permeability of aggregate and paste, respectively, influence the orientation and amount of ice needles.

In the theories of cement paste it is assumed that the layer between air voids has a uniform temperature, which is justified from the small dimensions of the body. As the aggregate has much greater dimensions, the nonuniform temperature distribution may have considerable influence upon the direction of water movement.

The study is further complicated in paste with high amounts of water surrounding coarse aggregate with low porosity, as the heat released by the fusion of ice may delay the penetration of frost in the paste in comparison with the penetration of aggregate. Hence the hypothesis is put forward that coarse aggregate may serve as centers of low temperature, which may extract water from the unfrozen paste in all directions and thereby give rise to formation of rather thick coatings of ice in the early stages of hydration.

It is to be hoped that a well-equipped laboratory will study this problem in the future.

Necessary Prehardening to Avoid Damage From Freezing

Available information seems to indicate that the macroscopic ice segregation in green concrete is possible until the degree of hydration corresponds to a stage somewhere between initial and final set. On the other hand, the concrete may be damaged, even if ice segregation is not observed, and below a survey is given of some test results from laboratory experiments to determine the degree of hydration where concrete is undamaged by the first freezing. The presentation is largely based upon an unpublished report prepared by G. Möller [4].

Graf [66] in Germany made experiments on mortar specimens which were exposed to freezing at varying ages. The compressive strength was determined after thawing and additional curing. From his test results Graf drew the conclusion that concrete exposed for a very small number of freezing-and-thawing cycles should have a compressive strength of 80 kg/cm² before the first freezing. Concrete exposed to a great number of cycles of freezing-and-thawing should have obtained at least 150 kg/cm^2 before exposure. Kreüger in Sweden [67] also made experiments with mortar, and he concluded that concrete should be cured at least 24 hr at 20 °C before being exposed to first freezing. Some of his results are shown in figure 14. Both Graf and Kreüger made the tests on mortar and applied the results to concrete, which may not be correct because the contact layer between paste and aggregate is especially vulnerable to ice segregation.

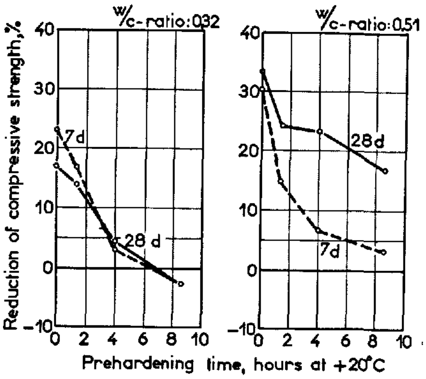

FIGURE 14. *Relation between prehardening time and reduction of compressive strength in percent of normal cured specimens at two water-cement ratios.*

Tested after 7 and 28 days curing. Kreüger's results [67] as presented by Möller [4].

Scofield's Tests

Scofield [68] has carried out tests to determine the necessary prehardening. He expressed the compressive strength of frozen 15- × 30-cm cylinders as percent of the strength of normally cured specimens. For specimens placed in the freezing room immediately after manufacture, he found a reduction in compressive strength from 25 to 65 percent for portland cement. During the cooling period, the specimens obtained a maturity corresponding to 1½ to 2 hr curing at +20 °C. His test results are given in figure 15.

If we accept a compressive strength of 95 percent of that of the normally cured specimens as a criterion for no damage, it will be seen in the lower part of the figure that the necessary prehardening time for concrete with a water-cement ratio of 0.76 is between 12 and 17 hr. For the high water-cement ratio of 1.05 the necessary prehardening period is longer, i.e., from 48 to 60 hr. When the prehardening took place in the moist room, considerably longer periods were necessary as shown in the upper part of figure 15. The figure shows only the compressive strength after curing periods of 28 days or longer, where the effect of delayed hardening due to the low temperature is less important than at earlier ages. It will be seen that even after 96 hr curing at 21 °C the concrete with the water-cement ratio of 1.04 has not gained sufficient strength. In this case air entrainment has not been used, but the test results demonstrate very clearly that prehardening under conditions that permit a reduction of the degree of saturation is very beneficial for the concrete.

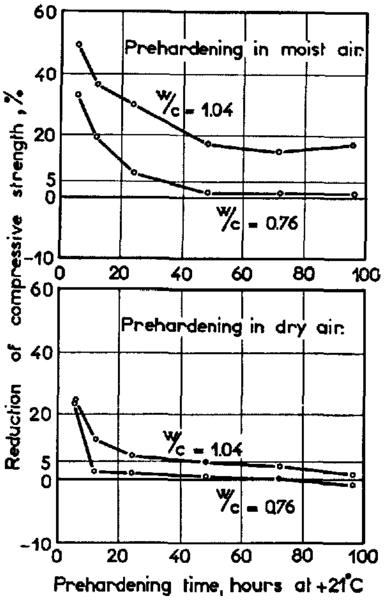

FIGURE 15. *Relation between prehardening time and reduction of compressive strength in percent of normal cured specimens for two water-cement ratios and two curing conditions.*

Scofield's results [68] as presented by Möller [4].

McNeese's Tests

McNeese [69] has also carried out tests to determine the necessary prehardening time on non-air-entrained concrete. The concrete had a cement content of 275 kg/m^3. Portland cement Type I was used. The water-cement ratio was 0.6. The concrete had a slump of 7.5 cm (~3 in.) and no air-entraining agent was added.

Cylinders having dimensions $B=15$ cm, $H=30$ cm, were exposed to freezing after 0, 1, 3, and 6 hr of prehardening at +22 °C or +4.5 °C. Four different temperatures of freezing were used within the range of −4 to −26 °C, and the length of freezing was 3 days. The specimens were then cured in moist air at a temperature of +22 °C until the compressive strength was determined at ages 3, 7, and 28 days without taking into consideration the period during which the concrete temperature was below +10 °C. The test results were expressed as percentages of the strength of companion specimens cured at 22 °C. Möller has shown that the frozen specimens had obtained a little extra curing period corresponding to 5 hr at 22 °C.

McNeese's test results are given in figure 16 as presented by Möller. It will be seen that the lower freezing temperature seems to require a longer prehardening time. If we permit a reduction in compressive strength of 5 percent, the necessary prehardening time for this type of concrete seems to be between 8 and 12 hr.

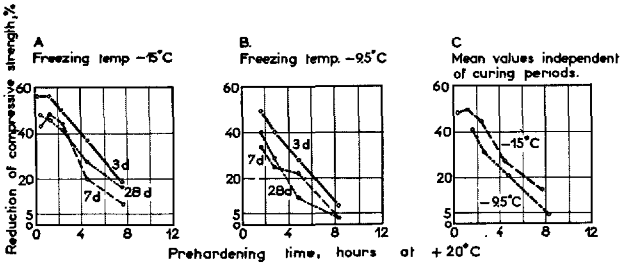

Figure 16. *Relation between prehardening time and reduction of compressive strength in percent of normal cured specimens as influenced by freezing temperature and length of after-curing period in days.*

Water-cement ratio=0.6. McNeese's test [69] as presented by Möller [4].

Bernhardt's Tests

Bernhardt in Norway [63] carried out a comprehensive investigation including variation in water-cement ratio, consistency, amount of accelerators, air-entraining agent, freezing temperature, freezing period, curing period after freezing, and the prehardening period. The prehardening took place in air at +18 °C in the laboratory for 24 hours and later in moist air at +20 °C. His results have been treated by Möller as reproduced in figure 17. Applying the criterion of a permissible reduction of strength of 5 percent, the necessary prehardening time is about 8 hours for water-cement ratio 0.4 and increases to about 24 hr for the highest water-cement ratio of 1.0.

Bernhardt reached the conclusion that air entrainment did not have any beneficial effect on the resistance of concrete to early freezing.

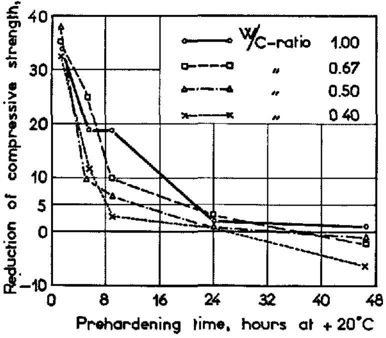

Figure 17. *Relation between prehardening time and reduction of compressive strength in percent of normal cured specimens.*

Mean value of Bernhardt's test results [63] as treated by Möller [4].

Möller's Tests

A comprehensive investigation was carried out at the Swedish Cement and Concrete Institute by G. Möller in order to determine the necessary prehardening time for concrete exposed to freezing at early ages. The investigation was sponsored by the Swedish Institute of Building Research on account of the great economic importance to all the northern countries of establishing how the cost of concreting in winter can be reduced.

During the investigation extreme care was taken to test the specimens from the freezing series at the same degree of hydration as the blank specimens cured at normal temperature.

One type of maturity function has been proposed by Saul [70], Nurse [71], and Bergström [72]. In the maturity function developed by these authors it is assumed that hydration will take place even at a temperature down to −10 °C. The maturity is computed as

$$M=\Sigma(t+10)\cdot\Delta a_t \qquad (8)$$

where $\Delta a_t=$ the curing time at the temperature t °C. This function has been modified by Nykänen [73].

A different way of computing the maturity or degree of hardening has been proposed by Rastrup [61], where the curing time a at a fixed temperature t may be computed from the formula

$$a=\Sigma 2^{\frac{t_v-t}{10}}\cdot\Delta a_v \qquad (9)$$

where $\Delta a_v=$ the intervals of curing time at the varying temperature t_v. The different maturity functions were discussed at length at the RILEM Symposium in Copenhagen [13].

Although none of the proposed maturity functions take all the variables pertaining to cement hydration into consideration they seem to be of very great help in making comparisons between concrete specimens exposed to low temperature or a number of freezing-and-thawing cycles and the corresponding blank specimens cured at normal temperature. By the use of the Saul-Nurse-Bergström maturity function, G. Möller is able to exclude the influence of low temperature upon the strength development. Consequently, when expressing the strength obtained in the freezing series as percentage of the strength of normally cured specimens, a reduction is exclusively considered to be caused by the freezing damage.

In Möller's experiments the cement content varied between 200 and 300 kg/m³, the water-cement ratio varied between 0.49–0.90, the consistency as measured by the slump test was 1–8 cm. The tests included series with and without air-entraining agent. In the latter case the air content was approximately 2–3 percent by volume. When air-entraining agent was used, the air content was 4.3–6.6 percent by volume.

As criteria of the freezing damage were chosen: (1), the reduction in the modulus of rupture in percent of that of normally cured specimens; (2), the reduction in dynamic modulus determined by resonance-frequency method; and (3), the dilation during freezing. For each mix the reduction in the modulus of rupture and dynamic modulus were plotted against the prehardening time in a similar way as shown in figure 17, and, applying the same level of permissible reduction in strength of 5 percent, the required prehardening time was determined.

The results are found in figure 18 together with all the previously mentioned tests. The required prehardening time is plotted against the water-cement ratio, which in Möller's opinion is the most decisive factor for obtaining early resistance to freezing. Taking into consideration that test conditions have varied with regard to cement type, fineness, curing, rate of cooling, and strength determinations, it must be admitted that the scatter of test results is not so high as could be expected.

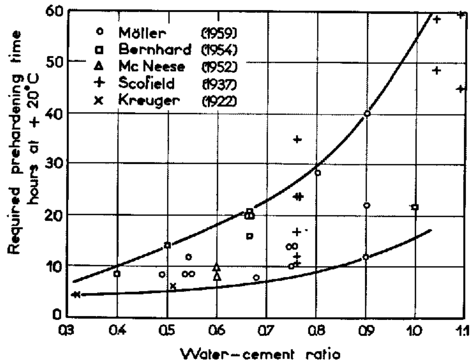

FIGURE 18. *Relation between the required prehardening period and the water-cement ratio.*

As presented by Möller [4].

Möller has computed the strength values which correspond to the required prehardening periods, determined by his own tests. He found that the required compressive strength is of the order of 25–30 kg/cm^2 and the modulus of rupture should be at least 5 kg/cm^2.

The effect of air entrainment was not very clearly demonstrated by the strength testing, as the observed reduction of the required prehardening time could be explained from the reduction of the water demand. The effect of the air was, however, very clearly demonstrated in the measurements of dilation.

The method used was to pour the fresh concrete in rubber balloons and determine the change of volume by the pycnometer method.

The test results are given for series A in figure 19. The concrete had a cement content of 200 kg/m^3, a water-cement ratio of 0.90 and the amount of entrapped air was 2.7 percent. The curves to the left indicate the dilation during the first cooling period from +20 °C to −5.5 °C and the numbers of the curves indicate the length of the prehardening period at +20 °C.

The diagram to the right indicates the relationship between the number of freezing and thawing cycles (−5.5 °C to +5.5 °C each day) and the remaining dilation after the specimen has been brought back to the +5.5 °C level. The values are not corrected for variation of the specific gravity of the pycnometer fluid (water-spirit mixture or ethylene glycol), but it is nevertheless possible to see that the dilation is diminishing with increasing prehardening time.

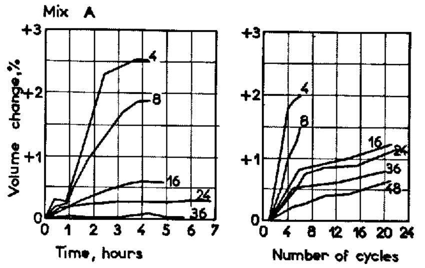

FIGURE 19. *Volume change of concrete during first cooling (left) and remaining dilation after cycles of freezing and thawing (right) after prehardening periods in hours at +20 °C as indicated on each curve.*

Non-air-entrained concrete (L=2.7%) of 200 kg cement/m^3 and w/c=0.90 (Möller [4]).

In figure 20 are given the results from a concrete with the same cement content as in figure 19. The amount of entrained air was 6.6 percent, and, as the water demand was reduced due to the entrained air, the water-cement ratio was 0.80.

By comparison of the two concrete mixes it is readily seen that the entrained air (fig. 20) reduces the dilation to one-fifth of the value obtained for the non-air-entrained concrete (fig. 19) for the testing after 4 hr prehardening.

The observations may be explained by the earlier-mentioned theories [6, 12, 23].

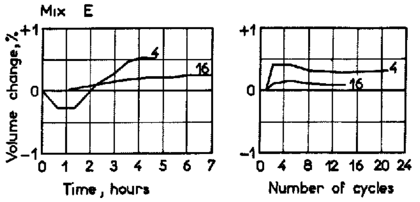

FIGURE 20. *Volume change of concrete during first cooling (left) and remaining dilation after cycles of freezing and thawing (right) after prehardening periods in hours at +20 °C as indicated on each curve.*

Air-entrained concrete (L=6.6%) of 200 kg cement/m^3 and w/c=0.80 (Möller [4]).

Johansen in Norway [74] made freezing tests on grouts for injection of cable ducts in post-tensioned concrete and found that the entrained air had a very beneficial effect in preventing expansion, when freezing took place after 3 days' curing at +5 °C.

Möller [4] has determined the relationship between the maximum increase in volume during the first freezing and reduction of the modulus of rupture (fig. 21).

From the reported data of decrease of the volume weight due to freezing in Graf's investigation [66], Möller has computed the permanent increase in volume and plotted these results against the reduction of compressive strength (fig. 22).

In both cases the reduction of strength is much greater than that corresponding to the increase of porosity.

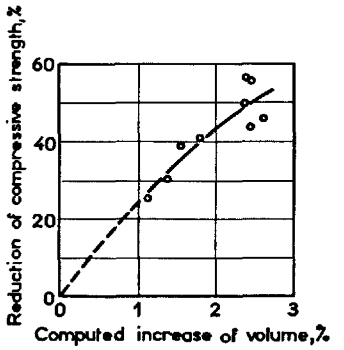

Figure 21. *Relation between the reduction of compressive strength in percent of that of normal cured specimens and computed remaining dilation.*

(Graf's results [66]) as presented by Möller [4].

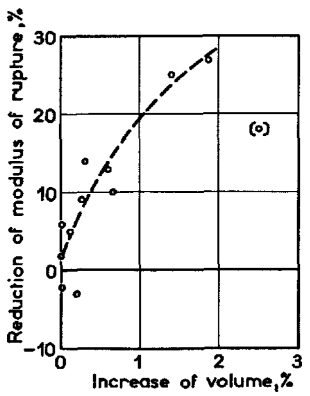

Figure 22. *Relation between the reduction of modulus of rupture and maximum dilation during the first cooling.*

(Möller [4])

Conclusions

Frost action in concrete has in many countries caused serious damage to exposed structures. Studies of the frost resistance of mortar and concrete have consequently been started in early periods of the concrete age, but it has not been the intention of the writer to give a historical review of testing procedures and the test results obtained in this early period.

The present paper is also incomplete insofar as many important reports on noteworthy developments may have escaped the writer's notice. This may especially be the case if the paper has been published in languages other than English, French, German, or the Scandinavian languages.

It cannot be avoided that selection of papers and the presentation of general principles and concepts are greatly influenced by the writer's own opinion on the subject. The theories and concepts which take full advantage of the highly increased knowledge of the basic physical properties of cement paste have a prominent place in the present review, although it has been almost impossible to present all these ideas in such a way that all the implications may be understood from this review. It is strongly recommended that the readers study the theoretical papers to which references have been made in the text.

It will be understood that the writer is in favor of using air-entraining agents in concrete structures exposed to freezing conditions, even if it has been possible in earlier days and may still be feasible to produce a concrete without air-entraining agent and still obtain a reasonable resistance to freezing under moderate climatic conditions. The incorporation of a reasonable amount of air, which is well distributed in the concrete, is, however, a very easy and economical way of obtaining a safeguard against frost damage which involves only small disadvantages if any with regard to reduction of strength. To obtain the full advantage of this—at least in Europe—relatively new development, recommendations of the mix design, control of air content, and the properties of air-entraining concrete should be prepared on a national scale based upon the climatic conditions prevailing, as the results from the laboratory tests should be adjusted to the actual climatic conditions. Tentative recommendations of this type were published in 1952 by the Danish Institution of Civil Engineers, and to the author's knowledge Denmark was the first country in Europe where an official organization accepted the use of air-entrained concrete for certain structures.

The air-entraining agents may be further developed, and the methods of mix design may be refined, but at the moment it seems that the resistance of hardened concrete now depends more than ever upon the properties of the aggregate, and further research is needed in this field. A few observations indicate that even dense stone and granite after crushing have been brought to such a state that the natural weathering process affecting all types of rocks may be accelerated after the incorporation of the particles in concrete, but no definite conclusions can be drawn as yet.

Freezing of concrete at early ages has recently been the subject of research in Scandinavia. Some relations between curing periods and resistance to freezing and thawing have been established, but further research is needed. No definite conclusions can be drawn with regard to the time at which macroscopic ice segregation will be prevented during the progressing hardening process. The influence of entrained air on frost action in concrete at early ages is still the subject of discussion.

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The Portland Cement Association has sent me reports, which were difficult to obtain in Denmark. The Danish National Institute has supplied the photographs No. 1, 11, and 13 and among the staff members, Mr. N. M. Plum and Mr. Jørn Jessing have been specially helpful. Mr. Folke Sandford, Swedish Silicate Research Institute, has permitted the reproduction of figure 8. Mr. G. Möller, Gullhögen, has permitted the writer to draw freely on an unpublished report. Mr. C. Nymand made the drawings and Mrs. K. Steen Kristensen typed the manuscript.

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Discussion

R. A. Helmuth

A question of very great importance in research concerning frost action in concrete is how ice formation produces stresses in the porous structure of the hardened cement paste. According to the hydraulic pressure hypothesis (HPH), [1][1] freezing first fills all the pore space with ice and unfrozen water (actually aqueous solution), and then develops pressure which is generally prevalent throughout the pores in the paste, instead of producing stress concentrations at the frozen (larger) capillaries. As discussed in Poul Nerenst's excellent review paper, work in this laboratory led to the formulation in 1953 of an extended theory of freezing of water in hardened cement pastes and the protective effect of entrained air [2, 3]. This theory included two mechanisms: (1) the HPH, i.e., generation of pressures by ice formation and the relief of these pressures by saturated hydraulic flow to air voids, and (2) (osmotic) accretion of ice in capillaries and macroscopic segregation of ice in air voids by unsaturated flow. There are two unsaturated flow mechanisms: suction and surface diffusion. They are the result of free-energy differences between air-void ice and water and ice in the pores of the paste. Nerenst's review indicates that this extended theory represents "notable" progress, yet there have been several quite thorough studies since 1953 in which only the HPH is considered, no doubt because the mathematical formulation makes experimental results more amenable to analysis.

It is the purpose of this discussion to question whether saturated flow occurs in mature air-entrained cement pastes even in the early stages of freezing in pastes which are as nearly water-saturated as possible. This question is directly related to the question of how ice formation produces stresses. Stress concentrations resulting from saturated flow alone would be spaced according to the void spacing factors, which are about 0.25 mm or 250 μ in pastes with entrained air. On the other hand, stress concentrations at the sites of ice formation would be spaced according to the spacing of the capillaries, which in mature cement pastes are believed to be of the order of 0.01 μ in diameter and perhaps several times as far apart. According to the extended theory, dilation might be produced during saturated flow because of the hydraulic pressure and during unsaturated flow by highly localized osmotic pressures at the sites of ice formation. That the flow is almost entirely unsaturated even during the early stages of freezing will be shown using both the older data on which the extended theory was based and more recently obtained data.

Effect of Entrained Air Voids on Freezing Expansions

Examination of the formulation of the HPH reveals that the variables s, the saturation coefficient, U, the rate of ice formation, R, the rate of cooling, and $\overline{L}$, the void spacing factor, are variables that control the pressure and dilations during freezing. Experimentally both s and U are apt to be difficult to control because of moisture distribution changes produced by temperature change [4] and capillary size restrictions on ice formation [5]. Therefore, tests of the hypothesis should be designed to vary only R or $\overline{L}$ with s and U held constant. The most easily reproduced value of s is unity. This can be obtained if the paste is cured in water at the freezing temperature, or if the air voids contain free water that may be absorbed by the paste to maintain saturation in cooling from the curing temperature to freezing temperatures. Present consideration will be confined to results for pastes having only rather high air contents because pastes of low air content became somewhat desiccated as a result of cooling from room temperature, whereas high air content pastes with water in the air voids apparently remained water-saturated in cooling to freezing temperatures. Furthermore, the pastes of high air content and therefore small void-spacing factors, showed only relatively small expansions which were probably almost completely elastic.

An example of the kind of results obtained is given in figure 1, which shows a complete cooling-warming cycle for a paste with small void-spacing factor. Many tests of this kind were made. In every case the beginning of freezing is indicated by an expansion and temperature rise (or temporary cessation of cooling) caused by release of latent heat of fusion. Inspection of the curves reveals that subsequent length changes are functions of paste characteristics, air-void-spacing factor, and cooling rate.

Summary plots of most of these freezing curves are presented in figures 2, 3, and 4, which show the effect of variation of void spacing factor. The expansions produced by freezing are seen to yield to shrinkage at a rate much greater than the thermal contraction of the paste at temperatures above freezing, which indicates that the paste has been dried internally by accretion of ice in the air voids. A line of slope $35\times10^{-6}/°C$ has been drawn through the origin in each of these plots to show how closely the curves of small spacing factors approach this line. This close approach occurs regardless of paste porosity, except for the very impermeable pastes of w/c=0.45 in which these cooling rates must have been so high that the shrinkage appreciably lagged the changing temperature.

This shrinkage during freezing is taken as positive evidence that the flow of moisture to air voids at low temperatures is *unsaturated* flow.

The possibility of *saturated* flow to air voids in the early stages of freezing will also be examined.

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[1] Figures in brackets refer to the literature references at the end of this paper.

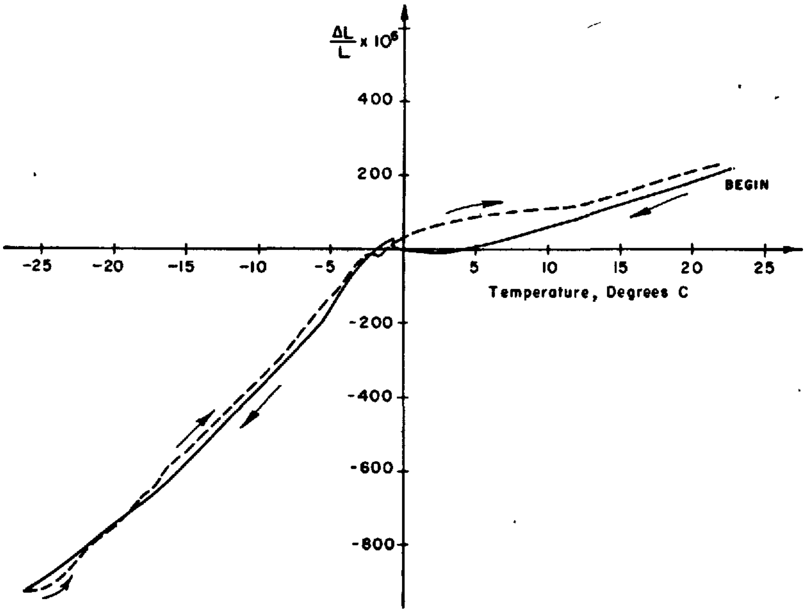


FIGURE 1. *Freezing-cycle test of specimen 4_1 b.*

w_t/c was 0.669; w_n/c was 0.161; 14.8 percent air with a void-spacing factor of 0.0226 cm and ϕ (L)of 1605 cm². Cooling and warming at 0.25 °C per min.

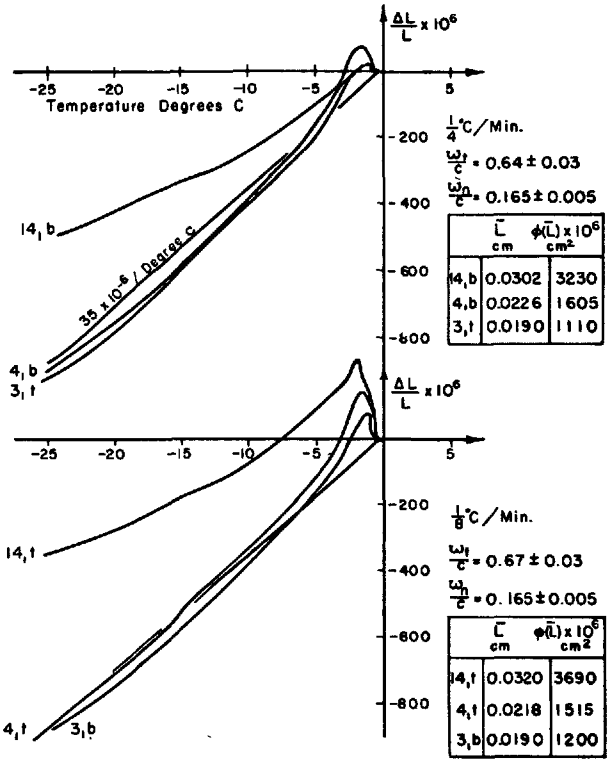


FIGURE 2. *Effect of spacing-factor variation in high-porosity pastes.*

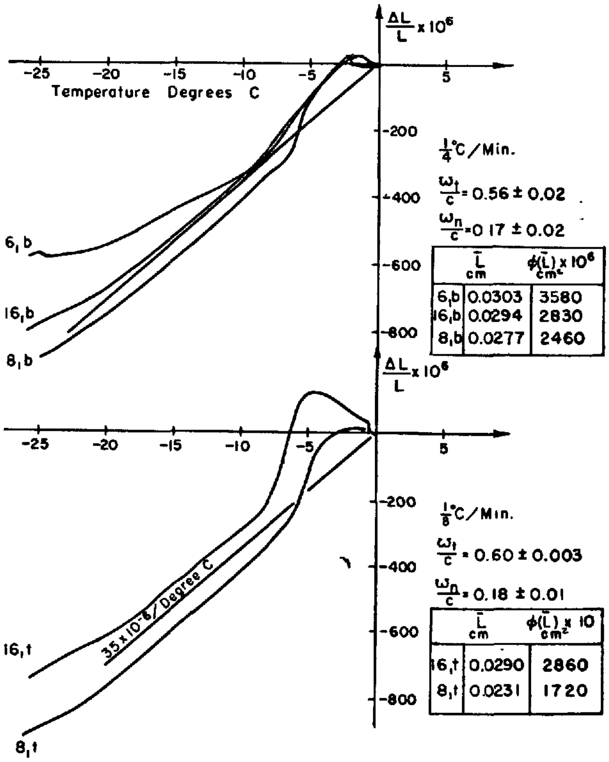
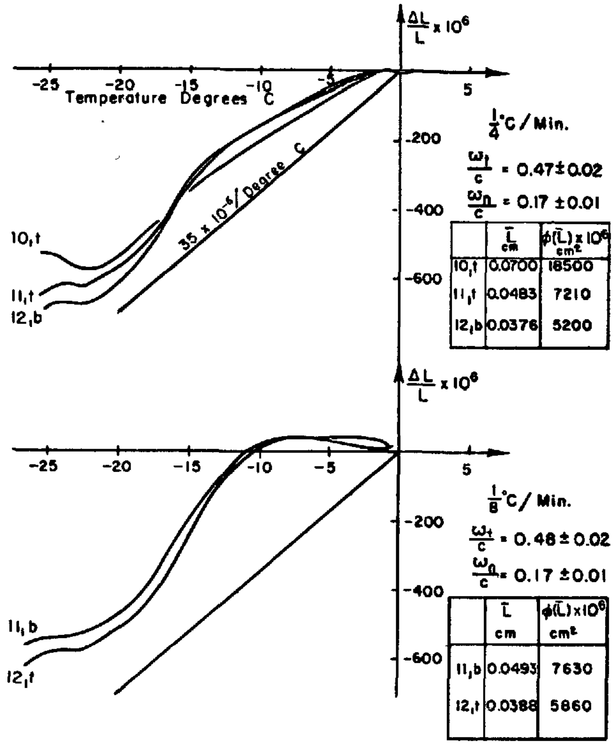


FIGURE 3. *Effect of spacing-factor variation in medium-porosity pastes.*



	$\bar{L}$ cm	$\phi(\bar{L}) \times 10^6$ cm²
10,t	0.0700	18500
11,t	0.0483	7210
12,b	0.0376	5200

	$\bar{L}$ cm	$\phi(\bar{L}) \times 10^6$ cm²
11,b	0.0493	7630
12,t	0.0388	5860

FIGURE 4. *Effect of spacing-factor variation in low-porosity pastes.*

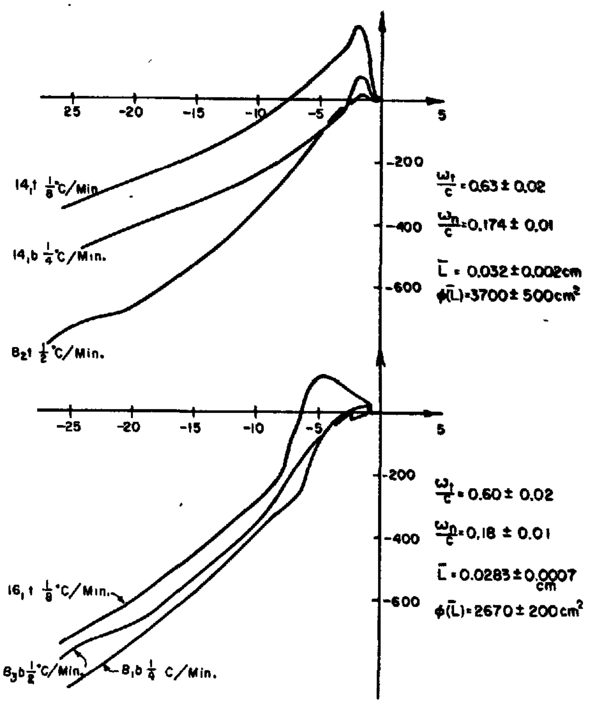


FIGURE 5. *Effect of rate-of-cooling variation on freezing expansions.*

In Powers' formulation of the hydraulic pressure hypothesis it was shown that for constant paste characteristics, the rate of cooling R and the spacing factor function $\phi(\bar{L})$ determined the maximum pressure generated by freezing the paste. As $\phi(\bar{L})$ or R increase, the maximum expansion should also increase. The results shown in figures 2, 3, and 4 are in accord with the deduction that the maximum expansion increases with the spacing factor function $\phi(\bar{L})$. Figure 5 gives plots of results at approximately constant paste characteristics and void spacing factors at three cooling rates. The top set of curves shows that for pastes of $w_t/c = 0.63 \pm 0.02$, $w_n/c = 0.174 \pm 0.01$ and $\bar{L} = 0.032 \pm 0.002$ cm, the maximum expansions *decrease* as the cooling rates increase. When $w_t/c = 0.60 \pm 0.02$, $w_n/c = 0.18 \pm 0.01$ and $\bar{L} = 0.0283 \pm 0.0007$ cm as in the lower set of curves the same is true of the maximum expansions, though the behavior at lower temperatures results in contractions not related in the same way, probably because the cooling rate of specimen 8_1b dropped considerably below the nominal ¼ °C/min in the vicinity of −6 °C and this permitted more shrinkage than would have occurred with better control.

At the highest cooling rate used, ½ °C/min, the freezing expansion is almost completely absent in both sets of curves. This would be decisive evidence against the HPH if it were not for the fact that during cooling before freezing, moisture tends to move into the gel from capillary cavities in the paste, thus reducing the capillary saturation coefficient and the freezing expansion. When the air voids contain some water (as in all of these specimens) the paste can imbibe water from these voids and remain saturated during cooling, but this process takes time and if cooling is rapid it is possible some "desiccation" may result, even with water in the air voids. However, the differences in capillary saturation coefficients in these six specimens at the beginning of freezing are believed to have been very small because each began the progressive freezing expansion at a temperature much higher than comparable air-free pastes which could not imbibe water from air voids during cooling. For this reason these results are taken as strong evidence that no saturated flow occurred in these tests.

Though the expansions of pastes with entrained air vary qualitatively with void spacing factor as would be expected from either mechanism, the freezing expansion results with rate of cooling variation at constant void-spacing factor indicate that the expansions are limited by a mechanism different from that of freezing in place and saturated flow to air voids. The results are in accord with the theory of osmotic accretion by unsaturated flow.

In 1953 we believed that in the early stages of freezing, when ice formation was rapid, saturated flow of water occurred so easily that no appreciable pressures or dilations were produced. Then we could explain the observations without abandoning the HPH, which seemed to us too reasonable to deny. However, it seems now that not only these results can be explained without assuming saturated flow but that there are other results which indicate that the dilations must be produced only by stress concentrations at the sites of ice formation. These results show that expansions are produced in pastes free of entrained air even when there is ample empty space in the capillaries to accommodate the excess volume produced by ice formation.

Initial Formation of Ice in Slightly Supercooled Air-Free Pastes

In a paper [5] supplementary to Nerenst's review paper, the initiation of ice formation in the capillaries of hardened cement paste is discussed in some detail. There it is shown that the water in the pores supercools unless it is seeded by ice crystals. When it is seeded at sufficiently low temperatures, there is rapid freezing of a small amount of water, w_f. This amount can be estimated readily from the observed temperature rise ΔT_f, and the specific heat of the paste, C_p.

If the water that freezes in the capillary spaces undergoes the same volume change as pure bulk water does when it freezes, the volume change of ice formation is

$$\Delta V_i = 0.09\ w_f. \tag{1}$$

This volume change may then be compared with the fraction of the capillary space which is empty. If ΔV_i is greater than the volume of the empty capillary space, ice formation should develop pressure in the capillary water, at least in the capillaries where freezing occurs. Such pressure should expand the paste structure more than the thermal expansion alone.

The volume of the empty capillary space in the paste can be calculated from the fraction of the capillary space which is filled with water, or the capillary saturation coefficient, s_c, for pastes cured in certain ways. For self-desiccated pastes Copeland and Bragg's [6] work yields:

$$s_c = \frac{0.99 w_c}{0.99 w_c'} = \frac{w_o - 1.74 w_n}{w_o - 1.49 w_n} \tag{2}$$

in which 0.99 is the specific volume of the capillary water, w_c is the mass of the capillary water, w_c' is the mass of the capillary water for the paste when water-saturated, w_o is the mass of the original water, and w_n is the mass of the nonevaporable water. The fraction of the capillary space which is empty before freezing is then $(1-s_c)$.

Table 1. *Comparison of the volume change of initial ice formation with available volume in self-dessicated pastes*

Specimen	s_c	$\frac{0.09\ w_f}{0.99\ w_c'}$	$\frac{0.09\ w_f}{0.99\ w_c'(1-s_c)}$
51_2b	0.989	0.00132	0.12
52_1t	.953	.00097	.02
55_2t	.940	.00063	.01

In the supplementary paper [5] some results of freezing experiments with self-desiccated pastes are presented (figs. 5, 9, 10, and 11 of that paper), in which the initial ice formation could not have filled all the available capillary space, yet sustained expansions occurred in these unsaturated pastes. In table 1 the volume increase produced by the amount of ice formed in the initial freeze is compared with the volume of empty capillary space for three specimens which showed definite expansions at the initial freeze. The w_f values were given in the supplementary paper. The volume increase was calculated from w_f and eq (1), then expressed relative to the volume of capillary space, 0.99 w_c', and also relative to the empty capillary space, 0.99 w_c' $(1-s_c)$. In all three cases the ratio of the volume increase of ice formation to the volume of empty capillary space is much less than unity. Nevertheless, these freezes produced expansion not only during the initial freeze, but sustained expansions with further cooling. It seems necessary to conclude that the expansion after the initial expansion occurred because of lateral growth of the original dendrites, or some other slower form of crystal growth, in the initially frozen capillaries even when there was considerable empty capillary space in the paste. That is, the expansion was not produced by a generally prevalent pressure in all of the evaporable water in the paste, but was a result of local pressures produced in the capillaries where freezing occurred. This seems to be true even in the water-soaked pastes, in which we must take account of the transfer of moisture from capillary space to gel pores that occurs during cooling to freezing temperatures. The reduced value of s_c resulting from moisture movement from capillary spaces to the gel during cooling of these specimens to 0 °C from room temperature was calculated from [5]:

$$s_c = 1 - \frac{0.0194 w_g' + 0.0024 w_c'}{w_t' - 1.74 w_n} \tag{3}$$

in which w_g' is the water content of the gel when saturated, and w_t' is the total water content of the paste when saturated. This reduction of the capillary saturation coefficient is more than enough to accommodate the excess volume generated in the initial freeze, which is shown in table 2 for a group of water-soaked pastes, cited in the supplementary paper.

Table 2. *Comparison of the volume of initial ice formation with available volume in water-soaked pastes*

Specimen	s_c	$\frac{0.09\ w_f}{0.99\ w_c}$	$\frac{0.09\ w_f}{0.99\ w_c\ (1-s_c)}$	Initial Expansion$\times 10^6$
63_2t	0.9944	0.0017	0.30	120
60_2t	.9929	.0005	.07	26
61_1t	.9917	.0000	.00	0
57_1t	.9863	.0000	.00	3
59_1t	.9833	.0008	.05	50

These specimens were cured in water at 5 °C, but in preparation for the test they were in contact with water at about room temperature. At the time the tests were made it was believed that though the equilibrium water content of the specimens would be lower at room temperature than at 5 °C, it would require many hours for the specimen to lose an appreciable quantity of water when warmed to room temperature after curing at 5 °C. It was later discovered by weighings at 0 °C, 5 °C, and 25 °C that this change occurred rapidly. Hence it is believed that the water contents of these specimens were those required for saturation at 25 °C and not at 5 °C. Even if this is only approximately true, the results of these calculations indicate that there was much more empty space in these pastes than necessary to accommodate all the excess volume produced by ice formation in the initial freeze, yet there immediately followed large progressive expansions.

The data in tables 1 and 2 indicate that stress concentrations at the sites of the initial ice formation are responsible for the dilations because the amount of ice formed was too small to fill all the pore space with ice and water. Confidence in this interpretation is enhanced by the rather good correlation in table 2 between the initial expansions and 0.09 w_f/0.99 w_c, regardless of the amount of empty space.

Conclusions

The results presented above indicate that the expansion-producing mechansim in moist, hardened pastes, both with and without entrained air, is *not* the development of pressure in the water in all the pores, but is the production of localized osmotic pressures at the sites of ice formation. This appears to be true not only in the later stages of freezing, as shown in 1953, but even in the early stages.

The results with mature pastes containing entrained air showed no dilations caused by hydraulic flow. Nevertheless, it could be argued that saturated flow to air voids did occur, but with such little resistance that no dilations due to hydraulic pressure occurred. However, results with air-free pastes showed that dilations were observed even when the paste was unsaturated; therefore, saturated flow to even the much more closely spaced empty capillaries cannot occur so easily that no dilations result. Hence, when dilations are prevented, it must be because the pastes are even more unsaturated. This must mean that in the tests of pastes containing entrained air, unsaturated flow to air voids occurred early enough and to such an extent that positive pressures and saturated flow did not develop.

The reasons for the lack of saturated flow are: (1) the lack of water-saturation, which is caused by (a) the drying effect of ice in air voids [2] at temperatures below 0 °C, (b) self-desiccation caused by hydration of cement during curing, and (c) "cooling desiccation" resulting from moisture absorption by the gel during cooling to freezing temperatures; and (2) the very limited amount of freezing *in situ* that can occur during cooling because of capillary size restrictions on ice formation in the pores of the paste. These effects combine, in moist pastes with small void spacing factors, to dry the pastes before freezing can produce positive pressures and saturated flow of the water in the paste surrounding the air voids. Therefore, the dilations result from accretion alone, and the flow is unsaturated flow to capillary ice and air-void ice.

The above conclusions are based primarily on data obtained with water-soaked pastes of normal porosities with entrained air. Further investigation may reveal that hydraulic pressure is an important factor in the production of dilations (and saturated flow) in pastes without entrained air, in pastes of abnormally high porosity, or in immature cement pastes. Though we have made no thorough study of this question using immature pastes, a limited amount of available data for pastes with and without entrained air suggests that the above conclusions are also valid when as little as 20 percent of the cement is hydrated.

References

[1] T. C. Powers, The air requirement of frost-resistant concrete, Proc. Highway Research Board **29**, 184–211 (1949).

[2] T. C. Powers and R. A. Helmuth, Theory of volume changes in hardened portland cement paste during freezing, Proc. Highway Research Board **32**, 285–297 (1953).

[3] G. Pickett, Flow of moisture in hardened cement paste during freezing, Proc. Highway Research Board **32**, 276–284 (1953).

[4] R. A. Helmuth, Dimensional changes of hardened portland cement pastes caused by changes of temperature, to be published in the Proc. Highway Research Board **60** (1961).

[5] R. A. Helmuth, Capillary size restrictions on ice formation in hardened portland cement pastes, this Symposium, paper VI–S2.

[6] L. E. Copeland and R. H. Bragg, Self-desiccation in portland cement pastes, Am. Soc. of Testing Materials Bull. **204**, 34–39 (1955).

Discussion

Ulf Danielsson

In the principal paper "Frost Action in Concrete," Nerenst has made an excellent review of this complex field. However, I should like to comment upon one minor point. The equations given for the maximum hydraulic pressure set up at freezing contain the factor $\left(1.09-\frac{1}{s}\right)$, where s is the coefficient of saturation. A closer examination of the case of partial saturation shows, however, that the coefficient s should appear in the equations in a less simplified form.

In the paper "The Frost Resistance of Cement Paste as Influenced by Surface-Active Agents" [1] a formula for the rate of generation of water volume by freezing has been derived:

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[1] U. Danielsson and A. Wastesson, The frost resistance of cement paste as influenced by surface-active agents, Swedish Cement and Concrete Research Institute, Proceedings No. 30, 40 pp. (Sweden. 1958).

$$\mathscr{H}=\left(\frac{1}{\gamma_f}-\frac{1}{\gamma_w}\right)\left(-\frac{dz}{dT}\right)\left(-\frac{dT}{dt}\right)\frac{\gamma w_w}{(1-A)(1+w_0)}, \qquad \text{(A)}$$

where:

$\mathscr{H}$=rate of generation of water volume by freezing, cm^3 water/cm^3 paste and sec.,
γ_f=density of frozen water, g/cm^3 ($\gamma_f=0.917$ g/cm^3),
γ_w=density of unfrozen freezable water, g/cm^3 ($\gamma_w=1.000$ g/cm^3),
z=weight ratio of frozen water to freezable water at temperature T,
T=temperature, °C,
t=time, sec.,
γ=density of the paste including air pores, g/cm^3,
w_w=total weight of freezable water per unit weight cement,
A=total volume of air pores per unit volume of paste, and
w_0=water-cement ratio of the paste.

In the case when the paste is unsaturated before freezing starts ($s<1$), $\mathscr{H}$ is zero until the voids have been filled. This occurs when $z=z_0$, where:

$$z_0=\frac{\gamma_f}{\gamma_w-\gamma_f}\left(\frac{1}{s}-1\right). \qquad \text{(B)}$$

Equation (A) is thus valid only in the range $z_0 \leq z \leq 1$. The maximum value for $\mathscr{H}$ is generally obtained at temperature T_0, corresponding to $z=z_0$, and we obtain:

$$\mathscr{H}_{\max}=\left(\frac{1}{\gamma_f}-\frac{1}{\gamma_w}\right)\left(-\frac{dz}{dT}\right)_{z_0}\left(-\frac{dT}{dt}\right)_{T_0}\frac{\gamma w_w}{(1-A)(1+w_0)} \qquad \text{(C)}$$

where z_0 and T_0 depend on the saturation.

From eq (B), and with the condition $z \leq 1$ it follows that the water flow vanishes when the saturation is below $s=\frac{\gamma_f}{\gamma_w}=0.917$. The factor $\left(1.09-\frac{1}{s}\right)$ becomes zero for the same limiting value. Also in the case of saturated paste ($s=1$), there is agreement between eq (C) and that part of eq (2) in the paper under discussion corresponding to the source of the flow.

When, however, the saturation lies between 0.917 and 1, it is tacitly assumed in eq (2) that the function expressing the strength of the source, or the hydraulic pressure, is a linear function of $1/s$, which is not necessarily correct. The general behavior is given by eqs (B) and (C). Admittedly, in experimental work one usually tries to keep the test specimens saturated, but unsaturated conditions are often met with in practice, and therefore I feel that it is worth while to point out this inconsistency.

(Ed. note: *Because of the illness of its author, the above discussion was not submitted in time to permit a response by the author of the paper under discussion.*)

Paper VI–S1. Deterioration of Cement Products in Aggressive Media*

J. H. P. van Aardt

Synopsis

The chemical and compound compositions of various hydraulic cements are discussed in relation to chemical attack. Data are presented in regard to the corrosion of hardened hydraulic-cement mortars in aggressive media, such as solutions of sulfates and chlorides, acids, and soft waters.

In the corrosion of cement mortars in sulfate, chloride, and other salt solutions, the nature and the function of the cations in the systems are important. The behavior of mortars made with different hydraulic cements is compared, and it is shown that the state of equilibrium and curing have marked influences on the resistance of cement mortars to aggressive agents; the effects of high- and low-pressure steam curing, curing under water, and curing in humid atmospheres are discussed. The carbonation of mortars made with portland cement is found to be beneficial, and the substitution of a calcareous aggregate for a siliceous aggregate improves the resistance of cement mortars to sulfuric acid attack. High density and low permeability in mortars reduce their vulnerability to corrosion, and it is stressed that good quality of the mortar is of prime importance in any corrosive environment. Bad practice in this respect can outweigh improvements aimed at by the use of more corrosion-resistant cements.

Résumé

La composition chimique d'oxydes et de composés de différents ciments hydrauliques est discutée par rapport à l'attaque chimique. Des données sont présentées en ce qui concerne la corrosion de mortiers durcis de ciment hydraulique en milieux agressifs, tels que les solutions de sulfates et de chlorures, les acides et les eaux douces.

Quand on étudie la corrosion des mortiers de ciment dans les solutions contenant le sulfate, le chlorure et des autres sels, la nature et la fonction des cations dans les systèmes sont importantes. Le comportement des mortiers confectionnés de différents ciments hydrauliques est comparé, et l'on voit que l'état d'équilibre et de conservation ont des influences marquées sur la résistance des mortiers de ciment aux agents agressifs. Les effets de conservation à la vapeur sous haute et basse pression, la conservation sous l'eau et la conservation en atmosphères humides sont discutées. On trouva avantageuse la carbonatation des mortiers confectionnés de ciment portland et la substitution d'un agrégat calcareux à un agrégat siliceux améliore la résistance des mortiers de ciment contre l'attaque de l'acide sulfurique. Une haute densité et une basse perméabilité dans les mortiers réduisent leur aptitude à la corrosion et on souligne la première importance de bonne qualité des mortiers en tout milieu corrosif. A cet égard une mauvaise pratique peut l'emporter sur les améliorations recherchées par l'emploi de certains ciments résistants à la corrosion.

Zusammenfassung

Die chemische Zusammensetzung und die Verbindungen, die man in den verschiedenen hydraulischen Zementen findet, werden in ihrer Beziehung zu chemischen Angriffen besprochen. Angaben der Korrosion erhärteter hydraulischer Zementmörtel in zerstörenden Medien, wie Sulfat- und Chloridlösungen, Säuren und weichem Wasser, werden angegeben.

Bei der Korrosion der Zementmörtel in Sulfat-, Chlorid- und anderen Salzlösungen ist die Natur und die Wirkung der Kationen in den Systemen von großer Bedeutung. Das Verhalten von Mörteln, die aus verschiedenen hydraulischen Zementen hergestellt worden sind, wird verglichen, und es wird gezeigt, daß der Gleichgewichtszustand und das Aushärten einen großen Einfluß auf den Widerstand der Zementmörtel gegen angreifende Mittel haben; die Wirkungen des Aushärtens mit hoch- und niedriggespanntem Dampfe, unter Wasser und in einer feuchten Atmosphäre werden behandelt. Die Einwirkung der Kohlensäure auf Mörtel, die mit Portlandzement hergestellt worden sind, muß als wertvoll bezeichnet werden, und die Einführung eines Karbonataggregats an Stelle eines Silikataggregats verbessert den Widerstand der Zementmörtel gegen Schwefelsäureangriff. Ein hohes spezifisches Gewicht und eine niedrige Permeabilität der Mörtel macht diese weniger korrosionsanfällig; es wird betont, daß in einer korrodierenden Umgebung eine gute Qualität des Mörtels die Hauptsache ist. Wenn man hier falsch verfährt, kann man alle Verbesserungen, die durch die Anwendung korrosionswiderstehender Zemente hervorgebracht worden sind, wieder zunichte machen.

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* Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the South African Council for Scientific and Industrial Research, Pretoria, S.A.

Introduction

The main object of this paper is to show how various chemical and physical factors influence the durability of cement products and how diverse studies have contributed towards improved durability and greater usefulness of such products. The heterogeneous mixture of cement, water, and aggregate is a very complicated one, and it is not surprising that many conflicting data and observations concerning resistance to aggressive conditions are to be found in the literature. Slight variations in materials, methods, and experimental conditions can lead to major differences in results and conclusions. For this reason close control of variables and clear descriptions of experimental procedures and conditions are essential.

The corrosion of cement products is influenced not only by the chemical composition of the components but also by their physical state and nature, and hence it is a field of study involving chemistry and physics, as well as applied technology.

General Discussion on Chemical Composition in Relation to Chemical Attack

Susceptibility of Various Cement Compounds to Attack

It has long been known that the behavior of cements in aggressive media is largely determined by their compound composition. Thus it is now well established [1, 2, 3, 4, 5][1] that the C_3A content of portland cement determines its resistance to solutions containing sulfate ions, in that cements with low C_3A contents are more resistant than those with high C_3A contents. Often experimental results do not show a linear relationship between C_3A content of portland cement and the resistance of the cement products to attack by sulfates, but this lack of correlation is probably due to errors in estimating the C_3A content [6] and to the effect of physical factors such as density and permeability.

The reaction of sulfates with other constituents of portland cement has also been investigated [7, 8, 9, 10]:—C_4AF is found to be vulnerable to sulfates but to a lesser extent than C_3A, and, furthermore, crystalline C_4AF is reported to be more resistant than C_4AF in the glassy state. In addition it has been shown that the hydrates of the silicates, C_3S and C_2S, are more resistant to sulfate attack than those of C_3A and C_4AF.

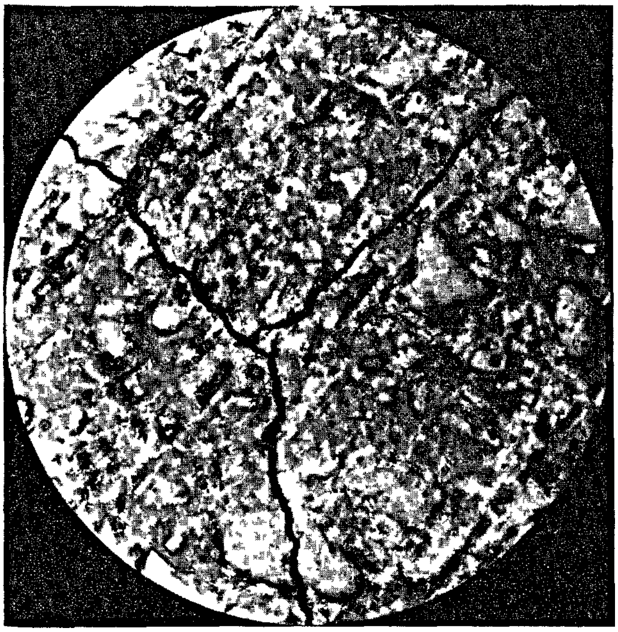

FIGURE 1. *Photomicrograph showing unhydrated cement particles.*

(×220)

Influence of Equilibrium Conditions on the Nature of Hydrated Cement Compounds

When anhydrous cement compounds are brought into contact with water, reaction and decomposition take place with the formation of hydrates. Supersaturated and unstable solutions are formed which slowly tend to equilibrium. However, when the mass sets and hardens, the mobility of the various ions is reduced and the attainment of equilibrium is very slow. For instance, figure 1 shows a neat cement specimen in which unhydrated particles of cement are still present after 28 days curing under water.

It was stated earlier that the nonlinear relationship which has been found between C_3A content and sulfate resistance might be due to errors in estimating the C_3A content and to physical factors such as denseness and permeability of the hardened cement product; a further possibility is that the nonlinear relationship might be due to the existence of different forms of hydrated aluminates. When anhydrous aluminates react with water, metastable equilibrium conditions prevail and platelike metastable aluminate hydrates are formed. On prolonged storage under appropriate conditions, the metastable compounds alter to stable materials. It is conceivable that the metastable and the stable compounds will react differently in an aggressive environment. Numererous investigators have studied the system Al_2O_3–CaO–H_2O either at room temperature or at elevated temperatures and have shown that different hydrated aluminates are formed, depending on the conditions of the experiments.

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[1] Figures in brackets indicate the literature references at the end of this paper.

Other investigators, notably Malquori and Cirilli [11] and Jones [12] have worked on the system $3CaO{\cdot}Fe_2O_3-H_2O$ and have produced evidence that hydrated compounds similar to the hydrated calcium aluminates are formed. In the system $4CaO{\cdot}Al_2O_3{\cdot}FeO_3-H_2O$ solid solutions of aluminate hydrates and ferrite hydrates are produced.

The reaction of the hydrated cement compounds with various chemical media is of considerable importance with respect to corrosion of hydraulic cement, but, since many of the compounds are metastable, and their formation depends on the conditions of hydration, it is difficult to predict with absolute certainty the behavior of a cement of known composition for different conditions of use.

Corrosion in Sulfate Solutions

The action of sulfates on cement compounds is dependent not only on the compound composition but also on the type of sulfate [13]. Furthermore, it should be realized that the speed of reaction and, in many instances, the nature of the reactions, are modified by the physical state of the cement product.

Practical experience has shown that the resistance of cement products to sulfates is dependent in no small measure on the cement content, the density, and the permeability of the product. Figure 2, for instance, illustrates how an asbestos cement pipe made with an ordinary portland cement with an average C_3A content, has withstood the action of sulfates; a layer of calcium sulfate half an inch thick has built up inside the pipe over a number of years. Except for a few circumferential cracks the pipe was still in good condition.

Ever since it was first observed that hardened portland cement was vulnerable to attack by sulfates, the system $CaO-Al_2O_3-CaSO_4-H_2O$ has been extensively investigated. It was shown by early workers that the calcium sulfoaluminate which is responsible for the deterioration of hardened portland cement in sulfate solutions is identical to the naturally occurring mineral ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$). A low-sulfate form was prepared and identified by Lerch, Ashton, and Bogue [14]. Subsequently, Jones [12] has studied the system and has shown that a solid solution series involving $C_3A{\cdot}3CaSO_4{\cdot}32H_2O—C_3A{\cdot}Ca(OH)_2{\cdot}12H_2O—C_3A{\cdot}CaSO_4{\cdot}12H_2O$ exists. More recently, J. D'Ans and H. Eick [15] have shown the existence of mixed crystals of $C_3A{\cdot}CaSO_4{\cdot}12H_2O$ and $C_3A{\cdot}Ca(OH)_2{\cdot}12H_2O$ in the system $CaO-Al_2O_3-CaSO_4-H_2O$.

This information shows that, although the alumina content of a cement is of considerable importance, the state of equilibrium after hardening with respect to the hydrated aluminates, and especially with respect to $C_3A{\cdot}3CaSO_4{\cdot}32H_2O$, will influence vulnerability to sulfate ions. Hydrated supersulfated slag cements are rich in $C_3A{\cdot}3CaSO_4{\cdot}32H_2O$ and are stable in the presence of sulfate ions. On the other hand, it has been shown that the cations in the solution have a marked influence on the nature and speed of reaction during attack by sulfates, and in this connection van Aardt [16] has shown that it is incorrect to say that supersulfated slag cements are resistant to sulfates; it should rather be stated that they are resistant to attack by the sulfate ion.

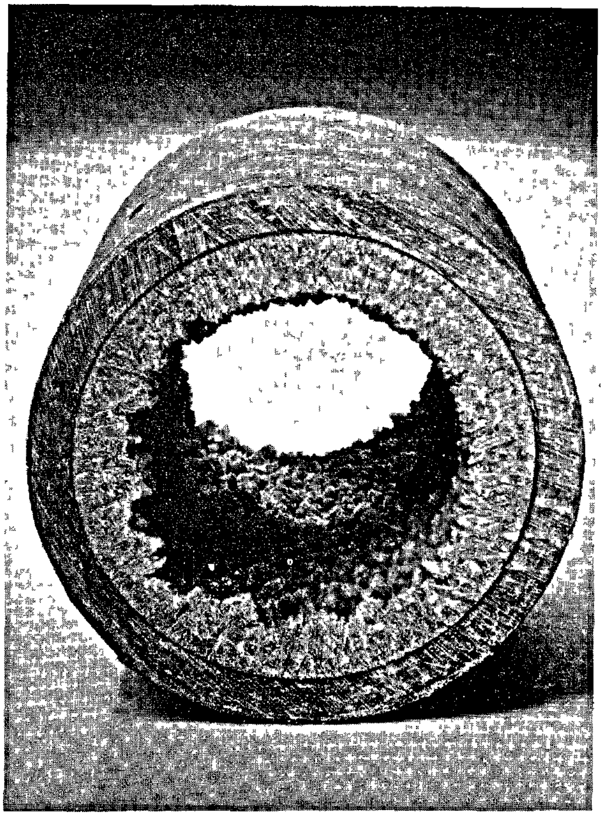


FIGURE 2. *Crystalline calcium sulfate deposit in an asbestos cement pipe.*

Figures 3A and 3B illustrate the behavior of a supersulfated slag cement mortar in sodium, magnesium, and ammonium sulfates, while figure 3C shows the severe attack by magnesium sulfate. The data presented in this figure, and the further experimental data given in subsequent sections of this paper, were obtained by methods and procedures as described by van Aardt [17].

Similarly, extensive work on portland cement, carried out at the National Building Research Institute and elsewhere, has indicated how incorrect it is merely to speak of sulfate resistance or sulfate attack without qualifying the statement by mentioning the cations involved. It has been found that all cements of the portland type so far examined are corroded by magnesium sulfate, and in many cases it is not a sulfate-ion attack but decomposition of the cement by other chemical

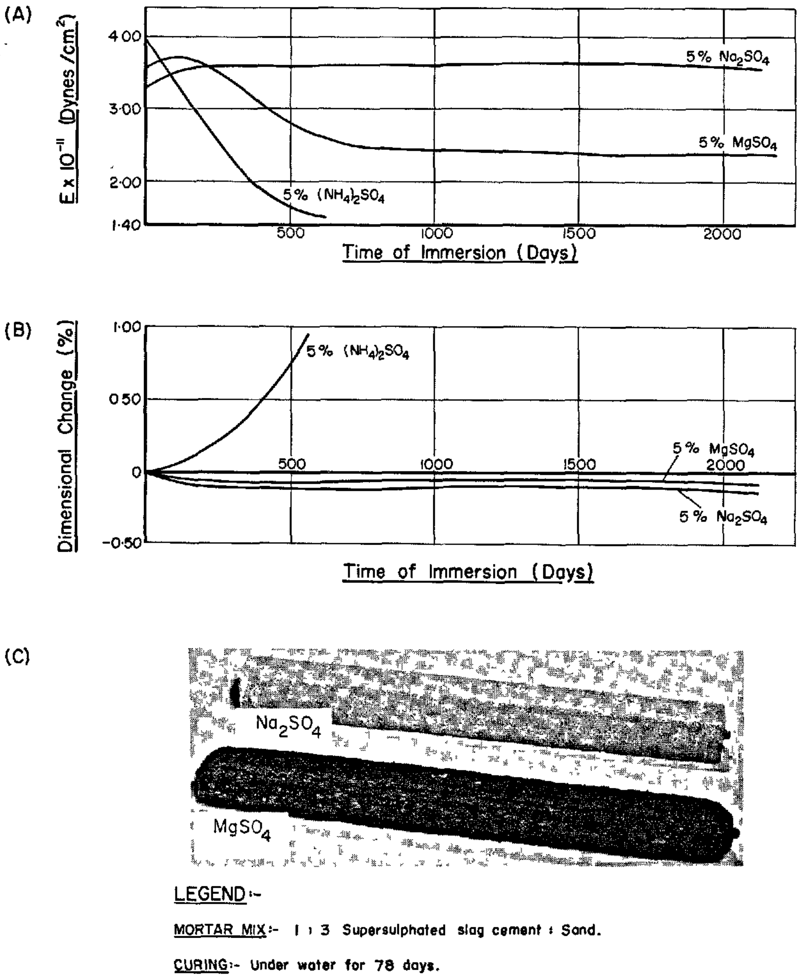


FIGURE 3. *Behavior of supersulfated slag cement mortar in 5 percent sulfate solutions.*

A. Relationship between time of immersion and dynamic modulus of elasticity.
B. Relationship between time of immersion and dimensional change.
C. Specimen showing attack by magnesium sulfate solution.

actions. These cements are in fact chemically stable only in a liquid environment of *p*H above approximately 11.5. At lower values a labile state exists, and reaction with salts such as magnesium sulfate is possible; this salt will react with the hydrated silicates to form magnesium hydroxide and calcium sulfate, while free silica is deposited. A reaction of this nature will decompose the binder.

Van Aardt [16], in studying the behavior of mortar specimens, has found that up to an expansion of about 0.4 percent, the rate of expansion for a particular cement in 5 percent magnesium sulfate solution was approximately constant for all specimens cured under water. The rate of expansion is, however, not constant throughout the entire period during which a specimen is immersed in such a solution.

The initial rate of expansion, i.e., after short immersion periods, can often provide an indication of sulfate vulnerability, since specimens which show rapid expansion are generally more susceptible to an aggressive environment than specimens which show a slow rate of expansion. Even though the ultimate expansion of the latter may be considerable this expansion does not seem to affect the quality of the material adversely. To demonstrate this fact, use has been made of the following method of measuring quality of mortar specimens. If, when a specimen deteriorates, there is only slight variation in dimensions, the natural transverse frequency of vibration is directly proportional to the dynamic modulus of elasticity, i.e., the quality of the material; the drop in frequency is, therefore, a measure of deterioration. Figure 4 illustrates that specimens which show considerable expansion can still be of high quality if the expansion has taken place slowly. It is suggested that this is due to the fact that the material can take up slow expansion, possibly by creep, without disruption taking place. With a slow rate of expansion there may also be some autogenous healing of cracks. However,

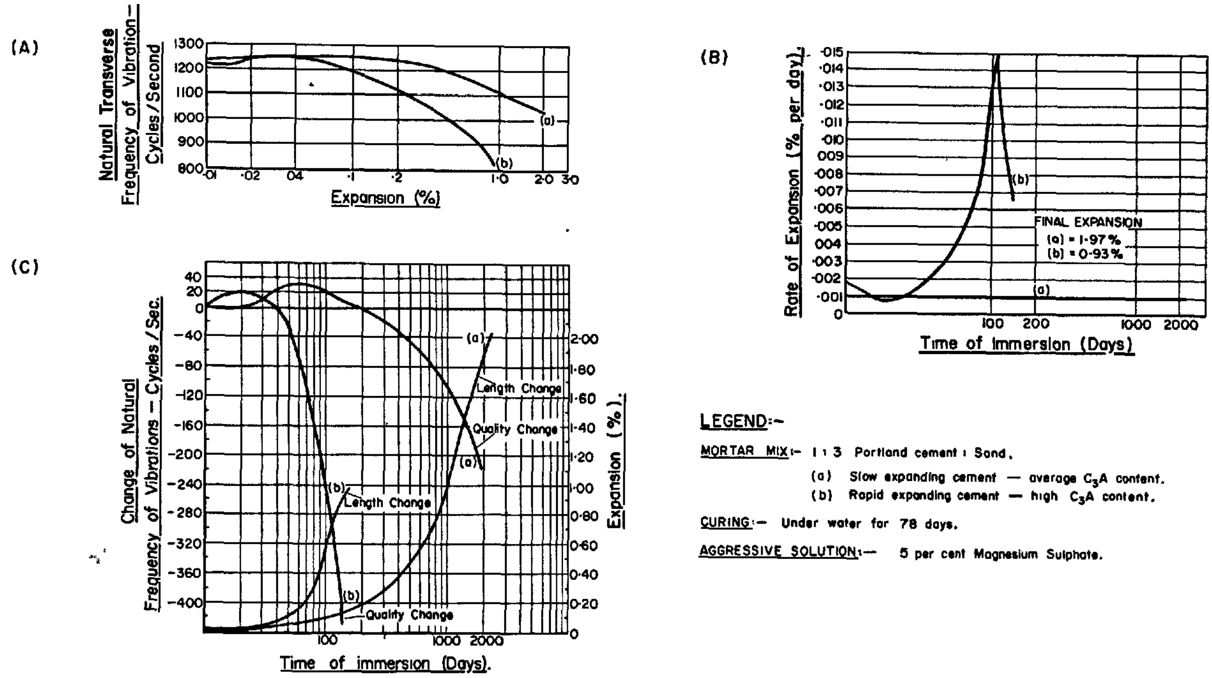


FIGURE 4. *Behavior of specimens in 5 percent magnesium sulfate solutions.*

A. Relationship between natural transverse frequency of vibration and expansion.
B. Relationship between rate of expansion and time of immersion.
C. Relationship between quality change, length change, and time of immersion.

disruption occurs if substances are present which can yield $CaSO_4 \cdot 2H_2O$ and $C_3A \cdot CaSO_4 \cdot 32H_2O$ at a rapid rate. The deterioration by chemical decomposition of the cement compounds in the interior of a dense mortar or concrete, for instance, under mildly acid conditions, is apparently a slow process compared with the disruptive action due to the formation of $CaSO_4 \cdot 2H_2O$ and $C_3A \cdot CaSO_4 \cdot 32H_2O$. Specimens in magnesium sulfate clearly deteriorate by the action of two distinct processes, namely by expansion and subsequent disruption, and by destruction of the silicate hydrates due to chemical action. The second process causes a disintegration which first becomes evident by the crumbling of the edges and surface layers, extending to greater depths over longer exposure periods.

The nature of the action of sodium sulfate on portland-cement products is sometimes unpredictable. If a small permeable region in a good quality specimen allows the penetration of sodium sulfate, local expansion, disruption, and subsequent cracking can destroy the mortar, in the fashion apparent from figure 5(a). Figure 5(b) shows a well-compacted portion of the same specimen.

With high-alumina cement it was found that the corrosion resistance to sulfate ions is dependent on the state of equilibrium reached during hydration; the metastable aluminates are more resistant to sulfate attack than are the stable compounds. It is, however, not clear why the stable form of calcium aluminate hydrate, namely tricalcium aluminate hexahyhrate ($C_3A \cdot 6H_2O$) should be more vulnerable in this instance than the metastable hydrated aluminates, while with portland cements it was found that when stable conditions are reached, for instance by autoclaving, the cement product is more resistant to sulfate ions.

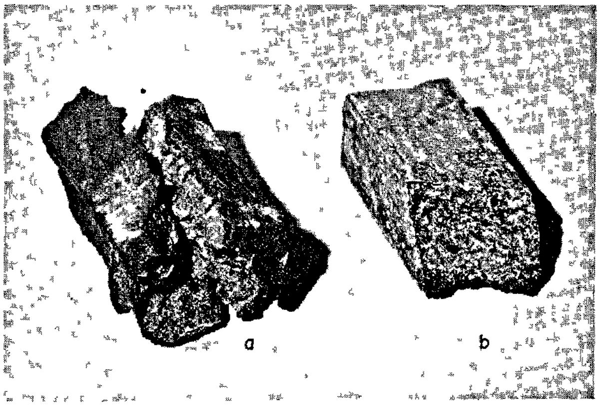


FIGURE 5. (a) (Left) *Expansion and disruption occurring in 5 percent sodium sulfate.* (b) (Right) *Well-compacted portion is practically unaffected.*

As with other hydraulic cements, corrosion of high-alumina cement by sulfates depends on the type of sulfate involved, but the relative vulnerability in some cases is changed as compared to the other cements, e.g., high-alumina cement is more resistant to ammonium sulfate and magnesium sulfate than are the other cements. In 5 percent sodium sulfate solution, its behavior is apparently markedly influenced by the nature of the hydrates as determined by the state of equilibrium reached under the conditions of hydration.

The resistance of high-alumina cement to sodium sulfate can be good, but under certain circumstances it may be poor. It is known that hydrated high-alumina cement is vulnerable to caustic alkalies and the formation of sodium hydroxide is possible if high-alumina-cement products are subjected to sodium sulfate solutions. Figures 6A and 6B illustrate the behavior of high-alumina cement mortars in various sulfate solutions. Figure 6C shows the extent of deterioration by sodium sulfate.

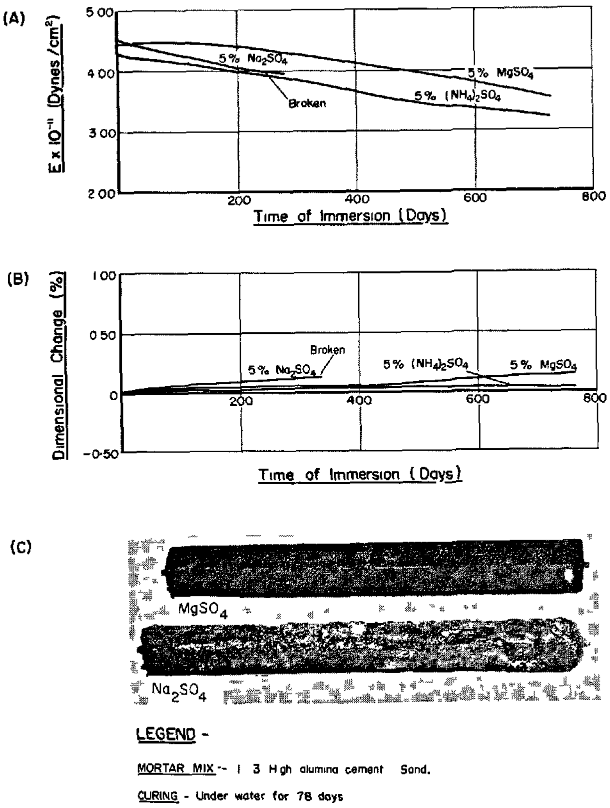


Figure 6. *Behavior of high-alumina-cement mortars in sulfate solutions.*

A. Relationship between dynamic modulus of elasticity and time of immersion.
B. Relationship between dimensional change and time of immersion.
C. Specimens showing attack by sodium and magnesium sulfate solutions after 650 days.

Corrosion in Chloride Solutions

In chloride solutions, as with sulfates, the cations of the aggressive medium have a significant effect on the corrosion of cement products.

Figures 7 and 8 show the behavior of 1:3 cement-mortar specimens, made with various hydraulic cements, in 5 percent solutions of sulfates and chlorides. Over the periods of these tests, magnesium chloride seems to have very little effect on high-alumina cement; there is a slow expansion but no deterioration in quality. The portland-cement specimens showed a marked initial drop in quality, whereas the supersulfated slag cement showed an initial drop and a subsequent increase to a constant value of quality, while the sulfate-resisting cement showed no change in quality. The cements showed a slow expansion in magnesium chloride solutions; the largest expansion was observed for the portland cement, followed by the sulfate-resisting portland cement.

In 5 percent sodium chloride, high-alumina-cement specimens showed a marked initial drop in quality and a slow surface disintegration. The quality of the other cements remained fairly constant during the time of exposure. Especially for the portland cement and the high-alumina cement, however, there was expansion. In ammonium chloride there was a similar drop in quality for specimens made with the various cements, and the specimens showed slight shrinkage, the largest shrinkage being observed for the sulfate-resisting portland cements.

Corrosion in Mixtures of Sulfates and Chlorides

It has previously been suggested [16, 18] that chloride ions might have the effect of decreasing attack on portland cement products by sulfates, but it now appears that this effect is insignificant and that sulfate expansion and deterioration proceed in the presence of large amounts of chloride ions. The data presented in figures 7 and 8 seem to verify this last observation although there was a slight reduction in length change, but this can be attributed to the lower sulfate concentration, as chloride ions were substituted for some of the sulfate ions in these experiments.

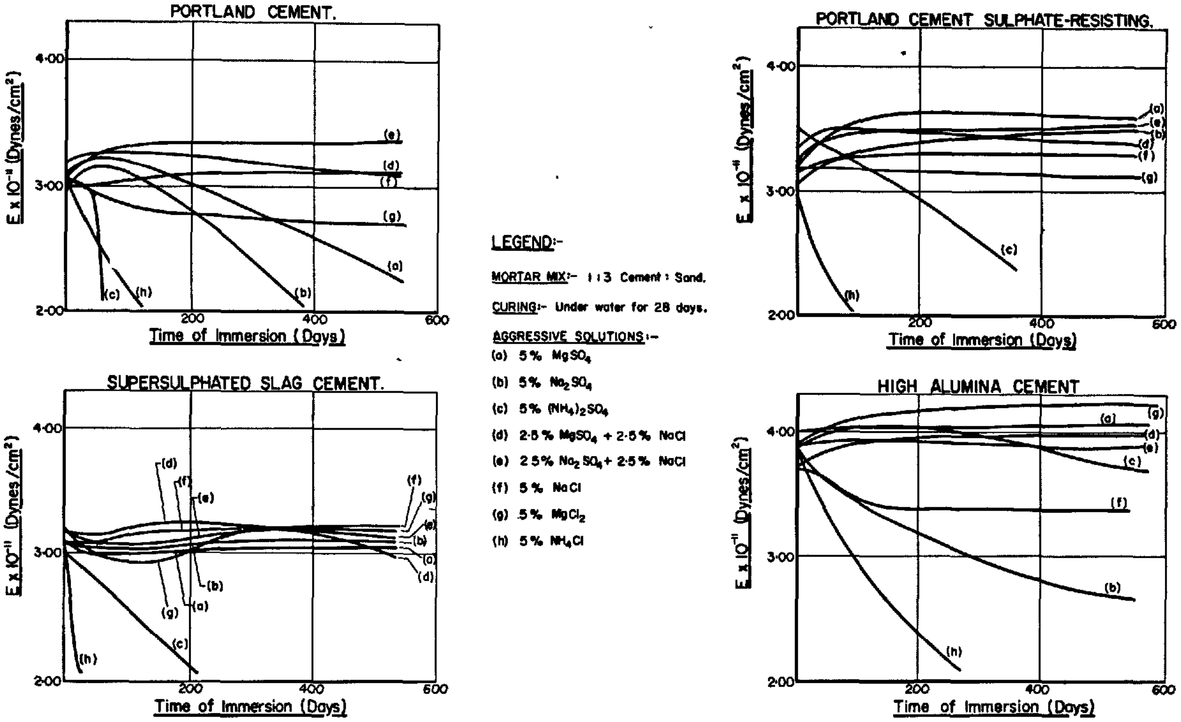


FIGURE 7. *Behavior of various cement mortars in aggressive solutions.*
Relationship between dynamic modulus of elasticity and time of immersion.

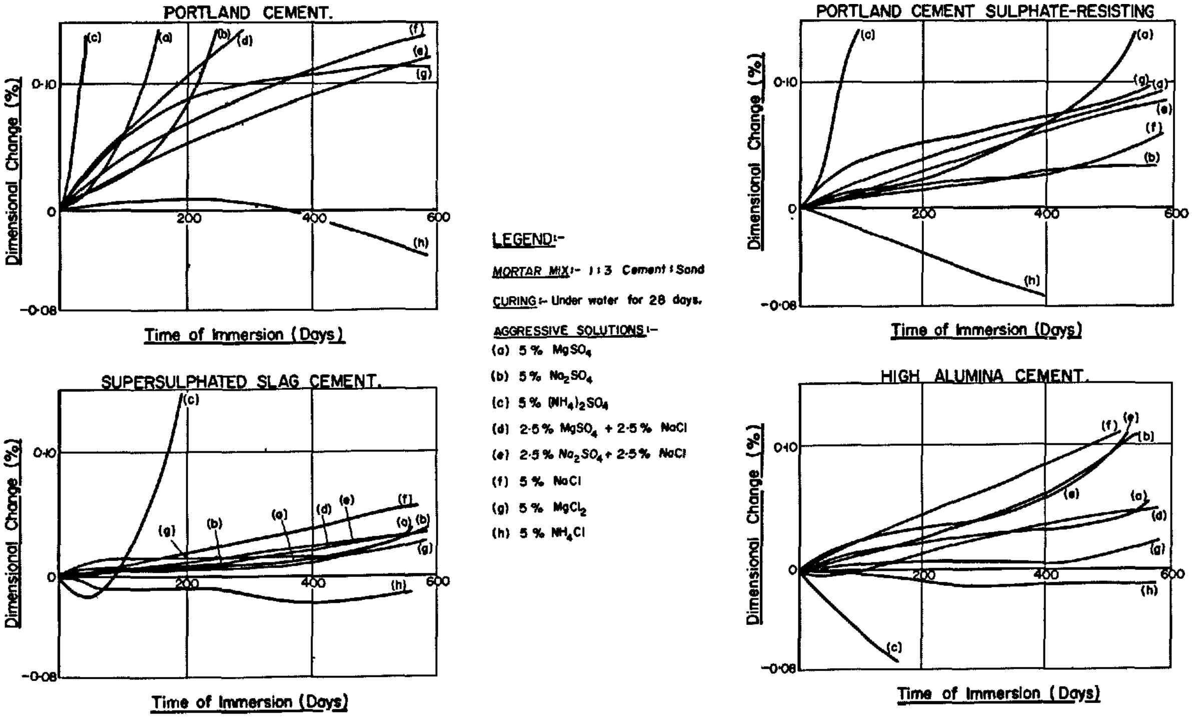


FIGURE 8. *Behavior of various cement mortars in aggressive solutions.*
Relationship between dimensional change and time of immersion.

Since hydraulic cements are basic materials, it can be expected that they will be vulnerable to strong and even weak inorganic and organic acids. It is, however, interesting to study the nature and speed of attack of various acids on such cements and, furthermore, such a study has furnished useful information, since cement products are in fact often subjected to acid environments. Due to the basicity of hydraulic cements, acids cannot penetrate dense mortars or concrete without destroying the material as they they travel inwards into the material, while at the same time the acids are neutralized. Thus, unless the product is very open-textured, purely acid destruction takes place from the surface inwards and this type of corrosion is more markedly influenced by concentration of the aggressive media than in the case of salt attack. If the acid is of a type containing an anion which attacks cements, the anion penetrates the product and causes destruction ahead of the acid front. It is thus apparent that some acids have a twofold attack on cement products, namely the purely acid attack and the salt attack.

Figure 9 illustrates the behavior of portland-cement mortars in various acid solutions. The data show that neither dimensional change alone nor weight loss alone is always a true measure of deterioration. Furthermore, it is not uncommon for a cement product to be destroyed by salt action before any significant portion of the cement is neutralized and destroyed by the acid attack. This destruction often takes place in low acid concentrations, while in high acid concentration the acid attack is predominant, and the specimen is destroyed before any marked salt action can occur.

This relative acid-salt attack is conveniently illustrated by immersing normal portland cement mortars in 1 and 5 percent sulfuric acid solutions. It is found that most of the damage is done by sulfate attack in the 1 percent acid, while the acid attack is mainly responsible for the destruction in the 5 percent acid solutions.

These considerations are of significant practical value and explain many of the observations made when various hydraulic cements are in contract with acid solutions. In fact there is generally very little difference in the resistance of various hydraulic cements to acids only, and the fact that some of these perform better than others in particular acids, depends on whether or not secondary reactions occur.

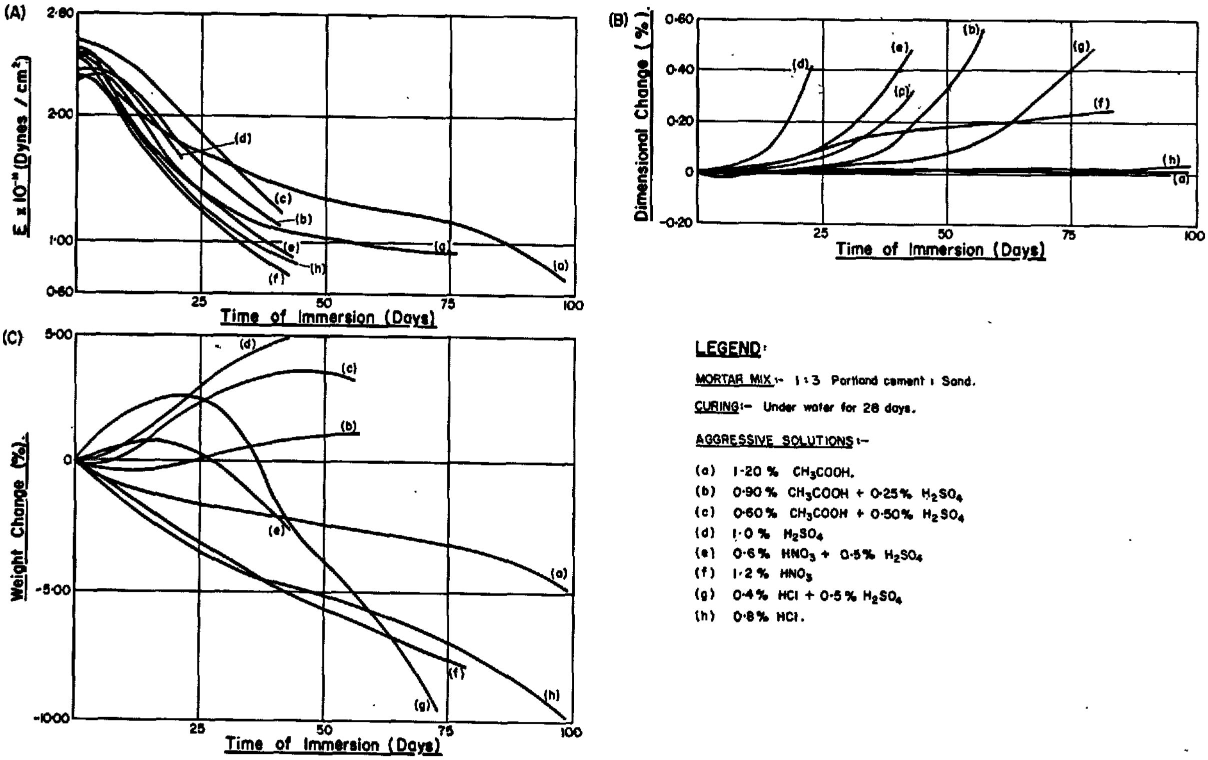


Figure 9. *Behavior of portland cement mortars in various solutions.*

A. Relationship between dynamic modulus of elasticity and time of immersion.
B. Relationship between dimensional change and time of immersion.
C. Relationship between weight change and time of immersion.

Deterioration of Cement Products in Soft and Pure Waters

Since hydrated cement compounds are slightly soluble in water, it follows that they will be slowly removed from a cement product by solution. Furthermore, the hydrated compounds are, in general, incongruently soluble in water and certain components of the hydrated cement will be removed preferentially. Since hydrated silicates are unstable in contact with water having a low *p*H, slight decomposition takes place until the calcium hydroxide content of the liquid in contact with the silicate is at the equilibrium level. If this liquid is replaced by fresh water, more decomposition will take place, and, if the process is repeated over a long period, this leaching of calcium hydroxide will result in complete decomposition of the hydrated calcium silicates. Only insignificantly small quantities of lime will be removed in this way if the water is hard, but incrustation might occur. In moderately hard water the action is negligible.

Soft water, however, is aggressive, the aggressiveness being a function of the calcium carbonate, calcium bicarbonate, and carbon dioxide contents and of the *p*H of the water. The rate of dissolution in soft water is high if the aggressive carbon dioxide content is high. The aggressive carbon dioxide is that portion of the free carbon dioxide in excess of the quantity required for the stabilization of the carbonate-bicarbonate equilibrium.

$$CaCO_3 + H_2CO_3 \rightleftharpoons Ca(HCO_3)_2$$

The higher the concentration of calcium bicarbonate, the higher will be the quantity of free carbon dioxide required for stabilizing the equilibrium, and hence, for the same amount of free carbon dioxide, the lower will be the amount of aggressive carbon dioxide.

Reaction of Inorganic and Organic Anions and Acid Radicals With Hydraulic Cement Minerals

Since cement is often used in contact with various organic and inorganic acids and since these substances combine with the calcium and aluminum ions in the cement to form calcium-aluminum hydroxy-salts, a thorough understanding of their characteristics is essential. Their significance in the field of cement chemistry has long been realized; they have an influence on the setting and hardening of cement and on the durability and resistance of cement products to attack. Some characteristics are probably significant in regard to the corrosion of steel in concrete. Much has already been said about the two sulfate double salts of calcium-aluminum, namely $C_3A \cdot 3CaSO_4 \cdot 31H_2O$ and $C_3A \cdot CaSO_4 \cdot 12H_2O$, but many others, such as chloride, carbonate, nitrate, are known.

Savvina and Serb-Serbina [19] have shown how the calcium-aluminum hydroxy-chlorides have an influence on the durability of hardened cement in concrete. Feitknecht and Buser [20] have distinguished and described two types of calcium-aluminum hydroxy-salts, namely needle-shaped and plate-shaped materials. Little work has been done on calcium-aluminum hydroxy-salts involving an organic radical. A plate-shaped picrate was described by Feitknecht and Buser [21].

Using the method of preparation described by Feitknecht and Buser, a number of double salts containing inorganic and organic anions were prepared and examined. Plate-shaped nitrite and sulfite crystals similar to the chloride and nitrate were obtained.

The work was extended to benzoates, including substituted benzoates. All these gave plate-shaped crystals except *p*-nitrobenzoate which gave needle-shaped crystals. X-ray diffraction diagrams of the various salts are given in figure 10.

The calcium-aluminum hydroxy *p*-nitro-benzoate crystals are similar in shape and appearance to ettringite. Calcium-aluminum hydroxy *p*-nitrobenzoate was also prepared by mixing calcium *p*-nitrobenzoate with C_3A, $C_3A \cdot 6\ H_2O$, portland cement, or high-alumina cement. Needle-shaped crystals, as shown in figure 11, and similar to those of ettringite, were obtained.

The Influence of Curing Conditions on the Behavior of Cement Products in Aggressive Media

The importance of thorough curing in obtaining cement products which are resistant to attack has been realized and demonstrated, yet in practice full advantage of thorough curing is not always taken. It is often assumed that the mixing water is sufficient to achieve this; in practice, however, especially in arid and hot climates, loss of moisture due to evaporation and, in plasters and mortars, due to absorption by the materials on which they are used, can lead to inadequate curing.

Furthermore, the curing procedure per se has a marked influence on the resistance of cement products to aggressive agents.

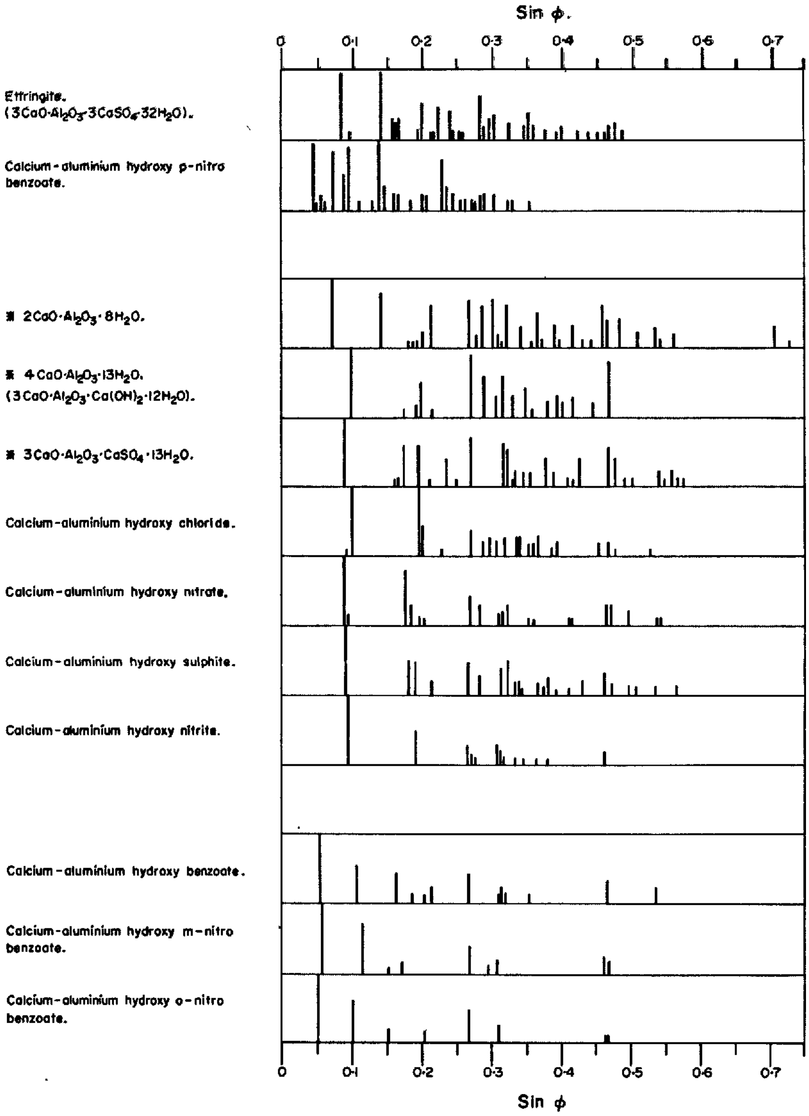


FIGURE 10. *X-ray diffraction diagrams of various calcium-aluminum hydroxy-salts.*

(Radiation—Copper $K_{\alpha 1}$; λ = 1.54050A).

* Zement-Kalk-Gips No. 12, p. 517, table 2 (1957).

Steam Curing

High-Pressure Steam Curing

Steam curing and, in particular, high-pressure steam curing has an advantageous effect on the resistance of mortars and concrete to sulfate solutions. This improvement is largely attributable to the formation of more stable, low-lime hydrates and also to reaction between silica and lime, which decreases the amount of free lime in the hardened product and thus reduces vulnerability. The formation of silica-alumina-lime complexes is also advantageous. It can be demonstrated, however, that although the resistance of steam-cured products to, for instance, sodium sulfate, is vastly increased, such products are still vulnerable to magnesium sulfate, as shown in figure 12. In figure 13 it is apparent that the substitution of a dolomitic calcareous aggregate for a siliceous aggregate in similar high-pressure, steam-cured mortars, made with the same cement, did not reduce resistance to magnesium sulfate but rather increased it. This observation seems to indicate that the lime-silica reaction is not the major factor contributing to the greater resistance of autoclaved specimens to this sulfate.

Low-Pressure Steam Curing

It was found that steam curing under atmospheric pressure did not have a significant influence on the behavior of cement products in aggressive solutions when compared with similar products cured in a humid atmosphere.

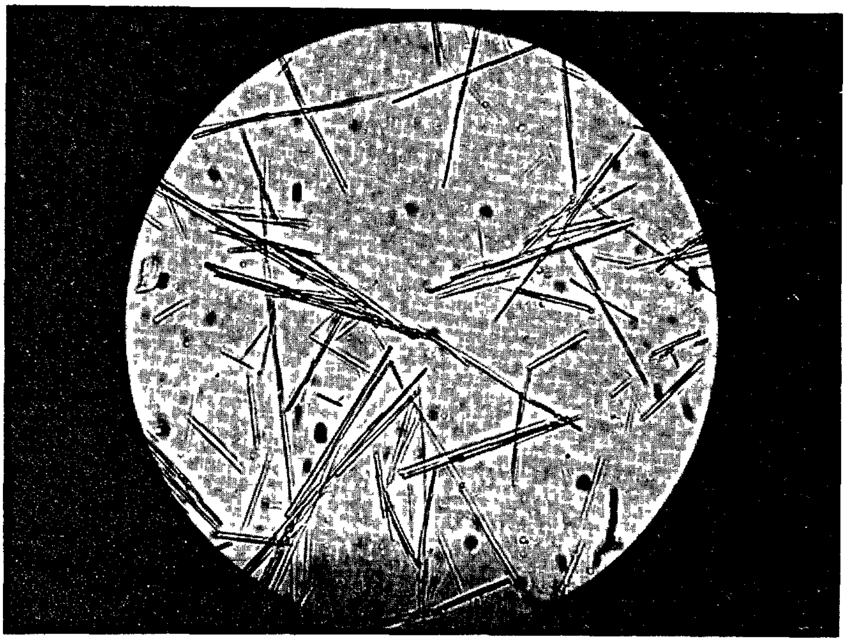


FIGURE 11. *Photomicrograph showing crystals of calcium-aluminum hydroxy p-nitro-benzoate.* (X395).

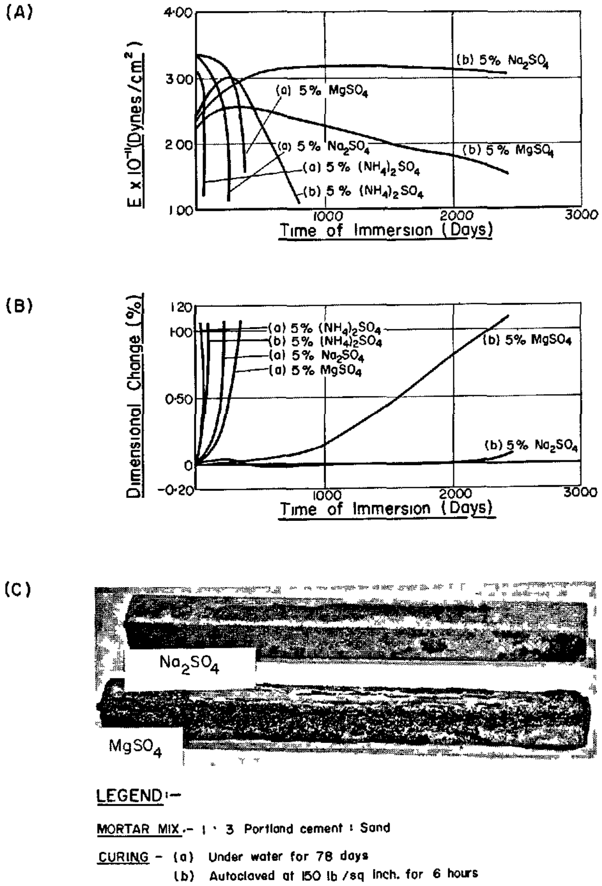


FIGURE 12. *Behavior of autoclaved and water-cured portland-cement mortars in sulfate solutions.*

A. Relationship between dynamic modulus of elasticity and time of immersion.
B. Relationship between dimensional change and time of immersion.
C. Autoclaved specimens showing attack by 5 percent sodium and magnesium sulfate solutions after 7 yr.

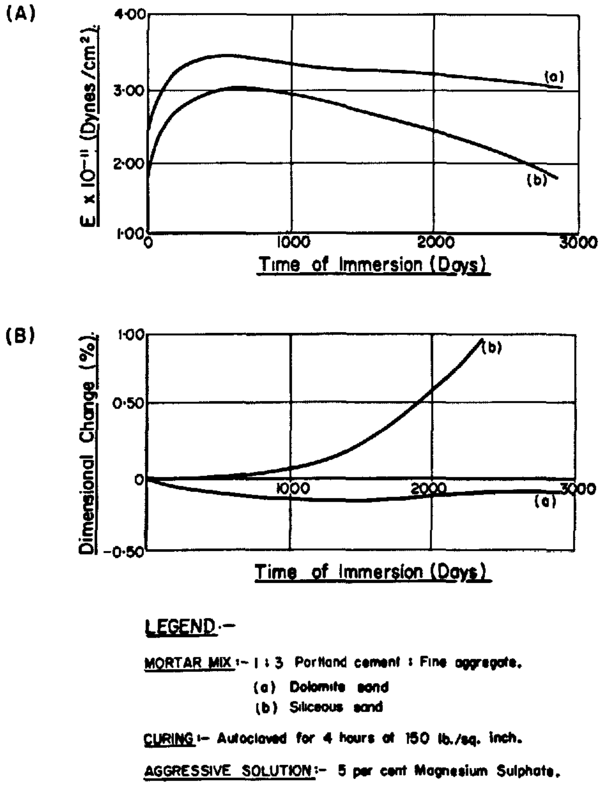


FIGURE 13. *Behavior of autoclaved cement mortars containing dolomitic and siliceous sand in 5 percent magnesium sulfate solution.*

A. Relationship between dynamic modulus of elasticity and time of immersion.
B. Relationship between dimensional change and time of immersion.

Underwater Curing and Humid-Atmosphere Curing

Van Aardt [17] has shown that mortar specimens cured under water, prior to immersion in sulfate solutions, were more vulnerable than specimens cured in an atmosphere of 80 percent rh. For specimens cured in saturated air the resistance to sulfates was less than for those cured in the 80 percent rh environment, since in saturated air, underwater conditions are approached. Figure 14 illustrates the behavior of two portland-cement mortars, cured under different conditions, when immersed in a 5 percent solution of magnesium sulfate.

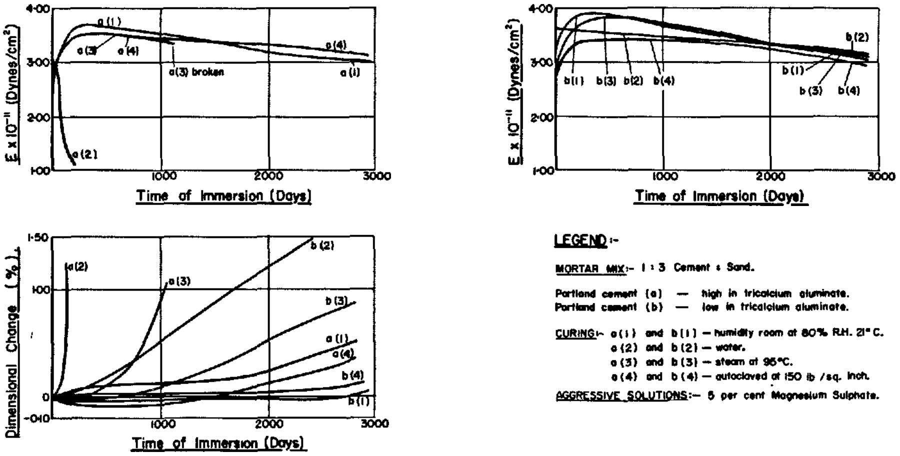
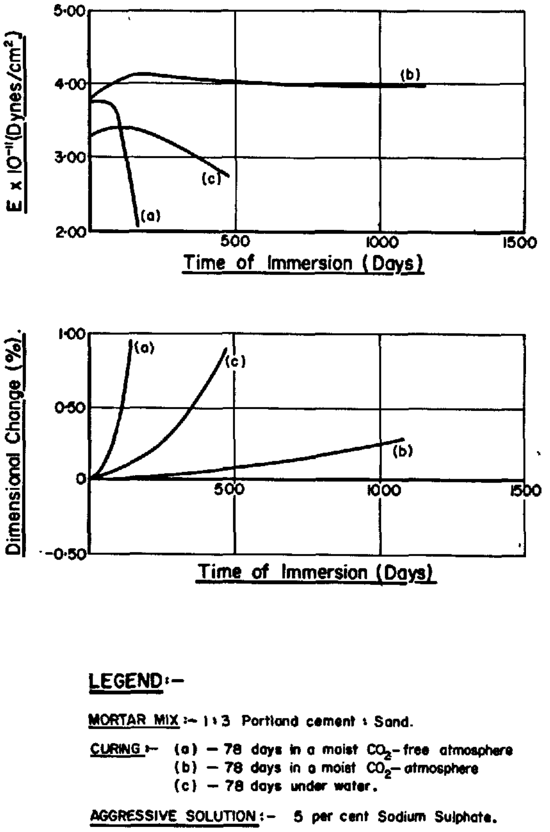


Figure 14. *Dynamic modulus of elasticity and dimensional changes of two portland cement mortars cured under different conditions.*



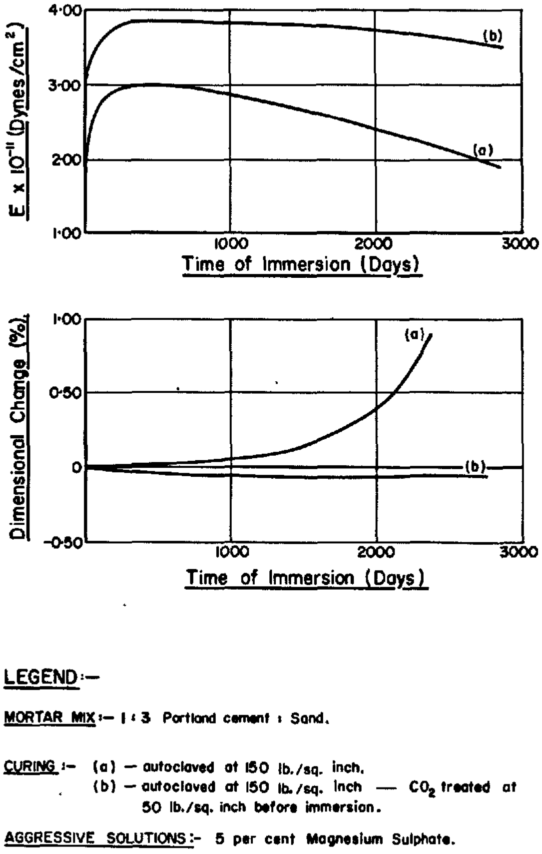


Figure 15. *The effect of carbonation on the resistance of portland cement mortars in 5 percent sodium sulfate solutions.*

Figure 16. *The effect of carbonation on the resistance of autoclaved portland cement mortars in 5 percent magnesium sulfate solutions.*

Carbonation of Cement Products During and After Curing

Leber and Blakey [22] have determined the effect of gaseous carbon dioxide on the strength and shrinkage of mortars and concretes. They found that strength is increased and shrinkage decreased if specimens undergo a period of curing in carbon dioxide immediately after demolding. Results obtained by Verbeck [23] showed that carbonation of hydrated portland-cement pastes had advantageous effects on the products with regard to strength, hardness, permeability, and volume stability.

Carbonation of hydrated portland-cement products also improves their behavior in aggressive media. Portland-cement mortar specimens cured in a carbon dioxide-free environment have poor resistance compared to carbonated or partially carbonated specimens. This observation is illustrated in figures 15 and 16. In contrast to the above, early carbonation has an adverse effect on the quality of supersulfated slag cement products, and carbon dioxide should be excluded during the early curing period when these cements are used.

The Influence of the Nature and Type of Aggregate on Corrosion Resistance

The important finding that the substitution of a calcareous aggregate, such as good quality limestone or dolomite, for a siliceous or other noncalcareous aggregate has a very significant beneficial effect on the corrosion of cement products in certain aggressive media, has been extensively studied. In acid solutions the useful life of the product can be extended appreciably by the use of calcareous aggregate; this can be seen from figure 17. It appears that not only does the acid-soluble aggregate "protect" the cement in that it aids in neutralizing the acid, but it also has a retarding effect on the expansion resulting from sulfate attack in acid solutions; the carbon dioxide produced when the acid reacts with the carbonate aggregate apparently reduces the formation of tricalcium sulfoaluminate.

If portland-cement products made with a nonsiliceous aggregate are autoclaved, the materials produced generally have lower strength than those made with siliceous aggregates, but research has shown that they have good resistance to sulfuric acid and sulfates.

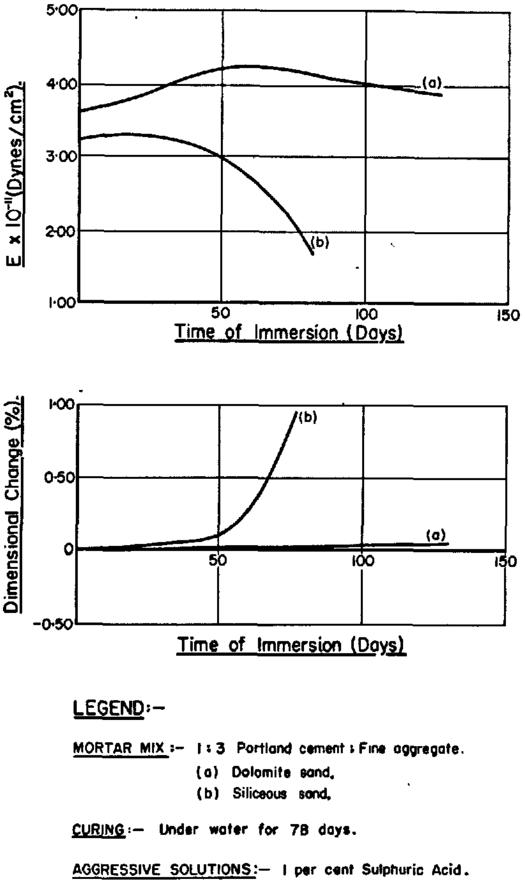


FIGURE 17. *Comparison of the behavior in 1 percent sulfuric acid solution of portland cement mortars made with dolomitic and siliceous sand.*

General Remarks on Corrosion Studies

Studies aimed at evaluating the corrosion resistance of hydraulic cement products are difficult owing to the complexity of the problem; it is not sufficient to determine the chemical reactivity of the unhydrated neat cements or hydrated neat cements, because they are in practice not subjected to aggressive environments in these states. Therefore the accelerated tests of the kind described in this paper can serve only as a guide and should be considered as such.

An attempt was made to evaluate cements in a state in which they are used, but since cement products are so variable with respect to quality, even when made under strictly controlled conditions, it is practically impossible to produce in the laboratory products which are in all respects comparable with those made in actual practice, and hence statistical correlation, between laboratory results and long-term practical exposure and use, is essential. Furthermore, it is difficult to simulate in the laboratory the varied conditions of exposure found in practice.

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Discussion

T. D. Robson

When testing high-alumina cement mortars or concretes in sulfates or salt solutions there are one or two points which may need attention if apparently contradictory results from different workers are to be avoided.

As the author has said, the resistance of specimens containing the normal hexagonal calcium aluminate hydrates may be different from that of specimens kept in conditions where substantial conversion to the stable cubic hydrate can occur. The resistance properties obtained from each of the two types of hydrate should therefore, in our opinion, be first examined separately. Accordingly, if the normal resistance properties of high-alumina cement are to be tested in this way, there is much to be said for making and storing the specimens at a controlled low temperature (say, below 70 °F) so that any possible effect of conversion can be eliminated from initial consideration.

For example, tests carried out at an unspecified temperature range, at "room temperature" or "in the laboratory," may cause confusion between investigators in different parts of the world, since local temperature conditions may be sufficient, in some cases, to cause appreciable conversion to cubic hydrate within the test period. The effect of total conversion of hydrates on the sulfate resistance of high-alumina cement can best be determined as a separate operation by keeping the specimens in test solutions maintained at over 85 °F or by fully converting the hexagonal hydrates, by heat treatment, before placing the specimens in the solutions.

When this is done, it has been found that the properties of the "fully converted" high-alumina cement specimens (including the chemical resistance properties) are chiefly dependent on the water-cement ratio used [1, 2]. Roughly speaking, specimens made with a water-cement ratio below 0.4 still show high chemical resistance even if all the hydrate is converted to the cubic type, but those made with much higher water-cement ratios usually give reduced resistance if kept in conditions where appreciable conversion takes place.

In brief, specimens made with either high or low water-cement ratios give excellent chemical resistance if one is dealing with the normal hexagonal hydrates, but the resistance obtained under conditions causing conversion is largely dependent on the water-cement ratios.

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Discussion

L. R. Blair and Julie Chi-Sun Yang

In the paper of J. H. P. van Aardt entitled "Deterioration of Cement Products in Aggressive Media," much has been said concerning the chemical stability of cement and cement products. Our laboratory has devoted much effort to a study of the chemical stability, particularly in sulfate media, of asbestos-cement products, and the results of these investigations are summarized below.

Prior to beginning a discussion on the chemical stability of asbestos-cement materials, it is necessary to emphasize the fact that these products may be cured by one of two different procedures. The type of curing has been found to exert a strong influence on product stability in various chemical environments. The first of these is termed "normal" curing, which is generally conducted at atmospheric pressure either under water or in a moist atmosphere for periods of time usually in excess of 28 days. The second type of curing is accomplished by first storing in a moist atmosphere for 24 hr and then treating in an autoclave operated at pressures between 100 and 200 psi under saturated steam conditions for periods of 16 hr or more.

The starting formulations as well as the final chemical assembly of asbestos-cement products vary with the curing conditions. If a product is to be normal-cured, its starting dry formulation usually contains approximately 20 percent of a fiber blend and 80 percent of portland cement, normally of the Type I variety. Autoclave-cured formulations, on the other hand, contain approximately 20 percent of the fiber blend and 80 percent of a quartz flour-portland cement mixture in a ratio of 0.6 quartz to 1.0 portland cement. There is a vast difference between the chemical stability of normal and autoclaved asbestos-cement products, the autoclaved products being generally superior. In addition to laboratory test results, field results also emphasize this point. Two field experiences will be discussed briefly to illustrate this conclusion.

In the first instance a normal-cured asbestos-cement pipeline was installed by the town of Ordway, located in southeastern Colorado. This line was installed in 1934 in a high sulfate-containing soil. Approximately 6 yr later the walls of the pipe eroded in spots, causing leaks and ruptures in the line. A stretch of this line, which was peculiarly situated in relation to pumps and stand towers, was subjected to alternate wetting and drying from the inside. This portion was particularly troublesome, although occasional breaks in other portions of the line also occurred. A portion of the disintegrated pipe removed from service is shown in figure 1. Approximately 13 yr after original installation, the damaged line was replaced with autoclave-cured asbestos-cement products. The new line was located approximately 1½ ft from the old line and ran in a parallel direction. The autoclave-cured material has been in continuous service since that time under conditions duplicating those which cause deterioration in the normal-cured pipe. Recent inspection (1960) has shown there is no visible evidence of sulfate attack.

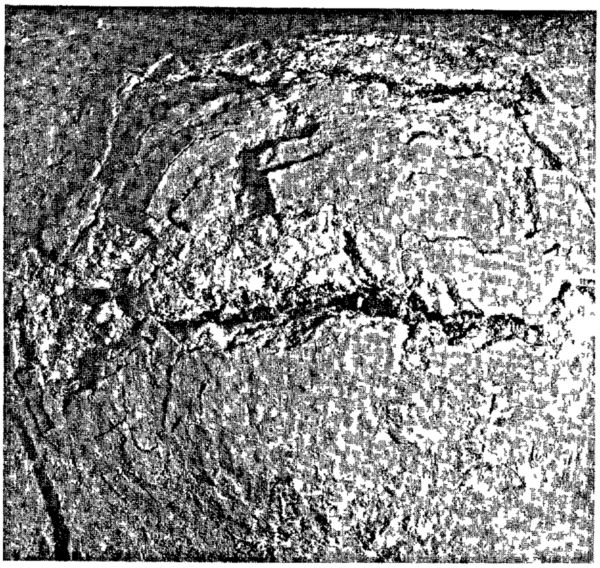

Figure 1. *Close-up of corroded normal-cured pipe removed from service at Ordway, Colorado.*

The second long-term field test also illustrates the improved stability of autoclaved products toward a high sulfate chemical environment. In 1931, as part of an extensive program of the study of sulfate attack on cements and concretes [1],[1] Miller also conducted tests on normal-cured asbestos-cement pipe. By 1936 he found that this material did not have ". . . more than normal resistance . . ." to sulfates [2]. Manson [3] stated that these materials were severely attacked in this period of time. At this time autoclave-cured asbestos-cement pipe was introduced to the American market, and Miller decided to test the new products. He and Manson placed 30 sections of the autoclave-cured material under water at Medicine Lake, South Dakota, for tests similar to those used previously on the normal-cured material. The waters of Medicine Lake at that time contained about 12 percent of sulfates, of which two-thirds was magnesium sulfate and one-fourth sodium sulfate.

The crate in which these pipes were submerged became separated from the main body of crates and was lost. It remained at the bottom of the lake until early in 1960, when it was accidentally located and returned to the University of Minnesota for observation and test. After 24 yr in this severe environment, these pipes appear to be physically sound and free from defect.

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[1] Figures in brackets indicate the literature references at the end of this paper.

Although field experience is of necessity limited to attack by sodium and magnesium sulfate solutions, laboratory tests also indicate that autoclave curing increases resistance to attack by other sulfate media, and also by bicarbonate solutions and distilled water.

There are many factors which are thought to contribute to the superior stability of autoclave-cured portland cement products. These are:

(1) The elimination of free calcium hydoxide;

(2) The formation of a better crystallized calcium silicate hydrate;

(3) The elimination of small amounts of hydrated sulfoaluminates; and

(4) The probable elimination of C_3AH_6 as indicated by the fact that it is not detectable by X-ray analysis.

The first two of these factors will be discussed in detail in this paper. Factor 3 has been well covered in previous investigations [4], and factor 4 will be dealt with in a future publication.

The Elimination of the Free Calcium Hydroxide

It has been found that portland cement hydrates rapidly in saturated steam at 100 psi and above, liberating free hydrated lime. Since silica flour is incorporated in the autoclave formulation, this liberated calcium hydroxide in turn reacts rapidly with the quartz to produce a calcium silicate hydrate of the tobermorite variety. Free hydrated lime is also liberated when a cement product is normally cured. However, because there is no silica in the formulation, the calcium hydroxide remains in the product in the free crystalline form. Incorporating silica in a normal-cured formulation does not help the situation since it does not react in detectable amounts with free lime at these low temperatures. Analyses of various autoclave- and normal-cured products show that the former contain not more than 1/2 percent free lime, whereas the latter commonly contain between 13 and 18 percent.

As early at 1897 Candlot [5] found that cements containing free lime disintegrated in salt solutions. This was followed in 1902 by the work of Deval [6] who found that the presence of free lime in a cement reduced its resistance to attack by sulfate environments. These publications have been followed by the work of numerous investigators who have confirmed the original findings [7]. From these investigations it is apparent that calcium hydroxide content is a prime factor in causing sulfate deterioration. Sulfate attack is usually due to chemical reactions within the cement which produce compounds of a greater volume than those originally present, thus causing an expansion and disruption of the cement bond. Any free hydrated lime which is present will react with the soluble sulfates to produce either calcium sulfate with a resultant 200 percent volume increase or ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32\ H_2O$) with also a 200 percent volume increase. These reactions are illustrated in the following formulas:

$$Ca(OH)_2 + SO_4^{=} + 2\,H_2O \longrightarrow CaSO_4 \cdot 2\,H_2O + 2(OH)^-$$
$$1 \text{ volume} \longrightarrow 2.97 \text{ volumes} \qquad (1)$$

$$6\,Ca(OH)_2 + 2\,Al^{3+} + 3\,SO_4^{=} + 26\,H_2O \longrightarrow 3\,CaO \cdot Al_2O_3 \cdot 3\,CaSO_4 \cdot 32\,H_2O$$
$$1 \text{ volume} \longrightarrow 3.04 \text{ volumes.} \qquad (2)$$

Examinations of the deteriorated portions of the Ordway pipe indicate that reaction 2 took place in this instance. Large amounts of ettringite and traces of calcium carbonate were found by microscopic and X-ray examination in the blistered sections. Gypsum was not detected.

Other data also indicate that the presence of free lime results in the deterioration of asbestos-cement products in distilled water and bicarbonate solutions.

The results of tests made by leaching crushed portions of asbestos-cement pipe which contained 13.0 and 0.03 percent free lime in bicarbonate solutions are presented in figure 2. After 9 days, 64 percent of the total lime had been leached out, compared to 40 percent for the sample containing 0.03 percent free lime.

To test the comparative resistance of the same two products in distilled water, portions of pipe were cut into pieces approximately 2 x 3 x ½ in. These portions were immersed in distilled water and the water was changed every 24 hr to simulate

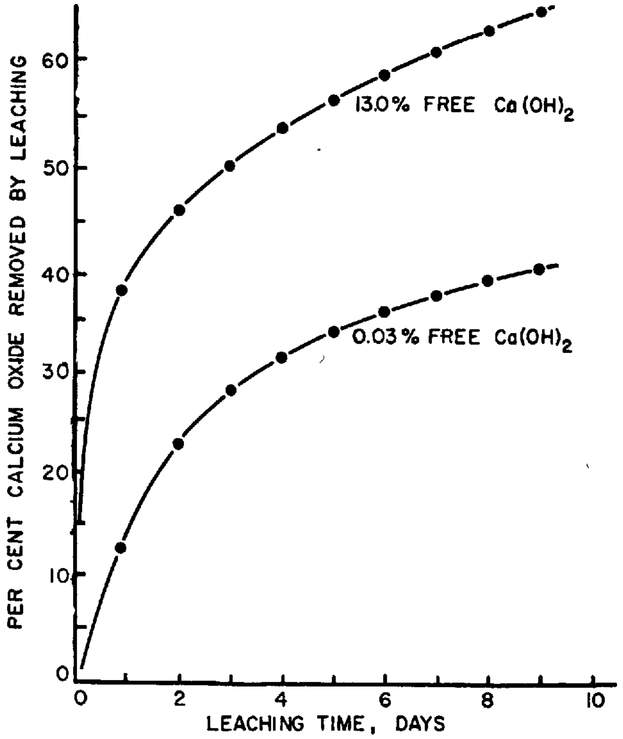


FIGURE 2. *$Ca(OH)_2$ removed from asbestos-cement samples by continuous leaching of powdered sample with bicarbonate water.*

($NaHCO_3$, 2.2 g/l; NaCl, 2.6 g/l; CO_2 added to bring *p*H to 6.1) flow conditions in the pipe. The samples were removed from the solution at weekly intervals, dried, and weighed. The weight losses are plotted in figure 3. Here the material containing 13 percent free lime lost approximately 8 percent of its weight at the end of 4 weeks. The material containing 0.03 percent free lime lost but 2 percent.

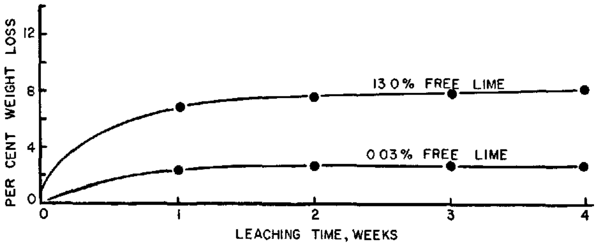


Figure 3. *Resistance of asbestos-cement products to leaching by distilled water.*

The calcium hydroxide contents of autoclave-cured and normal-cured asbestos-cement sag cakes made with Type I and Type V cements and their comparative sulfate resistance, as indicated by U.S. Bureau of Reclamation tests, are shown in table 1. It is interesting to note that normal-cured Type V cement (said to be sulfate resistant) is superior to normal-cured Type I cement. However, when either of these cements is autoclave-cured, differences between the two types are no longer apparent, and the autoclave-cured results are superior to the normal-cured in each instance. Thus, Type V cement does not appear to improve the sulfate resistance of an autoclave-cured product. The chemical analyses of the two types of cement which were studied and their calculated compositions are presented in table 2.

The limit of calcium hydroxide which may be tolerated in a product subjected to sulfate conditions is difficult to specify. However, it is apparent that any amount of free hydrated lime is detrimental, and therefore the limit should be set as close to zero as practical.

Table 1. *Test data—free lime content and sulfate resistance of normal- and autoclave-cured cements*

Sulfate resistance test, U.S. Bureau of Reclamation

Type of cure	Silica/ cement	Cement type	Free $Ca(OH)_2$	Total expansion after 28 cycles
			%	%
Autoclave, 125 psi, 16 hr	0.6/1.0	I	0.4	0.03
		V	.5	.03
Normal cure, underwater 28 days.	.0/1.0	I	15.5	.16
		V	13.7	.11

Table 2. *Chemical and calculated compound compositions of type I and type V cements investigated*

Constituent	ASTM cement type	
	I	V
	Percent	*Percent*
Ignition loss, 1,800 °F	3.8	1.6
SiO_2	19.5	22.3
Fe_2O_3	2.9	5.5
Al_2O_3	5.9	3.1
TiO_2	.2	.2
P_2O_5	.3	.1
CaO	61.0	62.0
MgO	2.2	2.1
Na_2O	.5	.2
K_2O	.8	.5
SO_3	2.7	2.2
Tricalcium silicate	49.0	48.0
Dicalcium silicate	19.0	28.0
Tricalcium aluminate	11.0	0
Tetracalcium aluminoferrite	9.0	17.0

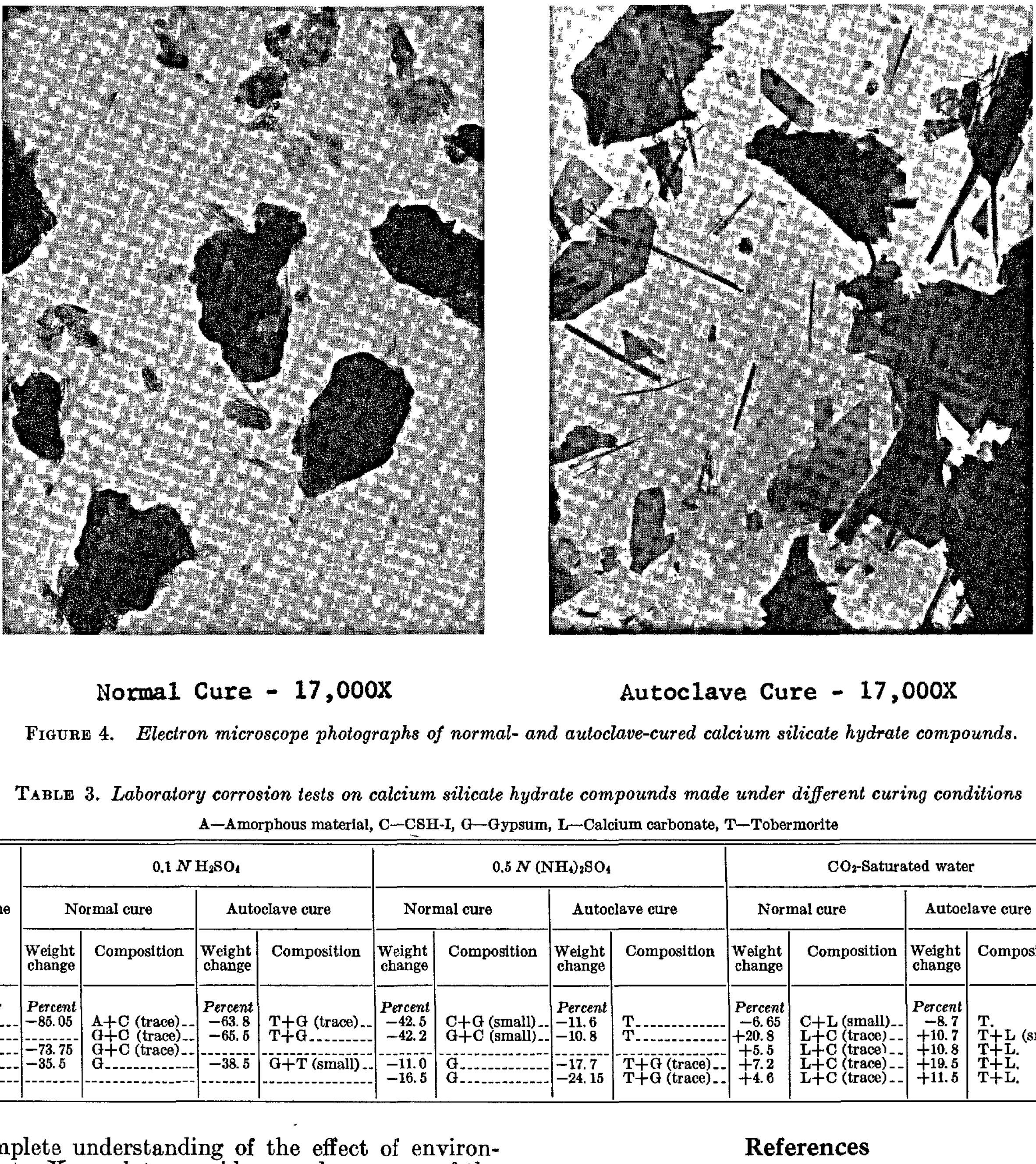
The Formation of a Better Crystallized Calcium Silicate Hydrate

It would be expected that the apparent solubility of a compound or its resistance to change caused by aggressive media would be dependent to some extent on its physical condition. For example, a finely divided form of a material would have a higher surface area and therefore should go into solution or react at a faster rate. Also, as the degree of crystallinity increases, the lattice energy of the compound also increases. This increasing lattice energy is accompanied by a decreasing tendency for a compound to undergo change, since greater energies are required for dissociation. It is reasonable to expect that the form of calcium silicate which is produced under autoclave conditions, which has a reduced surface area and better crystallinity, would exhibit greater resistance to attack than that produced under normal cure conditions.

To demonstrate this possibility, two calcium silicate hydrates were prepared. Each had a calcium to silica ratio of 1:1, and was reacted in excess water. The first sample was treated in saturated steam at 100 lb/sq in. pressure for 16 hr, while the second sample was allowed to react at room temperature for 28 days. X-ray analysis showed the first to be tobermorite or well-crystallized CSH-I, and the second poorly crystallized CSH-I. Electron microscope photographs of these two materials are shown in figure 4.

The solubility of the two products was tested in 0.1 *N* sulfuric acid, 0.5 *N* ammonium sulfate, and carbon dioxide-saturated water with a *p*H of 4, by placing 200 mg of the sample in a 4-oz polyethylene bottle and adding 50 ml of the appropriate solution. The bottles with their contents were shaken for periods of time ranging from ½ hr to 3 days. The suspensions were filtered, the residues washed with acetone, dried at room temperature, weighed, and studied by X-ray diffraction. The results are summarized in table 3.

From the data it is seen that weight change is not the prime consideration for evaluating the stability of a substance. Weight loss is indicative of solubility and weight gain indicates reaction with the environment. Therefore, when both take place together the weight change results must be accompanied by other data to obtain a



Normal Cure - 17,000X

Autoclave Cure - 17,000X

FIGURE 4. *Electron microscope photographs of normal- and autoclave-cured calcium silicate hydrate compounds.*

TABLE 3. *Laboratory corrosion tests on calcium silicate hydrate compounds made under different curing conditions*

A—Amorphous material, C—CSH-I, G—Gypsum, L—Calcium carbonate, T—Tobermorite

Time	0.1 N H_2SO_4				0.5 N $(NH_4)_2SO_4$				CO_2-Saturated water			
	Normal cure		Autoclave cure		Normal cure		Autoclave cure		Normal cure		Autoclave cure	
	Weight change	Composition	Weight change	Composition	Weight change	Composition	Weight change	Composition	Weight change	Composition	Weight change	Composition
Hr	*Percent*		*Percent*		*Percent*		*Percent*		*Percent*		*Percent*	
½	−85.05	A+C (trace)	−63.8	T+G (trace)	−42.5	C+G (small)	−11.6	T	−6.65	C+L (small)	−8.7	T.
1		G+C (trace)	−65.5	T+G	−42.2	G+C (small)	−10.8	T	+20.8	L+C (trace)	+10.7	T+L (small).
5	−73.75	G+C (trace)							+5.5	L+C (trace)	+10.8	T+L.
24	−35.5	G	−38.5	G+T (small)	−11.0	G	−17.7	T+G (trace)	+7.2	L+C (trace)	+19.5	T+L.
72					−16.5	G	−24.15	T+G (trace)	+4.6	L+C (trace)	+11.5	T+L.

complete understanding of the effect of environment. X-ray data provide a crude measure of the breakdown of the original material and the new compounds which are forming.

General Remarks

Field test results provide a measure of the reliability of laboratory conclusions on corrosion resistance. Both field and laboratory tests show that autoclave curing improves the resistance to attack of asbestos-cement materials. The results discussed above are in excellent agreement with the conclusions of van Aardt concerning the effects of high-pressure steam curing.

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Paper VI–S2. Capillary Size Restrictions on Ice Formation in Hardened Portland Cement Pastes*

R. A. Helmuth

Synopsis

T. C. Powers' model of the pore structure of hardened portland cement paste is used to discuss the conditions that must be met for ice formation in capillaries of various sizes. It is proposed that initial ice formation in supercooled water in the capillaries occurs dendritically, just as it does in bulk water, through only those sufficiently large capillaries which are contiguous with the initially seeded capillaries. Subsequent growth of this dendritic network of ice crystals and resulting expansions during cooling depend primarily on freezing in smaller capillaries at lower temperatures. This theory is supported by the results of experiments in which freezing propagation rates and temperature rises were measured during tests with supercooled pastes, and by experiments in which dimensional changes were measured during cooling and warming through freezing temperatures.

Résumé

Le modèle proposé par T. C. Powers sur la structure des pores de la pâte de ciment portland durcie est utilisé dans la discussion des conditions nécessaires à la formation de glace dans les capillaires de différentes dimensions. Il est proposé que la formation de glace initiale dans l'eau sous-refroidie dans les capillaires se produit dendritiquement, exactement comme dans l'eau en large volume mais seulement à travers les capillaires suffisamment larges et attenant aux capillaires précédemment ensemencés. La croissance ultérieure de ce réseau dendritique de cristaux de glace et les expansions qui résultent pendant le refroidissement dépendent en premier lieu de la congélation dans les plus petits capillaires aux basses températures. Cette théorie est supportée par les résultats d'expériences dans lesquelles les vitesses de propagation de la congélation et les élévations de température étaient mesurées pendant des essais avec des pâtes refroidies, et par des expériences dans lesquelles les changements de dimensions étaient mesurés pendant le refroidissement et le réchauffement à travers les températures de congélation.

Zusammenfassung

Das Modell, welches T. C. Powers für die Porenstruktur einer erhärteten Portlandzementpaste angegeben hat, wird benutzt, um die Bedingungen klar zu machen, unter denen eine Eisbildung in den Kapillaren verschiedener Größe vorkommen kann. Es wird vorgeschlagen, daß die erste Eisbildung in unterkühltem Wasser in den Kapillaren sich dendritisch ereignet, ganz so wie sie in einer offenen Wasseroberfläche sich ereignen würde, aber doch nur in den verhältnismäßig großen Kapillaren vorkommt, die an die Kapillaren, in welchen der erste Eiskeim entstand, anstoßen. Das darauffolgende Anwachsen des dendritischen Gitters der Eiskristalle und die davon herruhrende Ausdehnung während des Kühlens hängen überwiegend vom Gefrieren in kleineren Kapillaren bei niedrigeren Temperaturen ab. Diese Theorie wird durch die Experimentalbefunde unterstützt, in welchen man die Fortpflanzungsgeschwindigkeiten des Gefrierens und die Temperaturerhöhungen in Versuchen mit unterkühlten Pasten festgestellt hat; in anderen Experimenten hat man die Dimensionsveränderungen während des Abkühlens und des Erwärmens in der Nähe der Gefriertemperaturen gemessen.

Introduction

A study of the freezing of water in hardened portland cement pastes with and without entrained air was undertaken some years ago to obtain experimental verification of T. C. Powers' hydraulic pressure hypothesis [1, 2].[1] There were some perplexing features of those data [3] which have been elucidated by subsequent experimental work. In particular, the manner in which freezing is initiated in the capillaries in the cement paste was not determined and the rates of expansion and ice formation during cooling were found to be much smaller than expected from the melting data obtained earlier by Powers and Brownyard [4]. This difference indicated the existence of certain restrictions on ice formation during cooling that required further examination. In earlier papers [3, 5], it was assumed that ice formed in capillaries *without* seeding by an existing ice phase. Examination of the nucleation and crystal-growth processes leads to a rather different view of the freezing process in the early stages of ice formation.

The manner in which freezing begins in a supercooled, moist, porous solid should resemble the freezing of supercooled bulk water. Dorsey [6] made a systematic study of the freezing of supercooled samples of bulk water in which he found that the freezing depended on the size and nature of small solid particles in the sample and on some

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Research and Development Laboratories of the Portland Cement Association, Skokie, Illinois.

[1] Figures in brackets indicate the literature references at the end of this paper.

features of the walls of the container. If there are no particles present, or if the solids are ineffective nucleating agents, supercooling to very low temperatures results.

Chalmers has studied the dendritic nature of ice formation in supercooled water. He writes [7] that the ice-water interface forms ". . . a series of separated spikes, each of which has its axis in a well defined crystallographic direction, and with branches in other equivalent directions." This arrangement results in rapidly growing, fernlike structures in supercooled water as shown in figure 1, [8].

FIGURE 1. *Dendritic ice formation in supercooled water.* (Courtesy of Prof. B. Chalmers and *Scientific American*.)

Studies of the freezing of water in foods, soils, building stones, concrete, and hardened cement paste show that supercooling is commonly observed even in the presence of various solids which might be expected to serve as nucleating agents [4, 9, 10, 11, 12].

In Powers' model of cement-paste structure [13] the capillary spaces are described as the residues of originally water-filled space in the fresh cement-water mix. They are much larger than the pores between particles of cement hydration products formed around cement grains, which are called gel pores. Powers and Brownyard argued that the ice in cement pastes formed in the relatively large capillary spaces in their model of cement paste structure, but not in the small (20–40A) pores in the gel produced by cement hydration. In addition they argued that the melting temperature of any ice crystals small enough to be contained in the gel pores would prevent freezing until very low temperatures were reached.

In this study it is proposed that the water in the capillaries in cement pastes supercools before freezing because of restrictions on ice crystal growth through the pore structure and that the initial ice formation occurs dendritically through water in capillaries. After the initial freeze, the subsequent extension of the network of frozen capillaries also depends on the capillary size restrictions on ice formation. Hence, data from freezing experiments provide more information about the pore structure of the paste, as well as about the freezing process.

Theory

Porosity of Hardened Pastes

According to Powers' model of cement-paste structure all cement pastes contain gel pores which, when filled with water, contain a mass of gel water given [14] by:

$$w'_g = 0.74 w_n \tag{1}$$

in which w_n is the mass of nonevaporable water, which is essentially the water of hydration, and is commonly about 0.2 g per gram of cement for complete hydration. The prime notation on water-content symbols will be used to designate values of water-saturated pastes. The constant 0.74, which depends on the cement composition, was determined on the same Type I cement (15754) used in this study. This quantity of gel water is equivalent to 2.38 monolayers adsorbed on the solids in the paste if the surface area of the solids is taken as that determined by the BET method [15]. In addition to the gel pores, cement pastes contain much larger capillary spaces which, when filled with water, contain a mass of water w'_c. The total mass of water in a paste, saturated or not, is:

$$w_t = w_c + w_g + w_n \tag{2}$$

in which w_c and w_g are the water contents of the capillary and gel spaces, respectively, and the sum of w_c and w_g is w_e, the evaporable water. The total porosity of the paste can be divided into the porosity of the gel and the capillary porosity, p_c. Copeland [16] has shown that the specific volume of the capillary water in saturated cement pastes is 0.99, which is the value to be expected from the presence of the small quantity of alkali metal hydroxides in solution. Then the capillary porosity is given by:

$$p_c = \frac{0.99 w'_c}{V_p} \tag{3}$$

in which V_p is the paste volume.

The Capillary Saturation Coefficient

When the paste is partly dried, the remaining water distributes between capillary spaces and gel pores, but at high relative vapor pressures most of the water lost is from the capillary spaces [17]. The capillary saturation coefficient is defined as:

$$s_c = \frac{w_c}{w'_c} = \frac{w_t - w_g - w_n}{w'_t - w'_g - w_n} = \frac{w_t - 1.74 w_n}{w'_t - 1.74 w_n} \tag{4}$$

in which w_t' is the total water required to saturate the paste, and it is assumed that the gel pores remain water-saturated. If the specific volume of the capillary water is independent of this saturation coefficient, this equation also gives the volume fraction of capillary space which is filled with water.

If a cement paste is maintained in a water-saturated condition from the time it is cast

$$w_t' = w_o + 0.254 w_n \tag{5}$$

in which w_o is the original water content [16]. Hydration of the cement produces self-desiccation of the paste if it is cured in a sealed mold from the time it is cast. In such cases w_t is the original water content w_o, but w_t' is given by eq (5), so

$$s_c = \frac{w_o - 1.74 w_n}{w_o - 1.49 w_n} \tag{6}$$

for self-desiccated pastes [17].

When a water-saturated cement paste is cooled from 25 to 0 °C, moisture moves from the capillary spaces into the gel. Capillary space emptied can be filled by soaking in water. The resultant increase in weight is given [18] by:

$$\Delta w = 0.0194 w_g' + 0.0024 w_c'. \tag{7}$$

If the paste is not soaked in water, Δw is the amount by which w_c' is reduced to w_c, and eqs (4) and (7) can be used to obtain the fraction of the capillary space which is empty of water. Then

$$s_c = 1 - \frac{0.0194 w_g' + 0.0024 w_c'}{w_t' - 1.74 w_n} \tag{8}$$

for pastes cooled from 25 °C without additional water imbibition.

Supercooling and the Initiation of Freezing

Freezing of water can be initiated in any of three ways, by (a) homogeneous, or thermal nucleation [19], (b) heterogeneous nucleation, such as by oriented adsorption of water in an ice structure over a sufficiently large area on a solid surface [20], or (c) seeding with a piece of ice. At every temperature below 0 °C there is finite probability of homogeneous nucleation in any finite time interval. This probability is extremely small for the specimen size, temperature range, and time intervals considered here [21]. Specimens in this study have been supercooled to temperatures as low as −15.0 °C. There is apparently no feature of the structure of the paste which can serve as a nucleation site for ice formation at temperatures higher than this. Hence, when freezing does begin at higher temperatures it is most probably initiated by some external means, such as by seeding the supercooled water in the pores with an ice crystal. At the specimen surface an external ice crystal can seed ice formation in surface pores, but in the interior pores only ice in adjoining pores can act as seeds. Hence it seems that if seeding is necessary, ice formation must be propagated as a continuous phase through the pore structure of the paste.

Propagation of a continuous ice phase through the pore structure of the paste depends on whether ice can be formed of such size and shape as to be stable at the freezing temperature. These ideas have been discussed by Penner [22], Gold [23], and Jackson and Chalmers [24], with respect to ice formation in soils. In materials with finer pore structure the problem is complicated by the presence of an unfreezable film of water adsorbed on the solid. Powers and Brownyard showed that even when the water in the paste came to equilibrium with stress-free ice there remained u molecular layers of unfrozen water adsorbed on the solid surfaces of the hydrated cement, where u has a value of about 4.0 and varies slightly with the temperature. Hence an ice crystal in any small capillary must not only be smaller than the capillary diameter, D (assuming it is more or less circular in cross section), but smaller than $(D-2ut)$ in which t is the thickness of a monolayer of adsorbed water. Volmer [25] discussed the stability of small crystals in their melts below the normal melting point in terms of Thomson's equation, which can be written

$$T_r = T_s \exp\left(-\frac{2\sigma M}{r_c Q d}\right) \tag{9}$$

in which T_s is 273 °K, T_r is the fusion temperature of an ice crystal with radius r_c, σ is the interfacial energy between ice and water, Q is the molar heat of fusion, d the density and M the molecular weight of ice. If we take $\sigma = 10.2$ dynes/cm, $Q = 14{,}400$ cal/mole, $d = 0.917$ g/cm^2 and $M = 18.02$ g/mole, the values for r_c corresponding to the values of T_r given in table 1 can be calculated. D can then be computed as $(2ut + 2r_c)$, the diameter of the capillary required to contain the smallest ice crystal stable at the temperature T_r. The value taken for t was 3.1 A which corresponds to the density of bulk water, which is believed to be at least approximately correct. If the ice crystal is a dendrite, r_c is the radius of a sphere inscribed in the crystal at the growing end. It is this end which must penetrate the constrictions in the pore structure.

TABLE 1. *Size of capillaries required for propagation of ice formation at temperature t_r*

$T_r - T_s$	u	ut	r_c	$(2ut+2r_c)$
°C		A	A	A
−2	[a] 4.5	13.9	90	208
−5	4.0	12.4	29	83
−10	3.7	11.5	18	59
−15	3.2	9.9	12	44
−20	[a] 2.7	8.4	9	35

[a] By extrapolation.

In supercooled bulk water, freezing is known to occur dendritically. In a porous solid the crystal growth must be restricted not only by the crystal habit of the ice but also by the solid surfaces which the dendrites encounter during their growth. The lateral growth of the dendrites is much slower than the longitudinal growth [26] because the latent heat of crystallization is dissipated into the supercooled water much more rapidly from the tip of the dendrite than along its length. Then the initial rapid formation of ice should cease when the dendrites have penetrated all the sufficiently large capillaries contiguous with the initial ice seed. The immediately subsequent ice formation should be much slower.

The initiation of freezing in a supercooled paste at some temperature, T_f, should produce rapid dendritic growth of ice crystals which must be at least as large as those given by eq (9). These dendrites can grow through only those constrictions in the interconnected capillary system which are larger than this size. During this rapid freezing heat is liberated which raises the temperature of the supercooled paste by ΔT_f to a temperature, T_m, at which the size of thermodynamically stable dendrites is larger than any remaining constrictions in the unfrozen water-filled capillaries. At this temperature the rapid dendritic growth must cease, and only the much slower lateral growth can occur. If freezing is initiated at a temperature at which the ice crystals can be, by eq (9), only slightly smaller than the constrictions in the largest capillaries, only a very limited network of capillaries will freeze. In this case the temperature rise will be very small. Alternatively, if freezing is initiated at a considerably lower temperature, ice crystals can grow through smaller constrictions and more ice can form in the initial freeze. If the largest water-filled capillaries are sufficiently numerous the temperature will rise to the same temperature as it did when freezing began at the higher temperature. The maximum temperature reached, T_m, should be independent of the initial freezing temperature, T_f, or:

$$T_m \neq f(T_f) \tag{10}$$

if the largest water-filled capillaries are sufficiently numerous. If the largest capillaries are *not* sufficiently numerous, they will all be frozen at some temperature lower than T_m. In the unfrozen smaller capillaries, freezing can occur only at lower temperature; therefore, the freezing will stop at a temperature lower than T_m.

The heat liberated by this rapid ice formation is $C_p\Delta T_f$ per gram of specimen, in which C_p is the specific heat of the paste. If it is assumed that the heat liberation is so rapid that the heat loss to the specimen surroundings is small enough to be neglected during the time of the temperature rise, the mass of frozen water must be:

$$w_f = \frac{C_p\Delta T_f}{q}\,(w_t + c) \tag{11}$$

in which q is the heat of crystallization of 1 g of ice, c is the mass of cement, and (w_t+c) is the mass of the paste. If w_f is much smaller than w_t, C_p may be regarded as a constant.

Since the dendritic structure is a very open one, only a small amount of the water in the frozen capillaries should freeze initially. Then eq (11) can be used to obtain w_f and we should expect $w_f/w_{cf} \ll 1$ for the initial ice formation, where w_{cf} is the water content of the partially frozen capillaries. Though w_{cf} is unknown, we know that $w_{cf} \leq w_c$ and we should expect:

$$\frac{w_f}{w_c} \ll 1 \tag{12}$$

if the growth is dendritic. If eq (12) is found to be true it does not necessarily mean that the growth is dendritic because eq (12) could be true even if $w_f/w_{cf} \sim 1$, if only a few capillaries were frozen.

Experimental Procedures

The specimen casting, curing, and analytical methods have been described in detail elsewhere [18]. All pastes used in this study were free of entrained air. The cement paste specimens on which extensometer measurements were made were cast in molds consisting of 25-cm lengths of 29-mm glass tubing with a 12-mm rubber core mold fitted axially in the glass cylinder between the rubber stoppers at each end. The test specimens were 7.6-cm and 2.5-cm lengths cut from the hardened-paste hollow cylinders.

Length changes of the hollow cylinders were measured with a calibrated extensometer built around a transducer made by Statham Laboratories as previously described [18]. During tests the extensometer was partially submerged in a 4-liter temperature-control bath so that the specimen was completely immersed in kerosene and the transducer was well up in the room air. The kerosene used as the bath fluid in the first experiments had been dried by shaking with flake calcium chloride (for Wagner turbidimeter use) and probably contained a small amount of this salt. The presence of the salt had a considerable effect on the freezing behavior of the specimens, and it was found necessary to extract water soluble impurities from the kerosene. This was done by adding water to the bath, emulsifying it in the kerosene with a high speed stirrer, allowing it to settle to the bottom where it coalesced, and removing it with a suction tube. This operation was repeated whenever new kerosene was added to maintain the bath level after it was realized that this procedure would inhibit supercooling. The results presented were obtained in kerosene that had been so treated, unless otherwise noted.

The special experiments performed to measure the rate at which the initial freeze propagated through the specimens were made with specimens which were cast without hollow cores. Only specimens 3-9b, 3-14b, 3-20b, 76_1, 78_1, 80_1, 81_1, and

81_2 were of this group. The three water-saturated specimens used for measurements of freezing propagation rates, 3-9b, 3-14b, and 3-20b were cut from solid cylinders of paste cured under water for 7 yr at 23 to 25 °C. After the mold was removed they were cut to a length of 110 mm. Four holes for thermocouples were drilled in the specimens with a No. 54 (1.397 mm) drill. The holes were 9 mm deep, perpendicular to the cylinder axis, and situated 29 mm apart along a line parallel to the axis. The first and fourth holes were equally distant from the ends. The specimens were stored in limewater at 0 °C for 4 days before the tests, to insure water saturation at the freezing temperature. Before immersion in the bath, the specimens were wiped free of water and copper-constantan thermocouples made with No. 30 wire were placed in the drilled holes. The thermocouple leads were wrapped so that they fitted snugly in the ends of the holes. Ice formation in the bath and on any surface film of water on the specimen was prevented in these experiments by emulsifying 40 ml of 2 molal calcium chloride solution in the bath. It is believed that the concentration of salt in any remaining film of water on the specimen increased enough before the initiation of freezing to preclude ice formation in any such film.

In each of the measurements of propagation rates in water-saturated pastes the specimens were suspended with a burette clamp in the kerosene temperature-control bath at about +1 °C. The bath was cooled at 0.5 °C/min to freezing temperatures no lower than −8.5 °C. Freezing was initiated by touching the top end of the specimen with a piece of ice held with forceps. The position of the freezing wave front was taken to be between two thermocouples when one had indicated freezing and the next farther away from the seeded end had not. The distance between the thermocouples and the seeded end was known, and the recorder channel printing at the time of the seeding was noted, which defined the time of seeding. From these data it was possible to compute the average rate of advance, or rather the upper and lower limits, because of the uncertainty of the position of the wave front between two thermocouples. In most cases the rate was so great that only a lower limit could be determined.

The propagation rate measurements with the self-desiccated specimens 76_1, 78_1, 80_1, 81_1, and 81_2, were done in much the same way. These specimens were cured at 23 °C. After they were removed from the stoppered molds care was taken to prevent moisture loss by keeping them either in screw-capped jars or wrapped in tin foil, with only momentary exposure to room air during transfer operations. Ignition loss determinations showed no indication of drying during the preparatory manipulations. The geometry of these specimens was similar to that of the water-saturated specimens with the exception that the holes were 25 mm apart, 15 mm deep, and made with a No. 60 (1.016 mm) drill. The thermocouple junctions were at the bottom of these holes and therefore on the axis of the cylinder since the specimens were 29 mm in diameter.

After fitting the thermocouples in the holes, each specimen was mounted in the bath at 23 °C, cooled at 0.5 °C/min to +5 °C, held there about 10 min, then cooled at 0.5 °C/min to about −8 °C, then warmed at 1 °C/min to +5 °C, and held there again for about 10 min. This cycle was repeated two to five times.

Experimental Results

The Initial Formation of Ice in Hardened Pastes

In most of the freezing experiments made in this study, freezing was not initiated by any deliberate operation but was left somewhat to chance except for control of the temperature and certain other features of the environment. In the first experiments, the specimens supercooled to temperatures ranging from −5 to −15 °C before freezing began. Freezing was indicated by an abrupt expansion and temperature rise. After about 8 weeks of daily testing it was found that the initial freezing temperatures had gradually increased to about −1.5 °C, and this temperature was independent of the porosity or other characteristics of the different specimens. It was also observed that some water (perhaps 50 ml) had accumulated in the kerosene bath by dripping of condensed atmospheric moisture from upper parts of the bath cooling coil. This water, which was emulsified in the kerosene by the stirrer during tests and settled out between tests, had apparently inhibited supercooling of the water in the specimens. At temperatures below 0 °C this water in the bath formed frazil-like ice that tended to collect in a mass of fine crystals around the extensometer.

Some experiments were performed to test whether or not the frazil ice in the bath was seeding ice formation in the specimens. In these experiments it was found that the hardened pastes froze at about −1 °C when water-soluble impurities were extracted from the kerosene, as described above, if there was some free water in the kerosene, and that these same pastes supercooled to temperatures as low as −7.0 °C when concentrated NaCl solutions were emulsified in the kerosene.

To investigate this apparent seeding at the specimen surface and propagation of ice formation to the specimen interior in the preceding experiments, additional experiments were performed to measure the rate of propagation of ice formation through supercooled pastes after touching one end with a piece of ice. The results presented in table 2 were obtained with 7-yr-old, water-saturated specimens. For comparison, the results obtained by Hillig and Turnbull [27] for ice-crystal growth rates in supercooled water in glass capillary tubes and by Lindenmeyer, Orrok, Jackson, and Chalmers [28] for free growth in supercooled bulk water are given corresponding to the temperature, T_f. Both of these refer to growth perpendicular to the c-axis of ice, i.e., the rapid growth direction.

TABLE 2. *Freezing propagation rates in supercooled water-saturated hardened cement pastes*

Specimen	w_t/c	w_n/c	T_f	T_m	Propagation Rates (mm/sec)			
					At least	At most	Linden-meyer et al.	Hillig and Turnbull
			°C	°C				
3-9b	0.640	0.221	−4.9	−4.0	8.7	-----	10	23
3-14b	.541	.219	−2.7	−1.5	5.1	11	2.5	8.6
3-14b	.541	.219	−5.4	-------	8.1	------	13	27
3-20b	.477	.219	−2.6	−2.2	11	------	2.4	8.2

Specimens 3–9b and 3–14b were found to contain cracks after the tests of table 2. To determine whether freezing propagation could be detected even when such damage could not occur, self-desiccated pastes with capillary saturation coefficients less than 0.91 were used. (Even these pastes were sometimes damaged by freezing when greatly supercooled. However, in such cases the maximum temperature reached was the same during the first freeze, when supercooling was slight, as during subsequent freezes when the supercooling was great. Therefore, the damage incurred could not have had much effect on the initial freezing process. Perhaps the cracks did not result from stresses developed directly by ice formation but resulted from thermal stresses across the freezing wave front. These may have been quite high when the supercooling was great.) Figure 2 shows the strip chart record of the thermocouple outputs during the sixth freeze of specimen 76_1. The results of computation of the propagation velocity from the strip chart data and the specimen water contents are given in table 3. In some cases the upper and lower limits on propagation rates coincide because the recorder happened to record just at the time the temperature was changing at a thermocouple and this defined the position of the wave front much more exactly than in the other cases.

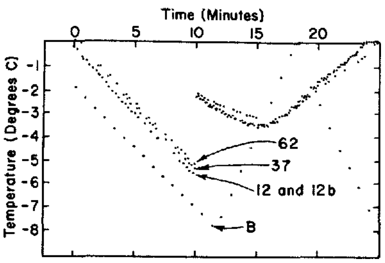

FIGURE 2. *Strip chart record of thermocouple EMF's during freezing of specimen 76_1.*

B indicates thermocouple in the bath; 12, 37, 62, and 12b indicate the thermocouple in the specimen, 12, 37, and 62 mm from the top and 12 mm from the bottom, respectively.

TABLE 3. *Freezing propagation rates in supercooled self-desiccated hardened cement pastes*

Specimen	w_t/c	w_n/c	Freeze	Temp. of bath	Propagation Rates mm/sec.			
					At least	At most	Linden-meyer et al.	Hillig et al.
				°C				
76_1	0.469	0.118	1	−5.0	3	4.6	11	24
			2	−4.8	3	4.6	10	22
			3	−6.9	7	14	23	41
			4	------	------	------	------	------
			5	−4.4	2.1	3.5	8	19
			6	−7.1	14	------	29	43
78_1	.460	.120	1	------	------	------	------	------
			2	−5.2	3	4.6	12	25
			3	−8.0	14	------	32	54
			4	------	------	------	------	------
			5	−6.8	14	14	22	40
80_2	.457	.138	1	------	------	------	------	------
			2	−8.1	7	7	33	55
			3	------	------	------	------	------
81_1	.550	.134	1	------	------	------	------	------
			2	------	------	------	------	------
			3	−5.3	7	14	12	26
			4	−7.0	14	------	27	42
			5	−4.4	7	7	8	19
81_2	.561	.152	1	------	------	------	------	------
			2	−5.8	5	5	15	31
			3	−7.1	7	7	29	43
			4	------	------	------	------	------
			5	−7.1	7	7	29	43
			6	------	------	------	------	------

The purpose of the experiments of table 3 was only secondarily to measure the propagation rates. The primary purpose, and the reason for placing the thermocouples so deep in the specimen, was to measure the maximum temperature reached during the rapid initial formation of ice. These results are plotted in figure 3 versus the initial freezing temperature. Table 6 contains a summary of all the T_f and ΔT_f measurements presented in the tables and figures in this report.

Dimensional-change measurements made during freezing with supercooling reveal that the expansion rate during the initial freeze is rather small

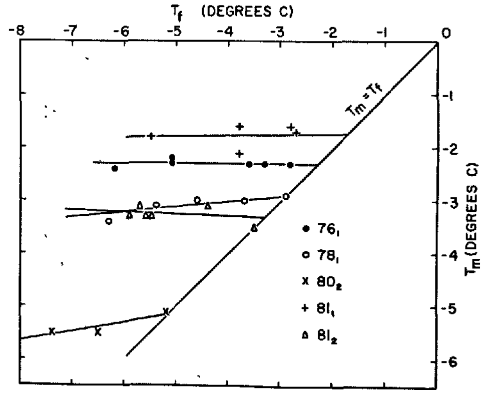

FIGURE 3. *T_m, maximum temperature reached during initial freeze of supercooled cement pastes frozen at different temperatures T_f.*

even though the rate of ice formation, as indicated by the rapid rise in the specimen temperature, is much greater than during the subsequent progressive expansion. Figures 4 and 5 show the temperature-versus-time and length change-versus-time curves for specimens 55_2t and 63_2t. These 0.45 water-cement ratio pastes were cured at 5 °C for 4 days. Specimen 55_2t was cured without additional water and thus became somewhat self-desiccated. Specimen 63_2t was cured with lime-water in the hollow core of the specimen, which maintained water saturation during hydration. The beginning of freezing is indicated in each case by an expansion and a coincident break in the temperature-time curve.

Table 4 gives the initial freezing results of three nearly completely hydrated specimens of high water content. These specimens were cured in water at room temperature and were of approximately equal porosities. Water-soluble impurities had not been extracted from the kerosene bath at the time the tests of specimens HVb and AAVb were made. The initial expansions increased with the amount of supercooling which preceded freezing. In each case, further cooling produced much larger total expansions. The complete freezing-thawing results for a similar paste are given in figure 12. Specimen AAVb was frozen again 2 days after the test of table 4.

Table 4. *Expansions produced by freezing of supercooled pastes*

Specimen	w_t/c	w_n/c	T_m	T_f	ΔT_f	Initial expansion
			°C	°C	°C	
IVLt	0.683	0.220	−0.6	−0.9	0.3	0×10^{-6}
HVb	.692	.228	−3.9	−4.8	0.9	100×10^{-6}
AAVb	.721	.233	−7.1	−8.8	1.7	$>320\times10^{-6}$

It supercooled to −15.0 °C before the second freeze.

Three typical cases of freezing of pastes of low porosity are shown in figure 6. Water-soluble impurities had not been extracted from the kerosene bath at the time the tests of specimens SVb and UVb were made. Specimen SVb was cooled at 0.25 °C/min from 22.8 °C, and test conditions were such that it supercooled to −6.0 °C before freezing. The plot shows both a 40 x 10^{-6} expansion and an increase in the temperature of the interior of the specimen to −5.4 °C. Specimen UVb was cooled at 0.25 °C/min from 22 °C and supercooled to only −1.4 °C before freezing. An expansion of 20 x 10^{-6} accompanied a temperature rise to −1.0 °C. No perceptible temperature rise occurred when specimen 9_1b was frozen. Freezing at −0.7 °C was apparent because of an increased temperature gradient in the specimen and an expansion of 10 x 10^{-6}.

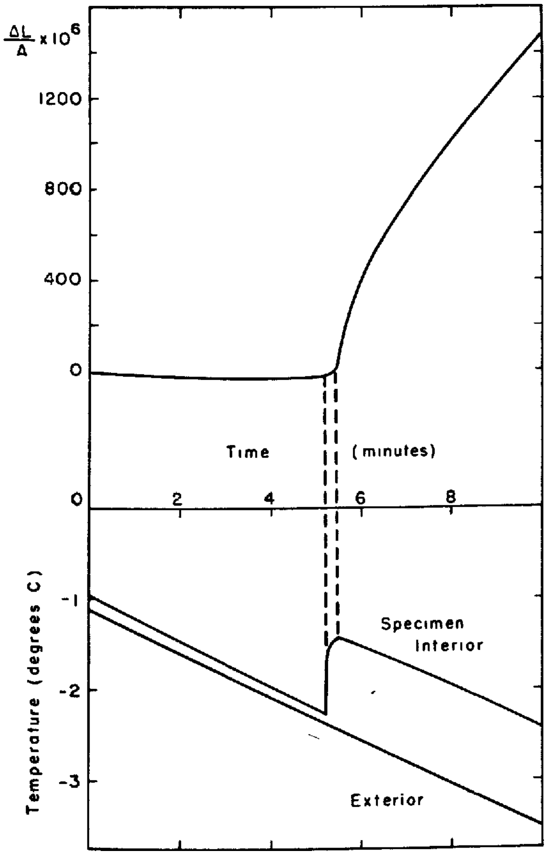

Figure 4. *Results of freezing specimen 63_2t.*

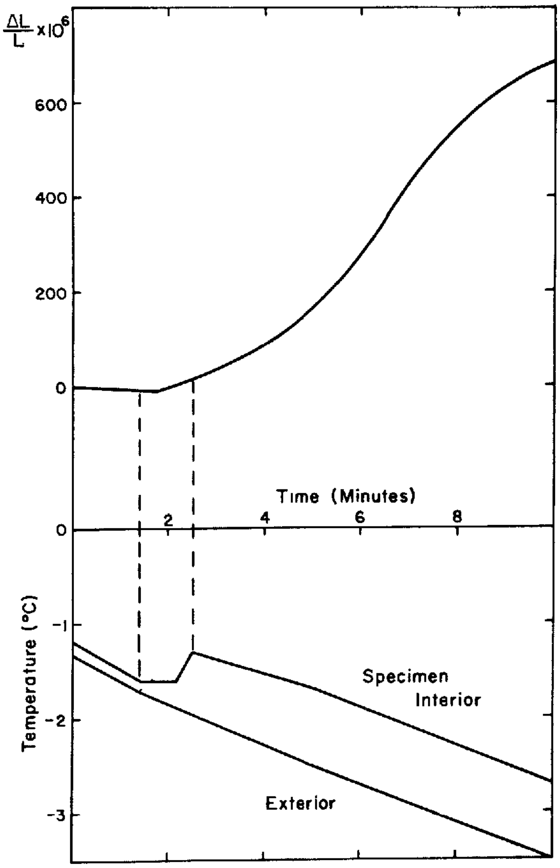

Figure 5. *Results of freezing specimen 55_2t.*

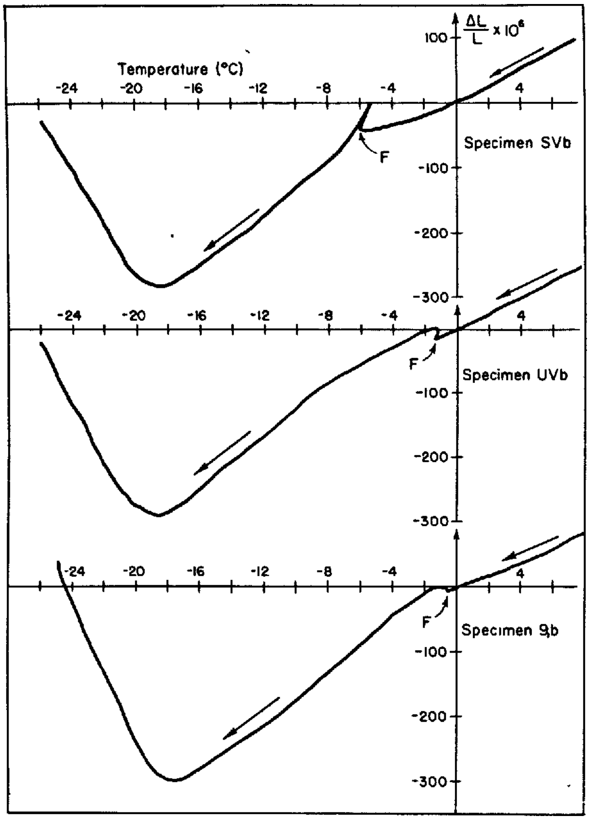

FIGURE 6. *Freezing curves of 0.45 water-cement ratio pastes.*

Cooling at 0.25 °C/min. F indicates the beginning of freezing.

These specimens were all of 0.45 water-cement ratio. A similar specimen, TVt, was subjected to the same kind of test after storage in ice water for 4 days. The initial expansion of 100 x 10^{-6} resulted in a temperature rise from −2.7 to −1.4 °C. The curve was otherwise very similar to that of specimen SVb.

Ice Formation Immediately Subsequent to the Initial Freeze

Figure 7 shows the results of length change and temperature measurements obtained during freezing tests of five water-soaked cement pastes. The specimens were 2.5-cm sections of hollow cylinders of pastes of 0.45 water-cement ratio, cured at 5 °C with water in the central core for periods ranging from 7.8 to 870 days. Each of the specimens was cooled at 1 °C/min from room temperature (to which it had warmed during preparation for the test) to +1 °C where it was held long enough to reach constant length. Then it was cooled at 0.25 °C/min to −10 °C, or even lower temperature.

More detailed information obtained with specimen 57_1t of figure 7 is given in figure 8 which shows ΔT, the difference between the temperature of the specimen interior and the bath temperature. This difference is directly related to the rate of ice formation in the specimen since the cooling

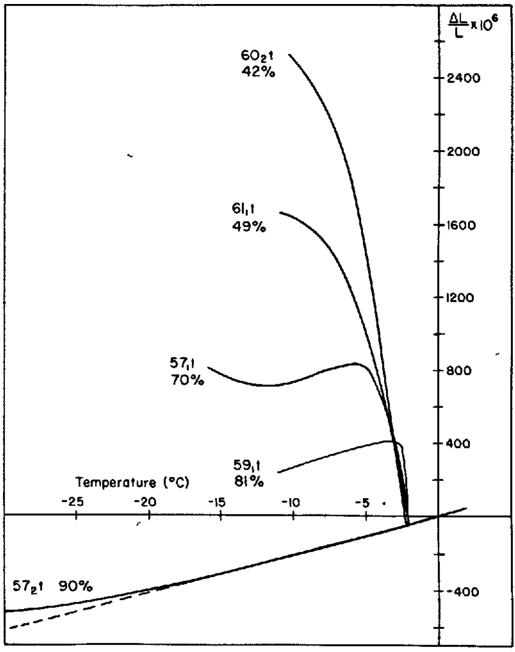

FIGURE 7. *Freezing expansions of water-soaked pastes with percent hydration as indicated by* w_n/c.

w_o/c=0.45.

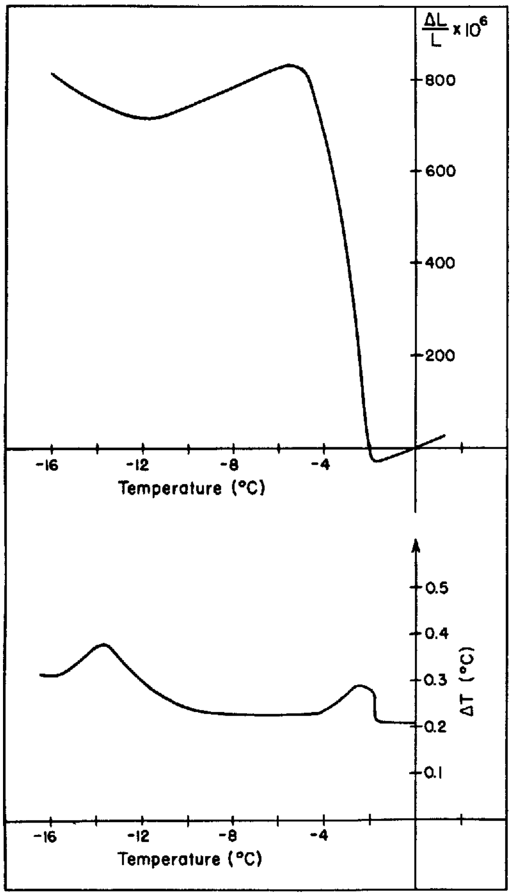

FIGURE 8. *Results of freezing specimen 57_1t.*

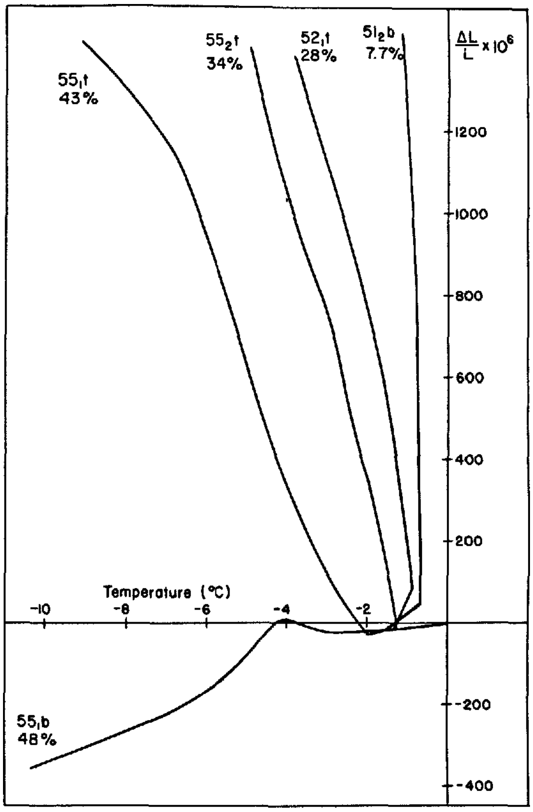

FIGURE 9. *Freezing expansions of self-desiccated pastes with percent hydration as indicated by* w_n/c.

$w_o/c=0.45$.

was done at a constant rate and other conditions remained essentially constant.

Figure 9 shows the results of freezing tests of self-desiccated pastes of $w_o/c=0.45$ cured 1 to 10 days at 5 °C. Each of the 2.5-cm specimens was cooled at 1 °C/min from room temperature (to which it had warmed during preparation for the test) to +1 °C and allowed to come to constant length. Then it was cooled at 0.25 °C/min to −10 °C and the temperature again held constant. The freezing expansion was almost entirely eliminated after 10 days of hydration, at which w_n/c was 0.110. In fact, freezing produced shrinkage in addition to thermal contraction after the small expansion. In the test of specimen 55_1t the expansion did not begin until −2.0 °C was reached, though a change in the temperature gradient and slope of the contraction curve indicated that freezing had begun at −0.7 °C. In the test of specimen 55_1b freezing began at −0.9 °C though the progressive expansion did not begin until −3.0 °C. These results are shown clearly in figures 10 and 11.

Progressive Extension of the Initially Formed Ice Network

Figures 12, 13, and 14 show the results obtained with 7.6 cm, nearly completely hydrated specimens of various w_t/c which were frozen and thawed at 0.25 °C/min. These specimens had been thoroughly leached of soluble alkalies. The fact that the large progressive expansions in these tests began at low temperatures for pastes of low

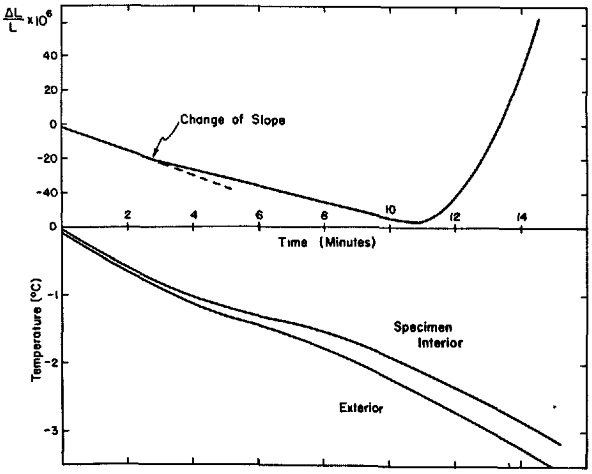

FIGURE 10. *Details of the freezing curves of specimen* 55_1t.

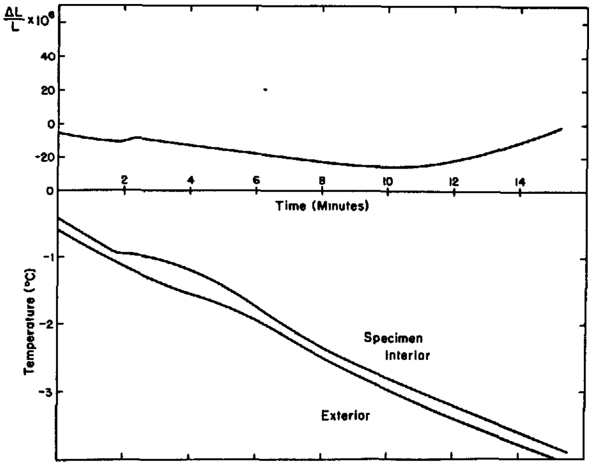

FIGURE 11. *Details of the freezing curves of specimen* 55_1b.

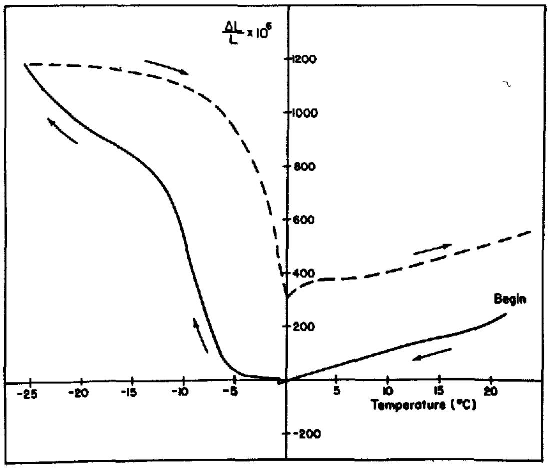

FIGURE 12. *Freezing cycle test at 0.25 °C/min.*

Specimen IVLb; w_t/c was 0.610, w_n/c was 0.220.

porosity was a general feature of all the tests made with water-soaked pastes without entrained air. One group of specimens was cured in a closed tank at 23 °C by standing in about 3 cm of water with the hollow core of each specimen packed with wet paper tissues. Self-desiccation was prevented because this wick kept the specimen surface wet during hydration. Figure 15 shows the relationship between the temperature at which the large progressive expansion (not the "pip" signifying initial ice formation) began and the capillary porosity of the most porous (upper) part of the test specimen. The figure shows results for pastes at different w_n/c and different cooling rates.

The results of testing a mature paste cured at 23 °C in a sealed mold to permit self-desiccation are given in figure 16. The original water-cement ratio was 0.432, so the results may be compared with those of the water-saturated pastes of figure 6.

The total water contents, nonevaporable water contents, and curing methods of specimens referred to individually in the various figures and tables are compiled in table 5.

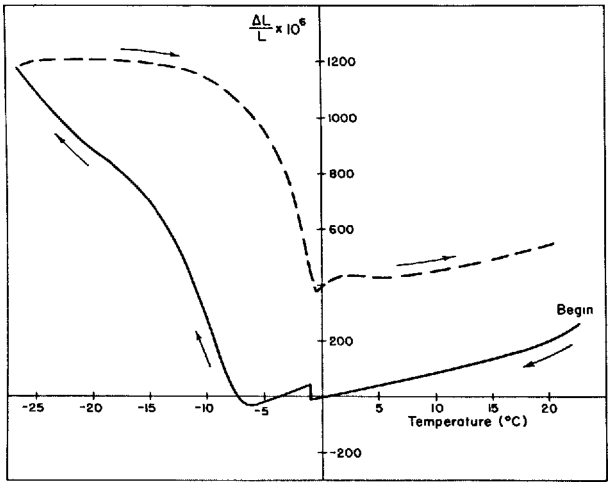

FIGURE 13. *Freezing cycle test at 0.25 °C/min.*

Specimen HVLb; w_t/c was 0.583, w_n/c was 0.222.

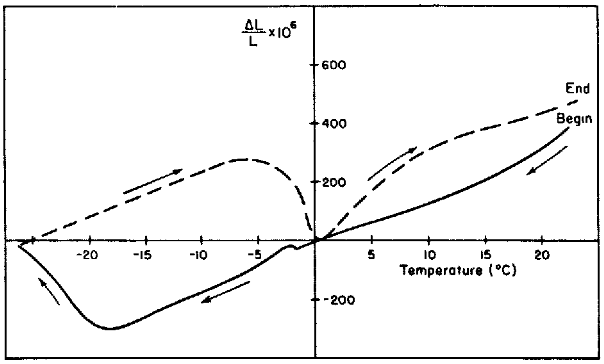

FIGURE 14. *Freezing cycle test at 0.25 °C/min.*

Specimen KVLt; w_t/c was 0.505, w_n/c was 0.215.

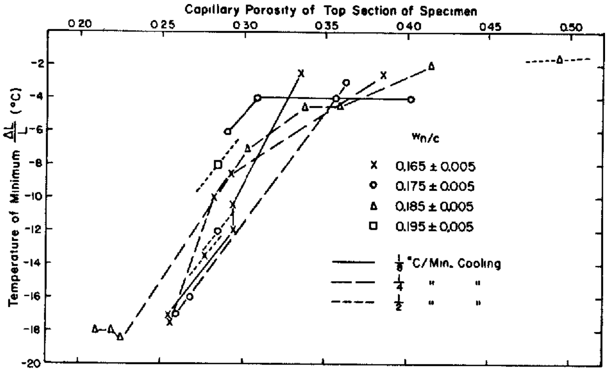

FIGURE 15. *Effect of capillary porosity on the temperature of the beginning of progressive expansion.*

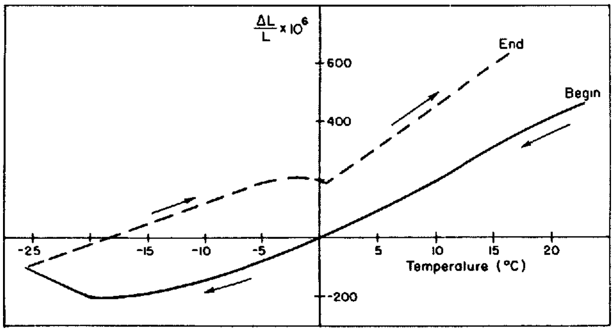

FIGURE 16. *Freezing cycle test of self-desiccated specimen 29_1b.*

w_t/c was 0.432 and w_n/c was 0.199. Cooling and warming at 0.25 °C/min.

TABLE 5. *Summary of specimen data*

Specimen	w_t/c	w_n/c	Curing [b]	Curing temperature
				°C
AAVb	0.721	0.233	C+L	23
HVb	.692	.228	C+L	23
SVb	.49 [a]	.225	C+L	23
TVt	.49 [a]	.224	C+L	23
UVb	.49 [a]	.225	C+L	23
HVLb	.593	.222	C+L	23
IVLt	.683	.220	C+L	23
IVLb	.610	.220	C+L	23
KVLt	.505	.215	C+L	23
9_1b	.484	.168	W	23
29_1b	.432	.199	S.D.	23
51_2b	.440	.018	S.D.	5
52_1t	.440	.064	S.D.	5
55_1t	.446	.099	S.D.	5
55_1b	.429	.110	S.D.	5
55_2t	.440	.077	S.D.	5
57_1t	.488	.162	C	5
57_2t	.483	.207	C	5
59_1t	.495	.187	C	5
60_2t	.465	.097	C	5
61_1t	.472	.113	C	5
63_2t	.443	.072	C	5
76_1	.469	.118	S.D.	23
78_1	.460	.120	S.D.	23
80_2	.457	.138	S.D.	23
81_1	.550	.134	S.D.	23
81_2	.561	.152	S.D.	23
3–9b	.640	.221	M	24
3–14b	.541	.219	M	24
3–20b	.477	.219	M	24

[a] Estimated from orignal water-cement ratio and w_n/c.

[b] *C*=Cured with water in hollow core of specimen.
W=Cured with a water-soaked wick in the specimen core.
S.D.=Cured in a sealed mold to permit self-desiccation.
L=Leached of soluble alkalies by storage in 60 liters of limewater for 18 mos.
M=Solid cylinders cured under water in mold.

Discussion of Results

The Initial Formation of Ice in Hardened Pastes

Three kinds of evidence have been presented to show that ice formation in the paste requires seeding and is propagated as a continuous phase through the interconnected pores of the paste. First, it was shown that preventing ice formation in the bath emulsion around the specimen prevented freezing of the water in the interior of the paste specimens to temperatures as low as −15 °C. It seems reasonable to suppose that the frazil-ice crystals formed in the bath, seeded ice formation in water in surface pores of the specimens, and that supercooling was pronounced in the early tests because (a) the kerosene originally contained a little calcium chloride which depressed the "freezing point" of any water in the bath, and (b) there was so little water in the bath that the probability of an ice crystal forming and striking the specimen was not very large until temperatures lower than about −5 °C were reached.

Second, it was shown that touching a supercooled specimen with a piece of ice produced ice formation throughout the specimen, and in fact the speed of propagation of freezing could be measured. The results presented for water-saturated pastes agree reasonably well with those given by Hillig and Turnbull [27] for ice growth rates in glass capillary tubes and by Lindenmeyer, Orrok, Jackson, and Chalmers [28] for free growth of ice crystals in supercooled bulk water. The latter authors found that the growth rate was influenced strongly by the thermal conductivity of the supporting medium, presumably because the formation of ice was limited by the extraction of the latent heat of crystallization, so Hillig and Turnbull's results are thought to be more appropriate for comparison with cement-paste results. The propagation speeds measured with the self-desiccated pastes were only about one-tenth that found in saturated pastes. Perhaps this difference occurred because the thermal conductivity of the partially dried pastes was less than that of the saturated pastes and because the ice formation may have followed a more tortuous path through the pore structure of the dried pastes than through the water-saturated pastes.

Third, additional evidence that the initial freezing propagation must have occurred through the pore structure of the paste was shown in table 4 and figure 6. Although the abrupt temperature rise and expansion are quite small when supercooling is slight, they do indeed indicate the beginning of freezing of water in the pores of the specimen, because increasing the porosity increases both the expansion and the temperature rise when the supercooling is great. Such variation could hardly be explained in terms of freezing of a film of water on the specimen surface. However, since specimens as porous as those in table 4 were always badly damaged in the freezing tests, it is conceivable that freezing occurred in the interior only through cracks opened up by freezing in surface pores. For this reason results of tests with pastes of low porosities were given in figure 6. It is not thought that such specimens were damaged by the initial freeze because even after large expansions at −25 °C these specimens showed no permanent dilation, and visual inspection revealed no cracks. The results with the self-desiccated pastes of figures 3 and 5 and table 3 also indicated that freezing occurred in the interior of the specimens, and such pastes are not usually damaged by freezing. This point is also substantiated by similar results obtained with pastes containing closely spaced, entrained air voids [3]. Such pastes show initial freezing "pips" indicating ice formation in the specimen, but they show no evidence of damage by freezing.

The computation of the propagation speed from the distance between thermocouples and the measured time interval is perfectly straightforward if the wave front shape is nearly planar or if the thermocouples are near the surface, as in the results in table 2. However, if the wave front is far from planar, the shape of the wave front has an effect on the velocity along the axis because of propagation along the specimen surface. During these tests the temperature of the surface was about 1.5 °C lower than that along the specimen axis. According to the results of Lindenmeyer, Orrok, Jackson, and Chalmers, ice-crystal growth should be about twice as fast at the temperature of the specimen surface as at the temperature along the axis. Hence the wave along the surface should get far ahead of the wave front proceeding down the axis. At some distance from the seeded end there should develop a steady state wave front configuration which propagates at the rate of the surface wave. Then the rate along the axis varies along the specimen and the average rate is *not* that characteristic of the temperature along the axis. We can, however, compute the propagation rate *along the surface* by consideration of the geometry of the specimen and an estimate of the shape of the wave front. The estimate is believed to be justified because the rates computed in this way have about the same temperature dependence as the rates measured by Lindenmeyer, et al. These computed rates correspond to the temperature of the surface, or the bath temperature, and not the specimen interior temperature.

Powers, Copeland, and Mann [29] concluded from a study of the permeability of hardened pastes that the originally water-filled space in the fresh mix became individual capillary cavities separated by cement gel produced by hydration unless the water-cement ratio exceeded 0.70, in which case they remained as part of a continuous, interconnected network of capillaries. However, the freezing-propagation results indicate that even mature pastes of 0.45 water-cement ratio contain at least a few continuous capillaries. Simple calculations indicate that these few continuous capillaries would not be detectable by permeability measurements of the kind reported by Powers, Copeland, and Mann, except perhaps in pastes of very low porosity.

Figures 2, 3, 4, 5, 6, 8, and 9 show that in pastes containing enough water there is an initial rapid formation of ice which produces a rapid temperature rise, ΔT_f. Ice formation then continues at a much lower rate which depends partly on the rate of heat extraction. In some nearly completely hydrated pastes, such as in figures 8, 13, and 14, the ice formation virtually ceases after the rapid initial freeze and some immediately subsequent ice formation. Equations (1), (2), and (11) were applied to various results to calculate w_f/w_c from the specific heats and temperature rise in the initial freeze. The specific heats of the pastes were estimated from data given by Siegmann [30] and are tabulated in table 6 with the calculated values of w_f and w_f/w_c. The values of w_f/w_c calculated for the initial freeze are all quite small, the greatest being 0.109 for specimen 76_1 when it was supercooled to −6.2 °C before freezing. Since the w_f/w_c values are all so small, these provide direct evidence that some aspect of the paste structure imposes a restriction on the amount of initial ice formation. We may conclude that either very few of the capillaries are frozen, or that very little ice forms in the capillaries that do freeze, or that both of these possibilities are true. The results are also consistent with the hypothesis that the initial ice formation is dendritic because the immediately subsequent ice formation is much slower than the initial freezing.

In the section on theory it was proposed that if the largest capillaries are sufficiently numerous, rapid ice crystal growth should continue through these capillaries until a T_m characteristic of this capillary size is reached, and this T_m should not depend on T_f, the initial freezing temperature. The results in figure 3, obtained with immature self-desiccated specimens, show that such independence is observed in these pastes. This provides additional evidence that ice formation is restricted by the sizes of the capillaries in the paste.

The cessation of the rapid formation of ice in the initial freeze cannot readily be explained in terms of formation of a solution of the concentration required for a local equilibrium between the ice and solution in the capillaries. If such concentrated solutions were formed in the initial freeze we should expect w_f/w_c to be greater when ΔT_f was greater, which means the unfrozen solution would be more concentrated and T_m would be lower. However, T_m could not then be independent of T_f unless w_f/w_c was very small in every case, which would mean that T_m would have to be very close to 0 °C. Since the observed values of T_m are not close to 0 °C we must conclude that rapid ice formation ceased for some other reason.

TABLE 6. w_f/w_c *Calculated from* ΔT_f *and* C_p

Specimen	T_f	ΔT_f	C_p	w_f	w_f/w_c
	°C	*°C*	*cal/g of paste*	*mg/g of paste*	
AAVb	−7.1	1.6	0.48	9.6	0.049
HVb	−3.9	0.9	.46	5.2	.029
SVb	−5.4	.6	.39	2.9	.045
UVb	−1.0	.5	.39	2.4	.030
HVLb	−.9	.4	.43	2.1	.015
IVLt	−.5	.4	.46	2.3	.011
IVLb	−.6	.4	.44	2.2	.014
KVLt	−1.8	.0	.40	0	.000
9_1b	−.8	.0	.41	0	.000
51_2b	−1.5	.8	.42	4.2	.012
52_1t	−1.4	.5	.41	2.6	.009
55_1t	−.7	.0	.39	0	.000
55_1b	−1.0	.1	.38	0	.000
55_2t	−1.6	.3	.40	1.5	.005
57_1t	−1.8	.0	.41	0	.000
57_2t	−3.4	.1	.42	.5	.006
59_1t	−2.2	.2	.41	1	.009
60_2t	−1.8	.2	.42	1	.005
61_1t	−2.4	.0	.41	0	.000
63_2t	−2.2	.8	.41	4.1	.019
76_1	−3.6	1.3	.41	6.7	.037
	−3.3	1.0	---	5.1	.028
	−5.1	2.8	---	14.4	.081
	−6.2	3.8	---	19.5	.109
	−2.8	.5	---	2.6	.014
	−5 1	2.9	---	14.9	.083
78_1	−2.9	.0	.40	0	.000
	−3.7	.7	---	3.5	.020
	−6.3	2.9	---	14.5	.084
	−4.6	1.6	---	8.0	.046
	−5.4	2.3	---	11.5	.067
80_2	−5.2	.1	.40	.5	.003
	−6.5	1.0	---	5.0	.033
	−7.4	1.9	---	9.5	.064
81_1	−3.8	1.7	.43	9.1	.044
	−2.7	1.0	---	5.3	.026
	−3.8	2.2	---	12.4	.061
	−5.5	3.7	---	19.9	.097
	−2.8	1.2	---	6.5	.032
81_2	−3.5	.0	.43	0	.000
	−4.4	1.3	---	7.0	.037
	−5.5	2.2	---	11.8	.062
	−5.9	2.6	---	14.0	.074
	−5.6	2.3	---	12.4	.065
	−5.7	2.6	---	14.0	.074
3-9b	−4.9	.9	.47	5.3	.034
3-14b	−2.7	1.2	.43	6.4	.061
3-20b	−2.6	.4	.41	2.0	.031

The specimens of table 4 were all of high porosity and water saturated at 23 °C, yet they exhibited T_m values that did decrease with the freezing temperature, T_f. Water froze in one case at −0.6 °C, yet rapid freezing stopped at −3.9 and −7.1 °C in the other cases. To explain this behavior we must note that these pastes were nearly completely hydrated, and therefore the largest capillaries were *not* sufficiently numerous to permit ice formation up to a T_m characteristic of that size. In fact, Powers, Copeland, and Mann's study of paste permeability would indicate no interconnected capillaries in such fully hydrated pastes, whereas their work indicates that the specimens of figure 3 contained enough interconnected capillaries to affect strongly the permeability.

The same argument can be applied to the results obtained with the low water-cement ratio pastes shown in figure 6.

It is interesting to compare the initial freeze of the immature self-desiccated pastes in figure 9 with the similar water-soaked pastes of figure 7.

The T_m values of the pastes of figure 9 decreased steadily as the extent of hydration increased from 8 percent to 48 percent. The values were −0.6, −0.9, −1.3, −2.0, and −3.0 °C, the −2.0 °C occurring at 43 percent of the ultimate value of w_n/c, 0.230. In four of the water-soaked pastes of figure 7 expansions also began with T_m values of −2.0 °C; the extent of hydration ranged from 42 percent to 81 percent in these cases. These results indicate that up to about 42 percent of the ultimate value of w_n/c the largest capillaries of the self-desiccated pastes contain appreciable amounts of water which can be frozen, just as in the saturated pastes. It also indicates the existence of a network of large (−2 °C corresponds to 200 A diameter) capillaries, the sizes of which are not much dependent upon the extent of hydration, at least up to 81 percent of the ultimate w_n/c. However, the progressive reduction of the expansion indicates that this network of contiguous capillaries becomes less continuous as hydration proceeds.

Ice Formation Immediately Subsequent to the Initial Freeze

The results shown in figures 4, 5, 7, 8, and 9 show that the initial rapid formation of ice produces immediate expansions in pastes containing sufficient water. Though these expansions are not very large, immediately subsequent there are large progressive expansions which must be a result of the subsequent growth of the original dendrities.

Powers, Copeland, and Mann interpreted the reduction of paste permeability with hydration as resulting from the reduction of capillary continuity by filling of capillaries with products of cement hydration. The systematic reduction of the immediately subsequent expansions of the water-soaked paste as shown in figure 7 can be interpreted in the same way. The initial expansions began in each case at about −2 °C but were reduced to zero between the w_n/c values of 0.187 and 0.207 (81 to 90 percent of the cement hydrated).

The results presented in figure 9 are intrepreted to mean that freezing of water in these pastes began at about −1 °C, but only in specimens 55_2t, 52_1t, and 51_2b did the initial ice formation fill the spaces in which the freezing occurred. In the tests of the two other specimens, 55_1t and 55_1b, the freezing apparently did not occur in many water-filled capillaries until −2 and −3 °C respectively, because large expansions did not occur until these temperatures were reached, though continuing ice formation was evident at higher temperatures from the time-temperature curves in figures 10 and 11. Analysis of the variation of T_m with w_t/c and w_n/c for the self-desiccated specimens of figures 3 and 9 indicates that the temperatures at which the large expansions began in the tests of 55_1t and 55_1b are very nearly the T_m values that would have been observed if these specimens had not been seeded at higher temperatures. This result indicates that the large expansions began when it was cold enough for ice crystals to penetrate into many large water-filled capillaries, rather than by the filling up of partly empty capillary spaces by progressive freezing of the solution in these capillary spaces.

Progressive Extension of the Originally Formed Ice Network

The preceding discussion has been almost entirely concerned with the initially formed network of ice crystals in the capillaries of the paste. The effect of subsequent growth and thawing of this network is illustrated in the results shown in figures 12, 13, and 14. Additional ice formation was indicated by a progressive expansion at a temperature that depended on the capillary porosity as shown in figure 15. The additional expansion is believed to occur because a temperature is reached at which additional stable ice crystals can be formed in the smaller water-filled capillaries connected to those in which ice formed initially.

These specimens did not contain entrained air voids, but the specimen geometry provided escape boundaries with an equivalent void-spacing factor of 0.4 cm. Though this is too large to prevent destructive expansions it was small enough to reduce considerably the large progressive expansions of high water-cement ratio pastes. Specimens of such pastes without hollow cores yielded results similar to those with hollow cores but showed greater expansions. Nevertheless, these results show typical freezing-thawing hysteresis and permit calculation of the fraction of the capillary water which froze at the beginning of freezing. Neither of these aspects of the results is believed to be invalidated because of the moisture lost to the surface during freezing, though the magnitude of the expansion was affected by the loss.

Figure 15 shows a rapid decrease in the temperature of the progressive expansion between capillary porosities of 0.30 and 0.26. This decrease is no doubt partly a result of moisture movement from capillaries to gel during cooling. Such movement can have only little effect in pastes of high porosity because there is so much more capillary water in them than required to maintain the gel saturated during cooling. Even in pastes of low porosity the moisture redistribution with temperature does not seem to have a significant effect on the large progressive expansions at low temperatures because specimens TVt and SVb (of fig. 6) showed very similar freezing expansions beginning at about −18 °C, even though TVt had been stored in ice water before the test and SVb had not. Even more convincing are the results obtained with specimen 29_1b of figure 16. Though the capillary saturation coefficient of this paste was calculated to be only 0.82 at 23 °C, the large progressive expansion began at −19

°C, only 2 degrees C lower than that of the companion water-soaked specimen of figure 6, 9_1b. This result indicates that the temperature of the beginning of progressive freezing is more closely related to the pore structure of the paste than the saturation coefficient, though at very low porosities the effect of cooling on the capillary saturation coefficient must become very important.

Figure 15 indicates that even in pastes of relatively low porosities freezing resumed at about −17 °C. Table 1 indicates that at this temperature freezing could occur through capillaries of about 40 A diameter, which is not much greater than Powers' estimate of the average size of the gel pores in cement pastes from porosity and surface area considerations [31]. Since large freezing expansions occurred at this temperature in all water-saturated pastes tested, there must be a relatively large number of pores of this size in such pastes. It has also been shown that even pastes of low capillary porosity have some very large capillaries, those which permit a limited amount of ice formation near −1 °C. Capillaries of intermediate sizes were apparently not very numerous in these low water-cement ratio pastes. There seem to be two principal kinds of pores in these cement pastes, which Powers has called gel pores and capillaries. Figure 8 is a particularly good illustration of the effect of the binodal character of the pore-size distribution on freezing behavior during a single test.

The freezing-thawing hysteresis evident in figures 12, 13, and 14 is readily explained in terms of capillary size restrictions on ice formation. Water in many of the larger capillary spaces does not freeze until low temperatures are reached because they are not connected to the existing ice network through any capillaries large enough to contain stable ice crystals. Once they have become frozen at a lower temperature they will not melt until a temperature corresponding to the size of each particular frozen capillary is reached, and this temperature is apparently considerably higher than the temperature at which it became frozen. In actual experiments the freezing-thawing hysteresis curves are complicated by diffusion of water from unfrozen pores to ice in the frozen capillaries. The fact that expansions, supposedly resulting from this diffusion, can be observed is further evidence for the existence of certain pores in the paste in which the ice phase cannot be nucleated.

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Paper VI–S3. Comparison of Chemical Resistance of Supersulfate and Special Purpose Cements*

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Synopsis

Mortar specimens made with five supersulfate cements were exposed to solutions of various salts and acids, and their performance as judged by sonic measurements, weight loss, and appearance was compared with the performance of specimens made with portland blast-furnace slag, portland-pozzolan, sulfate-resistant, and high-alumina cements exposed to the same solutions. The testing solutions were prepared from magnesium sulfate, sodium sulfate, sugar, and lactic, sulfuric, citric, and acetic acids. A saturated solution of CO_2 in water was also used. Differences were observed in the resistance to attack of the various cementitious materials in the different solutions. The special-purpose cements appeared to resist attack as well as, and in some solutions better than, the supersulfate cements.

Résumé

Des spécimens de mortier faits avec cinq ciments sursulfatés furent exposés à des solutions de sels et d'acides variés, et leur comportement, apprécié par des essais soniques, la perte de poids, et l'aspect fut comparé au comportement des spécimens confectionnés avec un ciment portland au laitier de haut fourneau, un ciment portland-pouzzolanique, un ciment "sulfate-resistant" et un ciment alumineux, exposés aux mêmes solutions. Les solutions d'essais étaient préparées à partir de sulfate de magnésium, de sulfate de sodium, de sucre, et d'acides lactique, sulfurique, citrique et acétique. Une solution saturée de CO_2 dans l'eau fut également utilisée. On observa des différences dans la résistance à l'attaque des matériaux cimentaires variés dans les différentes solutions. Les ciments à but spécial semblèrent résister à l'attaque aussi bien, et dans certaines solutions certains étaient plus résistants que les ciments sursulfatés.

Zusammenfassung

Mörtelprobenkörper, die von fünf Sulfathüttenzementen hergestellt waren, wurden mit Lösungen verschiedener Salze und Säuren behandelt, und ihre Leistung, die durch Tönungmessungen, Gewichtsverlust und Aussehen bestimmt wurde, wurde mit der Leistung anderer Probenkörper, die aus Hochofenzement, Portlandpozzuolanzement, sulfatbeständigem Portlandzement und Tonerdezement hergestellt wurden, verglichen. Die Prüflösungen wurden aus Magnesiumsulfat, Natriumsulfat, Zucker, Milchsäure, Schwefelsäure, Zitronensäure und Essigsäure hergestellt. Eine gesättigte Lösung von CO_2 in Wasser wurde auch angewandet. Die verschiedenen Zementmaterialien zeigen verschiedenen Widerstand gegen den Angriff solcher Lösungen. Die Spezialzemente zeigten in vielen Fällen denselben Widerstand wie die Sulfathüttenzemente, und einige von diesen zeigten sogar einen besseren Widerstand in manchen Lösungen.

Introduction

There are a number of exposure conditions where concrete made with regular portland cement does not give satisfactory performance. Sea water, sulfate ground water, carbonated water, and water containing organic acids are detrimental to concrete. In dairies and wineries, either special coatings to protect the surface from attack, or special cements which offer greater resistance, are in use. Sulfate-resistant cement, pozzolanic cement, portland blast-furnace slag cement, high-alumina cement, and supersulfate cement are examples of the cements used. Various reports have been made relative to the use and durability of each of these types of cements, but no direct comparisons of all of them have been made. In order to make such comparisons, physical and chemical tests were made on a number of these cements. Since supersulfate cements are relatively unknown in the United States, although extensively used in Europe, several were included in order to obtain a range of properties of such cements. Mortar specimens made with the cements were exposed to solutions of various salts and acids, and the performance of the cements was judged by sonic measurements, weight loss, and change in appearance.

Materials

Five supersulfate cements were obtained for this study, four being commercial brands from Europe, and one an experimental cement produced in the United States. All possible precautions were taken to protect the cements during shipment. The cements used for comparison were a blend of 25 percent calcined shale and 75 percent Type I

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the National Bureau of Standards, Washington, D.C.

cement, a portland blast-furnace slag cement, a high-alumina cement, and a Type V sulfate-resistant cement. The chemical analyses are shown in table 1. The physical tests usually required in Federal and ASTM specifications for portland cement were also made; these test results are shown in table 2.

Mortar specimens made of each of the above cements and graded Ottawa sand were exposed for chemical attack in solutions prepared from reagent or U.S.P.-grade chemicals. The following solutions were used:

magnesium sulfate	20g/l
sodium sulfate	20g/l
sugar solution	170g/l
lactic acid	45g/l
CO_2 solution, saturated	
sulfuric acid (Sp. Gr. 1.84)	10g/l
sulfuric acid (Sp. Gr. 1.84)	20g/l
citric acid	10g/l
acetic acid (glacial)	10g/l
saturated magnesium sulfate	------

The CO_2 solution was kept saturated by introducing a slow stream of CO_2 into the storage container from a tank of compressed CO_2 gas.

TABLE 1. *Chemical analyses*

(percents)

204, 206, 208, 210, 212 Supersulfate cements, 213 Portland-pozzolan cement, 214 Portland blast-furnace slag cement, 215 High-alumina cement, 216 Type V cement

Cement No.	204	206	208	210	212	213	214	215	216
Ignition loss	1.33	1.59	0.89	0.94	0.82	2.77	1.53	0.82	0.87
Insoluble residue	(a)	(a)	(a)	(a)	(a)	(a)	(a)	(a)	.14
SO_3	8.72	7.77	7.27	7.81	6.40	1.44	2.69	.20	1.75
MgO	5.78	5.92	3.83	3.63	4.45	1.85	3.31	1.10	.96
SiO_2	24.64	24.96	27.80	26.10	29.99	28.89	26.17	11.34	22.82
Al_2O_3	14.70	14.54	13.55	12.75	10.40	5.80	8.09	38.26	4.12
Fe_2O_3	(a)	(a)	(a)	(a)	(a)	4.06	2.13	6.69	4.14
CaO	41.80	42.02	43.60	45.92	46.27	54.10	54.92	35.25	64.22
Na_2O	.64	.68	.23	.26	.14	.30	.08	.09	(a)
K_2O	.42	.41	.81	.49	.48	.92	.20	.11	(a)
S	1.13	1.12	.88	.98	1.33	.004	.74	.21	(a)
Mn_2O_3	.92	1.03	.43	.90	.38	.00	.69	.00	(a)
FeO	.38	.41	.80	.49	.50	(a)	(a)	(a)	(a)
C_3S	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	49.5
C_3A	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)	3.9

[a] Not determined.
[b] Not calculated.

TABLE 2. *Physical tests*

Cement No.	Normal consistency	Initial set	Final set	Specific gravity	Air entrainment	Air permeability fineness	Passing No. 325	Autoclave expansion	Compressive strength, 2-in. cubes						
									1 day	3 days	7 days	28 days	1 yr		
													Water storage	95 percent air [c]	50 percent air [d]
	Percent	*hr/min*	*hr/min*		*Percent*	*cm²/g*	*Percent*	*Percent*	*psi*	*psi*	*psi*	*psi*	*psi*	*psi*	*psi*
204	25.6	2:45	4:55	2.94	7.2	3,420	86.4	0.01	1,140	2,640	3,380	4,620	6,020	5,910	3,380
206	25.4	3:45	6:25	2.93	7.3	3,400	87.1	−.02	1,160	2,140	2,710	3,270	4,370	4,530	2,760
208	25.4	5:30	8:40	2.92	7.2	2,930	88.5	.06	700	2,590	4,370	6,420	7,980	8,350	4,780
210	23.0	5:15	8:15	2.97	7.0	4,030	93.7	−.00	1,100	3,070	6,510	8,430	10,220	10,390	8,540
212	(a)	1:55	4:40	2.95	5.8	6,750	99.8	.17	2,040	3,860	4,630	6,180	7,980	8,280	6,600
213	29.6	3:10	5:35	3.05	8.3	4,690	90.6	.11	840	2,120	3,330	5,740	7,380	7,420	5,620
214	27.4	4:05	6:15	3.03	8.2	3,980	98.7	.02	1,330	2,410	3,750	7,160	8,460	8,320	6,630
215	24.4	(b)	(b)	3.11	6.8	2,930	80.9	−.04	4,660	5,430	5,620	6,130	6,170	6,020	5,990
216	24.2	4:25	6.10	3.18	(e)	3,040	98.8	.01	990	2,040	3,250	5,070	6,440	7,670	5,470

[a] Could not obtain normal consistency, as the cement had a tendency to flash set.
[b] Did not reach initial set in 10 hr.
[c] One yr in moist cabinet, air at 95 percent rh, never in water.
[d] Six days in water, 49 wk laboratory air at 50 percent rh, then 2 wk in water.
[e] Not obtained.

Test Procedure

Test specimens were 40 x 40 x 160-mm prisms made with one part of cement and 2.75 parts of graded Ottawa silica sand in accordance with Method 2701 (May 1, 1957) of Federal Test Method Standard No. 158. The specimens were removed from the molds after 24 hr in the moist cabinet, then stored in water for 6 days. Control specimens remained in water storage thereafter. Three test specimens of each of the nine cements were made on the same day for storage in one of the solutions. Since exposure to air during setting causes a friable, dusty surface layer on specimens containing supersulfate cements, molds containing these specimens were placed in the moist cabinet in plastic bags, reducing the friable layer to a thin film. At 7 days, the specimens were weighed, and the fundamental transverse frequency determined (Method 4101 of Federal Test Method Standard No. 158). Specimens were than placed in glass jars, supported so that all sides were exposed, and covered with approximately 6 liters of solution; there was no agitation of the solutions during the test period.

Measurements of frequency and weight were made at 14, 21, and 28 days after the specimens were fabricated and each 28 days thereafter, and the appearance of the specimens was recorded at each measurement. The test specimens were placed in a fresh solution after each of these intervals. The acid solutions were probably neutralized before the end of each exposure period, so that the number of cycles of attack is more important than the age of the specimens. Specimens made with all nine cements were stored in the same jar of solution except the acetic acid, where an excessive black sediment from the high-alumina cement coated all the other specimens and obscured the identification number. Consequently these specimens were stored separately.

For the specimens exposed to saturated magnesium sulfate solution, a different schedule was adopted. Each 7 days a 3-day soaking period was followed by a 4-day drying period in laboratory air at approximately 73 °F. and 50 percent rh, measurements being made after drying. After the specimens were 28 days old, the soaking and drying periods were continued, but measurements were made only at 28-day intervals.

Test Results

The test results, in the form of average frequency measurements are recorded in table 3 which also shows the final average weight changes. Part of the test results are also portrayed in figure 1, which shows the relationship between fundamental frequency and cycles of exposure for the specimens in some of the solutions, as well as the frequency of control specimens at various ages.

Figure 2 shows the condition of the specimens at the end of the test in citric acid, sulfuric acid (20g/l), and saturated magnesium sulfate solutions. The following solutions appeared to have relatively minor effects on the specimens: sodium sulfate, magnesium sulfate (10g/l), sugar, and saturated CO_2 solution. Specimens containing the four commercial supersulfate cements showed minor loss of material from the corners and edges in the magnesium sulfate solution and slight surface pitting in the sugar solution. Increases in weight were not significant, and were generally less than the increase in weight of corresponding control specimens. The rate of increase of strength, as indicated by the fundamental frequency, was slower for specimens stored in the sugar solution than for the control specimens, those containing calcined shale indicating very little increase after 28 days, although the control specimens gained rapidly. In the sodium sulfate solution, specimens made with portland blast-furnace slag, portland-pozzolan, and Type V cements had higher rates of increase than the control specimens for the first four months, then leveled off at higher frequencies than the controls.

The specimens stored in sulfuric acid (10g/l) appeared to resist attack for four to six cycles, then showed progressive loss of strength. The high-alumina-cement specimens were badly eroded on the corners, edges, and faces and lost weight, although coated with sulfates. All of the other specimens increased slightly in weight due to sulfate deposits, although there was some loss of material from the edges and corners.

Lactic acid, acetic acid, citric acid, and sulfuric acid (20g/l) caused immediate and severe loss of strength in all specimens containing supersulfate and high-alumina cements. Specimens made with portland blast-furnace slag, portland-pozzolan and Type V cements showed a normal rate of increase of frequency for three cycles of exposure to citric acid and sulfuric acid (20g/l), then deteriorated slowly. In the lactic acid solu-

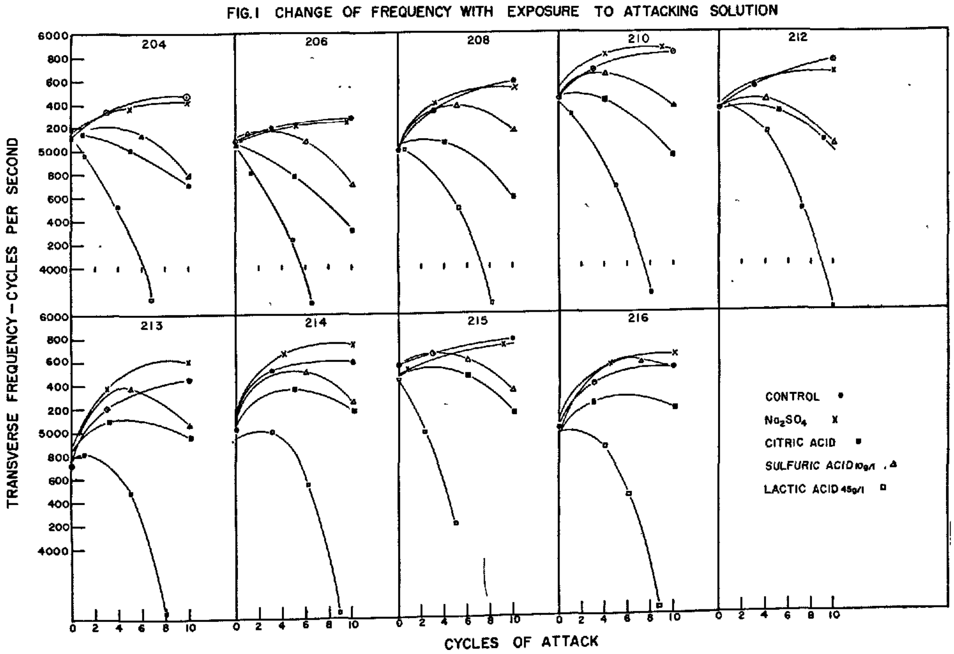

Figure 1. *Change of frequency with exposure to attacking solution.*

TABLE 3. *Transverse frequency of specimens stored in—*

Cycles per second

Cement No.	Age, days											Wt. change[a] g
	Initial	14	21	28	56	84	112	140	168	196	224	
$MgSO_4$ (20 g/l)												
204	5,070	5,150	5,180	5,190	5,200	5,210	5,200	5,200	5,210	5,210	5,200	+3
206	5,050	5,100	5,150	5,150	5,190	5,230	5,230	5,210	5,200	5,220	5,210	+3
208	4,980	5.250	5,320	5,350	5,440	5,460	5,490	5,490	5,490	5,490	5,480	+4
210	5,400	5,600	5,640	5,660	5,710	5,720	5,720	5,730	5,720	5,710	5,700	+2
212	5,390	5,480	5,500	5,520	5,580	5,620	5,640	5,660	5,660	5,680	5,690	+5
213	4,740	5,150	5,260	5,330	5,450	5,520	5,510	5,520	5,520	5,540	5,550	+7
214	5,020	5,430	5,530	5,580	5,680	5,720	5,730	5,750	5,750	5,750	5,750	+8
215	5,430	5,570	5,640	5,680	5,740	5,830	5,840	5,890	5,900	5,910	5,910	+6
216	4,930	5,290	5,420	5,480	5,580	5,650	5,660	5,690	5,690	5.700	5,700	+6
(Na_2SO_4 (20 g/l)												
204	5,130	5,250	5,280	5,300	5,350	5,360	5,400	5,430	5,430	5,430	5,440	+3
206	5,050	5,110	5,130	5,130	5,200	5,200	5,220	5,240	5,250	5,260	5,270	+3
208	4,980	5,210	5,300	5,330	5,430	5,470	5,500	5,510	5,540	5,540	5,540	+3
210	5,500	5,650	5,700	5,740	5,800	5,820	5,840	5,850	5,870	5,870	5,860	+3
212	5,370	5,440	5,510	5,510	5,570	5,590	5,600	5,620	5,650	5,650	5,650	+3
213	4,830	5,170	5,290	5,360	5,490	5,560	5,560	5,600	5,600	5,610	5,600	+6
214	5,010	5,400	5,480	5,590	5,680	5,730	5,750	5,750	5,750	5,750	5,760	+5
215	5,480	5,510	5,530	5,560	5,610	5,650	5,670	5,690	5,720	5,720	5,730	+5
216	4,970	5,310	5,420	5,470	5,610	5,660	5,670	5,700	5,700	5,710	5,730	+9
Sugar Solution (170 g/l)												
204	5,110	5,210	5,230	5,250	5,290	5,280	5,310	5,310	5,320	5,300	5,270	−0
206	5,050	5,110	5,140	5,150	5,170	5,170	5,180	5,180	5,180	5,150	5,110	−2
208	4,980	5,180	5,220	5,230	5,300	5,320	5,330	5,340	5,340	5,340	5,300	−8
210	5,430	5,520	5,540	5,570	5,610	5,620	5,640	5,640	5,640	5,650	5,630	−6
212	5,350	5,450	5,450	5,490	5,560	5,570	5,610	5,640	5,630	5,630	5,630	+4
213	4,770	5,000	5,040	5,100	5,190	5,140	5,120	5,130	5,160	5,150	5,140	+7
214	5,010	5,270	5,340	5,400	5,470	5,470	5,470	5,500	5,510	5,520	5,520	+5
215	5,530	5,550	5,550	5,560	5,580	5,580	5,580	5,600	5,610	5,620	5,650	+5
216	5,000	5,170	5,210	5,250	5,270	5,270	5,270	5,300	5,300	5,310	5,340	+3
Lactic Acid (45 g/l)												
204	5,140	4,960	4,810	4,800	4,520	4,340	3,860	3,600	3,320	3,040	2,740	−38
206	5,030	4,800	4,660	4,650	4,400	4,240	3,820	3,560	3,310	3,050	2,780	−37
208	5,010	4,940	4,860	4,850	4,630	4,500	4,200	3,940	3,670	3,380	3,100	−36
210	5,400	5,290	5,160	5,160	4,860	4,660	4,320	4,030	3,730	3,410	3,100	−35
212	5,380	5,310	5,220	5,220	5,120	5,000	4,730	4,460	4,100	3,930	3,620	−23
213	4,730	4,820	4,680	4,730	4,610	4,390	4,060	3,720	3,370	3,050	2,730	−29
214	4,960	5,000	4,950	5,000	4,960	4,780	4,530	4,160	3,760	3,340	---------	−28
215	5,450	5,220	4,990	5,070	4,540	4,180	---------	---------	---------	---------	---------	−81
216	4,950	4,980	4,870	4,920	4,830	4,670	4,430	4,060	3,700	3,310	---------	−34
CO_2 Saturated												
204	5,110	5,100	5,150	5,150	5,170	5,180	5,200	5,200	5,200	5,220	5,160	+2
206	5,070	5,010	5,050	5,050	5,080	5,080	5,100	5,100	5,100	5,090	5,030	0
208	5,000	5,040	5,110	5,140	5,210	5,230	5,240	5,260	5,270	5,260	5,210	0
210	5,400	5,490	5,540	5,580	5,620	5,640	5,660	5,670	5,680	5,680	5,680	0
212	5,360	5,410	5,460	5,470	5,490	5,500	5,500	5,520	5,510	5,510	5,460	+1
213	4,730	4,970	5,060	5,140	5,280	5,280	5,300	5,280	5,280	5,270	5,230	+1
214	4,990	5,290	5,410	5,450	5,540	5,540	5,540	5,530	5,530	5,530	5,480	+1
215	5,430	5,470	5,540	5,590	5,690	5,720	5,760	5,770	5,780	5,790	5,800	+4
216	4,960	5,210	5,320	5,380	5,480	5,490	5,500	5,490	5,490	5,480	5,430	+1
H_2SO_4 (10 g/l)												
204	5,100	5,180	5,170	5,190	5,200	5,160	5,160	5,050	4,970	4,870	4,790	+4
206	5,090	5,150	5,150	5,170	5,170	5,120	5,000	5,000	4,930	4,830	4,720	+6
208	5,000	5,260	5,320	5,360	5,410	5,360	5,350	5,320	5,280	5,240	5,160	+7
210	5,410	5,580	5,580	5,620	5,630	5,590	5,570	5,540	5,470	5,440	5,360	+8
212	5,340	5,400	5,390	5,440	5,410	5,360	5,320	5,270	5,170	5,110	5,040	+24
213	4,780	5,130	5,220	5,330	5,400	5,380	5,350	5,300	5,200	5,150	5,060	+24
214	4,960	5,300	5,430	5,500	5,570	5,550	5,530	5,470	5,410	5,340	5,270	+21
215	5,550	5,620	5,620	5,660	5,680	5,650	5,610	5,600	5,340	5,400	5,320	−22
216	4,960	5,290	5,380	5,430	5,560	5,590	5,600	5,580	5,550	5,550	5,500	+13

[a] Change in weight at 224 days, or at last age for which frequency is shown.

TABLE 3. *Transverse frequency of specimens stored in*—Continued

Cycles per second

Cement No.	Age, days											Wt. change[a] *g*
	Initial	14	21	28	56	84	112	140	168	196	224	
						H_2SO_4 (20 gl/)						
204	5, 150	5, 100	4, 970	4, 990	4, 900	4, 870	4, 720	4, 620	4, 470	4, 270	----------	+14
206	5, 110	5, 040	4, 910	4, 930	4, 800	4, 690	4, 540	4, 370	4, 170	3, 960	----------	+20
208	5, 053	5, 200	5, 160	5, 190	5, 060	4, 950	4, 820	4, 650	4, 460	4, 260	----------	+21
210 [b]	5, 470	5, 530	5, 340	5, 330	4, 950	[b] 5, 250	5, 000	4, 800	4, 420	----------	----------	−60
212 [b]	5, 380	5, 300	5, 010	5, 000	3, 630	[b] 5, 030	4, 660	4, 550	4, 290	----------	----------	−99
213	4, 830	5, 060	5, 180	5, 260	5, 200	5, 030	4, 900	4, 740	4, 550	----------	----------	−45
214	4, 990	5, 280	5, 360	5, 440	5, 330	5, 160	4, 990	4, 930	4, 750	4, 530	----------	−10
215	5, 520	5, 530	5, 340	5, 350	5, 140	4, 890	4, 650	4, 450	4, 220	4, 060	----------	−11
216	4, 980	5, 320	5, 310	5, 390	5, 410	5, 360	5, 230	5, 120	5, 020	4, 800	----------	−214
						Citric Acid (10 g/l)						
204	5, 170	5, 130	5, 040	5, 040	5, 050	5, 010	4, 950	4, 860	4, 820	4, 780	4, 700	−13
206	5, 110	5, 000	4, 920	4, 890	4, 880	4, 780	4, 680	4, 580	4, 490	4, 420	4, 320	−15
208	5, 040	5, 110	5, 060	5, 060	5, 090	4, 980	4, 930	4, 840	4, 750	4, 690	4, 590	−16
210	5, 430	5, 500	5, 430	5, 430	5, 430	5, 350	5, 260	5, 180	5, 100	5, 040	4, 950	− 16
212	5, 310	5, 390	5, 320	5, 330	5, 360	5, 320	5, 250	5, 170	5, 110	5, 060	5, 990	−14
213	4, 790	4, 990	5, 020	5, 080	5, 170	5, 080	5, 080	5, 060	5, 030	5, 020	4. 950	−105
214	4, 990	5, 220	5, 270	5, 320	5, 370	5, 350	5, 350	5, 240	5, 220	5, 220	5, 200	−60
215	5, 470	5, 510	5, 400	5, 480	5, 550	5, 520	5, 450	5, 390	5, 300	5, 230	5, 130	−45
216	4, 920	5, 140	5, 190	5, 220	5, 290	5, 300	5, 250	5, 220	5, 210	5, 090	5, 170	−50

[a] Change in weight at 224 days, or at last age for which frequency is shown.

[b] *Soft surface peeled off leaving hard surface.*

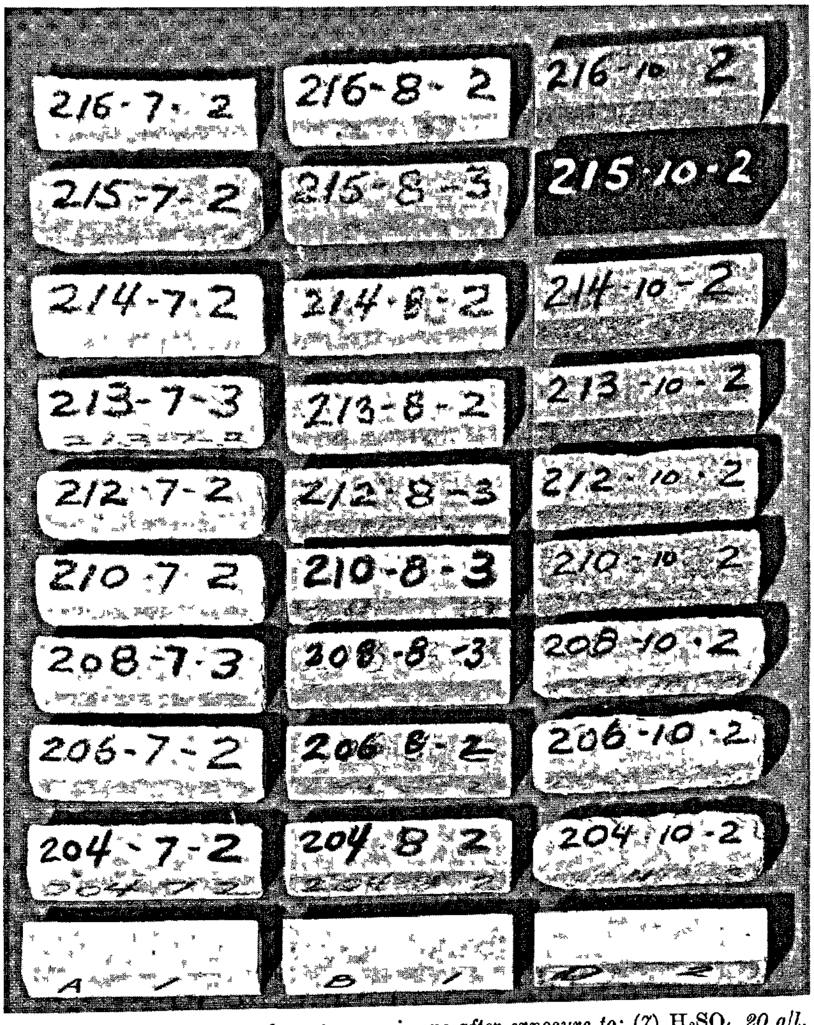

FIGURE 2. *Appearance of mortar specimens after exposure to:* (*7*) H_2SO_4, *20 g/l,* (*8*) *citric acid,* (*10*) $MgSO_4$, *wetting and drying.*

tion, the high-alumina-cement specimens were so badly eroded that they were removed after six cycles, but the other specimens showed only slight surface granulation accompanied by a considerable weight loss due to leaching. Specimens stored in acetic acid lost some weight, but showed no surface damage except surface granulation of specimens containing high-alumina cement. The citric acid caused moderate weight loss from all specimens, moderate coatings of calcium citrate on specimens made with supersulfate cements, and heavy coatings for the other specimens, except those containing high-alumina cement, which were not coated, but had a soft, spongy surface.

In the sulfuric acid solution (20g/l), specimens containing three of the supersulfate cements increased slightly in weight and were not eroded but the soft surfaces and the decrease in frequency indicated extensive loss of strength. The other specimens exhibited weight loss and surface damage. Spongy surface coatings made determination of the fundamental frequencies difficult. However, when the surface coatings were removed, clear patterns were obtained on the oscilloscope which indicated that the damage was limited to the exposed surface.

The frequency is dependent on the size of a specimen as well as the weight, strength, and shape. For most of the specimens and for most solutions, changes in size were so small that they could be disregarded. There were appreciable changes in the dimensions of the special cements in citric acid, and sulfuric acid (20g/l), and as smaller specimens should have higher frequencies, these specimens deteriorated more rapidly than indicated by the frequency change. Supersulfate cements in these solutions remained about the same dimensions, but became soft and granular.

In saturated magnesium sulfate solution with alternate wetting and drying, specimens containing three of the supersulfate cements deteriorated so rapidly that they had to be removed after three cycles. The other specimens showed a slight increase in frequency, those containing the high-alumina cement being closest to the control specimens. There was some pitting of the surfaces of specimens made with the other two supersulfate cements, and all specimens except those containing the high-alumina cement showed some loss in weight.

Discussion

In part because their resistance is superior to that of regular portland cement, supersulfate cements are used in situations where concretes are exposed to sulfate waters and where they are in contact with gypsum deposits. The principal constituents of these cements are blast-furnace slag, portland cement, and enough gypsum for a SO_3 content of 7 to 9 percent. The reaction of the granulated slag with water to form a hardened mass is slow unless accelerated by a small amount of lime, which is usually obtained from portland-cement clinker added to the cement in manufacture. The calcium sulfate also acts as an accelerator, as in portland cement when added in excess of the amount needed to retard the setting. Due to the low concentration of CaO and the high concentration of SO_4, the high form of calcium sulfoaluminate ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) is formed in supersulfate cement, to which the cement owes part of its strength and superior resistance [1].[1] In this form the alumina is not available to react with sulfate waters with resulting distress to the concrete. In portland cement the low form of calcium sulfoaluminate ($3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$) is formed during hardening, which can then further react with sulfate solutions.

In addition, supersulfate cement does not form large amounts of $Ca(OH)_2$ during hardening, as does portland cement by hydrolysis of di- and tricalcium silicate. Thus one of the claimed advantages for supersulfate cement [2] is that there is no $Ca(OH)_2$ free in the hardened concrete and available for leaching, with consequent increase of porosity of the concrete. However, it has not been proved [3] that leaching of the $Ca(OH)_2$ formed in hydrated portland cement is a factor in the sulfate attack of concrete, since cements of high tricalcium-silicate content may be sulfate-resistant if the tricalcium-aluminate content is low.

The hydrous calcium silicates of portland cement, approximately of the composition $3CaO \cdot 2SiO_2 \cdot nH_2O$, are relatively insoluble in comparison with sulfates and sulfoaluminates. The presence of the latter in hardened concrete would permit increased penetration and more rapid attack by acid solutions than would the calcium silicates in portland cement concrete. This factor may be responsible in part for the observed lower resistance of supersulfate cements to acid solutions.

Summary and Conclusions

Specimens of all of the cements tested showed good resistance to sodium sulfate, CO_2, and sugar solutions, except that the supersulfate cements underwent surface pitting in the sugar solution. Supersulfate cements did not resist the attack of magnesium sulfate solutions as well as did the other cements. In some of the acid solutions, particularly acetic and sulfuric (10g/l), the speci-

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[1] Figures in brackets indicate the literature references at the end of this paper.

mens of supersulfate cements remained the same size and showed only a slight loss of weight in the saturated condition. However the rapid decrease in frequency and the formation of a soft, granular surface indicated extensive damage to the internal structure of the mortar specimens. The high-alumina cement showed relatively poor resistance to lactic and sulfuric acid solutions. It is concluded that although the supersulfate cements offer excellent resistance to attack by sodium and calcium sulfates, they do not equal the resistance of the special-purpose cements to attack by magnesium sulfate and some of the acid solutions.

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[1] Léon Blondiau and Yvan Blondiau, Action du sulfate de calcium sur la prise des ciments métallurgiques sursulfatés et des ciments de haut fourneau. Revu. des matériaux construct. et trav. publ., No. 453, p. 165.

[2] Léon Blondiau, Les ciments métallurgiques sursulfatés et applications dans les travaux exposés aux agents agressifs. Quatorzième Congrès de Chimie Industrielle, Paris, October 21–27, 1934, p. 14.

[3] F. R. McMillan, T. E. Stanton, I. L. Tyler, and W. C. Hansen, Long-time study of cement performance in concrete. Chapter 5, Concrete exposed to sulfate soils, Special Publication of the Am. Concrete Inst. 1949; Research Labs., Portland Cement Assoc. Bull. No. 30.

Discussion

T. D. Robson

The testing of different cement mortars in even the most highly concentrated sulfate solutions is obviously justified as a practical procedure, since such concentrations can often be encountered by concretes under service conditions.

On the other hand, no hydraulic cement is claimed to be proof against moderately strong solutions of acids, and consequently there seems little point in testing the various cements at acid concentrations much stronger than those for which any of the cements could be recommended in practice.

Recommended acidity limits are usually about *p*H 4.0 for high-alumina cements and *p*H 3.0 to 3.5 for supersulfated cements (although concretes made with the latter cements can give good service in sulfuric acid of *p*H slightly below 1.0). Claims made for the superior acid resistance of both these types of cement apply only within some limits such as the above (which cover a wide range of industrial effluents, products of combustion, acid grounds, etc.). Once the restricted limits of acidity are grossly exceeded, all hydraulic cements are attacked to a degree which normally precludes their continued use, and a comparison of their resistance to stronger acids is rendered more irrelevant by the fact that the relative "order of merit" can change more than once with increasing acid concentration.

When specimens made from different types of cement are all immersed together in sulfate solution, there is always the possibility of secondary reactions which can, in effect, alter the test conditions to the detriment of one or more of the cements. In the investigation under discussion there is no indication of any such complication but the storage of different-type specimens in a common solution should probably be avoided.

Discussion

E. Burke

Tests on supersulfated cement have been carried out in our laboratories over the last 8 yr and the author's results can be confirmed where they overlap. This is particularly the case with solutions of magnesium sulfate in which its performance was inferior to that of sulfate-resisting portland cement of the type used by the authors. It was found that up to about 3 or 4 yr the supersulfated cement was apparently superior but that it deteriorated rapidly beyond this age (fig. 1). A similar effect was noticed in triple-strength sea water (fig. 2). It should be noted, however, that our tests were made on standard concretes totally immersed in the solutions, which were renewed at monthly intervals, as against the mortar specimens used by the authors. Quality of the concrete was judged by compressive strength tests.

In the case of sodium sulfate solutions no significant difference was observed in the resistance of concrete made with these two types of cement at 8 yr but the strength of the supersulfated cement was decreasing rapidly whereas the type V was steady (fig. 3).

For sulfuric acid solutions of 0.5 percent or greater strengths no difference was found in the resistance of concretes made with Type I, Type V, aluminous cement, or supersulfated cement. They all deteriorated rapidly. In these cases the solutions were maintained at full strength as it was found that, especially at early periods, the solutions were rapidly neutralized. It was found that if the solutions were not maintained in strength false results were obtained and it is suspected that some of the published results on the resistance of cements to acids suffer from this error.

There is a possibility that supersulfated cement has a superior resistance to weak acid solutions in the range of *p*H 2.5 and upwards. There is, however, a marked lack of experimental data in this range and it would be useful if the gap in our knowledge could be filled.

In the past, several workers have placed reliance on the expansion of mortar bars in sulfate solutions to show their resistance to attack. Although this can be quite a useful indication in the case of cements of the portland type, it is not of any value for supersulfated cements which can break up and disintegrate without any appreciable longitudinal expansion. This was pointed out by Dr. Lea some years ago.[1] We have found that the only really

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[1] F. M. Lea, The Chemistry of Cement and Concrete, pp. 302, 541 (1956).

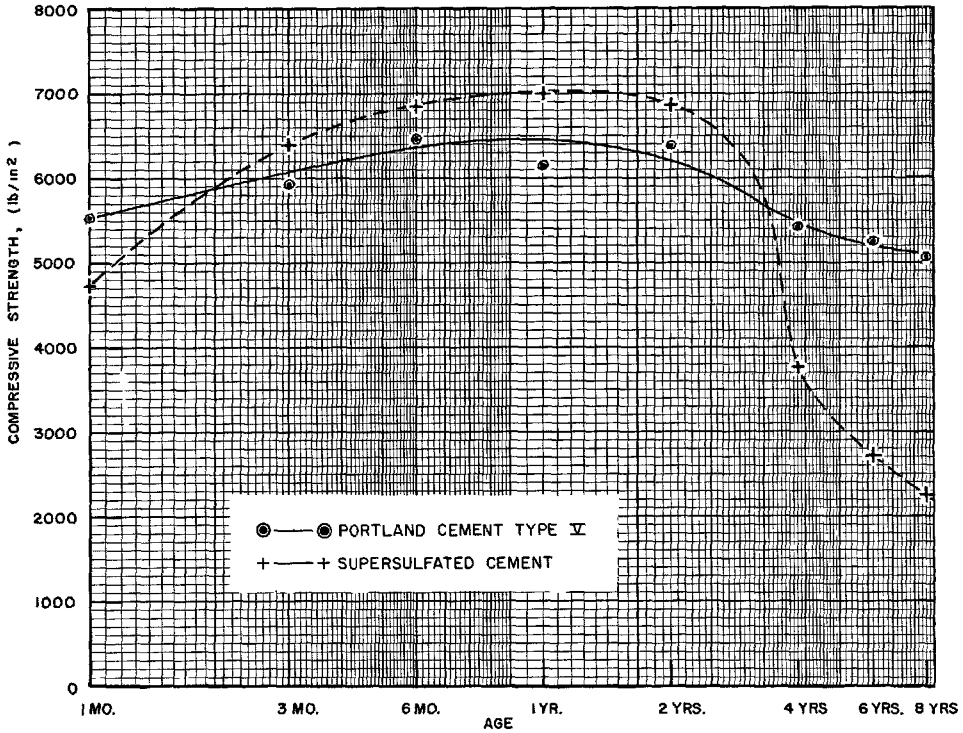

FIGURE 1. *Comparison of portland cement type V and supersulfated cement.*

Compression strength of 4-in. concrete cubes (1:2:4:0.58) stored in $MgSO_4$ solution (1.0% SO_4) after 7 days initial curing in water. Solid line, type V cement; dashed line, supersulfated cement.

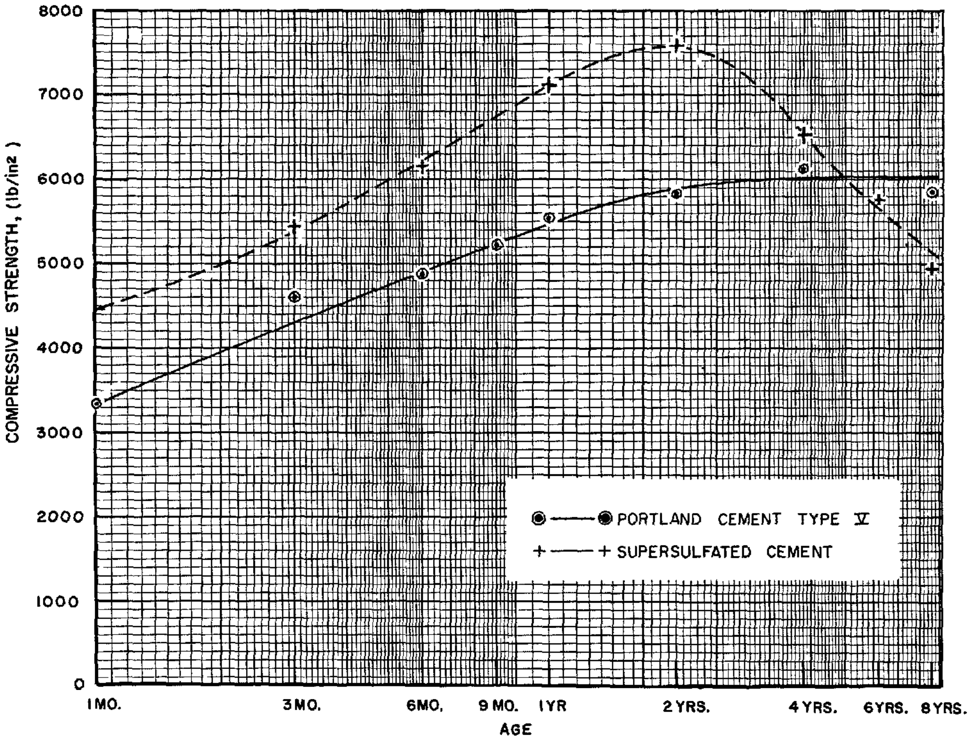

FIGURE 2. *Comparison of portland cement type V and supersulfated cement.*

Compression strength of 4-in. concrete cubes (1:2:4:0.58) stored in triple-strength sea water after 7 days initial curing in water. Solid line, type V cement; dashed line, supersulfated cement.

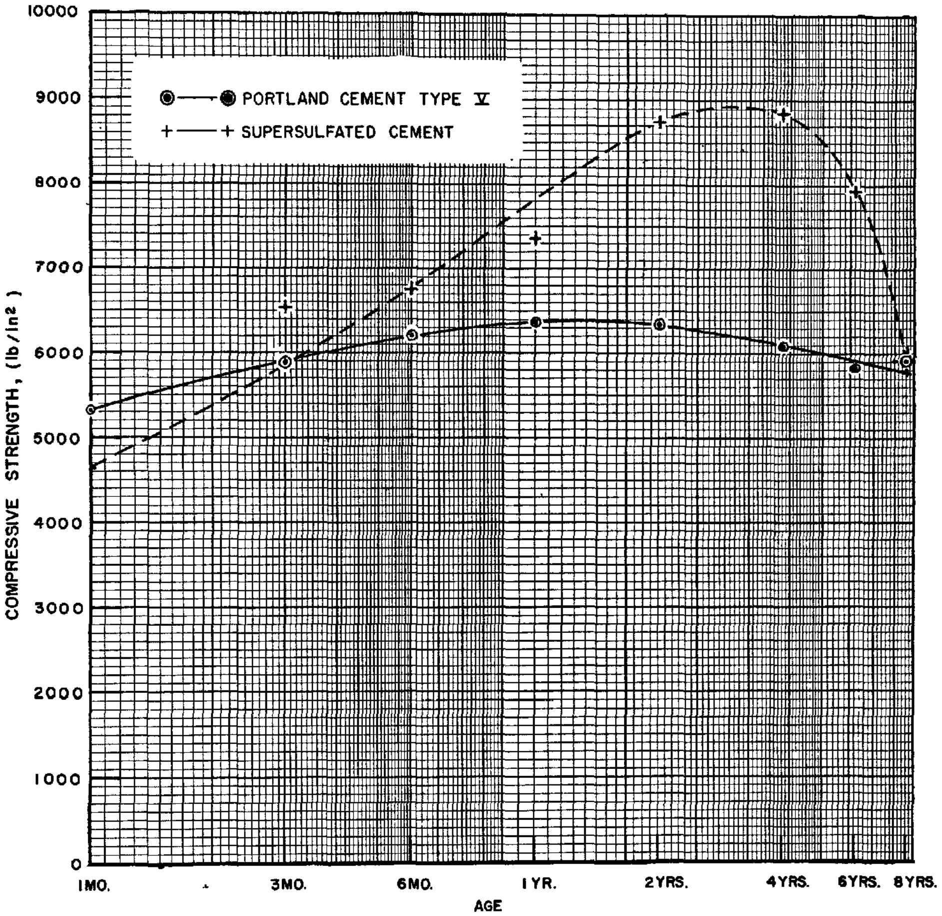

FIGURE 3. *Comparison of portland cement type V and supersulfated cement.*

Compression strength of 4-in. concrete cubes (1:2:4:0.58) stored in $NaSO_4$ solution (1.0% SO_4) after 7 days initial curing in water. Solid line, type V cement; dashed line, supersulfated cement.

reliable test, particularly when comparing different types of cement, is one that uses the compressive strength to judge the quality of the concrete.

The resistance of sulfate-resisting portland cement to magnesium sulfate solutions is surprising. One would expect that the presence of magnesium would lead to a much greater rate of attack than is the case. It is possible that the formation of magnesium hydroxide fills the capillaries in the mass, thus increasing the resistance to penetration of the aggressive solution.

Universal experience has shown that the greatest safeguard against aggressive attack is a dense concrete. A further safeguard is a resistant cement, particularly in the more aggressive solutions. In this connection I feel that the application of Powers' work will be of the very greatest importance and it is likely that the solution to many of the problems of aggressive attack will be found in his paper to this Symposium.

Discussion

Julie Chi-Sun Yang

In this discussion, I would like to describe some observations on the chemical resistance of supersulfated slag cement which resulted from our work at Johns-Manville Research Center on these cements.

Supersulfated slag cements are widely known for their chemical stability in aggressive media, especially sulfate-bearing environments. When these slag cements are hydrated at room temperature, ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$) is found to be the main contributor to the strength and the chemical resistance, as Messrs. Evans, Blaine, and Worksman indicated. However, it was found that ettringite was not stable in dilute acid solutions; it decomposed to form gypsum in large quantities, and great volume expansion accompanied the decomposition.

In the paper presented by Mr. Evans and others, the authors mentioned that all the specimens used for chemical resistance tests were cured in the moist cabinet for 24 hr and then were stored in water for 6 days, presumably at room temperature.

Up to the present time, our knowledge of the hydration of slag cement at elevated temperatures and pressures is not as far advanced as that which we have of portland cement. It is believed that the chemical stability of supersulfated slag cement can be further improved with regard to the action of dilute mineral acids and organic acids when the setting of the slag cement structures is controlled carefully. Following an initial setting period at room temperature, the process of autoclaving at elevated temperatures and pressures is recommended.

We found that these supersulfated slag cement structures, cured at room temperature under water or at highly humid conditions for a few hours to about one day and then autoclaved under saturated steam pressure up to 200 psi for 8 to 24 hr, have desirable chemical resistance.

Two commercially available supersulfated slag cements purchased from European countries were investigated (Frodingham cement from England and Sealithor cement from Belgium). They both consist of about: 89–90 percent glassy slag, 7–15 percent calcium sulfate as anhydrite, and up to 5 percent alkali activator. The major components are:

SiO_2	25 to 30 percent
Al_2O_3	11 to 15 percent
CaO	40 to 45 percent
MgO	up to 5 percent
SO_3	approximately 6 to 9 percent

From X-ray diffraction patterns and microscopic examinations, it was found that all the ettringite contributing to the early strength is decomposed, and from this, anhydrite, $CaSO_4$ forms. In the absence of silica, the remaining amorphous lime and alumina probably will interreact to form calcium aluminate hydrate $3CaO \cdot Al_2O_3 \cdot 6H_2O$. However, with the available silica from the disintegration process of the glass slag which is in a highly reactive form, hydrogarnet-like phases are formed with hydrated calcium silicates and calcium aluminates.

Hydrogarnets such as $3CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, $3CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 4H_2O$ and their solid solution series, including the corresponding partially iron-substituted compounds, are identified by their characteristic X-ray diffraction patterns.

Members of the hydrogarnet series are generally unreactive to sulfate solutions; our laboratory results also indicate that they are chemically stable to organic acids and dilute mineral acids. The details of the stability study of the hydrogarnets will be published in a separate paper.

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Paper VI–S4. Chemical Resistivities of Various Types of Cements*

Renichi Kondo

Synopsis

The chemical resistivity of cement should be very important especially in Japan, where there is a long coastline and consequently the concrete structures are frequently in contact with sea water. The chemical attack by 2 percent $MgSO_4$ solution on various types of cement mortar, where the cement sand ratio was 1:4, was examined with results as follows:

1. Sufficient durabilities were obtained with alumina cement, sulfate-resistant, and low-heat portland cements.
2. The durabilities of portland blast-furnace cement and portland silica cement were not always as high as those of normal and high-early-strength portland cements; therefore, special care should be taken in manufacturing the former two.
3. The durability of each portland, portland blast-furnace, and portland silica cement might be raised by increasing the addition of calcium sulfate nearly up to 2–4 percent as SO_3.
4. In the specimens containing portland blast-furnace cement, the external portion was severely cracked because of excessive expansion, while the internal part was intact, more stable than in the case of portland cement.
5. In the altered external layer, many needle-shaped gypsum crystals were found with ettringite.
6. In order to improve the resistivity of portland blast-furnace cement, it seemed desirable either to raise the amount of gypsum regardless of its modification, or to increase the slag content up to about 60 percent, or to grind the slag more coarsely than normal cement especially when the former was contained only to the extent of about 30 percent.
7. Though the external part of the specimens containing sulfated slag cement was finely cracked, the internal part remained entirely unattacked.

Next, the resistivity of hardened cement against neutralization is important, especially with the sulfated slag cement, because neutralization causes not only the risk of rusting of the reinforcing steel but also the reduction of bending strength and surface hardness.

These facts seemed to be related to the decomposition of ettringite by carbonic acid gas in air, with liberation of gypsum. The neutralization could be prevented by coating the surface thinly with water glass.

Résumé

Il faut souligner l'importance de la résistivité chimique du ciment spécialement au Japon où la ligne côtière est si longue et où les constructions en béton se trouvent par conséquent très souvent au contact de l'eau de mer. On a examiné l'attaque chimique d'une solution à 2% de $MgSO_4$ sur différentes sortes de mortier de ciment où le rapport ciment: sable était 1:4. Les résultats sont les suivants:

1. Des durabilités suffisantes furent obtenues avec le ciment alumineux, le ciment portland résistant aux sulfates et le ciment portland à faible échauffement.
2. Les durabilités du ciment portland au laitier de haut fourneau et du ciment portland-silice n'étaient pas toujours aussi hautes que celles des ciments portland normaux et à haute résistance initiale; par conséquent la fabrication des deux premiers devraient faire l'objet d'un soin particulier.
3. La durabilité du ciment portland, du ciment portland au laitier de haut fourneau, et du ciment portland-silice pourrait être élevée par l'addition accrue de sulfate de calcium allant jusqu'à 2–4% comme SO_3.
4. Dans les spécimens contenant du ciment portland au laitier de haut-fourneau on constata que la partie externe présentait des fissures importantes dues à la dilatation excessive, tandis que la partie interne restait fermement étanche, plus stable que dans le cas du ciment portland.
5. Dans la couche externe altérée, on trouva de nombreux cristaux de gypse aciculaires ainsi que de l'ettringite.
6. Afin d'améliorer la résistivité du ciment portland au laitier de haut fourneau, il a semblé désirable soit d'augmenter la quantité de gypse sans se soucier de ses modifications, soit d'augmenter la teneur en laitier jusqu'à un maximum d'environ 60%, soit de moudre le laitier plus grossièrement que le ciment normal spécialement lorsque le premier n'est contenu que dans la proportion de 30% environ.
7. Bien que la partie externe des spécimens contenant du ciment sursulfaté soit finement fissurée, la partie interne restait parfaitement intacte.

La résistivité à la neutralisation du ciment durci est importante, spécialement avec le ciment sursulfaté, parce que la neutralisation cause non seulement le risque de rouille pour l'armature en acier, mais aussi la réduction de la résistance à la flexion et de la dureté de surface.

Ces faits semblaient liés à la décomposition de l'ettringite par le gaz carbonique de l'air, avec libération de gypse. Un fin revêtement de verre soluble à la surface pouvait empêcher la neutralisation.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Tokyo Institute of Technology, Japan.

Zusammenfassung

Der Widerstand des Zements gegen chemische Angriffe ist für Japan ganz besonders wichtig, da dieses Land eine lange Küstenlinie hat, and da daher die Betonkonstruktionen häufig mit Seewasser in Berührung kommen. Der chemische Angriff durch eine 2% $MgSO_4$-Lösung wurde für verschiedene Zementmörteltypen untersucht, bei denen das Zement/Sand Mischungsverhältnis 1:4 betrug, und die folgenden Ergebnisse wurden erzielt:

1. Die Tonerdezemente, die sulfatbeständige Portlandzemente und die Portlandzemente mit niedriger Hydratationswärme sind beständig genug.
2. Die Beständigkeiten der Portlandhochofenzemente und der Portlandquarzzemente sind nicht immer so gross wie die der Normalportlandzemente und der Frühfestigportlandzemente; daher soll man in der Fabrikation der beiden erstgenannten sorgfältiger vorgehen.
3. Man kann vielleicht die Beständigkeit der Portland-, der Portlandhochofen- und der Portlandquarzzemente durch eine Zugabe von Kalziumsulfate, so dass das fertige Material bis zu 2–4% SO_3 enthält, erhöhen.
4. In den Probenkörpern, die Portlandhochofenzemente enthielten, war der Aussenteil mit Rissen durchgezogen da die Ausdehnung zu stark war, während der innere Teil, der immer zusammengedrückt war, stabiler als Portlandzement war.
5. In der veränderten aüsseren Schicht wurden viele nadelförmige Gipskristalle mit Ettringit zusammen gefunden.
6. Für die Verbesserung des Widerstandes des Portlandhochofenzementes ist es wünschenswert, den Gehalt des Gipses zu erhöhen, und es ist von untergeordneter Bedeutung, welche Modifikation hier angewandt wird; man kann auch den Schlackengehalt bis ungefähr 60% erhöhen, oder die Schlacke nicht so fein wie beim Standardzement vermahlen, wenn nicht mehr als 30% Schlacke anwesend ist.
7. Der äussere Teil der sulfatenthaltenden Schlackenzemente war mit feinen Rissen durchgezogen, jedoch ist der Innenteil völlig unversehrt geblieben.

Die Widerstandsfähigkeit des ausgehärteten Zements gegen Neutralisieren ist auch wichtig, besonders beim sulfathaltigen Schlackenzement, weil eine solche Neutralisierung die Gefahr des Rostens der Stahleinlage, und auch eine Verkleinerung der Biegungsfestigkeit und der Oberflächenhärte mit sich bringt.

Das scheint damit zusammenzuhängen, dass der Ettringit schon in Berührung mit Kohlensäure der Luft unter Gipsbildung zersetzt wird. Eine solche Neutralisierung kann doch durch eine Bedeckung der Oberfläche mit einer dünnen Wasserglasschichte verhindert werden.

Introduction

There are many causes affecting the durability of concrete, such as sulfate reaction, alkali-aggregate reaction, neutralization, shrinkage or cracking due to drying, repetition of drying and wetting, frost action, and so on. Among them, chemical resistance to sea water and to neutralization by air, and the cracking due to physical causes seem to be most important, especially in Japan, because of its very long coast line and many islands which demand a vast amount of structures such as embankments and submarine tunnels in contact with sea water, and as there is a necessity to prevent the rusting of reinforcing steel in concrete in order to deal with the risk of earthquake.

On the other hand, alkali-aggregate reaction gives rise to a great problem in the United States of America, but it is not regarded so seriously in Japan, as reactive aggregate is hard to find here.

A study of the chemical resistivity was, therefore, carried out to search for a suitable cement by factorial experiments. Portland blast-furnace cement and sulfated slag cement along with portland cement were chiefly chosen for this study because slag cement is generally regarded as most resistive to chemical action and the slag available for utilization is abundant here.

Resistivity to Sulfate Solutions [1] [1]

The chemical compositions and fineness of cements and the raw materials used in this experiment are shown in table 1.

Lean mortar specimens with cement-sand ratio 1:4, using various types of cement, were immersed in 2 percent $MgSO_4$ solution, after 7 days' water curing, for a prescribed duration, then the resistivity was measured by the decrease in mechanical strength and the change of outer appearance.

The data on strength are given in table 2.

An evaluation of the resistivities of various cements is given in table 3.

The data revealed that sufficient durability was attained by alumina cement, sulfate resistant, and low-heat portland cements, while portland blast-furnace cement and portland silica cement did not always show a higher durability than normal and high-early-strength portland cement. Also, the durabilities of portland and portland blast-furnace cements might be raised by increasing the addition of gypsum up to 2–4 percent as SO_3.

Figures 1–6 show various effects on the appearance of some specimens.

The specimen with commercial portland blast-furnace cement (fig. 1) gave excessive expansion and cracks. From the factorial experiment, this

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[1] Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. *Chemical composition and fineness of cements and raw materials tested*

Type and designation of cements	Cements tested																			Raw materials for cements prepared in laboratory				
	Commercial cements							Cements prepared in laboratory																
	Alumina cement	Silica cement	Portland blast-furnace cement	Sulfate resistant portland cement	Low-heat portland cement	High-early-strength portland cement	Normal portland cement	High sulfate portland cement	Portland blast-furnace cements								Sulfated slag cements			Granulated slag	"Beppu" white clay	Gypsum	850° C Calcined gypsum	Portland cement clinker
Cement Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19					
Chemical compositions, percent																								
Ig. loss		2.06	0.43	0.87	0.94	1.50	0.84	1.8	0.6	1.5	0.4	1.3	0.6	1.5	0.4	1.3		1.6		−1.06	8.0	20.53	0.04	0.35
Insol.		12.91	.41	.25	.25	.27	.49	.5	.3	.3	.2	.2	.3	.3	.2	.2								
SiO_2	5.55	19.23	25.01	25.40	24.01	21.59	22.51	21.3	25.9	24.0	27.8	26.6	25.9	24.0	27.8	26.6	28.0	39.2	28.0	32.10	87.7	0.22	.3	21.99
Al_2O_3	38.75	5.12	5.83	3.82	5.03	5.14	5.32	5.1	8.3	8.2	11.5	11.3	8.3	8.2	11.5	11.3	13.8	12.6	13.8	16.01	3.1	.06	.1	5.30
Fe_2O_3	16.73	2.66	2.35	4.08	4.37	2.70	3.24	3.1	2.7	2.5	2.1	1.9	2.7	2.5	2.1	1.9	1.3	1.1	1.3	1.41	.3	.02	.0	3.68
MnO			.56						.4	.4	.8	.8	.4	.4	.8	.8	1.2	1.0	1.2	1.35				
CaO	38.75	54.20	61.04	62.94	62.65	65.94	64.53	62.8	57.4	56.5	51.7	50.1	57.4	56.5	51.7	50.1	43.6	34.9	43.6	44.58	.3	32.60	40.9	65.51
MgO		1.39	2.23	.92	1.14	.96	1.01	1.0	2.3	2.3	3.6	3.6	2.3	2.3	3.6	3.6	4.7	3.8	4.7	5.44	.1	.14	.2	3.39
SO_3		1.61	1.44	.99	1.22	1.73	1.58	3.8	1.1	3.3	.6	2.9	1.1	3.3	.6	2.9	5.8	4.6	5.8		.1	46.63	58.5	.14
S			.53						.3	.3	.6	.6	.3	.3	.6	.6	.9	.7	.9	1.03				
Na_2O			.86			.24	.21	.2	.3	.3	.3	.3	.3	.3	.3	.3	.4	.3	.4	.44				.30
K_2O			.38			.30	.43	.4	.4	.4	.4	.4	.4	.4	.4	.4	.3	.2	.3	.34				.56
Total	99.87	99.70	101.07	99.27	99.61	100.37	100.16	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	101.64	99.6	100.20	100.0	101.20
Blaine fineness, cm^2/g																								
	4,220	4,750	3,390	2,150	3,600	4,720	3,050	3,250	3,660	3,860	4,270	4,470	2,930	3,130	2,820	3,020	5,450	8,130	3,330	Fine 5,090 coarse 2,660	16,850	6,910	9,110	3,570
Blending ratio																								
No. 7, portland cement								95	70	65	40	35	70	65	40	35								
Slag (fine)									30	30	60	60					87.5	70.0						
Slag (coarse)													30	30	60	60			87.5					
Gypsum								5		5		5		5		5								
Portland cement clinker																	2.5	2.0	2.5					
Calc. 850 °C gypsum																	10.0	8.0	10.0					
"Beppu" white clay																		20.0						

TABLE 2. *Compressive strength of mortar specimens*

	Commercial cements							Cements prepared in laboratory											
Type and designation of cements	Alumina cement	Silica cement	Portland blast-furnace cement	Sulfate-resistant portland cement	Low-heat portland cement	High-early strength portland cement	Normal portland cement	High-sulfate portland cement	Portland blast-furnace cements								Sulfated slag cements		
Cement No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Water curing (kg/cm²):																			
3 days	147	61	45	21	29	75	55	66	58	74	49	59	46	50	27	27	140	97	44
7 days	148	88	61	27	44	101	87	88	81	91	97	80	61	82	49	53	152	155	81
28 days	157	148	117	56	90	155	133	141	138	134	163	137	128	143	107	85	176	184	126
3 months	187	197	189	115	142	170	156	145	176	185	152	162	177	174	154	162	190	218	145
6 months	219	223	214	167	167	173	175	184	190	235	183	199	204	197	211	187	194	237	146
12 months	199	201	199	181	195	183	174	203	264	238	209	216	276	203	272	210	222	161	231
Immersed in sulfate solution (kg/cm²):																			
28 days	173	163	117	78	120	158	165	154	186	194	170	174	174	166	144	91	215	197	136
3 months	205	175	127	131	160	134	120	188	211	204	174	167	162	165	176	180	183	223	154
6 months	250	42	22	180	182	87	78	173	88	135	139	216	116	182	188	174	168	214	120
12 months	196	12	0	147	153	71	53	112	3	88	138	172	47	134	124	155	133	133	165
Ratio of strength: Sulfate solution immersion/water curing, percent:																			
28 days	110	110	100	139	134	102	117	109	135	145	104	127	136	116	134	107	122	107	108
3 months	109	89	67	114	112	79	77	130	120	110	114	103	92	95	114	111	96	102	106
6 months	114	19	10	108	109	53	45	94	46	57	76	109	57	92	89	93	87	90	82
12 months	99	6	0	81	79	39	30	55	1	37	66	80	17	66	46	74	60	83	72

TABLE 3. *Comparison of the corrosion*

(Age 12 months)

Classification based on the outward aspect of specimens		
Grade	Degree of corrosion	Cement No.
A	Thoroughly perfect	8 16 4 1
B	Almost unaltered	12 7 10 14 6 5
C	Slight cracking	11 13 15 17 18 19
D	Noticeable expansion and cracking.	9 3 2

Classification based on the decrease of the mechanical strength		
Grade	Ratio of strength: sulfate soln./water curing	Cement No.
	(Percent)	
A	>90	1
B	89–60	11 12 14 16 17 18 19 5 4
C	59–30	7 8 10 15 6
D	<29	9 13 3 2

unexpected result seemed to be due to the low amount of slag and gypsum in this cement.

With portland blast-furnace cement an altered layer 3 mm in depth was formed after 6 months, with large cracks, and many needle-shaped crystals were found in these cracks. They were hand-picked and determined to be gypsum. The altered gray layer was separated from sand, with an 88-μ sieve, and was identified as ettringite by X-ray analysis. The excessive expansion and cracks were also found on the specimens containing portland blast-furnace slag and immersed in 1.8 percent sulfuric acid. The reaction products were the same as in the sulfate reaction. More detailed studies on confirmation of the reaction products and the texture are now in progress.

The specimen of commercial portland silica cement (fig. 2) gave results similar to those obtained with the above cement.

Figure 3 shows a comparison of the effect of the amount of gypsum in the low slag portland blast-furnace cement. A larger amount of additional gypsum improved the resistivity remarkably.

The effect of the amount of slag in the portland blast-furnace cement was apparent in improving the resistivity with increasing amount of slag (fig. 4).

The fineness of the slag also had a significant effect; the finer the slag the less the resistivity (fig. 5).

Observations on the resistivity of portland blast-furnace cement may be summarized as follows: the external part was severely cracked, owing to excessive expansion, while the internal part was kept intact and was more stable than in the case of portland cement free from slag. Improvement of the resistivity seems possible, provided either that the addition of calcium sulfate is increased, or that the slag content is increased up to about 60 percent, or that the slag is ground more coarsely than is the case with normal cement, especially when the slag content is only about 30 percent.

FIGURE 1. *Commercial portland blast-furnace cement, No. 3.*

FIGURE 2. *Commercial portland silica cement, No. 2.*

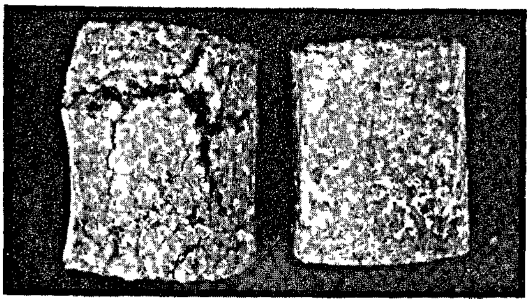

FIGURE 3. *Portland blast-furnace cement.*

Left—No. 9, with low gypsum content; right—No. 10, with high gypsum content.

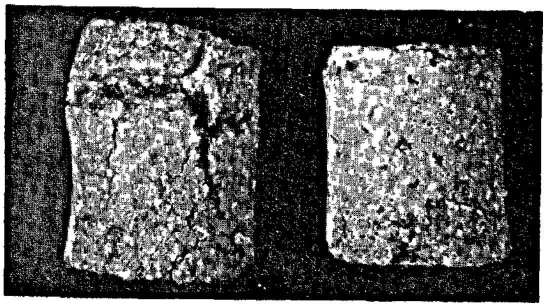

FIGURE 4. *Portland blast-furnace cement.*

Left—No. 9, with low slag content; right—No. 11, with high slag content.

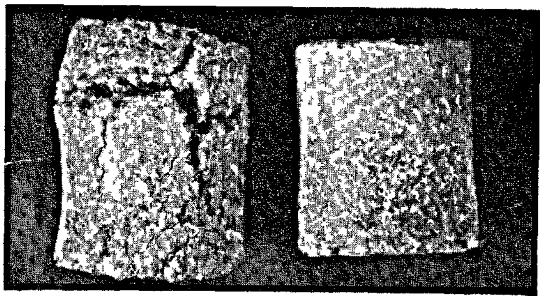

FIGURE 5. *Portland blast-furnace cement.*

Left—No. 9, with fine slag; right—No. 13, with coarse slag.

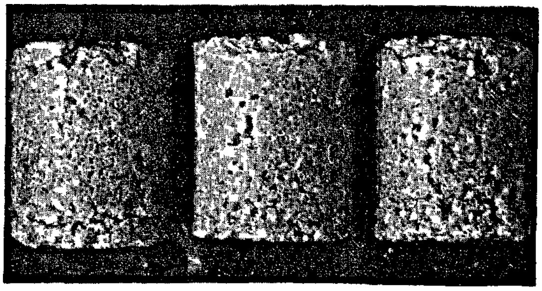

FIGURE 6. *Sulfated slag cement.*

Left—No. 17; middle—No. 18; right—No. 19.

(All of the specimens were 1 : 4 mortar immersed in 2% $MgSO_4$ solution for 12 months)

Thus, it becomes possible to keep the internal part of the specimen almost stable, as the result of the formation of a dense and stable protective layer over the surface. The superior durability of slag-gypsum admixture for various usages seems to be caused partly by its being coarsely ground and partly by the addition of gypsum.

Figure 6 shows a comparison of the resistivity of sulfated slag cement. Though the external part was finely cracked, the internal part remained entirely unattacked, the altered layer being not so thick as to induce heavy cracking.

Countermeasure to the Neutralization of Hardened Sulfated Slag Cement [2]

The harmful effect of neutralization is especially severe with hardened sulfated slag cement, which seems nevertheless to have suitable characteristics for the construction of massive or hydraulic structures. The decrease in bending strength and surface hardness of the hardened sulfated slag cement was ascertained to be due chiefly to neutralization, accompanied by the decomposition of ettringite, one of the main hydration products, into gypsum by the carbonic acid gas in air.

In order to prevent the neutralization, curing of specimens in gypsum solution was effective, but this method could not be practically applied to structures with vertical surfaces. Another pro-

TABLE 4. *Decrease in alkalinity and surface hardness of experimental cements*

Cement No.	Combination of raw materials					Depth of neutralized layer (mm)						Surface hardness (mm)					
						In air 3 months without coating			In air 3 months with water glass coating			28 days			3 months		
						Indicator											
	Portland cement	High-slag, blast-furnace cement	Separately ground slag	Calcium hydroxide	Anhydrite	Phenolphthalein	Methyl red	Methyl orange	Phenolphthalein	Methyl red	Methyl orange	In water	In air	With water glass coating, in air	In water	In air	With water glass coating, in air
	Percent	*Percent*	*Percent*	*Percent*	*Percent*												
A	100.0	--------	--------	--------	--------	0	0	0	--------	--------	--------	--------	--------	--------	--------	0.8–0.8	--------
B	97.5	--------	--------	--------	2.5	0	0	0	--------	--------	--------	--------	--------	--------	--------	0.8–0.8	--------
C	--------	100	--------	--------	--------	2.5	0	0	--------	--------	--------	--------	--------	--------	--------	1.7–1.6	--------
D	--------	95	--------	--------	5.0	1.5	0	0	--------	--------	--------	--------	--------	--------	--------	1.9–1.7	--------
E	--------	--------	79	1	20.0	4.0	.7	0	2	0.7	0	1.5–0.9	9.5–0.8	2.3–0.0	1.3–0.6	2.6–1.5	1.6–1.0

tective method was the application of a thin coating of water glass on the surfaces. A part of the experimental results is shown in table 4.

The resistivity decreased with the increase of slag content in cement. The defects of sulfated slag cement such as the rapid neutralization and low surface hardness were improved by this thin coating of water glass, to nearly the same degree as that of portland blast-furnace cement.

References

[1] Renichi Kondo and Toshiyoshi Yamauchi, The chemical resistivities of various cements . . . Special reference to the improvement of resistivity of blast-furnace cement, J. Ceram. Assoc., Japan, **62**, 656–665 (1954).

[2] Renichi Kondo, An attempt to improve the defects of portland cement and portland blast-furnace cement, Semento Gijutsu Nenpo, **14** (in press) (1960).

Discussion

E. Spohn

I would like to comment on a remark of Mr. Kondo on the sulfate resistance of slag cements. He said: "Slag cements are generally considered as most resistive". I am not prepared to show slides on that subject, but I wish to draw your attention to a publication in Zement-Kalk-Gips, 1960, page 310: "Die Beurteilung der Sulfatbeständigkeit von Zementen nach konventionellen Schnellmethoden" by W. Lieber and K. Bleher, and, in the same issue, page 317: "Ein Schnellprüfverfahren für Zemente auf ihr Verhalten bei Sulfatangriff" by A. Koch and H. Steinegger.

For a quick sulfate resistance test, Koch uses small prisms 1 x 1 x 6 cm, made from standard DIN mortar with a water-cement ratio 0.6. After 21 days water curing, the prisms are suspended in a 10-percent solution of $Na_2SO_4 \cdot 10\ H_2O$ for 56 days. This is a sufficient time for judgment of a cement. The result is obtained after 77 days altogether. Three methods have been applied to determine the sulfate resistance:

1. Titration of the SO_3 consumption.
2. Visual observation of cracks and disintegration.
3. Flexural strength development in relation to water storage.

All three methods render similar results. The flexural strength seems to be most acceptable.

The results of these tests do not agree with the general opinion which has been quoted by Mr. Kondo. It was found that:

1. Not all slag cements are sulfate-resistant. Some behave better, some worse than average portland cements.
2. High-early-strength slag cements generally tend to inferior resistance.
3. Different slags have an utmost different effect. Therefore, the percentage of slag used does not generally indicate the sulfate resistivity.

There are on the market slag cements with about 80 percent or more high reactive slag with excellent sulfate resistivity.

A certain low reactive slag with an Al_2O_3 content as low as 11.49 percent renders an excellent sulfate resistance in a percentage of 50 to 60 with type I clinker and does even better in combination with a type V clinker. Like ordinary slag cements, this cement compares favorably with portland cements including type V, when slightly acid aggression occurs. The high resistivity is attributed to the chemical composition.

I have the impression that the miniature prism method of Koch and Steinegger should be developed to a generally acceptable rapid method for determining sulfate resistance. It could be used for all kinds of cement. The tentative ASTM test can be applied to portland cements only, but not to slag cements and others. It is known that mixing of portland cement and supersulfate cement is not permissible, and this is exactly what is done in the ASTM test, when slag cement and gypsum are mixed. The miniature prism method does not have this disadvantage. Its results so far seem closely related to the relative behavior of different cements in concrete. Cements which seem to be entirely unaffected in good concrete have no or only a slight decrease in strength and show no cracks or disintegration after 56 days exposure with the miniature test.

Discussion

H.-G. Smolczyk

We congratulate Mr. Kondo on his very interesting research work. We are in full agreement with his opinion that a higher slag content and a better composition of the blast-furnace slag cements result in improving the resistance to aggressive fluids. In addition to this we would like to mention the following:

For many years attempts have been made to estimate the chemical resistance of cements and concretes by laboratory methods. But so far these efforts have not led to satisfactory results. Thus, a universal short-time test to determine the resistance of cements and cement concretes to chemical attack does not exist. So the Anstett test, which neither in France—where this test-method came from—nor in the United States is accepted as a standard method, cannot give accurate information data of the resistance to sulfate attack or even to other chemical aggressive agents, as pointed out by Fouilloux [1].[1] Even the results of investigations carried out by groups in Germany in the course of the last few years do not supply any standard test.

Consequently it seems to be possible to determine the chemical resistance of a cement only on the basis of long-time tests or even better by experiences and observations made on concrete structures which have been in direct contact with very aggressive waters for a long time. Here attention should be paid to the large-scale concrete structures along the coast of France and Belgium, which have been very resistant to the strong chemical attack of sea water and which were built by using preferably blast-furnace cements.

There is no need of discussing the fact that blast-furnace slag cement itself is much more resistant to aggressive solutions than can be expected of the clinker minerals and their hydration products.

If one tries to avoid the more vulnerable mineral component of the portland cement—the C_3A—by increasing the iron modulus, a certain improvement of the chemical resistance of these cements to sulfate attack can be obtained. This fact is confirmed by experimental results already obtained with ore cements in former times.

On the other hand, these portland cements develop a great amount of $Ca(OH)_2$ and it is a very well-known fact that therefore they are susceptible to the effects of other chemical aggressive agents—e.g., free carbonic acid.

In the case of blast-furnace cement—especially of the low-clinker blast-furnace cement—the C_3A content is reduced by the minor clinker content. Furthermore the very low CaO content is an advantage, but a more important one is the binding of the greater part of the $Ca(OH)_2$ by the slag component, thus making these cements more resistant to the influence of any chemical attack than any portland cement with its high $Ca(OH)_2$ content could be.

By taking these facts into consideration it is evident that a blast-furnace cement must possess very good chemical resistivity. In addition to the good properties resulting from the composition of the cement, the stability of a structure in concrete-aggressive surroundings also depends on the structural advantages to be obtained by this cement. Sea-water constructions are mainly structures with large diameters. In this case the stability does not depend on the resistivity of the cement only but to a high degree on a close-grained concrete structure, especially on a dense surface of the concrete that is free of cracks.

The very low heat of hydration of the blast-furnace cement allows the construction of mass-concrete structures of great diameters without the danger of obtaining cracks by temperature (heat of hydration) stresses; and without the necessity of preparing any cooling facility.

Large-scale measurements of the temperature in concrete constructions of different diameters [2, 3, 4, 5], carried out by the Research Institute for Blast Furnace Slags at Rheinhausen, Germany, have demonstrated the great importance of a low heat of hydration of the cements, in order to obtain a concrete shell free of cracks.

Furthermore, in the case of all concrete structures for which cracks on the surface are more than esthetic defects, the rise of temperature caused by the heat of hydration is to be taken into account when deciding on concrete technological considerations and provisions.

But, after all, the favorable elastic behavior of the blast-furnace cements, as has already been learned from the increased ratio of bending-tensile strength to compressive strength, guarantees a maximum of insensitivity to cracking due to contraction or temperature stressing.

There is no doubt that the very good experience with blast-furnace cements used for structures exposed to sea-water, is based on the low heat of hydration as well as on the good elastic properties.

The Netherlands, Belgium, and France, especially, are discontinuing the production of "sulfate-resistant portland cement with a reduced C_3A-content", for in these countries there is no need of it because of the extremely good results obtained by using blast-furnace slag cement.

References

[1] Pierre Fouilloux, Über die Widerstandsfähigkeit von Zementen bei verschiedenen Angriffsarten und über die Bedeutung, die der Anstettprobe hinsichtlich des Verhaltens der Bauwerke beim Abbinden gegenüber

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[1] Figures in brackets indicate the literature references at the end of this paper.

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[2] O. Eisemann, Zur Vermeidung von Temperaturrissen im Massenbeton, Die Bauwirtschaft, 23/24, June 1960

[3] R. Vinkeloe, Die Hydratationswärme und ihre Auswirkungen in Massenbetonbauwerken, Delivered at meetings and in the Research Institute for Blast Furnace Slags at Rheinhausen. (Publ. in prep.)

[4] Engler and Vinkeloe, Betontechnologische Vorteile einer niedrigen Abbindewärme des Zementes (Principal considerations, based on practical results in different structures). (Publ. in prep.)

[5] Hampe, Temperaturschäden im Beton, Die Bautechnik Aug. 1941.

Closure

Renichi Kondo

Mr. Spohn referred to the very recent publications on the miniature-prism method for the evaluation of cement regarding sulfate resistivity. I am glad to learn that this method gives good information in a very short period appropriate for concrete practice. It was also mentioned that the high-early-strength slag cements generally tend to inferior resistance. This result may be supposed to be due to the low slag content and finer grinding of slag in this type of cement. I cannot discuss, however, the effect of the difference in slags, as I have not done research on that point yet.

Mr. Smolczyk pointed out the valuable experience that concrete structures in Europe made of portland blast-furnace cements generally have very good resistivity against sea water. He also discussed the reasons. I have mentioned in my paper the excessive expansion of mortar caused by the reaction between hardened portland blast-furnace cement and sulfate solution. The factors governing this phenomenon were at the same time described there. I never intended to assert the general inferiority in resistance of the portland blast-furnace cements. I rather expected this experimental evidence to be useful in developing sulfate-resistant cements of much higher reliability than the ones now in production. Further fundamental investigations on this abnormal phenomenon would be also desirable.

Paper VI–S5. Durability of Concrete and Reinforced Concrete and Its Connections With the Composition of Cement, Concrete, and Construction Methods*

S. V. Shestopyorov

Synopsis (By editor)

The durability of concrete is best investigated by direct study of the frost resistance of materials and products not only in the laboratory but under the natural climatic conditions. Not only the concrete materials and the design of the concrete, but the construction methods and the curing of the concrete are important. Concrete made with freshly wet-ground clinker has certain advantages. The contraction that results from the reaction of cement and water produces minute air voids which improve frost resistance in the same way as intentional air-entrainment. Some plasticizers give beneficial results. Steam curing gives variable results and often lowers frost resistance. Many factors influence the durability of concrete and have to be taken into account. These various matters are discussed, and frost-resistance tests are reported for various concretes and for reinforced and prestressed concrete members.

Résumé

La meilleure méthode de recherches sur la durabilité du béton est l'étude directe de la résistance au gel des matériaux et des produits non seulement dans la laboratoire mais aussi sous les conditions climatiques naturelles. Ce ne sont pas seulement les matériaux du béton et sa composition qui sont importants, mais encore les méthodes de construction et la conservation du béton. Le béton produit de clinker fraîchement broyé à l'eau présente certains avantages. La contraction qui résulte de la réaction du ciment et de l'eau produit de vides minuscules remplis d'air qui améliorent la résistance au gel, ainsi que lorsque l'air est introduit volontairement. Certains plastifiants donnent des résultats favorables. La conservation à la vapeur donne des résultats variables et diminue souvent la résistance au gel. De nombreux facteurs influencent la durabilité du béton et il faut en tenir compte. Ces différentes questions sont discutées, et rapport est fait d'expériences sur la résistance au gel pour differents bétons et pour des éléments de construction en béton armé et précontraint.

Zusammenfassung

Die Beständigkeit des Betons wird vorzugsweise durch ein direktes Studium des Gefrierbenehmens der Materialien und Produkte nicht nur im Laboratorium, sondern auch unter natürlichen klimatischen Verhältnissen untersucht. Nicht nur die Betonmaterialien und die Mischungsverhältnisse des Betons, sondern auch die Konstruktions- und Erhärtungsmethoden des Betons haben ihre Bedeutung. Beton, der mit frischem nassvermahlenem Klinker hergestellt wurde, zeigt gewisse Vorteile. Die Kontraktion, die durch die Reaktion zwischen Zement und Wasser hervorgerufen wird, bringt kleine Luftporen hervor, die den Widerstand gegen Frostangriff erhöhen; dieser Effekt kann auch durch ein willkürliches Einverleiben der Luft erzielt werden. Einige plastifizierende Stoffe haben zu guten Resultaten geführt. Die Dampferhärtung kann verschiedenartige Erfolge zeigen; häufig wird der Gefrierwiderstand erniedrigt. Viele andere Faktoren beeinflussen die Betonbeständigkeit und müssen daher berücksichtigt werden. Diese Faktoren werden erörtert, und die Ergebnisse von Gefrierversuchen für mehrere Betone, Eisenbetone und Spannbetone sind beschrieben.

Introduction

Taking into account their life in the structures, reinforced-concrete constructions and details are designed and manufactured so that they may last for an indefinite time without repairs. The necessity of replacing properly designed and manufactured structures and details is caused only by their normal aging, not by destruction. This is verified by experiments *in situ*. Among the various methods of investigation of durability of concrete and reinforced concrete, including prestressed, the author considers that the best way of obtaining practical conclusions is direct study of frost resistance of materials in samples and products, including the possibility of performing experimental work under natural climatic conditions.

When investigating the frost resistance of concrete and reinforced concrete, it is impossible to limit the investigations to the materials used for concrete production and to concrete compositions. It is necessary to connect investigations of concrete durability with construction methods, including the curing of the concrete, which are often forgotten.

The highly efficient industrial methods of production of plain concrete and reinforced concrete

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Academy of Construction and Architecture, Moscow, U.S.S.R.

require a more progressive technology of production of concrete mixes.

Such technology includes the use of rapid-hardening, and in many cases. high-strength cements.

Change to industrial methods of production is needed both for reinforced concrete members and details and for plain concrete.

Waterproofing of concrete is a very active measure insuring primarily the creation of conditions for completion of the processes of hydrolysis and hydration of cement.

Freezing and thawing of concrete even several hundred times is insufficient for determining its durability. Concrete, during further testing, may lose its strength and be destroyed. During the combined action of water and frost, destruction which cannot be detected by a certain number of freezing-thawing cycles but which depends on the structure of the cement paste and the concrete texture may at some moment rise catastrophically. It is as if a preparatory period passes during which processes occur that determine the future destruction of the concrete. Destruction may be of various kinds; for instance, it may proceed in outside layers or inside the specimen.

Studies carried out by Powers (U.S.A.) are very interesting in relation to the frost resistance of concrete. For example, the idea is propounded of concrete destruction as a result of the hydraulic pressure developed in the concrete when the water freezes. Powers introduces many factors of great importance when considering this problem (contraction spaces, degree of saturation with water, conditions of water freezing in concrete, and others), this certainly being correct methodically. Powers, in some of his papers on concrete (cement), divides the observed destruction of this material into two kinds: internal and external (scaling). This division has also been noted in our investigations, but we consider that there are many more types of concrete destruction. The considerations on loss of concrete strength during freezing are interesting in the works of other scientists. Thus, for example, Wisey (1944) considered that loss of weight (connected with scaling or breaking of part of the sample at the edge), does not show loss of strength. We consider this point of view relative to the form of destruction correct, the latter being connected with the quality of the concrete. However, this does not mean that we agree with the opinions of Bergstrem that when the concrete is considered weak, invisible destruction of the structure is possible (loss of structural strength) in the entire sample and, consequently, in the entire volume of the structure, even though the latter is approximately the same size as the tested samples. Much work is being devoted to the problems of frost resistance of concrete (methodical work, tests with concrete, etc.). However, in our opinion, the trend and complexity which we are trying to realize, even though partially, in our investigations extending over many years, have in general been lacking. Possibilities for such investigations are widely offered to scientific workers in the USSR, where science is of unprecedented scope.

New efforts of investigators should be welcomed on this problem, which is of such great importance for construction. It should be noted that in the provisional American Standards on testing the frost resistance of concrete (C290–52T, C291–52T, C292–52T, C310–53T for different cases) the time of sample freezing varies ("slow freezing" and "rapid freezing"), as well as the conditions of freezing. Prismatic samples of concrete are tested. Principally, such an approach to testing creates the possibility of all-around evaluation of the results and, consequently, to a higher degree, approaches the needs of construction. Attention should be paid to the total duration of testing. For "rapid freezing" the highest requirement of frost resistance of concrete is 300 cycles, while, for "slow freezing," 200 cycles in water or 100 cycles in a saline solution are required. In this case it is considered that the test results may be estimated from the value of the dynamic modulus of elasticity of the frozen prismatic samples. The value of the modulus of elasticity should be not less than 60 percent of the initial value. We cannot agree with such a method of estimation of the frost resistance of concrete, and our viewpoint is verified by the results of our investigations described in the present report. Objections arise in relation to the routine use of one minimum freezing temperature during laboratory tests which differ significantly from requirements introduced in Dresden in 1886. It should be borne in mind that during recent years the use of reinforced concrete has grown immensely. Consequently, the types of structures have changed, as well as the conditions of work, even if only because construction is being carried out under natural conditions less satisfactory for the life of the material; and, besides, reinforced concrete is beginning to be widely used in industrial construction where strong aggression is possible against it. It is incorrect to consider that there is only one freezing temperature. There are as many freezing temperatures as there are types of capillaries, varying in diameter. It is natural that the denser the concrete, the smaller the diameter of the capillaries in it. When designing durable concrete, the problem arises of producing concrete with capillaries such that the water in them shall not freeze at the temperatures to which the structure will be exposed. Lengthy investigations that we have made with concrete have shown that it is possible to prepare such concrete.

As an original investigation of the frost resistance of building materials in Russia the work by K. J. Ilkevitch (1915) should be mentioned. The author of this work writes ". . . . the foregoing leads to the view that testing for freezing in various climates should be performed in different ways, namely, in conformance with the temperature conditions of each given locality. The frost resistance of materials for each locality should correspond, so to say, to its own requirements."

In 1956 a book was published by the Scientific Research Institute on Cement under the guidance of Prof. B. C. Skramtaev (author, G. I. Gorchakov). It should be noted that in this work our view on the lowering of frost resistance of concrete in conformity with the content of mineral C_3A is corroborated.

If, in many cases of practical construction, small requirements are made for frost resistance of concrete—100 cycles, for example—in many other cases a frost resistance of 1,000 cycles is considered insufficient. Knowing that it is possible to prepare concrete resisting several thousand freezing-thawing cycles, and seeking to establish the main reasons for difference in frost resistance, the following problems should be solved: (a) study of the essence of the processes proceeding in concrete that resists several thousand freezing-thawing cycles, to account for the durability of such concretes, and (b) determination of the correct criterion for the conditional freezing temperature of the water enclosed in the porous-capillary material, i.e., conditions of water freezing in capillaries of different diameters. Unfortunately for this aim, the sizes of the capillaries in concrete have not as yet been determined, and furthermore, concrete is not designed according to this criterion. We consider that the sizes of the capillaries, as well as the volume of entrained air, should be the basis of the physical properties of concrete. It is only necessary to work out a similar criterion for laboratory methods of concrete testing, modeling according to conditions in the structures. This criterion would make it possible to estimate the time factor, without which it is impossible to perform accurate design for durability of materials. We consider erroneous the view of many investigators that it is not necessary to test concrete by repeated freezing and thawing. Those proposing this view refer to the good condition of many reinforced concrete structures. Such references are unfounded, as the conditions of exposure of the materials to different climatic conditions and in different structures vary. As a rule, for proving concrete durability, the good condition of structures of mass concrete is considered sufficiently established when 200 cycles of freezing and thawing are withstood during a long period. However, no single case of destruction of reinforced concrete structures should be ignored.

We consider that the life, for example, of such prestressed reinforced-concrete products as sleepers, contact line posts, sheet piles, piles, and others should be determined only by their actual wear.

The absence of established life of structures and products leads to the lowering of requirements in projects, in standards and specifications on materials, and in construction-method rules. The durability and measures for preventive repair of structures are not taken into account.

Problems of increasing concrete durability in no case should be solved by increasing expenditures and prolonging construction delay.

For the correct use of a cement, builders should know its composition. The mineralogical composition, calculated on the basis of gross analysis, reflects the "ideal" limiting composition of the cement.

Actually, the structure of the cement clinker is characterized by the presence of certain sizes of crystals of the main minerals, connected by intermediate glassy substances.

When the degree of subdivision (grinding) changes, the mineralogical composition of the particle surface also changes. As all processes of hydrolysis and hydration proceed at the interface of the solid phase—polymineral cement—with the mixing water, this mineralogical composition is of principal significance.

Fine subdivision of cement has very important technical and economic implications. Thus, for example, it has been determined that using finely ground cements obtained by wet grinding, we basically change the structure formation in the hardened cement. By employing common dry grinding (even very fine) this effect cannot be obtained. With very fine grinding and thorough mixing of the cement paste and gypsum, the entire aluminate (C_3A) may be exposed and combined into hydrosulfoaluminate. Fine wet grinding makes it possible to free all the alite from the shielding shell of belite, while the latter, in turn, is hydrated to a very high degree. As a result, the structure of the hardened wet-ground cement obtained is of a quality differing from that of the hardened paste of dry-ground cement.

The production of fine cement by wet grinding essentially changes the process of cement manufacture by advancing it from the stage of clinker calcination to the stage of obtaining cement paste, thus bypassing the operation stage of obtaining ground cement clinker. Thus, the technology of cement manufacture, in this case, eliminates dry grinding, storage of cement in silos, and, in some cases, its packing, transportation in closed railway cars, and storage in closed premises. The clinker may be utilized directly after preparation, while for dry grinding, according to the existing conditions of cement manufacture, the cement should be stored for several days before grinding. For wet grinding, the grinding operation is transferred into the workshops of concrete plants. In these shops the most favorable conditions are created for avoiding dust from the mineral materials, thus improving hygienic labor conditions.

The manufacture of mortars and concrete from cement made by wet grinding significantly widens the possibility of improving quality on the basis of promoting accelerated and complete reaction of the hydrated tricalcium aluminate with the gypsum, thus forming hydrosulfoaluminate even during the period of the elastic-viscous-plastic condition of the cement gel.

In speaking about the new technology of manufacture, it is impossible to limit the consideration of the grinding process to the one aspect—the wet grinding. Investigation of the processes of direct structure formation in the cement gel shows the importance of combining fine disintegration with the peptization method of formation of a flocculent product, and correct incorporation of various electrolytes in the cement paste, in particular of gypsum, as well as hydraulic admixtures and nonhydraulic microfillers.

One of the most important advantages of the new technology should be improvement of uniformity of mortars and concretes manufactured at the plants. It should not be forgotten that the existing high safety factor is directly connected with the approved technology of cement, mortar, and concrete production. Variability in the strength of the control samples is taken as an inevitable evil during concreting.

It may be said that with the new technology the uniformity of concrete will be much better. Systematic and general production of mortars and concrete of uniform quality allows higher design values without raising the grade of the cement and, consequently, allows the design of structures of smaller section.

Contraction and Internal Vacuum in Cement Paste (Self-Desiccation)

It is obvious that contraction is closely connected with the frost resistance of hardened cement paste, mortar, and concrete. The possibility and degree of action in the cement paste of forces arising during the freezing of water in the capillaries and pores of the cement paste depend on the degree of their filling with water and air and on the action of newly hydrated formations. The air may penetrate into the structure of the cement paste as the reactions of hydrolysis and hydration of the minerals in the binding agent (setting and hardening of the cement paste) proceed, due to contraction, during which an internal vacuum is developed in the mass of new formations, thus making possible the entrainment of air in them, the air filling part of the volume of the capillaries and pores; the air serves as a microscopic damper during the plastic motion of ice in capillaries and pores.

The phenomena of contraction has been widely investigated in detail by V. V. Nekrasov.

The air layers in the structure of the cement paste are only effective in improving frost resistance when the solid phase with air inclusions is of high strength and does not change under the influence of the conditions of exposure.

According to the data of V. V. Nekrasov, higher contraction for one and the same time is usually observed for cement of higher mechanical strength with the same mineralogical composition but of different particle size after grinding. Increase of contraction corresponds well with increase of strength and frost resistance of cement when the size of the cement grains is lowered during grinding. This proposition is disputed by several scientists.

The introduction of an electrolyte—calcium chloride in certain amounts—increases contraction and is characterized by increase of the mechanical strength of the material. The introduction of mineral admixtures into the cement, for example, of ground quartz, lowers the contraction, changing the frost resistance similarly.

Frost resistance is directly connected with the extent of contraction of the cement paste of monomineral cements of alite and belite. For cement with a low content of C_3A, the contraction equals 14–15 ml per 300 g of cement after 30-day curing.

Further work performed for developing new premises on the relationship between contraction and frost resistance affords simple models of the frost resistance of concrete and mortars of the most various compositions.

V. V. Nekrasov showed that contraction was significantly lower for cement that was not fresh.

Lengthy storage significantly lowers the total content of nonhydrated material, this lowering being confirmed by the increased losses on ignition. However, in this case, a thin hydrated shell is formed on the surface of the cement grain, and when it becomes solid, the possibility is lost of further hydrolysis and hydration of the main part of the grain which has as yet not reacted. The formation of such solid shells is most probable with grains of the smallest size. Thus, for part of the cement grains, contraction practically stops, but not for grains of larger diameter. For such grains contraction proceeds later on during their chemical peptization, which is carried out during later periods.

The formation of a vacuum in a body of concrete, caused by contraction, is described by P. E. Franzman, who shows that the water film disappears from the concrete surface due to suction into the contraction spaces.

The changing of concrete properties under the influence of different air-entraining admixtures should be considered in estimating the phenomena of internal vacuum in the setting and hardening of cement paste. Actually, in this case, an additional quantity of air is held in the concrete or mortar mix, the air being redistributed in the hardening cement paste during the contraction caused by hydration of the minerals, creating in the structure properly located air voids, not filled in the future with water in the hardened material, the water being delivered along the capillaries during saturation.

The changing of the structure of the cement paste during the process of hardening compacts the material, hampering hydration and, consequently, in this case does not allow proper consideration of the changing vacuum in the sample during long observation periods.

Let us consider some characteristic cases of destruction of samples of cement mortar during freezing and thawing, and let us connect them with data on the degree of sample saturation with water and air as a result of contraction under different conditions. In speaking about contraction and the internal vacuum corresponding to it, we cannot forget that the spaces formed at this time, at normal atmospheric pressure, either will be filled with air or will contain water. If air is in these "contraction volumes," the structure of the paste will have a shock-absorbing volume for the expansion of frozen water. The paste structure will be destroyed during freezing if these volumes are filled with water. This conclusion is confirmed by the results of *in situ* tests.

Cube specimens with 7.07-cm. edges were made of cement obtained by grinding clinker "K" in the laboratory with 3 percent gypsum admixture. The fineness of clinker grinding is indicated by the 10 to 11 percent residue on a screen with openings of 85μ. Normal one-size sand was used. Flow-table spreading of the mortar mix for a w/c ratio of 0.36, and shaking, was 130 mm.

Tests have shown the importance of air—"air dampers"—in the structure of the cement paste, formed by contraction during cement hydration.

Cement made of clinker "K" was used for a series of specimens which were immersed in water every hour for 24 hr after manufacture. These samples were then left in water for 28 days and then were vacuum-treated and transferred to the freezing chamber.

It should be noted that destruction of cement mortars with w/c=0.35–0.45, which, for usual hardening conditions are frost-resistant, was quick and complete. Consequently, common destruction beginning at the surface is a result of "deairing" of the structure of the cement paste in very thin surface layers. Under these conditions, the samples crumble—adhesion is lost between the sand particles in the surface layer, which were previously glued together by mineral gel.

If, during production of the cement paste, the mortar or concrete sample (with any w/c ratio, however low, which permits placing into molds), after molding, is left to harden in water, and is deaerated, it is easy to obtain frost-susceptible samples.

Actually, in this case the entire additional pore volume resulting from contraction, distributed equally in the material, becomes filled with water and forms capillaries acting during freezing. Freezing of such a sample, preliminarily saturated with water, creates the conditions for deep destruction of the material throughout the sample, as in this case the water when freezing cannot expand in the capillaries and pores. Consequently, any excessive water (excessive value of w/c) in the cement paste simulates the tests mentioned. This excessive amount is understood to be the water not combined with cement by chemical forces (hydration and crystal water) or by physical forces (absorptive-cohesive water) and may migrate.

Investigation of Frost Resistance of Plain Concrete and Reinforced-Concrete Products under Natural Conditions

Frost Resistance of Concrete

For estimating the frost resistance of concrete under severe natural climatic conditions, two climatic stations were organized at water basins with differing salinity. At station No. 1, the concrete was under the action of water with a salinity equal to the salt content of the ocean (20–30 g per liter). At station No. 2, soft water with low salt content acted on the concrete. Minimum air temperature at station No. 1 was −32 °C, at station No. 2, −45 °C; the water had a temperature from +1 °C to 4 °C. When calculating the freezing-thawing cycles the number of passes through 0 °C was taken into account. When considering passing through −15 °C and lower, for station No. 1 the number of cycles was decreased by about four times.

A large number of specimens were made of gravel consisting of frost-resistant grains and of cement with frost-resistant structure of the cement paste.

The surface of the specimens was polished, coated, penetrated with bitumen, and painted with ethanol varnish. The samples were made of different binding agents and aggregates and were tested after long hardening periods. The number of specimens tested under natural conditions at the two stations was over 10,000. The resistance of the specimens was estimated from their external appearance by rating points (table 1), and, for part of the specimens, by repeated tests of mechanical strength.

The approved methods are provisional, but they permit rapid and simultaneous testing of a large number of concrete compositions. Estimation of the condition of the specimens by the 10-point system permitted daily determinations with sufficient accuracy. The provisional criterion for beginning of destruction of the specimen was the moment corresponding to passage from the ninth point to the eighth point. As the defects of the specimen appeared, testing for ultimate strength was stopped. As the specimens were not moved from place to place during testing, it was possible to observe the destruction process of the specimens at all stages. Determination of the strength of the specimens should not be overestimated. In many cases, significant scattering of test results was observed, this being natural in view of the changing quality of the concrete surface. On the other hand, lowering of the strength of the specimen under the influence of mechanical causes leads to the appearance of external defects. Separate tests were carried out for finding the strength of the specimens after a certain number of freezing-

TABLE 1. *Scale of frost resistance by rating points*

Estimation of frost resistance in points	Concrete: type of destruction	Estimation of frost resistance in points	Mortar: type of destruction
10	No destruction.	5	No destruction.
9	Small changes: scaling of sides, beginning of edge rounding.	4	Small initial crumbling of edges and corners.
8	The same, with pits due to destruction of grains of non-frost-resistant rocks.	3	Beginning of destruction of sides.
7	The same, only to a higher degree; specimen becomes rounded.	2	Pronounced destruction of edges at corners and sides.
6	Sample loses its cubic shape; destruction of sides for 30–40 percent, appearance of cracks and breaking of corners.	1	Presence of cracks and violation of monolithic structure of sample.
5	Destruction of all corners. Destruction of sides by 60–70 percent.		
4	Destruction of sides by 80–90 percent.		
3	Sides distinguished with difficulty.		
2	No sides seen.		
1	Complete rounding of specimen.		

thawing cycles. However, this method of testing is not justified, for at the time of the test one part of the samples is being strongly destroyed, and its strength cannot be determined, while for the other part no signs of destruction have as yet appeared. When testing reinforced-concrete sleepers, drawings were made of their external appearance, thus facilitating the analysis of causes of destruction when comparing the condition of the concrete cubes and estimating the operation of the technologic equipment, primarily the vibrating platform, and the approved technologic process.

When the concrete in various structures experiences severe climatic conditions, it may pass during one year through several hundred freezing-thawing cycles. At station No. 1, during one day, it is moistened with water twice and at station No. 2 six or seven times. Therefore, for these cases it is important to estimate the resistance of the concrete by the number of freezing-thawing cycles rather than by its resistance during many years of exposure.

Testing of cubic samples, for instance, with edges of 20 cm, in this case completely simulates the working conditions of concrete in non-mass structures, for example in sleepers, communication line posts, posts of electric power lines and contact line posts, sheet piles, piles and beams of such structures as moorings and piers, airfield and road pavements, curbstones, slabs on revetments, etc.

The destruction of concrete cubes of plastic mixtures, as a rule, begins from the upper edge (smoothed edge of specimen) where, due to slight sedimentation of the concrete mix, there is more water than in the rest of the specimen.

Destruction of non-frost-resistant gravel grains in the concrete is noted not only at direct contact of the concrete with water (with permanent capillary suction), but also during periodic action of atmospheric precipitation on the concrete. In tests over a period of 20 yr to determine the weather resistance of concrete of different compositions, performed with 1.5-m and 2.0-m cubes, several interesting features were observed relative to the destruction of non-frost-resistant gravel grains. Thus, for concrete cubes of portland cement with cement contents of 400 kg/m^3 and 280 kg/m^3 and alumina cement with a cement content of 280 kg/m^3, after about 7 yr signs of destruction of the concrete surface began to appear at locations of weak gravel grains, while for samples made of sand-pozzolan cement no destruction was observed.

Even when the concrete was gradually or incidentally saturated with atmospheric moisture and the specimen did not absorb liquid water, the presence in the structure of the cement paste of active capillaries caused destruction of the concrete texture due to freezing of the weak rock material in it, in the same way as when the concrete was constantly moistened with water, but in the latter case destruction proceeded at a higher rate. If "passive" capillaries prevail in the structure of the cement paste, through which the water flows freely, non-frost-resistant cement paste exposed to the same conditions should not be destroyed.

For concrete existing under conditions such that the aggregate may be saturated gradually with water, and the concrete experiences systematic freezing and thawing, non-frost-resistant rock materials should not be employed. The influence of contact density may be clearly seen according to the results of tests of concrete with large-size sandstone aggregate. The concrete has a lower frost resistance, even though the frost resistance of the rock is high. Checking of contact density was performed by determination of the impermeability of the concrete.

After 3,000 test cycles, the concrete samples saturated with bitumen were well preserved (9–10 points) (samples of low-aluminate portland cement of one cement plant with crushed gabbro and dolomite, w/c=0.65 and 0.68). This result demonstrates the high resistance of concrete in which the capillaries filled with bitumen are hydrophobized after hardening of the cement paste.

After 3,600 test cycles, the specimens with w/c=0.68 were destroyed. (They were made with crushed tough dolomite.)

The problem of the curing of hardening concrete is closely connected with the strength of the concrete and its resistance to various aggressive physical and chemical factors of the ambient media. It would be very foolish, when considering concrete resistance, to limit the requirements regarding it to an incomplete one-sided specification of the material composition and its quality for estimating the resistance of the concrete, without paying attention to the technology, in which the concrete composition, its molding, and the care of the concrete up to a certain time in the hardening period, with other conditions invariable, are of decisive importance.

Cement is a half-finished product, and the technical properties of the cement paste in the mortar or concrete are developed by the builder at the construction site. The idea of absolute and not relative value of concrete strength, obtained during the testing of concrete cubes, leads to underestimation of the importance of insuring the required thermal-moisture conditions for hardening of the cement paste in the mortar or concrete. There are examples where concrete of higher mechanical strength has lower frost resistance than concrete with relatively lower strength. It is important to know the relative strength—the ratio of the actual strength to the strength which would be obtained with the given cement under optimal conditions of manufacture, formation, and curing.

It is possible to show an example of destruction after 15 to 20 test cycles of several concrete specimens with an ultimate strength of about 400 kg/cm^2 made of alumina cement. Such insignificant frost resistance of concrete is explained by the fact that this concrete was placed under water.

There are several cases of defective concrete in various engineering structures after a relatively short period of operation. Destruction began owing to the use of concrete which conformed only with the requirements on strength.

Concrete begins to freeze in zones of the structures which are systematically saturated with water during the winter period. Repeated freezing and thawing of concrete leads to its destruction and to the need for repairs of the structure. It should be noted that concrete which was used for these structures resisted standard freezing tests.

Due to the increased use of prestressed reinforced-concrete structures, investigations have been started on the frost resistance of stressed concrete.

For these tests, cement "B" was used (table 2). It is of the high-aluminate type (C_3A=10.5%). Before making the samples the cement was stored for six months, which significantly lowered its activity. Before the specimens were made, the cement was reground with a small number of balls in a ball mill.

The mineralogical content of the cement, in percentages, was: C_3S, 50; C_2S, 20; C_3A, 10.5; other minerals, 19.5; no free lime.

Sand with a fineness modulus of 2.2 containing 2.5 percent of clay and silt was used for making the specimens. The voids in the sand amounted to 38 percent. Crushed granite was used as the coarse aggregate. The voids in the crushed rock in the loose condition amounted to 42 percent. For some concrete compositions, the influence of a plasticizer of sulfite cellulose extract was investigated, as well as the quantity of gypsum and active mineral admixture of tripolite, with respect to variation of the frost resistance of the cement paste structure. The lower limit of water content was determined by the consistency of the concrete mix on a CM–475 vibrating platform with amplitude of oscillations from 0.3 to 0.6 mm. As the cement content in the concrete increased, the minimum water content correspondingly increased. Thus, if the cement content was 50 kg/m^3, a water content of 110 kg/m^3 was sufficient for obtaining a concrete mix of the required consistency. When the cement content increased to 500 kg/m^3, the water content was increased to 140 kg/m^3. Twelve samples were made of each concrete composition (table 3).

Before the frost-resistance tests, the specimens hardened for 28 days under normal conditions, and then were in the air for 310 to 340 days.

All twelve specimens were molded simultaneously on the CM–475 vibrating platform. The molds were fastened to the vibrating platform by mechanical fastenings and electromagnets.

It was determined that by future care of the concrete it is impossible to remedy the defects in the cement paste structure which appear as a result of violation of the thermal regime required for proper progress of the processes of cement hydrolysis and hydration after mixing. As the plasticizer somewhat retards the hardening process in its initial stage, it is natural that violation of the hardening conditions of the specimen is reflected to a high degree in the structure of the plasticized concretes. Investigations have shown how the porosity of samples of a cement mortar made with

TABLE 2. *Characteristics of portland cement "B"*

Time of testing	Fineness of grinding (percentage residue on screens)		Normal consistency		Setting time		Liter weight		Ultimate compressive strength of mortar specimen (1:3) for various hardening times			
	No. 021 (900 openings per sq cm)	No. 0085 (2,900 openings per sq cm)	Cement paste	Mortar	Beginning	End	Loose	Dense	1 day	3 days	7 days	28 days
			Percent	*Percent*	*hr:min*	*hr:min*	*g/liter*	*g/liter*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*
When received from factory	1.0	4.52	26.75	7.69	4:30	5:30	1,025	1,256	199	371	490	565
After aging			21.50	6.37	3:55	6:55			128	303	408	535
After repeated grinding	.1	4.52	29.0	8.25	3:35	6:15	1,025	1,256	91	249	393	496

TABLE 3. *Concrete components for portland cement "B"*

Cement	Components of concrete			w/c	Content of cement admixtures	
	Water	Sand	Crushed stone		Gypsum	Tripolite
	kg/m³	*kg/m³*	*kg/m³*		*wt %*	*wt %*
250	110	approx. 575	approx. 1,490	0.44	----------	----------
	120			.48		
	130			.52		
	140			.56		
	150			.60		
323	110	approx. 476	approx. 1,490	.34	----------	----------
	120			.37		
	130			.40		
	140			.43		
	150			.46		
400	120	approx. 452	approx. 1,490	.30	5 and 10	----------
	130			.325		
	140			.35		
	150			.375		
	160			.40		
	180			.45		
450	130	approx. 486	approx. 1,370	.29	----------	10, 20, and 30.
	140			.31		
	150			.33		
	160			.356		
	180			.40		
500	140	approx. 300	approx. 1,490	.28	----------	----------
	150			.30		
	160			.32		
	180			.36		
	200			.40		

TABLE 4. *Influence of relative humidity on porosity of cement mortar*

Relative humidity, percent	Initial w/c	Total porosity at different times of hardening			
		2 days	7 days	28 days	90 days
75–80	0.29	12–13	13–14	14–15	13–15
	.27	8–11	12–15	14–15	14–15
	.25	12	16	17	16
	.23	18	18	17	17
100	.29	8–10	8–10	5–9	4–5
	.27	7–9	9–10	6–11	5–6
	.25	12	12	9	4
	.23	16	8	9	7

standard sand (composition 1:2, w/c=0.29–0.23) increases in case of air hardening at a relative humidity of 75 to 80 percent and in a water-saturated atmosphere. These tests were carried out on cement from "K" clinker obtained in the laboratory by dry grinding. The fineness of grinding of cement containing 5 percent of gypsum, as measured on the Tovarov apparatus, was 4,000 cm²/g.

The features of concrete (mortar) hardening kinetics as affected by admixtures of plasticizers should also be noted. These results confirm our hypothesis of retarding of hardening processes of the cement paste when introducing plasticizers. During the beginning of hardening (5 days), even when hardening at 100 percent relative humidity, the samples containing 0.2 percent plasticizer had a higher porosity than samples without a plasticizer and with 0.1 percent plasticizer. This observation suggests that the structure of cement paste of low-aluminate clinker worsens when 0.2 plasticizer is introduced. However, after 90 days of hardening, the porosity of samples with 0.2 percent plasticizer was lower than for the others. During normal hardening conditions in water the porosity of samples is significantly lowered after some time. When the samples are airhardened without moisture saturation their porosity systematically increases (table 4). Any increase of porosity influences the durability of the concrete. Therefore, even for optimal hardening regimes, it is important what structure of cement paste is designed. Moreover, when designing concrete, increase of porosity is of some importance since it leads to significant worsening of the structure of the cement paste and the texture of the mortar due to incorrect care of the molded material.

In the case considered, the porosity is increased due to a change in the quantity and size of the pores, thus varying the mechanical strength of the concrete. This change is clearly seen when the strength of concrete is determined at an age of at least 28 days. However, due to the hardening features of such minerals as tricalcium aluminate or aluminoferrite, the change of strength at the beginning (1–7 days) cannot be used to judge the variation of porosity.

The preceding shows the importance of curing in concrete hardening. It should be borne in mind that concrete with a high initial w/c, hardened for a long time under normal "aging" conditions, has a lower porosity and better structure than concrete with a lower w/c, hardened under conditions of insufficient humidity. The mentioned feature is of extraordinary importance for high-strength concrete of "stiff" concrete mixes, always being taken into account.

For certain climatic conditions it is possible to produce frost-resistant concrete by designing and preparing concrete with passive capillaries.

Due to the creative cooperation of the Department of Building Materials of the All-Union Institute of Transport Construction with scientific workers of the Institute of Theoretical and Applied Mechanics of the Academy of Sciences of Czechoslovakia (Prof. B. Gazar, B. Counovsky, A. N. Slovatsky, J. Jambor, and others), it was possible to investigate two plasticizers of the sulfite cellulose extract type, "C" and "vusal." This study is most interesting since, in spite of the various investigations widely carried out, the role of the plasticizer, universal in its action on the cement paste (mortar or concrete mix) and the hardened cement paste obtained from it (table 5), has been underestimated by some specialists in foreign countries.

These plasticizers were proposed and investigated by scientists in Czechoslovakia. Several papers have been published on the use of these plasticizers for construction. Wide investigations have been carried out in Czechoslovakia by J. Jambor.

The papers of the Czechoslovakian scientists noted the excellent properties of these plasticizers, which are similar to the properties of Soviet plasticizers. Simultaneously, some abnormal cases were noted when working with these plasticizers.

TABLE 5. *Influence of type "C" plasticizer on frost resistance of concrete*

Portland cement (laboratory index)	Amount of plasticizer (percentage of cement weight)	Number of freezing-thawing cycles	Estimation of condition of specimen	Ultimate compressive strength	
				Standard	After freezing
			Points	*kg/cm²*	*kg/cm²*
"Bl"	0.1	120	10–10p	490–634	495[a]–562
		222	10–10p		460[a]–544
		319	9–10p		412[a]
	.2	222	10	600–639	432–600
		350	10		386–622
		467	9–10		510–535
		567	9		540–568
	.3	222	10	466–540	443–547
		350	10		565–595
		467	9–10		550–600
		567	9–10		420–550
	.4	222	10	440–610	512–533
		350	10		466–497
		467	9–10		502–525
		567	9		402–500
"B"	.1	102	10	435–436	480–512
		193	9–10		428–450
	.2	193	10	505–626	445–512
		326	9–10		394[a]–520
		417	8–9		364[a]–386[a]
	.3	193	10	505–610	480–628
		326	9–10		518–575
		417	9		490–575
		106	10	476–500	396–440
		417	8		395–455

[a] Visible crack network on specimen.

Note: The best concrete composition for the last test (Mar. 1960) passed over 2,000 cycles without changing the external shape of the specimens.

The study of these cases confirms what is said above on the necessity of estimating the quality of the plasticized cements. Some cements have delayed initial and final set, especially at high w/c ratio. Delay of the hardening processes may be observed by determining heat emission.

The plasticizers positively influence impermeability, chemical resistance, and frost resistance of concrete, and lower the absorptive capacity of concrete (mortar). It is considered that the plasticizers, in particular type "C," "partially increase" the bond with the reinforcement; it is advised that this admixture be used for highly reinforced structures. The application of plasticizers improves the transportability of the concrete mix, insuring the absence of segregation and improving the quality of the injected mortar.

The introduction of plasticizers into concrete (reinforced concrete) with air-entraining (air-retaining) agents is a very effective technical measure. All kinds of cement should be manufactured with such admixtures. The application of plasticizer dosages to concrete, as mentioned above, should be performed only in accordance with the active mineralogical and chemical content of the cement.

The Frost Resistance of Reinforced Concrete Structures

Reinforced-concrete railway sleepers, parts of communication-circuit line posts, blocks for prefabricated tunnel lining, and roof slabs were delivered to station No. 2 for checking the frost resistance of reinforced-concrete structures. All products were made with sized crushed granite. Concrete of similar composition was used for manufacturing reinforced-concrete products parallel with testing of cubic specimens. Comparison of the results of testing of cubes and products affirm the following:

1. The influence of the molding conditions of concrete mixes.
2. The influence of the arrangement of reinforcement in the concrete on the frost resistance of products. In particular, during tamping of mixes special attention should be paid to the molding of the protective layer of the article, including the side surfaces of the sleepers. In this case it is necessary to maintain vibration of the mix such that the side walls of the mold do not move horizontally, causing the entrainment of large air bubbles in the mix.

It was only natural that the previously employed system of estimating the condition of structures should be changed, and this was accordingly done. Two kinds of destruction of different intensity may be observed. One, designated by the letter "a" relates to the destruction of sleepers at the sides with destruction of the protective layers along the entire length of the sleeper. Each kind of destruction is estimated according to a six-point scale, which fixes the condition of the sleeper ends (end 1 and end 2). Estimation in points is given in the form of a relationship of the points for each end of the sleeper. All cases of destruction were observed during the last five years of investigation of frost resistance when studying the problem of different methods of tamping the concrete mix. During the testing process it was required to find whether the proposal of the author of the present report was correct as to the possible difference in quality of concrete of one and the same composition, molded on one and the same vibrating platform, only with different oscillations of the mold.

Testing of sleepers for frost resistance was performed at climatic station No. 2. Significant changing of the sleeper edges was noted only after 400 cycles. At this time the ratings were estimated (at the ends of the sleeper) for two sleepers: $\frac{\text{IIa}}{\text{Va}}$ (sleeper No. 1) and $\frac{\text{I}}{\text{IIa}}$ (sleeper No. 2), while after 450 cycles the ratings were $\frac{\text{IIa}}{\text{VIa}}$ and $\frac{\text{unchanged}}{\text{Va}}$. In this case the highest rating is I.

The condition of both ends of the sleeper molded without shifting and repeated vibration, at 400 cycles was estimated as IIIa, and at 450 cycles as IIIb.

Repeated testing of frost resistance of sleepers manufactured from a concrete mix containing 450 kg/m³ of cement with a plasticizer (concentrated sulfite cellulose extract) gave similar results. Testing of these sleepers is being continued.

Cubes of size 10×10×10 cm from a concrete mix of the same composition were molded on a laboratory vibrating platform and tested for frost resistance in the laboratory freezing chamber. After 450 cycles, hair cracks appeared on the specimens. It should be noted that one end of sleeper No. 2 shows no signs of destruction, consequently, during molding of sleepers on the vibrating platform it is possible to obtain a concrete, the frost resistance of which is higher than for the "standard" specimens manufactured on the laboratory vibrating platform.

For samples of sleepers used for testing, freezing was performed on cubes of size 10×10×10 cm made from the same concrete mix as the reinforced-concrete sleepers. The water content in the concrete mix, in the samples used for freezing, was 105–160 kg, and the cement content was 350–500 kg/m^3. All sleepers except one were tested after 117–243 days. Testing showed that destruction of the sleepers begins as a rule at the face and side surfaces. Destruction proceeds on the sections where the concrete is not uniform. The product behaves as though made of different concretes, even though this effect does not appear under static testing. As indicated, it has different mechanical strength and frost resistance or sulfate-resistance, etc. During analysis of the results of testing the first 34 sleepers of a large lot delivered for testing, heterogeneity of the concrete appears as follows. During the given period of test, opposite ends of the same sleeper undergo destruction with different intensity; as a rule, destruction begins at the faces of the sleeper and at the side surfaces along the protective layers of concrete; sleepers molded from a concrete mix on vibrating platforms have higher frost resistance than sleepers molded by other methods; sleepers molded from a concrete mix with lower water content (lower w/c ratio) on vibrating platforms have higher frost resistance than sleepers from mixes with higher water content. The destruction of the latter has a local character, if the concrete mix has a low consistency limit, with low water content (less than 150 kg/m^3 of water). For example, in two sleepers, at the 85th cycle destructions rated at IIa were noted. These destructions, up to 400 cycles, did not develop further; but as the tests proceeded, the area of these places was destroyed. Consequently, the sleeper had non-frost-resistant weak sections after 85 test cycles, even though as a whole, the sleeper was frost-resistant. One of these sleepers was removed from tests of frost resistance after 490 cycles with rating I/IIIb and passed tests of multiple repeated loading which it resisted. These tests, as well as the testing of cubes, showed that ethanol varnish cannot protect concrete with defects in the structure of the cement paste and in the concrete texture. However, for manufacture of a good quality of sleeper, it is possible to produce concrete of high frost resistance. Coating the concrete with ethanol varnish cannot compensate for deficiencies in the quality of the materials used, the concrete mix, and the concrete. Coating partially prevents defects caused by unsatisfactory care of the hardening concrete. For example, coating the concrete with ethanol varnish eliminates the formation of shrinkage cracks, and for other conditions it aids in production of concrete of higher frost resistance.

Testing sleepers with stressed coil reinforcement, made by standard technology, with tamping by suspended vibrators, does not show good results. Sleepers of concrete containing 350 kg/m^3 of cement, with 2 percent of $CaCl_2$, and 126 kg/m^3 of water were covered with cracks at the 42d cycle. The concrete was severely destroyed under weak impacts, this being connected with nonobservance of the rules for curing of the concrete. Testing of frost resistance of sleepers with stressed wire reinforcement was performed by the standard technology production methods. Molding of the sleepers was carried out by internal electromechanical vibrators with motors on one shaft, CNJIS-type, and additionally by surface vibrators.

Testing of about 120 reinforced concrete sleepers at the climatic station showed that only "stiff," properly molded concrete mixes insured preservation of the sleepers under these conditions. Thus, for example, the concrete of sleepers with 150 kg water and 350 kg/m^3 cement, had the lowest frost resistance according to the results of testing of cubes which were destroyed after approximately the same number of cycles as the sleeper. If, for mass structures with great thickness of the protective layer, the concrete is destroyed by cracks or crumbling, scaling of the surface does not have a catastrophic character; but such destruction of concrete is not allowable in precast reinforced concrete structures, especially with prestressed wire reinforcement where the thickness of the protective layer is 15–25 mm. It should be noted that destruction of the concrete in the sleeper depends closely on the strength of the concrete after one day. The lower the strength, independent of the concrete grade, the lower the frost resistance. This behavior is only natural, until we can create hardening conditions for the sleepers of the same kind as for the control cubes and consequently obtain the same structure in relation to frost resistance during a long hardening period as for sleepers with high one-day strength. This problem is very important for practical purposes. Testing at the climatic station of the frost resistance of the control cubes for several sleepers is also interesting in some respects. In the following table are given the results of these tests, which were performed at the same time as the testing of the sleepers.

Two tenths of one percent of a sulfite-cellulose-extract plasticizer was introduced into the concrete.

As can be seen, on the basis of results up to the 128th cycle none of the cubes showed signs of lack of frost resistance of the outer layers of concrete, while local destruction was noted on one of the sleepers at the end (rating IIa). At the 176th

Results of tests on frost resistance of control cubes and of several sleepers

Item No.	Content of water and cement	Estimation in rating points, of condition of samples during the indicated number of test cycles							
		80	128	176	240	340	352	408	464
	kg/m³								
1	127:350	10	10	9	8	7	6	5	3
2	130:350	10	10	10	9	8	8	7	5
3	135:450	10	10	10–9	9–8	7	6	5	3
4	140:400	10	10	10	10	10–8	9–7	9–7	8–6

cycle, parts of the cubes were partly destroyed (rating 9), while the condition of the ends of both sleepers was estimated at IIIa. At the 400th cycle, destruction of the cubes reached rating 5 and, of the sleepers, rating IVa. At this point, the destroyed depth at the faces exceeded 11 cm, the reinforcement was bared, and large cracks appeared as well as a network on the part of the sleeper under the rail. At the 464th cycle, destruction was significantly enhanced, as was indicated for the cubes by a rating of 5 and for the sleepers by a rating of Va. The frost resistance of concrete cubes and sleepers hardened under the same unfavorable conditions was lower than that of concrete of the same composition hardening under favorable conditions. The tests have shown that it is possible to attain complete agreement of test results for cubes and products of the same concrete mix if there is elimination of defects connected with lack of uniformity of mix tamping during molding of reinforced concrete products and the arrangement of the reinforcement in the concrete.

Testing of sleepers of concrete with a high content of cement (550 kg/m³) and water (165 kg/m³) shows that with poor curing of the hardening sleepers the concrete does not possess high frost resistance. At the 100th cycle, sleepers of such concrete of rapid-hardening cement show clear signs of destruction—scaling of edges and corners below the rail. Calcium silicate sleepers, at the 100th cycle, also show insufficiently high frost resistance. At this time, splits form at the corners and edges and adjoining parts of the faces. Destruction of calcium silicate sleepers is similar to destruction of samples of mortar with partial de-aeration during hardening in water. This is only natural, as the effect of contraction for portland cement and calcium silicate differs, leading to different destruction procedures for these materials and different durabilities. It should be noted that coating, with ethanol varnish, a sleeper made of concrete containing 140 kg/m³ of water and 450 kg/m³ of cement with 0.2 percent plasticizer, results, after 600 cycles, in a good external appearance. This sleeper did not have any embedded members of wood (drift sleeves) which should in no case be allowed in reinforced concrete structures. The face parts of the sleepers should not have weakened places due to shifting of wires and anchor sections during manufacturing. During the testing of double-bar sleepers it was observed that destruction of concrete started at the places of fastening of the bar ends. Bunches of wires cause severe destruction of the sleepers.

On the basis of the preceding presentation it is considered that the problem of manufacture of prestressed reinforced concrete sleepers having a durability of 100 years and more, and capable of resisting over 400 freezing-thawing cycles, is solved.

Let us now consider some of the results of initial tests with other types of structures. The test samples of structures were posts made in wooden molds inserted into special steel shells. Molding was performed on two nonsynchronized five-ton platforms, type CM–476. The steel shells were fastened to the vibrating platforms by means of wedges. In this case the concrete mix was tamped without additional loadings. At the beginning of testing the concrete had different hardening periods, from 1 to 2 years. The tension of reinforcement was performed on the mold during concreting of the posts in a horizontal position. Besides these posts, the same type of prestressed post was tested without steaming and manufactured by standard technology. Wire tensioning was performed on special stops. The posts were made in steel forms on a vibrating platform, only this time in a vertical position. The thickness of the post walls was 50 mm.

On the basis of test results at the 100th cycle, only one specimen was destroyed. At the 200th test cycle, two samples, Nos. 1 and 3, did not show any signs of destruction of the concrete surface. On the other concrete specimens, only insignificant signs of destruction were visible in the monolithic structure in the form of disorientated weak cracks and longitudinal cracks. At the 300th test cycle, the strongest samples (Nos. 1 and 3) showed the same defects. Further destruction appeared in the form of crumbling of the concrete at the edges and faces. For samples Nos. 1 and 3, this crumbling was observed at the 400th cycle, and for the rest, at the 350th cycle. At 800 cycles all structural members were entirely destroyed, baring the reinforcement.

Testing of frost resistance was also performed with test samples of prestressed corner members for telegraph posts. The corner members (reinforced concrete parts in the form of wide flange angles) were made with "rapid" cement without gypsum. This cement had been stored for 1.5 years, but the time of initial set had not changed. For correction of this deficiency, gypsum (3 percent) was added. Concrete for corner members contained 158 kg of water and 400 kg of cement per cubic meter. During the first 14 days, the corner members hardened under conditions of usual production care, and then under natural conditions. At the age of 28 days, the corner members were tested for frost resistance. The strength of control samples R_{28} under compression was 460 kg/cm². At the 100th cycle of testing, severe destruction of the corner members began.

When steaming concrete or during common hardening in open air, worsening of hardening conditions is possible, leading to lowering of the content of lime in the concrete with simultaneous lowering of concrete density. Therefore, that type of hardening is considered the best which ensures observation of the mentioned conditions. We consider that in this case the best cement should be made by fine wet grinding, creating the conditions for more effective progress of processes, insuring dense, corrosion-proof structures.

After the 100th freezing-thawing cycle, definite advantages were evident relative to the concrete in post No. 3. Thus, when the concrete of posts Nos. 1 and 2, at a rating of several points, was crumbling, and the reinforcement was bared, the concrete of post No. 3 did not have such destruction. Cracks and networks of hair cracks were observed on all posts.

Special attention should be paid to the problem of preservation, near the reinforcement, of an alkaline medium. However, for some depth of the protective layer of concrete, especially during low-quality molding with "stiff" steaming regime, the lime is rapidly combined with carbon dioxide, this not being allowed for in establishing the entire depth of the layer.

When making sleepers and posts, special attention should be paid to correct selection of the time of transmission of stresses to the concrete, and for preventing water seepage paths. The face parts of the sleepers, posts and other structures should be tamped thoroughly. It is important to select the amplitude of oscillations of the vibrating platform, confining it to the range of 0.3 to 0.6 mm (for 3,000 oscillations per minute).

The amplitude of oscillations of the vibrating platform (vibrating stand) should be selected in a practical way, on the basis of the working conditions for molding. The amplitude of oscillations, in particular, depends not only on the weight of the form, and the mix, but also on the thickness of the tamped layer. Resonant oscillations, which create impacts and, consequently, prevent bond of the reinforcement with the concrete, should not be allowed. The optimal value for obtaining dense concrete, in application to concrete mixes with low consistency limits, should be considered (for example, 110–120 kg of water, 350 of cement per cubic meter). Molding of such concrete mixes should be performed on a double-frequency stand, choosing the optimum amplitude of oscillations and employing a dynamic additional load. Before tamping and during the first stage of tamping, the concrete mix should be in a vacuum. When tamping mortar and concrete mixes (with aggregate of various sizes), the thickness of the layer of the mix is of decisive importance.

In this respect, the tamping of concrete mixes is somewhat difficult in forms of variable section—in steel forms of I-beam section, in particular. A lower amplitude of oscillations is needed for the lower flange, while a higher amplitude is needed for the web. The flange has a variable height and it is, therefore, advisable that the amplitude of oscillations of the mix should vary with the height. It is, therefore, important to adjust the tamping conditions by using different frequencies and their combinations, since changing the oscillation amplitude at one frequency is still impossible.

Contact line posts with stressed deformed reinforcing bars, manufactured in the centrifugal machine at the laboratory shop of our Institute, were sent to climatic station No. 2 for testing for frost resistance. The posts were tested in half-immersed horizontal condition. Testing is now in the stage (300 cycles) where destruction of the inner layer of the post wall may be seen.

The duration of centrifuging was 20 min. Steaming of molded posts was performed at 80 °C. The surface of post No. 3, some days after steaming, was coated with two layers of perchlorvinyl enamel XB–26 (table 6).

TABLE 6. *Characteristics of cement "B" and concrete of experimental centrifugal contact line posts*

Post No.	Cement characteristics			Concrete components after centrifuging				Sulfite cellulose extract	Steaming regime
	Activity	Normal consistency	Term of storage	Cement	Water	Sand	Crushed stone		
	kg/cm²	*percent*	*mo.*	*kg/m³*	*kg/m³*	*kg/m³*	*kg/m³*	*percent*	*hr*
1	600	28	45	399	172	477	1,370	0.2	During 4 hrs 3+8+0
2	620	29.5	0	400	179	520	1,320	.2	During 8 hrs 3+10+0
3	595	29	25	414	149	585	1,310	.2	During 60 hrs 3+8+0
4	600	28	15	412	157	530	1,340	.2	During 4 hrs 3+10+0
5	600	28	15	404	175	510	1,300	.2	During 4 hrs 3+9+7

Notes:
1. Support No. 3 is coated with a steam-insulation layer.
2. The strength of each post after 28 days, in kg/cm²:

	No. 1	No. 2	No. 3	No. 4	No. 5
Initial	368	320	410	366	465
After centrifuging	445	539	440	430	---------

3. Posts Nos. 1 and 2 are reinforced with prestressed wires; the others are reinforced with bars, prestressed before concreting.
4. At one and the same w/c ratio (in initial amount of water) from the mix for post No. 3, 58 liters were discharged in comparison with 34 liters of sludge for post No. 5.

As expected, after 100 test cycles the strongest post was No. 3. However, even in this post, scaling of the mortar part of the concrete at the inner surface of the post was noted. The inner layers of concrete contain a relatively higher amount of water than the outer ones, this condition being caused by centrifuging. On post No. 5, destruction of this type proceeded to a depth of 20–25 mm. On all posts, except No. 3, at 100 cycles a network of longitudinal hair cracks appeared, with a smaller amount on post No. 4, the concrete of which contained a smaller amount of water in comparison with concrete posts Nos. 1, 2, and 5.

Extensive tests, performed with an industrial centrifugal machine in the laboratory shop of our Institute, have shown that during molding of posts by centrifuging it is possible to lower significantly the content of water in the concrete in comparison with the amount employed. Detailed instructions are given in the corresponding specifications for manufacture of centrifugal contact line posts. The importance of smooth changing of centrifugal speeds for compaction of the mix has been established.

The hardening regime, including steaming, is of exceptional importance for concrete durability.

Let us consider some of the results of our investigations of frost resistance of steamed concrete.

In 1955, the author began investigations on the influence of steaming on concrete manufactured from portland cement of high grade, and from rapid-hardening high-strength cements in particular. It was desired to establish the possibility of accelerating the process of manufacturing stressed reinforced products. Such investigations had never been performed previously. In various instructions on concrete steaming it has been mentioned that the lowest effect was that of steaming concrete made of portland cement (tables 7 and 8).

Several tests have been carried out for checking the frost resistance of steamed concrete on cement produced in vibratory mills. Cements "B" and "Bl" were used for making specimens of size 10×10×10 cm. The mineralogical content of cement "B" (in percentage) was C_3S, approximately 55 percent; C_2S, 20 percent; interstitial substance, 25 percent. The mineralogical content of cement "Bl": C_3S, 50 percent; C_2S, 20 percent; and interstitial substance, approximatley 25 percent. The specific surface (according to Derjagin) of initial cement "B" was 13,110 cm²/g and of cement "Bl," 13,180 cm²/g. After repeated grinding, the specific surfaces of the cements were 18,130 and 22,200 cm²/g respectively. During repeated grinding no additives were introduced into the cement.

TABLE 7. *Influence of steaming regime on strength of concrete with portland cement "B"*

Item No.	Content of water in concrete	Ultimate compressive strength of concrete at various times							Steaming regimes				
		Normal hardening			After steaming				Duration of stages				Strength of sample in percentage of R_{28} of normal hardened sample
		3 days	7 days	28 days	1-2 days	3 days	7 days	28 days	Preliminary duration	Temperature increase to 80 °C	Duration at 80 °C	Temperature drop to 52-57 °C	
	kg/m³	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*hr*	*hr*	*hr*	*hr*	*Percent*
1	135	415	462	548	289	---	482	558	---	2	2	2 [a]	52.6
2	135	415	462	548	493	466	477	522	---	3	2	10	89.5
3	135	415	462	548	433	---	477	522	---	2	2	10	80.5
4	135	418	462	540	494	---	---	---	3	3	10	1 [a]	91.5
5	135	418	462	540	530	---	---	602	3	3	2	10	98
6	140	375	471	506	455	460	492	---	---	3	2	10	89.6
7	140	375	471	506	241	460	492	---	---	2	2	1 [a]	47.8
8	140	375	471	506	328	460	492	486	---	2	2	1 [b]	64.8
9	150	466	467	534	442	416	464	484	---	3	2	10	83
10	170	354	458	509	356	464	507	496	---	3	2	10	70
11	190	278	357	375	268	338	339	390	---	3	2	10	71.5

[a] The samples were removed from the steaming chamber at T=70-80° C.

[b] The samples were left for 15 hr in an open chamber. The concrete contained 450 kg/m³ of cement for each test series.

TABLE 8. *Influence of steaming regime on strength of portland cement "Bl"*

Item No.	Concrete components		Ultimate compressive strength of concrete at various times							Steaming regimes				
	Water	Cement	Normal hardening			After steaming				Duration of stages				Strength of sample in percentage of R_{28} of normal hardened sample
			3 days	7 days	28 days	1-2 hr	3 days	7 days	28 days	Preliminary duration	Temperature increase to 80 °C	Duration at 80 °C	Temperature drop to 52-57 °C	
	kg/m³	*kg/m³*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*hr*	*hr*	*hr*	*hr*	*Percent*
1	135	460	403	550	565	289	---	468	535	---	2	2	2 [a]	51.3
2	135	460	403	550	565	451	---	468	535	---	2	2	10	80.0
3	135	460	403	550	565	516	---	409	564	---	3	2	13	91.5
4	135	460	403	550	565	518	---	499	544	---	3	2	13	91.5
5	135	460	403	550	565	528	528	---	525	3	3	2	12	93.5
6	135	460	403	550	565	491	---	---	519	3	3	10	2	87.0
7	150	450	---	---	527	450	---	---	502	---	3	2	13	85.4
8	160	450	---	---	483	417	---	---	517	---	3	2	13	86.4
9	170	450	---	---	427	343	---	---	510	---	3	2	13	80.6
10	190	450	---	---	---	220	---	332	369	3	3	2	12	---
11	190	450	---	---	---	239	---	---	---	3	3	10	2	---

[a] The samples were removed from the steaming chamber at T=70-80 °C. The strengths of the steamed samples Nos. 2-6 are compared with the strength of sample No. 1, which experienced normal hardening.

The samples were made of concrete containing 450 kg of cement and 135 and 157.5 kg of water per cubic meter (w/c ratio–0.30 and 0.35).

Crushed granite was used as the coarse aggregate. Before steaming, the samples were stored for 3 to 5 hr. Both increase and decrease of temperature were carried out during 4 hr. Some of the samples were hardened under normal conditions.

Testing of samples for frost resistance was carried out in a freezing chamber. The samples were inspected after each cycle and were systematically weighed.

The hardening conditions play an important part in influencing the frost resistance of the concrete. If the hardening regime of concrete does not insure deep hardening, the frost resistance of the concrete is lowered. Similar destruction is observed in concrete hardening at the usual temperature with evaporation of water from it, and in concrete steamed at insufficient relative humidity.

The results of the tests show that concrete made with cement "Bl" was of lower frost resistance than concrete made with cement "B". This is clearly seen when testing specimens of concrete with high water content (157.5 kg/m^3). Whereas, for specimens made with cement "B", none of the investigated regimes of steaming significantly influenced frost resistance, the samples made with cement "Bl", with changed steaming regime and increase of temperature from 60 °C to 80 °C, and duration of isothermic heating of 12 hr, show sharply lowered frost resistance. The trend of lowered concrete frost resistance with cement "Bl" is shown also with specimens made with lower water content (135 kg/m^3), both for hardening under normal conditions and for steaming under various regimes. In both cases, a relatively low frost resistance was observed. Our numerous experiments with mortar and concrete samples, with synthetic (single-mineral and polymineral) cements, and with cements produced in laboratories and factories by grinding (the usual dry grinding, vibratory disintegration, and wet grinding), have shown that in several cases, the concrete (mortar) with a significantly lower cement content has an incomparably higher frost resistance. This fact, we consider, is connected in particular with increase in the cement of the active quantity of tricalcium aluminate, with its tendency to form coagulation structures that are not frost resistant. The introduction into the cement of plasticizers and an additional quantity of gypsum should lead to increase of the density of the reground cement and to increase of its frost resistance. However, at the present stage of investigation, not knowing the precise ratio of active quantities of gypsum and aluminate in the hardening process, we still cannot prove this beyond contradiction. The high frost resistance of concrete with cement "B" probably could be explained by the consideration that after its regrinding to a specific surface of 18,130 cm^2/g the ratio between the active amount of tricalcium aluminate and gypsum was more optimal (smaller amount of coagulation structure in the hardened cement paste), than in cement paste with cement "Bl", reground to a higher surface (22,200 cm^2/g). The above-mentioned conclusion is verified in particular by tests of the frost resistance of mortar specimens made with other kinds of cement from the same factories.

The tests performed have shown that steaming has a variable influence on the frost resistance of concretes of different compositions, manufactured from different cements.

The frost resistance of concrete manufactured from cement "B" and subjected to steaming by the mild regime, which insures obtaining a strength 73 percent of that of R_{28}, was not lower than the frost resistance of concrete hardening under normal conditions.

The testing of concrete manufactured from cement "Bl" has shown that its frost resistance depends on the water content. Concrete hardened under normal conditions, with a lower water content (135 kg/m^3), had a higher frost resistance. For concrete containing 157.5 kg/m^3 of water, the best results were obtained with samples steamed 16 hr at 60 °C. However, this concrete cannot be employed for products and structures subject to conditions of frequent and systematic freezing and thawing.

The conditions of concrete hardening influence to a very high degree the durability of the concrete. Therefore, when evaluating the rapid regimes of hardening of concrete it is necessary to determine the conditions of the hardening process (creation of structure) of the cement paste in the concrete.

The grade strength of the concrete is necessary as a criterion when estimating the conformance of design data to the actual strength of the concrete in the structure or product.

However, when estimating the quality of the concrete by the grade strength, in the majority of cases another technical-economic value of the same importance is forgotten—the relative strength of the concrete. The latter is directly connected with the degree of utilization or reaction of the cement in the process of concrete hardening up to 28 days. It is known that concrete of the same grade may be obtained with different kinds and grades of cement with significant degree of cement utilization. As a rule, after obtaining concrete of the required grade, the builder is not interested in further increase of concrete strength, just as the person designing the concrete composition is not interested in the problem of further increase of concrete strength, and in economy in relation to cement consumption. However, the increase of concrete strength, both during the first 28 days and for a longer time, is an objective indication of the quality of design, preparation, strength, and durability of the concrete.

Concrete, the strength of which increases systematically and with high intensity, will be of higher density and, consequently, of greater durability. If the concrete hardens for one day or for seven days under normal conditions, its strength after 28 days in both cases may be about the same, while the frost resistance will differ. This is natural and results from the simple determination after a long time of the strength of concrete specimens hardened under normal (100 percent relative humidity) conditions for a different time after preparation. Concrete hardening under normal conditions for 28 days continues to harden thereafter (naturally up to a certain limit). Concrete that hardens under normal conditions for only 7 days practically stops becoming stronger after 28 days. An even worse result is obtained in case the concrete hardens under normal conditions for less than 7 days. By grinding the cement and insuring normal conditions for concrete hardening, it is possible to lower the duration of the period of care (curing) of concrete and to increase its relative strength. In no case should the water be allowed to evaporate from the freshly placed concrete. If the steaming regime of concrete conforms to this condition and allows for full contraction in the cement paste, the latter is obtained with strong and durable structure, which simplifies and accelerates the technological process of manufacture of products. However, violation of the steaming regime is accompanied with intensive water evaporation from the concrete, leading to a low coefficient of utilization of the cement, lowering of relative strength and density of the concrete and, consequently, to lowering of durability.

Let us consider the results of testing the frost resistance of samples of plastic cement mortars (1:3) made with Volsk-type normal sand. The consistency of mortar mixes was similar in all cases. The mortars were made with portland cements "B" and "Bl". Cements produced at factories as well as those reground in vibratory disintegrators were used. Some lots of cement were reground with gypsum and plasticizers. The specific surface (according to Derjagin) of cement "B" produced in factories was 18,050 cm^2/g, and of cement "Bl", 14,730 cm^2/g.

As a rule, specimens with additives of gypsum and plasticizers came through the frost-resistance test with strengths nearly the same as those of corresponding specimens—standards—hardening in water.

The strength of specimens made without these additives was lower than that of the corresponding "standard" specimens.

The tests showed that, with one and the same cement, it is possible to obtain mortars possessing different frost resistances. They also verified the influence of the fineness on the lowering of frost resistance, when not combined with organized direct hardening of the cement paste.

Thus, for example, specimens made with cement containing an additive of 3 percent gypsum and 0.2 percent sulfite cellulose extract, and having a specific surface of 21,050 cm^2/g, reached after 300 test cycles a strength of 557 kg/cm^2, while the corresponding "standards" showed 678 kg/cm^2.

Specimens made with cement not containing additives, and having a specific surface of 25,260 cm^2/g, already after 250 cycles had lower strength in comparison with the "standard." The latter had a significantly lower strength than the specimens made with coarsely ground cement but containing additives. As a result of repeated grinding in vibratory mills three lots of each cement were obtained differing in degree of fineness. The specific surfaces of the different lots of cement "B" were 15,730, 13,130, and 20,330 cm^2/g; of cement "Bl", 18,600, 21,050, and 25,260 cm^2/g (tables 9 and 10).

The specimens of cement mortars were first tested for frost resistance in a freezing chamber and then at climatic station No. 2, where they passed 50 to 200 freezing-thawing cycles. At the same time that the strength of the specimens that had frozen was being determined, corresponding specimens stored in water under normal conditions were tested. Testing of the specimens was stopped after the edges and corners became rounded (rating point 3). During testing of samples in compression, scattering of results was observed, this being explained by the imperfection of the test procedure. In several cases lowered strengths were obtained owing to the distorting influence, in the press, of the destroyed surface layer of the cement mortar, even though as a whole the test specimen was not destroyed.

In the specimens that were under the action of aggressive media, it was necessary, before the compression test, to determine the hardness of the surface layers, in order to avoid the influence of the latter on the strength. It was also necessary to polish the surface of the sample prior to compression testing, in order to create comparable conditions for testing.

Hardening of concrete under conditions hampering the hydrolysis and hydration processes of cement reduces the quality and leaves a remainder of unreacted cement. It is incorrect to solve the problem of correct content of cement, and manufacture of durable concrete, by fine grinding of the cement, by vibration of the concrete mix at different frequencies, etc., without taking into account the importance of self-compaction of the concrete during the hardening process. This problem has seldom been considered in the technical literature.

Curing of structures of precast reinforced concrete is of very great importance, since their cross sections are small. Lately, in the technical literature, an outstanding problem has been the durability (strength) of concrete and the role of protective layers over the reinforcement, which is also connected with the use of precast structures. The mechanical strength of concrete is referred to as "stability," in order to accentuate the possibility of its impairment as time passes. However, these articles do not consider the importance of the conditions and time of hardening of concrete, plain

TABLE 9. *Frost resistance of plastic mortars (1 : 3) of portland cement "Bl"*

Item No.	Specific surface of cement	Additive		w/c ratio	Compressive strength of sample							
					After the indicated number of test cycles [a], [c]							At climatic station additionally after 50 to 200 test cycles
		Sulfite cellulose extract	Gypsum		100	150	200	250	300	350	400	
	cm²/g	*Percent*	*Percent*		*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*
1 [b]	13,050	---	---	0.5	$\frac{200}{308}$	$\frac{249}{383}$	$\frac{201}{362}$	$\frac{203}{494}$	$\frac{245}{390}$	$\frac{270}{449}$	$\frac{293}{473}$	$\frac{218}{429}$
2 [b]	15,730	---	---	.5	$\frac{300}{382}$	$\frac{185}{385}$	$\frac{177}{377}$	$\frac{171}{381}$	$\frac{224}{450}$			$\frac{218}{429}$
3	15,730	0.2	3	.37	$\frac{413}{410}$	$\frac{403}{425}$	$\frac{390}{455}$	$\frac{314}{436}$	$\frac{368}{500}$	$\frac{395}{508}$	$\frac{449}{488}$	$\frac{420}{498}$
4	15,730	.2	5	.4	$\frac{300}{278}$	$\frac{310}{392}$	$\frac{362}{430}$	$\frac{334}{438}$	$\frac{425}{498}$			$\frac{450}{439}$
5	18,130	---	---	.5	$\frac{285}{371}$	$\frac{204}{374}$	$\frac{220}{390}$	$\frac{217}{422}$	$\frac{77}{424}$			$\frac{222}{390}$
6	18,130	.2	3	.4	$\frac{424}{444}$	$\frac{355}{415}$	$\frac{332}{431}$	$\frac{422}{527}$	$\frac{364}{455}$	$\frac{493}{551}$		$\frac{430}{469}$
7	18,130	.2	5	.4	$\frac{401}{436}$	$\frac{300}{367}$	$\frac{379}{370}$	$\frac{316}{523}$	$\frac{382}{406}$	$\frac{429}{508}$		$\frac{429}{449}$
8 [b]	20,330	---	---	.5	$\frac{148}{410}$	$\frac{222}{450}$	$\frac{205}{484}$	$\frac{\text{---}}{444}$				$\frac{257}{410}$
9	20,330	.2	3	.4	$\frac{450}{460}$	$\frac{392}{488}$	$\frac{363}{535}$	$\frac{481}{541}$	$\frac{522}{537}$	$\frac{493}{527}$	$\frac{444}{552}$	$\frac{498}{527}$
10	20.330	.2	5	.45	$\frac{435}{420}$	$\frac{303}{480}$	$\frac{369}{337}$	$\frac{300}{284}$	$\frac{305}{367}$	$\frac{434}{498}$		$\frac{459}{596}$

[a] The value above the line shows the strength of the specimens after freezing, the value below the line shows the strength of specimens hardened in water at normal temperature.

[b] Testing of part of the specimens was stopped, as some were rated at point 3.

[c] The maximum values of strength are indicated.

and reinforced. Several Soviet and foreign authors have carried out interesting investigations in this field. In our book "Concrete Durability," it was shown that to obtain durable concrete it would be necessary to insure its hardening in a moist condition for at least 90 days (p. 338, table 130). In one interesting theoretical work by Powers, the conditions were considered under which the processes of cement hardening proceed with different intensity. However, due to the fact that this problem is very complex, a simple and expedient solution for construction purposes has not as yet been evolved. It is possible to agree with the view of Powers on the inadmissibility of water evaporation from the capillaries of the cement paste as, in this case, cement hydration stops, this being verified by our experiments and by lowering of the engineering properties of the concrete. Powers indicates that previously it was considered possible to allow evaporation of part of the water from the cement paste, due to the excessive amount of water in the concrete in comparison with the amount needed for the hardening process. At present, it is considered that cement hydration may proceed completely and at a high rate (at required temperatures) only in case the concrete or cement paste is completely saturated with water. We cite these opinions in order to emphasize the insufficient number of investigations devoted to this problem, which is, after all, decisive for the quality of concrete and reinforced concrete. Aside from the problem of migration of moisture in concrete, at the given stage of investigation it is possible to assume that the water introduced into the concrete should be available along with the cement for the required new formation, without evaporation.

The possibility of cement hardening, and of obtaining a material of the required grade of strength under practically any conditions, is dependent on the presence in the concrete of a sufficient quantity of fine cement fractions and of surplus water. However, in this case, the hardening process proceeds selectively. Such concrete, after some time, stops becoming stronger and it is not durable in aggressive media. Unfortunately, there are no detailed and systematic experiments on investigation of the influence of the hardening regime on the engineering properties of concrete made with different binding materials. One of the indications of the influence of hardening conditions, and, consequently, the degree of cement hydrolysis and hydration, may be change of the water permeability of concrete made with portland cement. In 1939 we had already performed several experiments. Water permeability of con-

TABLE 10. *Frost resistance of plastic mortars (1 : 3) of portland cement "B"*

Item No.	Specific surface of cement	Additive		w/c ratio	Ultimate compressive strength of sample									
		Sulfite cellulose extract	Gypsum		After the indicated number of test cycles [a], [c]									At climatic station additionally after 50 to 200 test cycles
					100	150	200	250	300	350	400	450	500	
	cm²/g	*Percent*	*Percent*		*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*	*kg/cm²*
1	14,730	----------	----------	0.5	$\frac{320}{385}$	$\frac{283}{380}$	$\frac{229}{319}$	$\frac{84}{354}$						$\frac{260}{430}$
2	18,600	----------	----------	.55	$\frac{310}{410}$	$\frac{253}{382}$	$\frac{251}{258}$	$\frac{119}{506}$	$\frac{80}{375}$					$\frac{381}{449}$
3	18,600	0.2	3	.42	$\frac{296}{462}$	$\frac{425}{535}$	$\frac{354}{582}$	$\frac{415}{542}$	$\frac{459}{576}$	$\frac{424}{571}$	$\frac{371}{517}$			$\frac{449}{489}$
4	18,600	.2	5	.39	$\frac{266}{437}$	$\frac{342}{485}$	$\frac{297}{532}$	$\frac{353}{560}$	$\frac{404}{542}$	$\frac{430}{545}$				$\frac{410}{508}$
5 [b]	21,050	----------	----------	.5	$\frac{349}{470}$	$\frac{385}{445}$	$\frac{256}{422}$	$\frac{279}{559}$						$\frac{280}{518}$
6	21,050	.2	3	.4	$\frac{495}{455}$	$\frac{465}{555}$	$\frac{402}{485}$	$\frac{473}{542}$	$\frac{557}{678}$					$\frac{488}{576}$
7 [b]	25,260	----------	----------	.53	$\frac{269}{419}$	$\frac{150}{405}$	$\frac{174}{507}$	$\frac{161}{400}$						$\frac{208}{449}$
8	25,260	.2	3	.46	$\frac{347}{430}$	$\frac{502}{599}$	$\frac{485}{512}$	$\frac{362}{477}$	$\frac{405}{537}$	$\frac{468}{610}$				$\frac{226}{518}$
9	25,260	.2	5	.5						$\frac{449}{432}$	$\frac{425}{532}$	$\frac{426}{503}$	$\frac{337}{488}$	$\frac{296}{469}$

[a] The value above the line shows the strength of the specimens after freezing; the value below the line shows the strength of specimens hardened in water at normal temperature.

[b] Testing of part of the specimens was stopped, as some were rated at point 3.

[c] The maximum values of strength are indicated.

crete made of low-aluminate cement and hardened in air was investigated at different ages. The amount of cement in the concrete was 250, 300, and 350, and of the water, 175 kg/m³. The ultimate compressive strength of the concrete was 260 to 440 kg/cm². Specimens tested after 80 days under a pressure of 5 atm, had a coefficient of permeability of $(0.110\text{–}0.300) \cdot 10^{-7}$. The same specimens, as well as control specimens, were tested after 230 days under the same pressure. It was found that the coefficient of permeability increased up to $(22.4\text{–}41.2) \cdot 10^{-7}$. These experiments may serve as obvious proof of the change proceeding in the cement paste and, in particular, in the gel component during evaporation of water from it with time. It is necessary to avoid the possibility of such changes by creating the appropriate hardening conditions. From this point of view we propose to consider the technological methods of operation, and acceleration of concrete hardening.

Given below are the final tabulated results of long-time testing at the climatic station of 20-cm. concrete cube specimens, made of cement from "K" clinker, ground in the CM–14 mill. Sulfite cellulose extract was added to the clinker during grinding. After 7 years of testing (5,000 cycles) the condition of the samples was estimated by rating point 9. In the majority of cases duplicate samples differed insignificantly from each other. For each composition 9 to 12 cubes were tested; 6 to 7 years of testing were passed without destruction by 25 lots of samples (table 11).

TABLE 11. *Characteristics of concrete resisting about 5,000 freezing-thawing cycles in situ*

Item No.	Concrete components		w/c ratio	Sulfite cellulose extract additive	Estimation of samples by rating points after the indicated number of years of testing					
	Water	Cement			1 yr	2 yr	3 yr	4 yr	5 yr	7 yr (5,000 cycles)
	kg/m³	*kg/m³*		*Percent*						
1	145	290	0.5	0.2	10–9	10–9	10–9	10–9	10–9	9–8
2	146	265	.55	.2	10–9	10–9	10–9	10–9	10–9	9–8
3	147	226	.65	.2	8	7–6	7–2	------	------	6–0
4	148	212	.7	.2	6	6–5	4–2	------	------	------
5	145	290	.5	.1	10	10–9	10–9	10–9	10–9	9–7
6	153	280	.55	.2	10–9	10–9	10–9	10–9	10–9	9–8

Testing of prestressed reinforced sleepers for frost resistance also verified the significant influence of the steaming regime on the durability of products and structures. The concrete contained 450 kg/m³ of cement and 145 kg/m³ of water. Some of the sleepers were steamed in pit chambers at a regime of 6+3+10+5 hr., and the rest were placed below a wooden hood, with leaking of part of the steam. After 100 test cycles the influence of the hardening regime on frost resistance was already detected. After 300 cycles the sleepers steamed under the hood were seriously deteriorated.

Principles of Designing Durable Concrete

Besides selecting the concrete components, according to the grade given in the project, it is also necessary to design the concrete mix in such a way that it conforms with other technical requirements.

The grade of durable concrete is understood to be the ultimate strength reached by the concrete in the structure after the designated life under actual ambient conditions, the aggressive action of which is determined during design of the structure and is taken into account in the design of the concrete. When designating the grade of durable concrete, the construction methods should be taken into account; namely, time of finishing the structure or part of it and loading with design forces; season of the year and climatic conditions when the concrete mix is being placed and the concrete hardens in the structure; massive or openwork type of the structure, construction methods, and type of reinforcement—common or prestressed. This is the first design stage.

The second stage of concrete design is the selection of materials for the concrete, the selection of the concrete composition, and its testing. There are some features distinguishing this work. At present, when selecting the components of concrete, only the ultimate strength of a laboratory specimen is considered without estimating the ultimate strength of the same specimen after it has been under the action of external aggressive influences. The author proposes a different principle of selection of the components of the concrete, consisting in selection based on the ultimate strength of a specimen hardened under conditions modeling in the laboratory the entire term and conditions of use of the concrete after erection of the structure. At present, when selecting the components of concrete for cases when, besides the grade, it is necessary to establish the fitness of the concrete for exposure to different aggressive media or to the action of different loads, estimation of the stability of the concrete specimen is accomplished not by testing it until it is destroyed, but up to some conditional limit.

In no case is the limit value of the load and time known, when the tested concrete is destroyed. This is true whether using concrete with insufficient or excessive stability against the action of the actual exposure after the structure has been erected.

The disadvantages of concrete under the action of ambient influences do not become apparent at once, but only after decades have passed. Unfortunately, in these cases, selective, periodic inspection of concrete does not allow of obtaining material for analysis of the causes of detected defects.

Conclusions

1. Of decisive importance for best results from use of cement in construction is the classification of the latter by the indications determining long-time behavior of the cement paste in the structure under various conditions of exposure and use. Though the conditions of use of the cement mortar or concrete vary, they may be and are necessarily estimated when certifying the cement for one or another structure. All of this may be accomplished by properly working out the cement mortar and concrete classification for producing cement at the site with properties corresponding to the working conditions, thus guaranteeing the quality indicated in the certificate, and by correct performance of concreting operations.

2. As the basis for using cement, the new classification should be adopted, taking into account the following:

(a) lack of waterproof capacity and, consequently, lack of frost resistance of hydrated tricalcium aluminate, hydrosulfoaluminate, and hydrated tetracalcium aluminoferrite;

(b) slow belite hardening;

(c) properties of active mineral additives for portland cement to increase impermeability and sulfate resistance of concrete and which affect its frost resistance;

(d) features of mono- and multi-component cement that make it impossible to obtain concrete of high frost resistance;

(e) the possibility of improving some of the building properties of cement by introducing plasticizers and air-entraining additives, and some new views and premises on the basis of investigations in this field.

3. When working out the new classification of cements having, as its aim, use in various structures of the most durable materials, the author proposes to use the principle of directed structure formation. The basis of correct use of this method is the consideration of actual properties of poly-mineral cement. The reaction processes should be the main part of the processes connected with the formation of the hardened cement paste and should be directed in the hardened material.

4. Thorough solution of the problem of durability of plain concrete and reinforced concrete will help to improve planning, distribution, and manufacture and delivery of cement, this solution being very important for obtaining concrete of much higher quality with lower cement content.

5. It is known that there is a widespread point of view that even in those cases where the cement does not conform in its properties to the actual conditions under which it is to be placed in the concrete, increase of cement content and corresponding lowering of the w/c ratio make it possible to obtain concrete of the required quality. In-

crease of the quantity of cement in laboratory tests shows increase of strength and some increase of stability of the samples, for example when testing them for frost resistance, but that is all. Practically, non-conformance of cement with external aggressive conditions is not overcome.

6. The use during scientific investigations of cement prepared according to new technology has led to several new solutions in relation to correcting some of the disadvantages of cement, cement with a high alumina modulus, for example. The idea of sulfate-resistant cement is a case in point. The same relates to the problem of obtaining mortars and cement with smaller shrinkage, expanding cement, and concrete with higher frost resistance in comparison with concrete of the same cements obtained in the usual way.

7. The main cause of insufficient introduction into production of the achievements of investigators in the field of technology of cement and concrete consists in the fact that these achievements are insufficiently reflected in the main technical documents—construction standards and specifications.

8. Correct estimation of the workability of the mix, and its design for application to actual conditions is of decisive importance for the progress of concrete work, and for obtaining structural concrete with the given technical characteristics (impermeability, frost resistance, etc.).

9. The formation of frost-resistant structures is directly connected, first of all, with use of the effect of contraction. Air is a required component of the cement paste, serving as a damper in the spaces formed during hydration of the cement minerals.

10. With frost-resistant coarse aggregate and unchanged concrete structure the hardened cement paste determines the stability of the concrete. The cement paste cannot improve the frost resistance if the rock material is not itself resistant to repeated freezing-thawing cycles.

11. Depending on which materials were chosen and on how well the plain concrete or reinforced concrete was prepared for the given grade of structure, the prevailing external influences may gradually destroy the concrete or may not have any aggressive action upon it.

12. When the proper conditions of mortar or concrete hardening are not observed in the structures their durability becomes uncertain.

13. It should be borne in mind that proper arrangement, in the structure, of prestressed reinforcement is essential and sometimes decisive for reliable behavior of reinforced concrete under the action of repeated alternating freezing and thawing.

14. Selection of the thickness of the protective layer should be determined not only by frost resistance, but mainly by the time of preservation, near the reinforcement, of an alkaline medium.

SESSION VII. CHEMICAL ADDITIONS AND ADMIXTURES

Paper VII-1. Some Chemical Additions and Admixtures in Cement Paste and Concrete*

H. E. Vivian

Synopsis

Important problems are encountered in the behavior of available cements and aggregates, in handling freshly mixed concretes and grouts, and in the properties of hardened concretes in various types of structures exposed to all types and combinations of weathering conditions. Any admixture or technique that can assist in overcoming these problems, without introducing further serious defects, has a useful place in concrete technology. It is not intended to advocate that admixtures should be used in all concrete or should eliminate the need for suitable mix design, handling techniques, or control of constructional operations; rather they should be used to counteract specific defects or problems and to confer additional advantages that will permit concrete to be used successfully or will assist concrete to carry out its designed function.

Chemical admixtures, which are usually added in relatively small quantities and generally interact chemically or physically with cement paste, are designed to affect a wide variety of paste and concrete properties. They may be used to vary setting times and rates of strength gain in order to meet particular construction requirements. Similarly the workability of freshly mixed concrete may be modified to meet specific construction requirements or methods or to produce specific types of products. It is in connection with improvement in durability that admixtures have been particularly useful. Entrainment of air in concrete is rightly regarded as a major factor in improved durability while attention is directed towards the new admixture field of inhibition of steel-reinforcement corrosion. Surface treatments which, although not strictly admixtures, are often closely allied in their action to waterproofers, may also modify concrete behavior and improve its durability.

On account of the lack of necessary basic data on the reactions that can occur in cement paste and on the mechanisms by which its physical properties develop, it is impossible to describe with certainty the various behavior mechanisms of many admixtures. Available data indicate that the major concrete problems are concerned with such properties as low tensile strength, volume instability, and cracking and durability. Further studies of the causes of these inadequacies and the development of techniques and admixtures for their improvement are clearly indicated.

Résumé

Le comportement des ciments et aggrégats disponibles, la manipulation des bétons et des coulis injectés, et les propriétés des bétons durcis dans différents genres de constructions exposées aux conditions atmosphériques les plus variées, présentent d'importants problèmes. Tout produit d'addition ou toute méthode qui peut contribuer à surmonter ces problèmes, sans introduire de sérieuses imperfections supplémentaires, a une place utile dans la technologie du béton. Il n'est pas dans l'intention de l'auteur de préconiser l'emploi des produits d'addition dans tous les bétons, ni d'affirmer qu'ils rendent inutiles la détermination des proportions du mélange, les méthodes de manipulation ou le contrôle des opérations de construction; leur emploi devrait plutôt avoir pour but de neutraliser certains défauts ou problèmes spécifiques et de conférer des avantages supplémentaires qui permettront d'utiliser le béton avec succès ou aideront le béton à remplir les fonctions qui lui sont dévolues.

Les produits d'addition chimiques, qui sont généralement ajoutés en quantités relativement petites et réagissent chimiquement ou physiquement avec la pâte de ciment, ont pour but d'affecter un grand nombre de propriétés diverses de la pâte et du béton. On peut les utiliser pour varier les durées de prise et les vitesses de l'accroissement de la résistance afin de satisfaire aux exigences de construction particulière. De la même façon la maniabilité du béton fraîchement malaxé peut être modifiée pour répondre aux exigences ou aux méthodes de construction spécifique, ou pour produire des produits spécifiques. Les produits d'addition ont été particulièrement utiles en ce qui concerne l'amélioration de la durabilité. On considère que l'entraînement d'air dans le béton est considéré à juste titre un facteur de première importance dans l'amélioration de la durabilité, tandis que l'attention est dirigée vers les nouvelles méthodes d'utilisation des produits d'addition pour empêcher la corrosion de l'armature en acier. Bien qu'on ne puisse les considérer comme des produits d'addition à proprement parler, les traitements de surface sont souvent très proches par leur action des imperméabilisateurs, et peuvent également modifier le comportement du béton et améliorer sa durabilité.

Par suite du manque de résultats fondamentaux nécessaires sur les réactions qui peuvent se produire dans la pâte de ciment et sur les mécanismes suivant lesquels ses propriétés physiques se développent, il est impossible de décrire avec exactitude les mécanismes variés du comportement de nombreux produits d'addition. Les résultats disponibles indiquent

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que les principaux problèmes du béton ont rapport aux propriétés telles que la basse résistance à la traction, l'instabilité volumétrique, la fissuration et la durabilité. Les études à poursuivre sur les causes de ces imperfections et le développement des méthodes et produits d'addition dans le but de les améliorer sont clairement indiquées.

Zusammenfassung

Bedeutende Probleme des Verhaltens der bekannten Zemente und der Zuschlagstoffe, der Behandlung frisch gemischter Betone und Mörtelschlämme und der Eigenschaften des gehärteten Betons in allen Konstruktionen, die den verschiedensten Arten von Wetter und Klima ausgesetzt sind, müssen noch gelöst werden. Irgendeine Beimischung oder Behandlung, die ein Problem löst und keine neue schlechte Eigenschaft hervorruft, wird in der Betontechnologie willkommen geheißen. Das muß nun nicht so verstanden werden, daß man in allen Betonen irgendwelche Beimischungen einverleiben und dann die Art und Weise der Mischung, die Verarbeitung und die Überwachung der Baukonstruktion vernachlässigen soll; nein, man soll Beimischungen nur für das Berichtigen bekannter Fehler benutzen, und um neue, bessere Eigenschaften hervorzubringen, damit der Beton dann mit vollster Zufriedenheit benutzt werden oder daß man wenigstens seine Benutzung anziehlicher machen kann.

Chemische Beimischungen, die meistens in kleinen Mengen hinzugefügt werden, und welche im allgemeinen mit der Zementpaste chemisch oder physikalisch reagieren, sollen mehrere Pasten- und Betoneigenschaften gleichzeitig verbessern. Sie können zum Beispiel für die Veränderung der Erstarrungszeiten oder Festigkeitszunahme zugegeben werden, sodaß man den Zement für Spezialkonstruktionen benutzen kann. In der gleichen Art und Weise kann man die Verarbeitbarkeit frischen Betons beeinflussen, sodaß dieser dann in Spezialkonstruktionen, für bestimmte Bauweisen oder für Spezialprodukte benutzt werden kann. Die Dauerhaftigkeit ist durch solche Beimischungen ganz besonders günstig beeinflußt worden. Man hat schon ganz richtig erkannt, daß ein hoher Luftgehalt im Zement die Dauerhaftigkeit sehr günstig beeinflußt, aber man schenkt das Augenmerk jetzt einigen neuen Beimischungen, die die Korrosion der Stahleinlagen verhindern sollen. Oberflächenbehandlungen sind genaugenommen keine Beimischungen, aber sie haben doch eine ähnliche Wirkung wie wasserabstoßende Mittel, daher können sie das Betonverhalten beeinflussen und die Betonbeständigkeit verbessern.

Da man die Reaktionen, die in der Zementpaste stattfinden können, noch nicht genau kennt, und da man nichts über den Mechanismus, der zur Entwicklung der physikalischen Eigenschaften führt, weiß, kann man nicht zu genau die Gründe beschreiben, warum diese oder solche Beimischungen diesen oder jenen günstigen Effekt hervorrufen. Von den Literaturangaben kann man herleiten, daß die Beimischungen meistens zur Verbesserung einer niedrigen Zugfestigkeit, mangelhafter Raumbeständigkeit, der Rißbildung und der Dauerhaftigkeit verwendet werden. Man muß daher die Gründe dieser Nachteile noch mehr erforschen und Verfahrensweisen und Beimischungen, die solche Nachtele überkommen sollen, entwickeln.

Introduction

The literature in the field of concrete admixtures is studded with specific instances of why some modification of concrete was necessary, certain claims that beneficial effects could be obtained with certain addition materials, discussions of the changes produced under different working or environmental conditions, and compilations of rules and recommendations for their use. A very useful summary of types of admixture materials, their purposes and rules for their use has been published by the American Concrete Institute Committee 212 [1] [1]. These published data are pertinent to the study and application of chemical additives and admixtures, and in addition the properties, uses, and effects of the more bulky admixtures (e.g., pozzolan and blast-furnace slag) have received considerable attention. Consequently it is intended that the present discussion should be confined to the effects produced by those admixture materials that are added in minor quantities to cement paste and concrete and will not include more than passing comment on economic or technological factors that naturally arise when large-scale use is attempted. Other papers to be presented at this Symposium are concerned specifically with the bulkier admixture materials, with false setting and the early hydration reactions, and with the properties of hardened paste and concrete. So as to avoid repetition, comment within these fields will be kept to a minimum.

To plan and carry out useful research on the use of admixtures in concrete it is necessary to recognize and assess the various problems that occur in cement paste and concrete as materials, that occur in the materials when handled in specific ways, or that occur in finished products or structures which are subjected to various environmental or operational conditions. It is clearly necessary therefore to inquire into the chemical and physical actions that admixtures impress on cement paste and concrete at all stages from the initial mixing until the useful life of a structure has ended.

As a beginning it would be desirable to examine briefly the faults and defects that appear to be inherent in cement-paste and concrete systems. With an understanding of the modifications required, it is possible to study the actions of some types of

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[1] Figures in brackets indicate the literature references at the end of this paper.

additives and to assess whether their effects are satisfactory in overcoming the defects without introducing further problems.

A discussion such as this also offers an opportunity for comment on possible future developments. Improvement in the intrinsic strength of hydrated cement and reduction in the importance of the allied problems, drying shrinkage and cracking are of great importance. Bond between cement paste and aggregate and between cement paste and reinforcement is being studied in order to improve structure performance. Methods by which concrete is rendered less easily penetrated by moisture or solutions should increase its stability and durability. Great importance is attached to possible future developments. Although it can be truly said that, while the properties of cement paste and concrete can be adapted and improved to meet the needs of today, the new uses to which concrete will be put tomorrow will place still greater demands on improved materials, properties and techniques.

Admixtures may be regarded as materials, other than the normally accepted ingredients of concrete, that are added to the mix immediately prior to or during mixing. There are certain treatments which, according to definition, are not admixtures. When applied to hardened concrete surfaces however, they may interact chemically or physically with the hydrated cement and induce effects that are similar to those of typical admixtures. It is considered justifiable therefore to make brief mention of some of the more useful of these surface treatments.

Hydrated Cement Paste and Concrete

Hydrating cement may be regarded as a dynamic system that has certain specific requirements, that may differ at different times in its history. These requirements may not be needed before a certain stage is reached or they may not be needed after a certain stage has passed. The effects induced however by a preceding action or treatment may be decisive in determining the later behavior of the concrete.

Cement paste and concrete, when freshly mixed, may be regarded as concentrated suspensions, which behave differently from dilute suspensions, because the paste is flocculated and cohesive. Powers [3] and Steinour [4] in their studies on the "bleeding" of cement paste postulated that it tended to behave as one large floc. On standing, the solids sediment and water "bleeds" at a rate that depends on its ease of escape from the paste. There may be considerable segregation within the sedimented-solids bed. These tendencies are, of course, carried forward and perpetuated in the hardened concrete. Workabliity, which is a very transitory requirement of any concrete mix, represents the ease with which the mass can be moved, deformed in shape, and compacted without its constituents undergoing separation or segregation. The resultant effects of the interaction between the concrete-mix properties and the method of placing, are "frozen" into the hardened concrete. Other minor effects, such as premature stiffening or false set, may also modify some of the desirable properties of cement paste and concrete and consequently either render normal placing techniques unsuitable or require the development of new equipment or methods.

The variability of cement, aggregates, and mixes as well as the multitudinous differences in types of work, methods of construction, and handling equipment have all accentuated the problems associated with freshly mixed cement paste or concrete. In many instances admixtures have been used to overcome specific difficulties, and a few types of operations may be quoted to illustrate the breadth of their potential use. The properties of the cement paste or concrete are generally modified by additives to permit pumping as grouts, linings for oil wells, or as linings for tunnels. Placing as a lining in pipes, on slopes for slip-forming, as pneumatically applied mortar, placing in narrow, heavily reinforced sections in contrast to open, unreinforced or lightly reinforced sections, have different requirements in regard to concrete properties, and these may sometimes be achieved more readily or effectively by the use of additives. It should be noted that the use of admixtures does not eliminate the need for designing the most suitable concrete mix with the available materials.

Hydration of cement is not an instantaneous process but occurs over a very long period of time during which chemical and physical changes occur within the mass. These changes depend to some extent on the environmental conditions to which the mass is subjected. The change from what may be regarded as a suspension of solid particles dispersed in water, which constitutes the continuous phase, to a solid mass in which water becomes the disperse phase, is a major one. It induces numerous problems mainly concerned with volume changes and strength development, starting from the time when stiffening commences, and remaining operative when hard set occurs and afterwards, since the hydration reactions proceed for a considerable time after the final set occurs. Such actions as drying shrinkage applied to a hardened mass of concrete that may be regarded as being rigid (within the short time scale usually employed) and of limited elasticity, must induce the development of numbers of cracks in positions of stress concentration. The basic questions about strength still remain unanswered. How strength is developed is unknown, the actual properties of the hydrated products and their associations are unknown, and the complex interactions of the chemical and physical actions are unknown. In short very little is known about the characteristics that confer strength and the way in which it is developed. Little more is known about the properties of clinker, especially its uniformity of behavior and whether cements produced from it can be made to act more effectively. It will be readily seen that when admixtures are studied in relation to these complex and largely unknown processes the results are generally confused and often not helpful. For these reasons the amount of work that has been done on the effects of admixtures on cement hydration and strength development has been limited. The more obvious and more easily measured changes in acceleration and retardation of setting and strength gain have been studied, but even in this more limited field the actions of the admixtures are incompletely understood.

The effect on sound concrete of environmental conditions is usually of paramount importance since they affect both the short term behavior of fresh concrete and the long term behavior of hardened concrete. Much emphasis has been rightly placed on the need for improved durability, and various additives have been used in attempts to achieve this end result. Undesirable properties such as low strength, excess mixing water, shrinkage stressing and cracking, and low bond between cement paste and aggregate and between mortar and reinforcement cause structure deficiencies and may lead to low durability. Under specific conditions of use or exposure, certain problems may become all important in their effects on concrete durability. Examples which may be given briefly include: (1) settlement of fresh concrete under large aggregate, under reinforcement, and in back-filling inverts which may cause lack of bond, with consequent reduction in mechanical properties, and increased permeability to water; (2) loss of workability in pumped concrete and grout, which interrupts the construction schedule and reduces compaction and strength as well as increases permeability; (3) volume changes in hardened concrete, which cause strength reduction or disruption (these volume changes being due to reactive aggregates, reinforcement corrosion, frost action, or aggressive salt action); and (4) abrasion resistance which is necessary to combat mechanical damage to surfaces. There are undoubtedly many more examples of special cases of concrete, under certain specific environmental conditions, either failing or giving an inadequate performance to meet the required demands. The use of admixtures, which are designed to assist the performance of concrete under the imposed conditions, will be discussed later.

Finally it would be desirable to note a few of the properties of cement paste and concrete that at present must be accepted as inevitable since they cannot be prevented. Engineering design will usually minimize the incidence of these effects as far as the structure is concerned; the chemical and physical effects on the material itself however remain unaffected. Some of these effects are discussed below.

Since the hydration reactions are exothermic, the accumulation of heat within a concrete mass makes curing extremely difficult or impossible to achieve ideally. The heat gradient in the mass regardless of curing tends to redistribute water within the concrete mass and between the concrete and the surrounding atmosphere. These effects together with differential thermal expansion in different parts of a structure may cause considerable volume changes.

Volume changes within the cement paste itself as a result of the hydration reactions and of drying shrinkage are inevitable. They occur largely after the concrete has hardened and become rigid, and consequent stressing causes cracks to develop. Changes in external dimensions, due to plastic deformation under applied stress, or "creep," are due to independent movement of different portions of the mass. The exact nature of creep in concrete has never been fully explained.

The hydration reactions of the various clinker minerals as well as other chemical interactions may proceed for a very long period of time. Moreover the hydrated clinker compounds appear to be capable of undergoing modification depending on their environmental conditions. These reactions are not all beneficial, and those tending to accentuate the unstable tendencies of hydrated cement, when taken to extremes, are detrimental to physical properties.

The particulate nature of hydrated cement which implies a certain amount of internal pore space, that may be filled by gas or liquid, induces a number of permeability problems associated with specific environmental conditions. These problems may sometimes be countered by the use of densifying admixtures or by surface treatments to reduce surface permeability.

Although it is not possible to deal with all the possible admixtures under all the possible conditions of exposure, it will be seen that there is ample scope for the use of admixture materials that confer specific properties on concrete. It is necessary to insure that these properties are adequate to overcome the effects induced by the environment and that in producing them other deleterious effects are not being introduced. With these background problems and requirements in mind, a discussion of certain types of admixtures and their effects in cement paste and concrete will now be attempted.

Admixture Actions

Admixtures added to concrete in small amounts may be classified very briefly according to the type of action that they produce. They may be described as:

1. Retarders or accelerators of hydration or other chemical reactions and of strength development.
2. Workability aids in freshly mixed pastes and concretes.
3. Surface-active agents and other materials that entrain air or act as waterproofers.
4. Corrosion inhibitors.
5. Miscellaneous admixtures.

Retarders or Accelerators of Hydration or Other Chemical Reactions and of Setting and Hardening

Little more than a few brief comments on the action of accelerators and retarders in cement and concrete can be given here. Steinour [2] in his review on the setting of portland cement has collected and arranged a vast amount of data, and this should serve as a basis on which future discussions and work can be planned. The introduction of other problems such as premature stiffening and "false" set need not be attempted here since these problems are the subject of a separate paper.

It is necessary however to point out that cement as normally used (i.e., as a mixture of ground clinker and gypsum) has generally undergone considerable modification when viewed against the behavior of the ground clinker alone. Gypsum may act with some clinkers and under some conditions as a retarder, whereas under other conditions and with the same or other clinker it may act as an accelerator. This lack of a consistent behavior pattern has been the main cause of the present confusion in connection with setting behavior of cements and with an overall mechanism to describe it. The subject is a difficult one on account of the large number of possible reactions that could occur either simultaneously or consecutively. When these reactions are complicated further by the addition of another admixture material, that either accelerates or retards the setting behavior, which may be regarded as normal, a completely new set of reactions may be induced or the admixture may accentuate one or more of the normal reactions or it may counteract one or more of the normal reactions. A short description of what is thought to happen may illustrate this point.

Finely ground clinker (without gypsum) may be either quick or slow setting. Although the causes of this difference in behavior are still obscure, it is apparent that clinker composition and the physical as well as the chemical nature of the hydration products affect setting. Quick setting is thought to be due to the very rapid hydration of tricalcium aluminate and the formation of a sufficient quantity of tricalcium aluminate hydrate to cause setting. Alternatively the coagulation of aluminates and silicates or their hydration products has been suggested as the cause of quick setting. Slow setting on the other hand, although just as obscure in mechanism, has been considered to be due to the presence of tetracalcium aluminoferrite (high Fe_2O_3:Al_2O_3 ratio in clinker) which hydrates to produce colloidal coatings, or to the production of protective coatings of tetracalcium aluminate hydrate on clinker particles when tricalcium aluminate hydrates in the presence of dissolved lime. The presence of sulfate in the clinker and lack of alkalies may also affect the setting times of clinkers.

Addition of gypsum changes the behavior of clinker so that quick-setting clinkers are retarded while slow-setting clinkers are sometimes accelerated. The action of gypsum may go beyond its effects on the setting reactions; it also appears to influence the development of early strength. It is considered that gypsum in the presence of hydrated lime acts as a set regulator retarding rapid setting by modifying the aluminate hydration products, forming calcium sulfoaluminate while it minimizes the formation of colloidal ferrite coatings which occur in slow-setting clinkers. It is not intended to pursue this discussion further here since it is the subject of another detailed paper. However it is clear that there are further reactions and possibilities which cannot be discussed here but which could affect the behavior of cement. The mechanisms of the reactions that occur in the first few minutes of hydration, the nature of the products formed and their function in relation to later reactions warrant much more detailed future study.

It can be seen now that the addition to cement of an accelerating or retarding admixture introduces further complication into a system that is already complex and very incompletely understood. The admixture reactions may be merely additional or counter to those occurring in cement or they may be of a completely different type. Much of the experimental work has been done with accelerators consisting of calcium chloride, sodium carbonate, or other inorganic salts and with retarders consisting of carbohydrates or other organic compounds and such inorganic compounds as phosphates and zinc oxide. The mechanisms of the actions of these compounds are not clearly understood but the overall effects induced in concrete and in oil well cements and grouts under specific environmental conditions are reasonably well known.

Calcium chloride is the most commonly used accelerating admixture. When added in small amounts, usually 2 percent, by weight of cement but sometimes in greater amounts up to 4 percent, it achieves the desired effects of accelerating set and strength development without seriously diminishing the ultimate strength attained. Small additions of sodium carbonate on the other hand accelerate setting but usually reduce the ultimate strength developed. Although the actions induced by these compounds are still largely unknown it is considered that they act in different ways. Calcium chloride acts as a retarder of flash set in clinker in much the same way as gypsum does, presumably due to the formation of calcium chloroaluminate. Its accelerating action in cement appears to be due (1) to the acceleration of the sulfoaluminate reaction between gypsum and tricalcium aluminate, and (2) to a depression of the *p*H, which accelerates the rate of hydration of the silicates. Sodium carbonate on the other hand reduces the calcium-ion concentration immediately, and under these circumstances the retarding action of gypsum is not operative while the

the quick setting of tricalcium aluminate hydrate becomes the major action. Further work is needed to elucidate these setting reactions.

Retardation of setting and strength development in excess of that provided by the usual gypsum addition may be achieved by the addition of various organic compounds. Carbohydrates such as sugars, starches, and cellulose products are most commonly used, while certain acids, particularly hydroxy-carboxylic acids and dicarboxylic acids, gums, albumen, and certain inorganic compounds, such as phosphates and borates, also have marked retarding actions. The action of the organic materials in retarding setting is not clearly understood. It is thought that some retard by adsorption through their hydroxyl groups while others act through their carboxyl groups. This explanation however is probably far too simplified since it does not indicate the mechanism of retardation. A limited amount of evidence has indicated that, after an initial delay, cement hydration proceeds at an approximately normal rate in the presence of sucrose. The development of strength is also delayed for various times which depend directly on the amount of added sucrose. This evidence suggests that initially the additive reacts rapidly with the cement and temporarily retards the rate of hydration. The additive may also affect the nature of the hydration products and the mechanism of strength development.

In the presence of inorganic salts, such as a soluble phosphate, at atmospheric temperature strength development is markedly retarded, but under steam-curing conditions, development of strength occurs readily. Although the cause of this retardation is not understood, it seems that the retarder could affect both the rate of hydration and the strength-developing properties of the hydrated products. Other inorganic salts, such as those of lead and zinc, are retarders. In these instances it is thought that they precipitate as gelatinous hydroxide or as hydrated oxide coatings on clinker surfaces and act as barriers which reduce the rate of hydration. There are sufficient anomalies in the field of accelerating and retarding admixtures to warrant caution in interpreting the available results. Future work should be directed towards determining, as a first step, whether it is the hydration rate or the nature of the hydration product that modifies behavior. Ultimately this work should be directed at understanding the basic mechanisms of acceleration and retardation.

Workability Aids in Freshly Mixed Concrete

It has long been recognized that workability is a property of a concrete mix that permits easy and homogeneous mixing, satisfactory handling and compaction, and suitable surface finishing. Equipment, such as mixers, buckets, buggies, pumps, vibrators, and surfacing screeds and trowels, has been designed to meet the needs of the concrete mixes used and the operations that must be performed. Modification in workability allows a wider choice of materials and mixes, improvement in concrete quality, and economies in power and time consumed in placing and finishing operations. For these reasons, and especially where cement economy is necessary, it is desirable to examine the effects and actions of workability admixtures in relation to costs and economies as well as cementing efficiency and concrete quality. It is these two latter effects that will be examined in greater detail here.

Workability aids may be classified according to their effects on cement paste as (1) dispersers, (2) flocculators, or (3) viscosity increasers.

Although workability depends on a vast number of factors that are capable of simultaneous variation, it will be seen that the most critical factors concern the properties of the paste fraction and the proportion of paste in the concrete mix. Other material factors, such as aggregate gradings, size fractions, and particle shape, also affect concrete workability, while such factors as temperature, cement properties, and standing time may also contribute additional complicating effects. However in this discussion all these factors will be mentioned only briefly since their effects on the two major factors will be largely self-evident.

In a fairly normal 1:2:4 concrete mix, made with reasonably graded sand and crushed stone or gravel of good particle shape and made with a water/cement ratio of about 0.6–0.7 by weight, the paste (cement+water) occupies about 28–30 percent by volume of the concrete. A change in the water/cement ratio alters the paste/aggregate ratio just as surely as a change in the total aggregate or cement. In lean mixes used for mass concrete the paste may occupy as little as 20 percent or sometimes less of the total volume of concrete. As the amount of aggregate is increased (or cement is decreased) the proportion of paste in the concrete becomes limiting in respect to workability, and the concrete becomes harsh and stony. It can be seen therefore that, for a mass of concrete to deform readily or for movement to occur between constituent particles within the mass, there must be some space in which particles can move in relation to each other or rotate without undue interference or interlocking. To allow this movement the concrete mix must contain a sufficient quantity of paste. Adding extra water to a concrete mix is the time-honored but least desirable way of increasing workability because such a practice does not fully achieve its purpose and it introduces a multitude of undesirable characteristics. These may be listed briefly as lowered early and ultimate strengths, increased segregation and bleeding and lack of cohesiveness, increased delay in finishing, increased drying shrinkage, reduced density within the mass, and greater permeability.

Reduction in water/cement ratio therefore appears to be a more logical way to achieve many of the desirable properties of concrete, but the problem of workability must be overcome. If workability is reduced to an extent that the cement paste becomes stiff and the concrete lacks cohesion and cannot be handled and compacted with the available equipment, the theoretical advantages of the lower water/cement ratio cannot be attained. The change in concrete workability as the water/cement ratio is decreased depends largely on the change in physical properties of the paste. Admixtures of various types affect the properties of the cement paste and in this way influence the workability of a concrete mix.

Under normal conditions cement particles in pastes and suspensions tend to be flocculated to some extent. On standing, the flocs sediment, and if the paste or suspension contains more water than can be accommodated within the sedimented bed, segregation occurs so that finally a layer of clear water stands above the bed of solids. Depending on its water content the paste will support aggregate particles of different sizes and density without undergoing deformation and allowing segregation of aggregate. At relatively high water contents pastes tend to be thixotropic, while at lower water contents they tend to exhibit dilatant tendencies. Any reactions that increase interparticle forces, such as premature stiffening or false set, tend to accentuate the dilatant properties of cement pastes. Dilatancy is probably the greatest difficulty to overcome in handling paste or concrete of low water/cement ratio. Unidirectional applied forces are not effective for moving and compacting concrete; vibration is generally much more effective, although excessive amounts may cause segregation.

Admixture materials, such as calcium lignosulfonate, calcium chloride, and many organic materials, which disperse cement particles, reduce viscosity or stiffness compared with that of a flocculated paste. There is a tendency for the finer cement particles to settle slowly in dispersed pastes but ultimately segregation into two layers, a bed of solids and a supernatant layer of water, occurs. On account of the dispersed solid particles settling as individuals, the packing in the bed is often denser than that of flocculated particles and consequently they tend to develop higher strengths. Segregation and bleeding however are much more likely to occur with dispersed particles, and with some dispersing admixtures, notably the carbohydrates, set retardation may be marked.

In concrete some of the defects, such as segregation and bleeding, may be lessened to some extent by reducing the mix water content which at the same time confers the advantages of improved strength and reduced permeability in the hardened paste due to its theoretically smaller capillaries. The workability of the concrete however is being reduced in two ways, (a) by a reduction in the volume of paste, and (b) by an increase in paste dilatancy. Concrete mixes containing dispersing admixtures are not particularly cohesive. Reproportioning the mix by increasing the cement factor may be neither economical nor desirable, since it increases the amount of paste that is capable of undergoing drying shrinkage, it does not entirely overcome the dilatant effects at low water contents, and it may accentuate the segregation problems at high water contents.

The action of dispersing admixtures appears to be due to the adsorption of charged ions onto the surfaces of cement particles which become mutually repulsive. It is possible that other effects may be induced by certain agents or additives that are adsorbed, and even though dispersion may occur it is sometimes masked by a more dominant action. For example, some air-entraining agents may also have a dispersing action, but the effects produced by entrained air exert the major effect on the properties of the paste or concrete mix.

Dispersing admixtures should be used with caution under carefully controlled conditions and for specific purposes where high-strength concrete is required and adequate means of handling and compaction are available. It is not a technique that can be adopted generally without introducing a number of additional problems.

Two new fields in workability improvement may also be discussed. These are concerned with admixtures that (1) increase the flocculation of cement paste, and (2) increase the viscosity of the paste by increasing the viscosity of the water phase.

In contrast with dispersion, enhanced flocculation of cement particles in pastes produces a different set of properties which change the behavior of concrete. Bruere and McGowan [5] have shown that increased flocculation of cement paste can be induced by the addition of various synthetic polyelectrolytes in small amounts which do not exceed 0.15 percent by weight of the cement. These admixtures consisted of various polymers such as polyacrylonitrile and polymethacrylic acid, and copolymers of vinyl acetate-maleic anhydride and isobutylene-maleic anhydride. These copolymers appear to be most effective in increasing the degree of flocculation of cement paste. Although the mechanism of their action is not fully understood, it is thought that these compounds, which have highly charged groups in their chains, are adsorbed on cement particles linking them together. The net result is equivalent to an increase in interparticle attraction which greatly increases the tendency of the paste to behave as one large floc.

The properties of cement paste and concrete which contain the vinyl acetate-maleic anhydride copolymer are of considerable interest and will be described here. Flow of paste containing this admixture, when measured on a standard flow table, was much reduced compared with that of a normal paste at the same water/cement ratio. As the quantity of the admixture increased the flow decreased. In addition, sedimentation volumes were increased as would be expected for strongly flocculated pastes. Pastes consisting of finely ground silica together with additions of this agent and a small amount of calcium hydroxide (0.2 percent by weight of silica) showed similar increased sedimentation volumes. Measurements of the bleeding rates and bleeding capacities of cement pastes made with water/cement ratios varying from 0.5–0.8 showed that the admixture additions increased the former and decreased the latter. Moreover the additions prevented the formation of bleeding channels through these pastes. Similar effects were observed in mortars, and in addition their increased cohesiveness was quite apparent. The action of the admixture on cement paste was maintained in concrete and clearly modified the properties of freshly mixed concrete. In rich mixes the admixture decreased slump and increased cohesiveness, while in lean, mortar-deficient mixes, although the slump was unaffected (zero in all mixes), the cohesiveness was markedly increased even though the water/cement ratio was as high as 0.79. Observation of bleeding and segregation tendencies in two series of concretes that were (a) rodded and (b) vibrated showed that all the control specimens tended to segregate and bleed copiously and to develop bleeding channels and surface craters. Addition of 0.1 percent of the agent to the concrete, however, reduced the bleeding capacity by up to 50 percent, and eliminated bleeding channels, surface craters, and segregation. Compressive-strength determinations indicated that the agent caused only minor changes; an increase for rich mixes and a decrease for lean mixes. The significance of these effects is questionable, and further test results would be desirable to evaluate them fully with respect to cement batch, aggregate types and gradings, mix proportions, compaction method, etc.

The vinyl acetate-maleic anhydride copolymer and other polyelectrolytes used as concrete admixtures possess a number of useful applications. Relatively high water/cement ratios may be used without the undesirable segregation and bleeding effects becoming serious. These are considerable advantages when back-filling inverts or when placing concrete in heavily reinforced sections. Such admixtures can also be used to overcome defects in fine aggregate gradings or particle shape and to reduce the segregation tendencies caused by overvibration. On account of the improvement it effects in workability and in the cohesiveness of lean mixes it could be useful in mass concrete especially as it reduces bleeding and the need for excessive surface cleanup between successive lifts. In transport of concrete, vinyl acetate-maleic anhydride copolymer as an admixture may prove most useful. While the concrete is being mixed or agitated it is readily deformable and workable. When mechanical work is stopped the concrete tends to "freeze" immediately. On this account cement paste or concrete containing this admixture may be regarded as thixotropic rather than dilatant. For this reason it should improve the behavior of concrete that is pumped over long distances as well as of that which is transported in buckets or buggies over long distances. Finally, the green strength of mixes containing the admixture are such that forms may be stripped as soon as placing has been completed and the products may be handled immediately. This advantage of early stripping could be most useful for slip-formed concrete, especially for arches in *in situ* concrete-lined, water-supply pipes.

From the foregoing it would appear that flocculating admixtures would be most useful in improving concrete properties. It should be noted that an admixture such as vinyl acetate-maleic anhydride copolymer does not entrain air and has only a very slight retarding action on setting. It is expected that, compared with normal concrete at equal water/cement ratios, permeability would be either unaffected or probably improved by additions of the agent and that drying shrinkage would not be changed significantly. Flocculating agents such as this admixture possess the useful advantage that they could be used generally and safely without excessive supervision.

Another class of admixture materials, notably those that increase the viscosity of the water phase of cement paste, may find uses in grouts or concrete produced for specific purposes. Compounds such as gum arabic, which increases the degree of flocculation of cement paste very slightly, and methyl cellulose which decreases the degree of flocculation slightly, tend to cause thickening, which is thought to be due to an increase in the viscosity of the water phase. Very little is known about the effects of these compounds on cement paste or concrete setting and strength-gain characteristics. It is considered that they could reduce the rate of segregation and water separation. For these reasons compounds of this type could be worthy of further investigation.

Air Entrainment

During the last 20 yr a tremendous field of work has grown up around the subject of deliberate air-entrainment in concrete. Addition of very small amounts of various surface-active agents to concrete during mixing causes the formation of large numbers of small air bubbles which are entrained in the paste. The presence of these air bubbles as well as the agent modifies the properties of both the freshly mixed concrete and the hardened concrete. The major advantages claimed for entrained air in concrete are improvement in concrete workability and a very considerable increase in durability, especially under adverse freeze-thaw exposure conditions. The importance of this technique warrants a detailed examination of the mechanism of air-entrainment and discussion of the effects produced.

Various types of surface-active agents, which are all long-chain carbon compounds, have been classified by Bruere [6] according to their chemical structures and assessed as air-entraining agents. The agents studied were as follows:

1. Anionic agents such as sodium dodecyl-,

tetradecyl-, and hexadecyl-sulfates and sodium abietate.

2. Cationic agents such as tetradecyl- and hexadecyl-trimethylammonium bromides, decyl- and dodecyl-amine hydrochlorides.

3. Nonionic agents such as polyalkylene ether alcohol and certain long-chain ether-linkage compounds.

4. Miscellaneous agents such as saponin, terpineol, octyl alcohol, and gelatin.

The anionic and cationic agents are all long-chain carbon compounds, which possess terminal active end groups and which are capable of ionizing in solution. The charge on the anionic agents is negative, while that on the cationic agents is positive. On account of their length these molecules display marked dipole characteristics, and at air-water, air-solid, and water-solid interfaces tend to orient in such a way that the hydrophilic end group is attached to the solid or remains in the water while the hydrophobic carbon chain tends to be unwetted and is oriented towards air. When adsorbed on solids these agents change the nature of the surfaces and may convert a hydrophilic or wettable solid surface into a hydrophobic or nonwettable solid surface. On this account these compounds are closely akin to waterproofers, but since the admixture quantities used are small and their solubilities, although small, are significant their waterproofing action is generally not permanent nor completely effective against water movement under a pressure head.

The available information about nonionic agents is very limited, owing in part to the fact that they are complex mixtures of condensates which are difficult to separate. The molecules consist generally of a chain of at least 10–12 carbon atoms comprising the hydrophobic portion together with a hydrophilic portion which contains 5 or more carbon atoms and a terminal hydroxyl group. Very considerable diversity of molecular weight and type (e.g., straight or branched chains) is possible. Although these agents possess polar characteristics, and orient at air-water surfaces, they are not chemically adsorbed on solid surfaces. Saponin and gelatin have good foam capacities and stabilities and appear to increase the surface viscosity of water. Terpineol and octyl alcohol are effective frothers in water since they are capable of causing rapid decreases in surface tension. Their foam stabilities and capacities in water and solutions however are extremely low.

Bruere [6,7,8] has described the effects produced by various surface-active agents when added to cement pastes and mortar. This work has led to a better understanding of the mechanism of air-entrainment in pastes and mortar and in fact forms the basis on which it should be possible to develop new techniques that are of practical significance for concrete.

There are three separate opinions concerning the mechanism by which surface-active agent admixtures alter the properties of fresh cement paste. These give emphasis (a) to the entrained air bubbles, (b) to the surface-active agent, and (c) to contributions by both entrained air and surface-active agent. The first theory, (a), postulates that the entrained air increases the volume and viscosity of the cement paste, and on this account concrete workability and cohesiveness are improved and segregation and bleeding are reduced. Since the entrained air bubbles are generally small and consequently possess a large total surface area, they are thought to behave somewhat like fine mineral admixtures. Their ability to deform under applied forces assists their lubricating action while their low density and consequent buoyancy is thought to assist in counteracting the settlement of solid particles.

The second theory, (b), suggests that the surface-active agent itself has the major influence in altering the properties of cement paste and that the entrained air has only a minor effect on such modified properties as workability, cohesiveness, and reduced segregation and bleeding. The surface-active agent is assumed to be adsorbed on cement-particle surfaces forming oriented hydrophobic films which act as boundary lubricants. In this way workability is thought to be increased. As a result of adsorption of surface-active agent on cement particles, the degree of flocculation of the paste is increased, and this increase is thought to be the reason for the observed reductions in segregation and bleeding in concrete.

Much of the evidence supporting these two different theories is indirect and was obtained by studying systems that contained both surface-active agent and entrained air. Hence the third theory, (c), which postulates that both the surface-active agent and entrained air contribute to the altered properties of cement paste and concrete, requires that the effects produced by the agent be studied separately from the compounded effects of agent and entrained air. Such a study could only be made when a technique had been developed for mixing cement paste reproducibly in the presence of surface-active agents without air bubbles being entrained. This method, which has been described by Bruere [7], has been used successfully and consists essentially of mixing cement paste in a virtually sealed vessel that is always completely filled, so that a vortex cannot form around the stirrer and air cannot be stirred into the paste. After a preliminary mixing the required amount of surface-active agent is injected into the paste and mixing is completed.

The viscosities of cement pastes, containing different surface-active agents added in a range of concentrations and without the complicating effect of entrained air, show some interesting variations. Anionic agents increase the paste viscosities significantly at low agent concentrations (0.01 percent by weight of cement). The agents are adsorbed on the cement particles, which tend to become hydrophobic, and on account of their increased interparticle attraction, flocculated to an increased extent. Flotation tests clearly confirm the adsorption of anionic agents on cement particles.

Cationic agents (e.g., hexadecyl-trimethyl ammonium bromide) also increased paste viscosity when used in low concentrations (below 0.05 percent by weight of cement). Under these contions the agent is adsorbed on the cement particles in such a way that the nonpolar ends of the molecules are oriented towards the water, the surfaces tend to become hydrophobic, the degree of flocculation increases, and the paste becomes more viscous. At higher concentrations of agent however a second layer of surface active molecules is adsorbed with the nonpolar ends oriented towards the particles and the polar ends oriented toward the water. Since the polar ends are hydrophilic there is a reversal in behavior and the paste becomes less viscous. It will be noted that with anionic agents cement paste does not show this reversal in behavior because the concentrations of the agents in solution are always low on account of their precipitation as sparingly soluble calcium salts.

Nonionic agents have virtually no effect on the viscosity of cement paste, while admixtures such as calcium lignosulfonate and saponin decreased paste viscosities at all concentrations. Both calcium lignosulfonate and saponin reduced interparticle attraction, the former by a dispersion mechanism and the latter by a protective colloid mechanism.

In the presence of entrained air and over a range of water/cement ratios the viscosities of pastes containing an anionic agent increased rapidly, whereas the viscosities of pastes containing saponin studied under the same conditions increased very slowly as the quantities of entrained air increased. Since it has been shown that air bubbles entrained in pastes containing saponin are not attached to cement particles, the increased viscosities in this instance must be due to the increase in surface area which follows from the fact that entrained air bubbles act as fine, weightless solid particles. The increase in paste viscosity due to entrained air only just exceeds the decrease in viscosity due to the action of saponin in reducing interparticle attraction. The increases in paste viscosities, which are produced by anionic agents in the presence of entrained air, exceed the sum of the effects caused separately by the interparticle attraction and the increased surface area due to air bubbles. Consequently at least one other factor must be operative. It is considered that these increases could be due, at equal air contents, to a smaller mean bubble size or to bubbles adhering to cement particles acting as bonds, which increase the aggregation of particles and form a large cohesive floc.

Examination of data showing the bleeding rates and capacities of pastes containing various surface-active agent additions with and without entrained air confirms the foregoing conclusions. In general the bleeding rates and capacities of cement pastes of limited water contents are reduced by amounts which depend on the degree of flocculation and the quantity of entrained air and the interaction of these two factors.

In connection with the mechanism of air-entrainment in cement pastes a considerable amount of data has been accumulated on the foam stability and foam capacity of various surface-active agents in contact with cement and their reactions with cement and silica particles. From all this data two major factors have emerged as necessities for air entrainment to occur. The surface-active agent must (1) possess some foam stability and foam capacity tendencies after coming into contact with cement particles and undergoing adsorption or chemical reaction, and (2) the surface-active agent should be adsorbed on the solid particles to render their surfaces hydrophobic so that air bubbles adhere to them. The significance of this latter factor can be readily demonstrated by the action of flotation activators and depressors on air-entrainment in silica pastes. An agent such as sodium dodecyl sulfate, which does not float silica and will not entrain air in a silica paste, can be made to do both by the addition of calcium hydroxide. The reverse behavior can be achieved with dodecylamine hydrochloride, which floats silica and entrains air in silica pastes, by the addition of gelatin. With anionic agents, such as sodium dodecyl sulfate in cement paste, the calcium salt, which is precipitated, appears to be capable of stabilizing bubbles and of sufficient solubility to produce the necessary foaming capacity in the solution.

Entrained air bubbles that are adsorbed on solid surfaces are very stable and cannot be readily removed. In hardened cement pastes cured under normal conditions, the bubble replicas retain their spherical shape. It is most likely that the adsorbed cement particles form a relatively undeformable coating on the bubble surfaces.

Saponin behavior in pastes according to the foregoing mechanism is anomalous because the entrained air bubbles are not attached to the solid surfaces. However saponin possesses a high foam capacity and forms fine bubbles which do not coalesce or escape readily, probably on account of the anomalous properties (e.g., viscosity) of thin films consisting of saponin-water mixtures.

A few brief comments may now be made on the effects of entrained air in concrete. Improvement in concrete workability is abundantly apparent on account of the modification of paste properties. The major defect of entrained air is its tendency to reduce strength, and this effect may be minimized by minor adjustments in mixing water and sand content. The major advantages in hardened concrete are decreased permeability and greatly increased resistance to frost action. These two advantages are probably interconnected. The mechanism by which frost action damages concrete is still incompletely understood. However two theories based on observation and experiment have been proposed and these suggest that damage is due to (a) development of hydrostatic pressure as a result of water freezing within limited spaces in the cement gel or (b) the formation of ice in zones where, by an increase in volume, mechanical disruption occurs. The former theory would apply to the more rapid rates of freezing whereas the latter would apply to slower rates of freezing and presupposes the presence of zones where ice can form. Frost damage can be alleviated by providing adequate spaces distributed throughout the concrete to accommodate the volume increase produced by the water-ice phase change. Entrained air bubbles distributed uniformly throughout the paste and spaced no farther apart than a minimum spacing distance (Powers [9]) are considered to be space into which water can move, and ice can form without building up disruptive pressures within the paste. There is now ample field evidence to show that air-entrained concrete possesses durability under adverse exposure conditions which far exceeds that of non-air-entrained concrete.

Future work on air-entrainment may well be developed along the lines of applying the theory of air-entrainment to solving problems that are concerned with concrete construction and durability. One line of work which suggests itself is contained in the work of Bruere [6] and concerns the uses of mixed surface-active agents which taken singly may be inefficient but taken together, so that their specific effects are additive, may be very efficient. An example of this type of action would be the use of a surface conditioner such as hexadecyl trimethyl ammonium bromide, and a foaming agent such as terpineol or octyl alcohol. If, by a judicious choice of admixture amounts of suitable agents, fine, stable air bubbles can be entrained in amounts that are constant and insensitive to agent concentration, and mixing vigor and time, the need for constant and rigorous control could be minimized without impairing concrete quality. Further, if bubbles that are sufficiently fine and uniformly distributed can be entrained in concrete, the total quantity of entrained air could be minimized. Such an advance would minimize strength losses and variations in concrete but at the same time permit the retention of the desirable properties such as permeability reduction and frost resistance.

Waterproofers and Permeability Reducers

Waterproofness, or the ability of concrete to resist the movement of water through it, is an important characteristic that is affected by two major factors, namely (1) the quality and condition of the concrete, and (2) the method by which water is made to penetrate it. In general it is found that compacted cement pastes made with a water/cement ratio no greater than about 0.27 and high-quality, fully compacted, and properly cured concrete are virtually impermeable to liquid. However in concretes there may be honeycomb areas, shrinkage cracks caused by drying, joints, poorly bonded areas under reinforcement, or large aggregate particles, and all of these constitute positions or flaws through which water under pressure may move readily. Consequently, procedures or admixtures that assist the production of dense, well-compacted, well-cured, and volumetrically stable concrete reduce permeability and increase waterproofness. Some such admixtures are not necessarily waterproofers. For example calcium chloride admixture may assist in reducing concrete permeability by improving workability and compaction, and by reducing damage that may result from inadequate curing. It is not a waterproofer in the true sense of the term. Air-entraining agents, although surface adsorbed on cement particles, are not necessarily good waterproofers either, even though they may assist in reducing concrete permeability. Their waterproofing action due to their conditioning surfaces is generally transitory on account of the small quantities used in concrete, their slight solubilities, and the tendency for large quantities of calcium hydroxide to be dissolved under moist conditions, and redeposited under drying conditions to mask or modify the conditioned surfaces. For many applications cement itself may be regarded as the best admixture, for an increased cement factor (richer mix) will often give adequately waterproof concrete.

Water penetration of concrete may occur under the action of a head of pressure or as a result of capillary forces. Under the action of pressure, water penetration usually takes place from one external surface while movement under the influence of capillary forces may occur in all directions. The quality of the concrete, and especially the density of the paste, affects both the rate and distance of penetration. The relationship between capillary movement and evaporation under suitable atmospheric conditions is an interesting one since it may induce the development of efflorescence on external surfaces in positions where the rate of evaporation equals the rate of water movement.

A number of different types of admixtures may be used to restrict water penetration and movement through concrete. These materials, which have different waterproofing actions, may be used as integral admixtures or as surface treatments on hardened concrete. Both types of treatment are useful; the former acts throughout the concrete mass while the latter forms only a surface film or skin which retains its effectiveness only as long as it remains undamaged. It may be noted here in passing that membrane curing compounds may be regarded as surface waterproofers which act in reverse, and constitute a useful technique for curing under difficult field conditions. Waterproofed concrete also demands that curing be continuous and commenced early because if it dries out it is virtually impossible to rewet it.

Integral waterproofing admixtures are of two major types; namely (a) water repellents (e.g., soaps), that may react with cement and tend to condition the surfaces of the solids, and (b) inert hydrophobic liquids such as mineral oils or asphaltic emulsions. The usual water-repellent-type admixtures generally consist of compounds such as calcium or ammonium stearates or oleates. The calcium compounds are practically insoluble in water but can be mixed with concrete. Care must be taken to insure that they are uniformly distributed throughout the mix. The ammonium compounds react very readily with cement and precipitate the calcium compounds. Both are added usually in small quantities (0.2 percent by weight of cement) because in large quantities they tend to cause severe frothing and to lower concrete strength. Butyl stearate, which is liquid at usual summer temperatures, does not usually cause such severe frothing as the other stearates and may be used in greater admixture quantities with less risk of serious strength reduction. It appears that butyl stearate is hydrolyzed slowly so that during the mixing period only a minor portion of the admixture quantity can react with cement; the remainder acts initially as an inert admixture liquid but slowly hydrolyzes and reacts with cement. Heavy mineral oils when used as waterproofing admixtures do not seriously reduce strength and appear to act as stoppers in capillaries. Asphaltic emulsions, which cause greater concrete strength losses than mineral oils, appear to act in much the same way when the concrete is allowed to dry sufficiently to permit the emulsion to break.

Although integral waterproofers have proved useful under some circumstances, especially in minimizing capillary movement, they have not always prevented water penetration and movement under applied pressures. The permeabilities of hydrated cement paste and concrete are not always completely overcome, and some reassessment of what is occurring is needed. The positioning of water repellents in the hydrated paste may not be particularly satisfactory since, as hydration proceeds, there is an enormous increase in new surfaces that may be completely unaffected by the admixture. Moreover as concrete undergoes cracking it is probable that the new crack surfaces are incompletely conditioned by the waterproofer. The inert admixtures would not be expected to be distributed more efficiently by the hydration process or to stop effectively any cracks that develop after the concrete has hardened.

A number of new types of material have been studied. Silicone compounds have some uses as water repellents but are unsatisfactory when used as waterproofers. Some types of rubber admixtures however appear to have possible uses as waterproofers.

On account of cost or to make the best use of their properties some film-forming materials may be used as surface coatings on hardened concrete to prevent water penetration. Various compounds have been used in this way, and some are known to penetrate into the concrete for considerable depths. Mineral or vegetable oils, waxes dissolved in solvents, bitumen emulsion or paint, and plastics have been used successfully to produce coherent films, which act as water barriers or strongly hydrophobic surface zones, while water repellents such as soaps and silicones have not proved successful as surface treatments. All surface coatings however suffer the defects of being exposed to weathering action, deterioration of bond with the concrete, nonuniform thickness, a tendency to rupture as a result of volume instability of the concrete or as a result of mechanical damage. Future work should be aimed at improving the action of water-proofers used integrally or as surface treatments. Such compounds could greatly assist in reducing attack by aggressive solutions and may simultaneously lead to improvements in such properties as concrete strength or abrasion resistance of surfaces.

Corrosion Inhibitors

Concern has been expressed at the corrosion of reinforcement steel in concrete subjected to certain environmental conditions. In recent times attempts have been made to prevent serious corrosion even under very adverse conditions of production, curing, and exposure by the use of admixture materials. The studies that have been made in this field seem particularly pertinent to the present discussion of admixture materials. In recent papers Shalon and Raphael [10] and Bäumel [11] discussed the action of dissolved salts as well as a number of other variables on reinforcement corrosion.

Under normal exposure conditions, steel reinforcement, covered by more than an inch of dense concrete which forms a continuous adherent coating on the steel surface, undergoes little or no corrosion due to chemical attack. The high alkalinity of the cement solution, which generally exceeds *p*H 12, produces a passive oxide layer on the steel and inhibits further corrosion. Carbonation of the hydrated cement proceeds at a very slow rate which diminishes further as the surface undergoes carbonation. In addition dense concrete is relatively impermeable to water. Incompletely compacted concrete or lean concrete is permeable to gases and water and does not afford satisfactory protection, and corrosion eventually occurs. Salts or compounds which reduce the solution *p*H to less than 12 promote corrosion, and in the presence of certain strongly ionized soluble salts an electrolytic cell action may occur and cause severe steel corrosion. Other corrosion mechanisms, such as the action of stray electric currents, are not of great interest here because they are due to installation leakages rather than to chemical action.

The practice of adding an accelerator, such as calcium chloride, to concrete tends to accentuate the risk of steel corrosion. Since it is a fairly general practice in concrete-products manufacture to steam cure with atmospheric-pressure steam, in order to accelerate strength development so that the forms can be stripped at early ages, the addition of calcium chloride as a set accelerator leads to marked corrosion of reinforcing steel. Steam curing appears to activate the corrosion reactions in the presence of calcium chloride and to accelerate their rates. Measurements of tensile strength can be made on mortar specimens in which the load is applied to two steel pins which are merely butted together in the center of the specimen. Under moist or wet curing conditions, even with calcium chloride admixture in the mortar, the tensile strengths are satisfactory after exposure for 1 yr. Steam-cured mortars however show very marked tensile-strength reduction when tested at 7 and 28 days depending on the amount of admixture added. These mortars, in contrast with those of high tensile strength, show numerous surface cracks filled with brown iron oxide; the steel pins are always severely corroded while those embedded in mortars cured under moist or wet conditions are relatively bright and uncorroded.

On account of the technological importance of accelerating setting and strength development by accelerator additions and steam-curing it is necessary to use a corrosion inhibitor which preferably also has the accelerating action of calcium chloride. Experiments in these laboratories have indicated that stannous chloride possesses all these desirable properties and can be substituted for calcium chloride as an accelerator that does not cause steel corrosion even under steam-curing conditions. Other salts such as cuprous chloride, chromous chloride, and cobaltous chloride possess similar but less marked acceleration and corrosion-inhibition properties. It appears necessary to use salts in the reduced condition and to ensure that the mortars are dense, otherwise their useful effects are nullified and corrosion occurs. The corrosion inhibition is thought to be due to the metallic ion tin, copper, chromium, etc. acting as a reducing agent and possibly plating the steel and protecting it from further chemical action.

There are also numerous possible combinations of corrosion inhibitors that can be used in conjunction with a setting and strength-development accelerator. In this instance calcium chloride could still be added as an accelerator while the corrosion inhibitor would be added to prevent reinforcement corrosion. These possibilities would seem to indicate a fruitful field for future work. The major criterion of successful action is an inhibitor which will prevent the corrosion of steel by calcium chloride under steam-curing conditions. If specimens are stored in a water-vapor saturated atmosphere after steaming, the optimum conditions for corrosion failure exist and a short testing period will be attained. Under these conditions control specimens containing calcium chloride are generally severely cracked within 10 days of steam-curing. Careful testing of corrosion inhibitors would be essential to ensure that they do not adversely affect the reinforcement-concrete bond or have other adverse effects on concrete. This whole subject is still in its early stages of development, and it is expected that a number of new compounds or procedures will be devoloped for controlling reinforcement corrosion.

Other Admixtures Used for Various Purposes

Apart from the admixture materials already discussed there are a number of other admixtures, added materials, or treatments that involve adding material to concrete, all of which have rather restricted uses for some specific purpose or product. Although it is not intended to give an exhaustive account of these admixtures or their uses, some of the more typical materials and techniques will be mentioned.

When quantities of gas, in excess of those that can be obtained by air-entrainment, are required in concrete, for example in lightweight or foamed concrete, it is usual to use a gas-forming agent such as finely divided aluminum powder. Alkali derived from the cement reacts with the aluminum to form hydrogen gas which is evolved as small bubbles which tend to bloat the concrete. Other gas-forming admixtures consist of finely divided metallic zinc and magnesium, or mixtures of hydrogen peroxide and bleaching powder. Care needs to be exercised in the case of all these agents on account of two major difficulties. Their rates of gas evolution are temperature dependent, and it is necessary to synchronize this with cement setting. In addition the gas bubbles, unlike those entrained with some surface-active agents, are unstable with respect to their size and position in cement paste. They tend to coalesce and escape readily. The technique of bloating to a limited extent may be used to counteract the settlement of concrete especially when used for back-filling or placing between vertically fixed points.

As a means of counteracting the drying shrinkage of portland cement much experimental work has been done, particularly in Europe, on expanding cements. Mixtures of sulfoaluminous cement and ground slag in varying proportions may be added to portland cement to give a delayed but controlled expansion. An admixture such as finely divided iron together with an oxidizing agent in the presence of moisture may also produce an expanding cement. The major problems with these materials and admixtures appear to lie in adequate control over the expansion processes and in insuring that internal expansion occurs in positions that adequately counterbalance drying shrinkage.

The use of finely ground limestone or chalk as an admixture in portland cement, sometimes in conjuction with an integral air-entraining agent, to produce masonry cement is fairly common. These cements have been developed to meet the specific requirements, namely a workable, cohesive, and water-retentive mortar for bricklaying.

Admixtures of various types may be used in concrete or other products or in certain parts of structures to improve or obtain desired properties.

Asbestos fiber used in asbestos cement products permits the production of relatively light sheets, pipes, and special shapes that possess suitable strength and flexibility. Recently plastic admixtures, such as polyvinyl acetate, have been used as surface densifiers and hardeners in floors subjected to heavy wear while rubber has been used in attempts to improve resilience. Pigments and artificially prepared colored aggregate may be used to achieve desired artistic and architectural effects.

In concluding this section some comment may also be made on the use of surface treatments on concrete. Although such treatments may not strictly be regarded as admixtures, the fact that in many instances the treatments penetrate for considerable distances into the concrete and modify the surface properties of the concrete very markedly in part at least justifies their inclusion here. Most surface treatments are applied for specific protective purposes. Concrete surfaces have been modified by the use of various materials as paints. Solutions of magnesium and zinc fluosilicate and sodium silicate, oils, bitumen, and mastics have been applied, usually as protective coatings but in the case of the solutions sometimes as surface densifiers and hardeners. There are however two other less well-known treatments that deserve mention. Gaseous silicon tetrafluoride penetrates concrete surfaces and reacts to form calcium fluosilicate which is relatively inert to acid attack. This treatment has been used as a means of protecting concrete in sewers from attack by sulfuric acid formed by bacterial oxidation of hydrogen sulfide gas. The other treatment consists of subjecting concrete to heavy carbonation. Carbon dioxide can be made to penetrate concrete for very considerable distances and may be used as a densifying and stabilizing treatment. In addition it has been observed to have a marked retarding effect on the rate of sulfate attack on treated mortar and concrete when immersed in aggressive solutions. It is expected that such treated concrete would behave satisfactorily if embedded in neutral or alkaline aggressive soils. Both of these gaseous treatments appear to be more effective than the application of appropriate paint treatments in achieving protection of hardened surfaces.

These comments are intended to indicate the broad and ever-increasing scope for the successful use of cement paste, mortar, and concrete. On account of the increasing number of possible uses for concrete there will undoubtedly always be a field for the development of new admixtures that improve specific properties of concrete, assist its production and handling, and permit the development of new products.

The Future

Any attempted assessment of the future developments and improvements that may be achieved by using admixtures must take into consideration the problems that are inherent in the materials, cement and concrete, and in the stages of development reached in the different and often separate fields in which concrete is used. The uses of concrete in different forms of construction, such as mass concrete, thin unreinforced slabs, reinforced and prestressed concrete, are varied while the handling and construction methods adopted, namely ready-mixed concrete, pneumatically applied mortar, tremie and pumped concrete, grouts, and the usual batch-mixed concrete, are similarly variable. Hardened concrete is exposed to extremely variable environmental conditions, such as being buried in soils and immersed in water of all types; it is subjected to a wide range of atmospheric conditions and to mechanical stressing and abrasion. Within limits the same materials are used for making concrete; the conditions, to which these materials and the structures made from them are exposed, are extraordinarily different and variable. The questions that arise here are what defects and problems arising from the materials, structure design, and the interaction between the structure and the environment are important and whether suitable admixture materials can be used or devised to overcome or alleviate these defects and problems.

The major problems encountered in concrete materials are concerned with strength, volume stability, and durability. Although improvements are desirable in many directions, it can be said that in general ways can be found to mix, handle, and place concrete reasonably satisfactorily. Structure design however is handicapped by the three above-mentioned major problems all of which are to a large extent problems that are inherent in hardened cement paste.

The strength of concrete is a complex property which has many different facets. The nature of the forces that produce coherence within the hydrated cement paste, in other words the intrinsic strength of the paste, are largely unknown. The behavior of cement paste or concrete under the influence of applied stresses, which is more generally regarded as its strength, has been studied extensively. These experimental determinations of mechanical strength have indicated clearly that cement paste and concrete are relatively strong in compression but relatively weak in tension. This weakness in tension can be counteracted by designing a composite unit that is adequately reinforced. The presence of steel reinforcement however introduces entirely new problems concerned with bond and stress transfer from concrete to steel. It is clear that unless the reinforced concrete behaves as a single unit its designed advantages will not be attained. Recently it has been shown that by the use of suitable treatments with epoxy resin the steel-concrete bond can be increased by several hundred percent. This increase is such that it has revealed once again the serious tensile weakness that is inherent in portland cement. Consequently new ways of increasing strength greatly in excess of that attainable at present need to be investigated. The use of strength-increasing admixtures and techniques appear to offer some possibilities of success since these may possibly be adapted to modifying the hydrated products and their properties, increasing the paste density, eliminating reactions that cause or contribute to internal stress, volume instability, and cracking, and increasing cement paste-aggregate bond.

The phenomenon of volume instability is another major defect of concrete. It has been noted already that cracking contributes to the low measured concrete strengths. Volume instability may be of two types, that induced by changes within the cement paste as a result of hydration and within the hydrated cement paste as a result of loss of water (drying shrinkage) or other reactions that may induce expansion, and that which is a characteristic of the mass but which occurs in the paste, known as creep or plastic deformation. Of all these volume changes, that caused by drying is probably the most serious because it is least amenable to control. While the presence of large aggregate in concrete undoubtedly minimizes the overall dimensional changes of the mass and restricts the number of major cracks developed as a result of drying shrinkage, it does not prevent the virtually discrete pockets of mortar within the mass from shrinking individually and developing large number of minor cracks. Consequently any technique or admixture that will minimize or prevent drying shrinkage or cracking must contribute enormously to future concrete technology. Increases in the intrinsic strength of hydrated cement may contribute considerably towards increased volume stability, and it is probable that creep, or plastic deformation under the action of applied forces, would be reduced. Further studies of the mechanism of creep are clearly indicated since these could assist in elucidating the weaknesses of hydrated cement paste and suggest methods for their correction.

The characteristic of cement paste and concrete that will receive greater future attention is durability. Much of the earlier discussion in this paper has been concerned with admixtures that, either in themselves or in the way that they assist in the handling of concrete or modification of hardened concrete properties, contribute to improved durability. It would not be amiss to indicate again here that admixture materials, such as more efficient air-entraining agent, workability aids, waterproofers and permeability reducers, reinforcement corrosion inhibitors, and treatments that prevent attack by aggressive solutions, will have a large and important part to play in the future of concrete.

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Discussion

K. R. Lauer

These comments pertain to that portion of the paper dealing with air-entrainment. In general the two major conclusions of Bruere were confirmed by laboratory investigation, namely the surface-active agent must possess some foam stability and foam capacity tendencies after coming into contact with cement particles and undergoing adsorption or chemical reaction; and the surface-active agent should be adsorbed on the solid particles to render their surfaces hydrophobic so that air bubbles adhere to them.

There is also evidence that the mixing procedure used has an important effect on the resulting air-entrainment. For example, the use of a Hobart N–50 mixer at high speed for 5 min readily entrained air with sodium lauryl sulfate in silica pastes. A $0.005M$ solution entrained 66 percent air in a paste with w/c of 0.60.

A method involving the use of a surface-tension–concentration curve for determining the concentration of an air-entraining agent in the filtrate proved successful. For the method of mixing used (Hobart N–50 at high speed for 5 min) and for representative agents of the anionic, cationic, and nonionic groups there appears to be a straight line relationship between the air content and the filtrate concentration of the mortar (fig. 1).

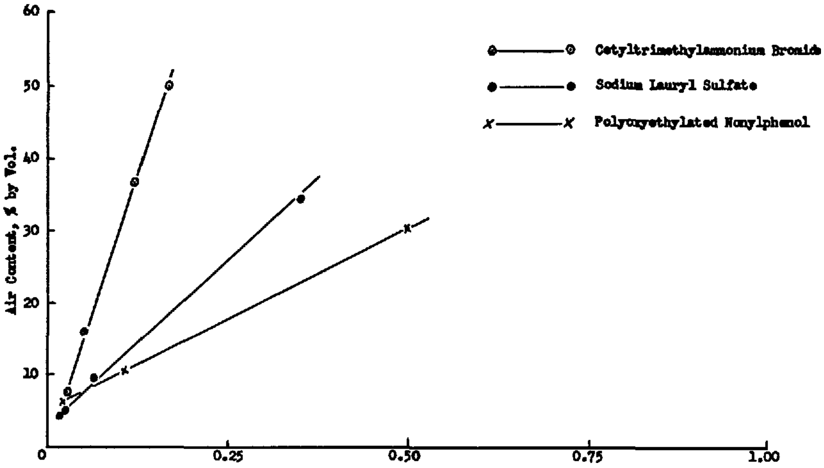

FIGURE 1. *Air content vs. concentration of agents in filtrate.*

The differences in mineralogical composition associated with such aggregates as limestone, quartz, and natural sand had little effect on the air entrained in mortars. Angular aggregate increased the air content of mortars compared to those containing rounded aggregate.

Discussion

J. H. Taplin

In his paper, Vivian mentions several types of materials which retard the hydration of portland cement. He suggests that hydroxyl groups are active in some compounds and carboxyl groups in others. Hansen [1] [1] suggested HO–C–H as the active group and Steinour [2] generalized this to the simple hydroxyl group in order to include certain inorganic substances. The data presented below indicate that HO–C–C=O is very active. In fact, it appears to be a general rule, that for an organic substance to retard cement, it must have at least two oxygen atoms each bound to a single but different carbon atom in such a way that the oxygen atoms can approach each other.

The data were obtained from paste specimens with a water-cement ratio of 0.30. Unless otherwise stated, the substances were added as one percent by weight of the cement. Soluble substances were dissolved in the mixing water, insoluble solid substances were mixed with the dry cement, and insoluble liquid substances were added simultaneously witb, or immediately after, the mixing water. The extent of the hydration was determined after 7, 17, 48, and 170 hr, by a method which involves determining the ignition loss at 540 °C of paste previously dried in an atmosphere of steam at 125° C. This method and the composition of the cement have been described previously [3]. The controls gave hydration values (H/C) close to 0.029, 0.069, 0.104, and 0.114 for the various curing periods. The paste stiffened at an H/C value of about 0.020 and hardened at about 0.050. With some substances (malic, α-ketoglutaric, gluconic, and dihydroxytartaric acids) the paste remained fluid ($H/C<0.010$) for more than a week, but with other substances the paste went stiff more or less rapidly, even though it may have taken several days to harden. If the H/C value at 17, 48, or 170 hr was 0.030 below that of the control then this retardation was considered significant. If the retardation was significant at only one curing period (usually 17 hr) then the substance was classified as a weak retarder. If the retardation was significant at two or three curing periods (which always included the 17-hr value) then the substance was classified as a strong retarder.

Table 1 is a classification of substances as retarders on this basis. Sections (a), (b), and (c) consist of simple compounds based on aliphatic chains of one, two, or three carbon atoms. It will be seen that all the retarding substances contain the group HO–C–C=O except glycerol. Oxalic and lactic acids are exceptional in that they contain the group but do not retard.

Section (d) contains substances based on a chain of four carbon atoms. Those which have the HO-C-C=O group retard. This section also contains retarding substances in which the oxygen atoms are not on adjacent carbons although, from the negligible activity of fumaric (as compared with maleic) acid, it would appear that the oxygen atoms must be able to approach each other.

Sections (e) and (f) contain some additional organic compounds. However caution must be applied in interpreting the results for substances such as quinone and pyrogallol which decompose rapidly in cement paste.

If we assume that organic substances retard by adsorption, then there are two alternative surfaces where this process might be effective:

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[1] Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. *Classification of substances in terms of their ability to retard the hydration of cement* [a]

Section	Retarding effect		
	Negligible	Weak	Strong
a	Methanol Sodium formate Formaldehyde (Diethoxy) methane		
b	Ethanol Calcium acetate Acetaldehyde Glycol Glyoxal Oxalic acid Dioxane		Glycol aldehyde Glycollic acid
c	*n*-Propyl alcohol Isopropyl alcohol Propane 1:3 diol Propane 1:2 diol Allyl alcohol Propionaldehyde Acetone Propionic acid Acryllic acid 2-Chloropropionic acid Malonic acid Hydracrylic acid Lactic acid	Glycerol Tartronic acid Butyl lactate Glyceric acid	Acetol Pyruvic acid Glyceraldehyde Dihydroxyacetone Ketomalonic acid
d	Fumaric acid Aldol Succinic anhydride	Maleic acid Erythritol Succinic acid Acetoin	Malic acid Maleic anhydride Tartaric acid Dihydroxytartaric acid Ethyl acetoacetate
e	Chloral hydrate EDTA (disodium salt) Glycine Urea Adipic acid 4-Hydroxypentane-2-one Cupferron	Diacetone alcohol Acetyl acetone Phorone 8-Hydroxyquinoline	α-Ketoglutaric acid β-Ketoglutaric acid Gluconic acid Citric acid 3 percent EDTA (disodium salt) Sucrose Glucose Fructose Sorbitol Pentaerythritol
f	Anthraquinone Phenol	Hydroquinone Salicylaldehyde Phloroglucinol Resorcinol 1:4 Naphthoquinone Chromotropic acid	Quinone Catechol Pyrogallol Gallic acid 1:2 Naphthoquinone Sulfonic acid
g	ZnO (in 3.6N $NaOH$ solution) BeO (in 3.6N $NaOH$ solution) As_2O_3 Sb_2O_5 Pb_3O_4 $CrCl_2$ $K_2Cr_2O_7$ Cu_2O CuO $HgNO_3$ $HgCl_2$ $SnCl_2$ NaH_2PO_2 $K_4P_2O_7$	$PbSO_4$ $Pb(NO_3)_2$ H_3BO_3 Sb_2O_3 CdO V_2O_5 $Cu(NO_3)_2$ $Na_2S_2O_5$ Potassium trithionate Sodium tetrathionate Sodium hexametaphosphate Concentrated ammonia	ZnO $ZnCl_2$ $ZnCO_3$ ZnO (in ammonium hydroxide solution) $BeSO_4$ PbO B_2O_3 As_2O_5 $Na_4V_2O_7$ Metaphosphoric acid Borax

[a] All substances added as 1 percent by weight unless otherwise indicated.

(1) on the surface of the clinker minerals so as to protect them from attack by water, and (2) on the surface of a coherent coating of hydration products so as to prevent the transport of material to or from the clinker surface. The explanation associated with this second adsorption process is similar to that suggested [3] to explain the limited hydration of low water-cement ratio paste. The explanation of this limited hydration phenomenon is that a rate-determining transport process through the hydration products ceases when the water voids become filled with products. (Although we can only speculate on the nature of the chemical species which might be involved in such a transport process, it appears unlikely that it would be water because of the relatively high concentration and mobility of this substance compared with, for example, calcium and silicate ions.)

Section (g) of table 1 contains inorganic substances. Substances such as boric oxide and the salts of the polythionic acids may provide anions which adsorb in the same way as organic retarders. However some inorganic substances such as zinc oxide and beryllium sulfate will not retard if they are added as solutions in alkali. It is not yet known if this is due to the presence of the alkali itself or because these substances can only act through their cations. These cations may exchange with those surface cations upon which the organic substances adsorb and both processes may have the same effect of either (1) stabilizing the clinker surface or (2) blocking the surface diffusion of material through the products.

References

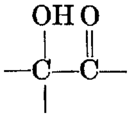
[1] W. C. Hansen, Oil well cements, Proc. Third International Symposium on the Chemistry of Cement, London, 1952, 598–627.
[2] H. H. Steinour, Discussion, ibid., 627–631.
[3] J. H. Taplin, A method for following the hydration reaction in portland cement paste, Australian J. Appl. Sci. **10**, 329–345 (1959).

Closure

H. E. Vivian

K. R. Lauer has indicated quite correctly that mixing vigor, which may be equated to speed of stirring, affects entrainment of air in pastes. It should be remembered, however, that both the consistency of the paste and the concentration of air-entraining agent will also affect the volume of air entrained. Bruère worked at rather lower concentrations of air-entraining agents than those used by Lauer. Although air can be entrained in silica pastes in the absence of calcium ions at high *p*H, the entrained air is unstable and on standing the paste readily segregates into separate layers. Undue emphasis should not be placed on the correlation between volume of entrained air and concentration of agent in the filtrate since very considerable difficulties are involved in obtaining reliable concentration data from surface tension measurements on filtrates from complex systems such as cement paste. It is considered that the surface area of sand particles is too small to affect the volume of air entrained in mortar significantly but that angularity in sand particle shape could increase the volume of entrained air by increasing local turbulence during stirring.

J. H. Taplin has noted that organic admixtures containing 2 oxygen atoms bound to adjacent carbon atoms as—



$$-\underset{|}{\overset{\overset{\displaystyle OH}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-$$

generally act, with few exceptions, as retarders. The mechanism of retardation of setting appears in many instances to be caused by adsorption of the retarder on solid surfaces in such a way that the rate of hydration is reduced. It is also possible that some admixtures may change the chemical composition of the hydration products and may modify their strength developing properties.

Since the original paper was written further work has shown that marked changes can be induced in the behavior of hydrating clinker compounds by the use of admixtures. The importance of all these studies cannot be overemphasized since they could lead to a clearer understanding of the chemical reactions and physical changes that occur as cement hydrates.

SESSION VIII. SPECIAL CEMENTS

Paper VIII-1. Stressing Cement and the Mechanism of Self-Stressing Concrete Regulation*

V. V. Mikhailov

Synopsis (By editor)

Soviet waterproof expansion cement, called WEC, was developed in 1942. It is obtained by dry grinding of high alumina cement, gypsum, and artificial hydrocalumite (C_4AH_{13}). Its functioning is based on quick formation of high-sulfate sulfoaluminate (ettringite). It quickly develops high strength, provides full shrinkage compensation, sufficient expansion, and great watertightness. It is excellent for repair and restoration of concrete structures, and as a waterproof layer.

Soviet stressing cement, called SC, is a more recent development, and research on it is continuing. It has three components: finely ground portland cement clinker, high alumina cement, and gypsum. Typical percentages are 66:20:14 when the portland cement has moderately high C_3A content. Use of a low percentage of water (25–30 percent) in 1:1 mortar gives good results under hydrothermic treatment (up to 100 °C) after a day of natural hardening. Low-sulfate sulfoaluminate forms first. Recrystallization to high-sulfate sulfoaluminate in the already hardened mass causes expansion, with retention of the bond to reinforcing steel, thus stressing the latter. High strength, watertightness, and prestressing possibilities make stressing cement a valuable binder for prestressed construction.

Theories of chemical action are presented, and research developments are discussed. Methods of producing self-stressed piping are described and compared.

Résumé

Le ciment expansif et imperméable soviétique a été développé en 1942. On l'obtient par brouage à sec de ciment alumineux, de gypse, et d'hydrocalumite artificiel (C_4AH_{13}). Son fonctionnement est basé sur la formation rapide de sulfoaluminate à forte teneur en sulfate (ettringite). Il développe rapidement une haute résistance, fournit la compensation complèt de retrait, une dilatation suffisante, et une forte étanchéité à l'eau. Il est d'un usage excellent dans la réparation et la restoration de constructions en béton, et comme couche imperméable.

Le ciment soviétique autocontraint est d'un développement plus récent, et continue à faire l'objet de recherches. Il a trois composants: du clinker de ciment portland finement broyé, du ciment alumineux, et du gypse. Des pourcentages typiques sont: 66:20:14 quand le ciment portland est d'une teneur en C_3A modérément élevée. L'utilisation d'un dosage peu élevé en eau (25–30%) dans le mortier 1:1 donne de bons résultats avec un traitement hydrothermique (jusqu'à 100 °C) après un jour de durcissement naturel. Le sulfoaluminate à faible teneur en sulfate se forme d'abord. La recristallisation en sulfoaluminate à forte teneur en sulfate dans la masse déjà durcie cause la dilatation, en maintenant l'adhérence à l'armature d'acier, causant ainsi la contrainte de ce dernier. À cause de sa haute resistance, son étanchéité à l'eau et ses possibilités de précontrainte le ciment autocontraint se trouve un liant valable pour les constructions précontraintes.

Les théories de l'action chimique sont présentées, et le développement des recherches est discuté. Les methodes de production de conduites autocontraintes sont décrites et comparées.

Zusammenfassung

Der in der Sowietunion hergestellte wasserfeste Expansivzement, wurde im Jahre 1942 entwickelt. Man erhaltet ihn durch trockenes Vermahlen von Tonerdezement, zusammen mit Gips und synthetischem Hydrokalumit (C_4AH_{13}). Das Benehmen einer solchen Mischung muss durch die schnelle Bildung des hoch sulfathaltigen Sulfoaluminats (Ettringit) erklärt werden. Dieser Zement entwickelt seine höchste Festigkeit schnell, zeigt vollständige Schwindungskompensation, hat eine genügende Ausdehnung und ist in hohem Grade wasserdicht. Man kann ihn gut für Reparaturarbeiten und Wiederherstellung von Betonkonstruktionen gebrauchen, und auch als wasserbeschützende Auflage.

Der in der Sowietunion hergestellte Spannungszement wurde viel später entwickelt; die Forschungsarbeiten sind noch im Gange. Drei Bestandteile sind darin enthalten: Feingemahlener Portlandzementklinker, Tonerdezement und Gips. Eine typische Prozentanalyse zeigt 66:20:14, wenn der darin enthaltene Portlandzement einen ziemlich hohen C_3A-Gehalt hat. Der Gebrauch von nur wenig Wasser (25–30%) in dem 1:1 Mörtel zeigt gute Erfolge bei der nassen Wärmebehandlung (bis zu 100 °C) nach einem Tage natürlicher Erhärtung. Zuerst wird ein Sulfoaluminat gebildet, mit einem niedrigen Sulfatanteil. Die Umkristallisierung zum hochsulfathaltigen Sulfoaluminat, nachdem die Masse schon hart geworden ist, bringt eine Ausdehnung hervor, und die Verbindung mit der Stahleinlage

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the U.S.S.R. Academy of Construction and Architecture, Moscow, U.S.S.R.

ist erhalten, was natürlich zur Folge hat, dass der Stahl gespannt wird. Die hohe Festigkeit, die Wasserdichtigkeit und die Möglichkeit, eine Vorspannung zu erteilen, tragen alle dazu bei, dass dieser Spannungszement ein wertvolles Bindematerial für vorgespannte Konstruktionen darstellt.

Theorien der chemischen Reaktionen werden erörtet, und der Erfolg der Forschungsarbeit wird besprochen. Die Methoden der Produktion selbstspannender Röhre werden beschrieben und untereinander verglichen.

Introduction

The fundamental consideration of engineers, who for many years have been working with no little success, has always been to create cements which bind natural and artificial rock, crushed stone, gravel, and sand, into a hard, strong concrete mass, quickly and reliably. The aim is to produce constant improvement of every available cement. Certain cements, intended to produce waterproof concrete, require special composition—to assure dense mineralogical cement paste and concrete structure. During setting and hardening, cement components are hydrated and acquire new structural forms, accompanied by concrete volume change.

At these changes, the internal stresses in the colloid particles, and between them, appear and are either partially or completely localized. Hence cement paste and concrete undergo uninterrupted volume changes.

Cement paste expansion, in consequence of so-called "inconstant volume", or of the influence of sulfate water, causes cracking, just as concrete shrinkage, highly undesirable, also leads to cracking.

Fargoing research has long been engaged in efforts to eliminate the harmful influence of shrinkage on reinforced concrete, or to provide conditions to obtain setting and hardening without shrinkage. Only in 1942 was this problem basically solved, when Soviet scientists created an expansion cement, now widely applied in construction. This cement is based on calcium hydrosulfoaluminate formation, which has interested many Soviet scientists (Baikov, Budnikov, Moskvin, Kind, Rehbinder, Orlov, Yoong, Yoodovich, Lapin, Kravchenko, Danelian, and others) as well as foreign scientists (Michaelis, Lafuma, Deval, Jones, Biehl, Sestini, Turriziani, Schippa, Wells, Clarke, McMurdie, D'Ans, Eick, Kalousek, Berkley, Lufsky, Klein, Troxell, and others).

Waterproof expansion cement, called WEC (author—V. V. Mikhailov) is a quick setting and quick hardening hydraulic binder, reaching high strength in several hours. This cement successfully withstands high hydrostatic pressure without any signs of water transmission.

WEC is obtained by combined dry grinding of high-alumina cement, gypsum, and artificial C_4AH_{13} (known as the mineral hydrocalumite). The latter is obtained by joint hydration of high-alumina cement and lime, followed by drying and grinding. The degree of expansion of this cement is largely regulated by change in the proportions of components.

Formation of calcium hydrosulfoaluminate $C_3A(C\bar{S})_3H_{32}$* (ettringite), known as "cement bacillus", concrete's most dangerous enemy [1][1] and the cause of considerable concrete building damage, is employed to solve this problem in cement expansion, not only for shrinkage elimination, but also to obtain active expansion. Calcium hydrosulfoaluminate appears in the early stages of WEC hydration and its formation is completed shortly after cement setting. Expansion thus begins and also ends in the short time of the cement paste stiffening, i.e., during the early period and first phase of cement hardening, thereby completely avoiding the harmful influence of ettringite formation.

It was in 1943 that WEC cement first came into use to rebuild war-destroyed reinforced concrete constructions; later in subway construction to replace lead for caulking joints of cast iron tubings, guaranteeing watertightness, high strength, and quick building. WEC cement finds use also in coal pit bracing. Good results were also obtained by expansion cement application in the repair and restoration of underground infiltrated concrete constructions.

To date we have worked out very simple and rapid methods of tamping cracks, holes, and cavities, which immediately stop water filtration, making the construction ready for use.

It is customary to apply waterproof cover as a concrete jacket in underground construction, when shotcreting with WEC concrete greatly simplifies the work.

An isolation layer of a WEC concrete, 3.5 cm thick, can be placed directly on the damp surface, promptly stopping water seepage. Such layers are applied to isolate dam surfaces, hydrostation tunnels and pipes, buttresses, tanks, and other underground and sea constructions. The method is applicable in building repair to restore to proper condition damp or submerged premises.

Thus, Soviet engineers have created a waterproof expansion cement which has become an industrial product, and has overcome the difficulties involved in concrete contraction. Again, this cement is used in various branches of construction to replace lead, metal, and other materials. Creation of this cement is an example of the profitable use of harmful factors in construction building, "cement bacillus" for example, whose formation and structural expansion are connected

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*The symbol $\bar{S}$ is here used for SO_3. The bar distinguishes from $S=SiO_2$.

[1] Figures in brackets indicate the literature references at the end of this paper.

with the initial period of WEC existence, when the colloidal formation in cement paste is maximum.

All known cements are now applied only to make strong stone from ballast, gravel, and sand, but these binders have unexplored qualities far beyond present applications.

Cement's "inconstant volume" and the possibilities of regulating nonelastic expansion are as yet not profitably employed. These factors establish a condition in concrete in which the reinforcement becomes extended and prestressed, making unnecessary the mechanical methods now practiced. This novel idea of creating self-stressing, obtainable by the help of stressing cement, opens wide horizons for application in building, and provides economy in materials and expenditure.

It must be pointed out that in world practice there has been very little research on binder compositions which cement by hardening and supplying sufficient energy to deform and stress the reinforcement. Therefore the achievements of Soviet scientists may be considered as the first step towards solving this problem.

Soviet stressing cement (authors—Mikhailov, Litver, and Popov) is a tricomponent binder made from finely ground portland cement, high-alumina cement, and gypsum, taken in optimum proportions. Mixed with a low amount of water, this cement sets and hardens quickly. Cured by hardening under the required hydrothermic conditions, stressing cement acquires sufficient strength and expands, carrying the reinforcement along and thereby creating self-stressed construction. High mechanical strength, watertightness, and prestressing possibilities make stressing cement a valuable binder for prestressed construction, assuring both watertightness and high tension resistance.

Any portland cement (in amounts of 60–70 percent) to which high-alumina cement and gypsum have been added in the proper proportions makes self-stressed cement.

We now turn to our research in expansion and stressing cement (production possibilities), and means of its use in building.

The Mechanism of Setting and Hardening of Portland Cement Binders

In considering the structure of high strength portland cement clinker we distinguish two structural varieties of clinker compound compositions:

(1) portland cement of high alumina content (fig. 1), in which polymineral structures C_3S and C_2S are glued with a glasslike mass of calcium aluminate (C_3A) and some calcium ferroaluminate (C_4AF),

(2) brownmillerite portland cement (fig. 2) in which polymineral structures C_3S and C_2S are glued with a glasslike mass of calcium ferroaluminate (C_4AF) exclusively. Here C_3A is absent.

To stabilize the technical properties and to regulate setting time, the portland cement clinkers are ground with a small amount of gypsum, which can react quickly with the alumina compounds of the clinker in water medium.

Any mixture of portland cement with water, as a result of absorption and chemical dispersion of the cement grains, which are splinters from the mechanical grinding of clinker compounds (fig. 3), disintegrates into separate micro and colloidal particles clearly described by P. A. Rehbinder [2]. Such a dissociation is accelerated by high solubility of alumina and ferroalumina glasslike matrix compounds and outwedging water action (Rehbinder), owing to penetration into numerous microcracks of cement splinters. As a result, active surfaces of cement grains quickly increase and hydration and hydrolysis are accelerated. Special investigations (A. Smirnov) with the application of radioactive isotopes have shown that 1 hr after mixing of C_3A with water (fig. 4), the active surfaces of cement increase from 3,000 to 300,000 cm^2/g, or by a hundred times. The explanation of these dissociations is that in chemical and mechanical processes cement particles less than 10 μ disintegrate fully into particles of colloidal size (0.1 to 0.01 μ), and form colloidal cement glue. Larger cement splinters of polymineral structure C_3S and C_2S, cannot fully dissociate even over a long time and always retain kernels of cement splinters, untouched by water. The cement glue layer, when the quantity of colloidal formation increases by new colloidal particle absorption, gives a saturated solution, and hydrated crystallization occurs directly around the remaining cement kernels, separated from the former by water diffusion layers, free of soluble salts. In the process of further dissolving, new hydrated ions and molecules of clinker salts are continuously ejected through this layer and are concentrated in the area of colloidal structure of hardened cement paste and are absorbed by the nearest crystalline hydrated formation. The hardened cement paste forms structures where the former cement, new formation, free water, and air are reacting [3]. The role of the latter is also important because hydration speed and volume change, which continuously accompany the structure changes, largely depend on the air distribution in the structure. A schematic drawing (fig. 5) shows the hardened cement paste structure, conditionally, after the alumina compound formations are fully hydrated, which requires little time. By this time, C_3S, and to a small degree C_2S kernels, decrease by hydration from the surface. As the hydration process of C_3S kernels develops, the water diffusion layer diminishes and the process slows down and finally stops because of water

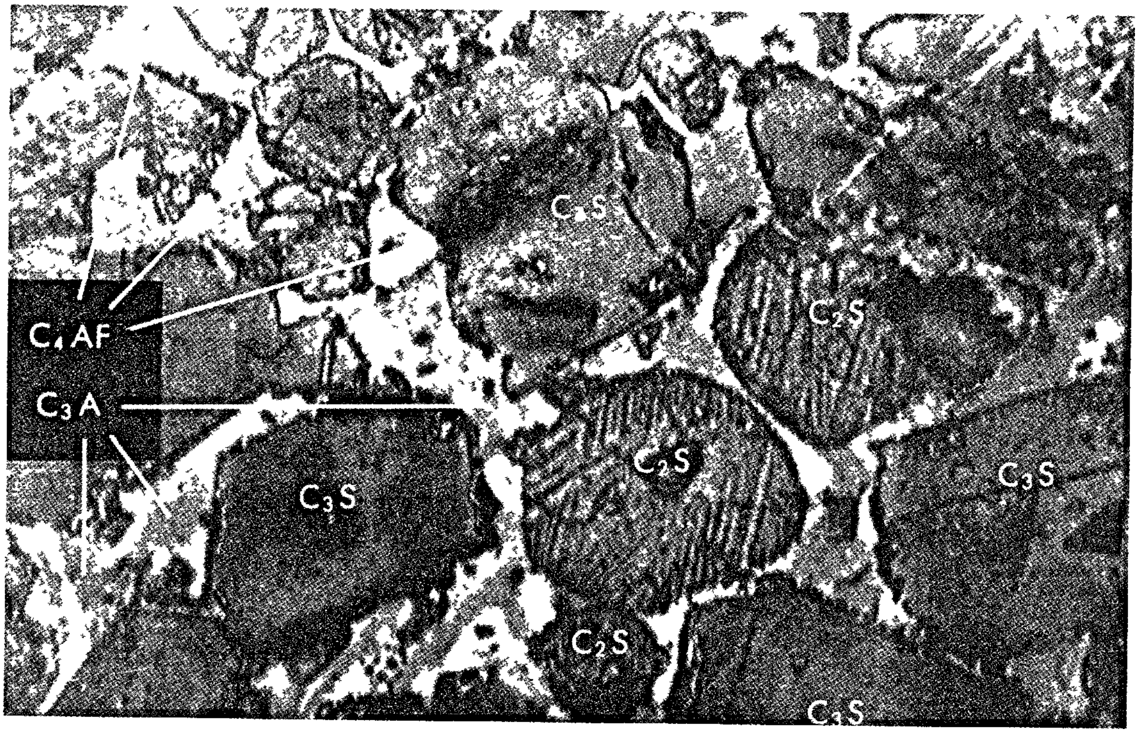

FIGURE 1. *High alumina portland cement structure, rich in* C_3A *and* C_4AF.

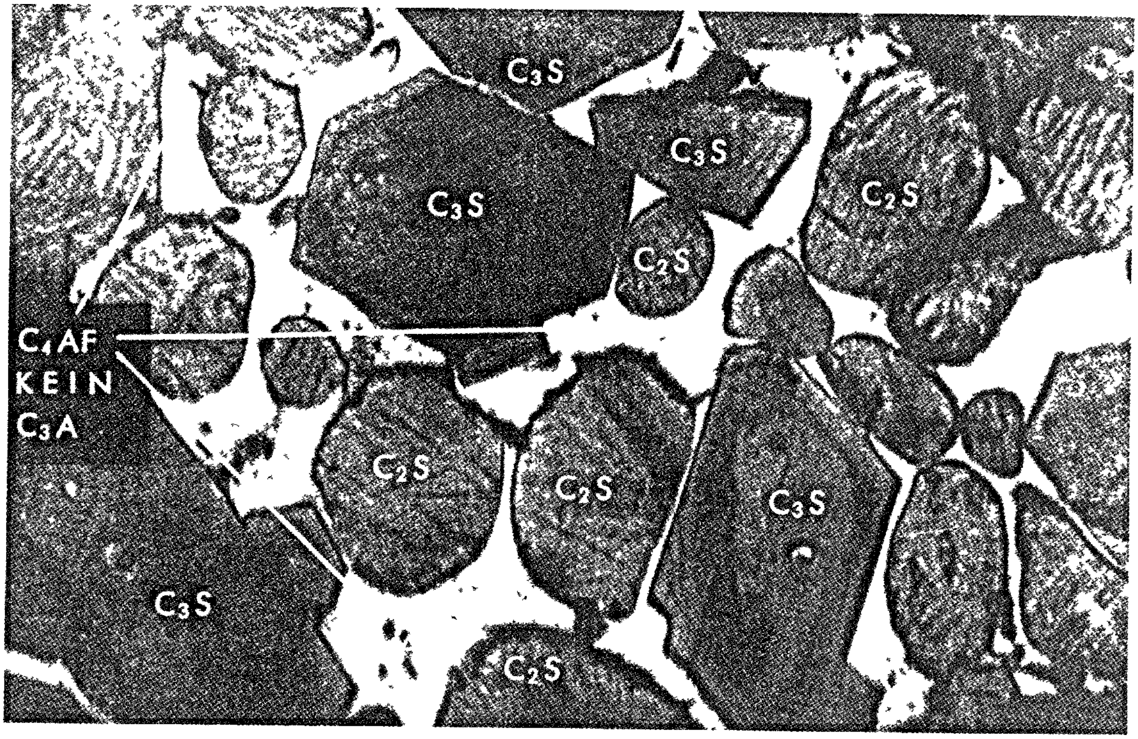

FIGURE 2. *High alumina portland cement structure,* C_3A*-free.*

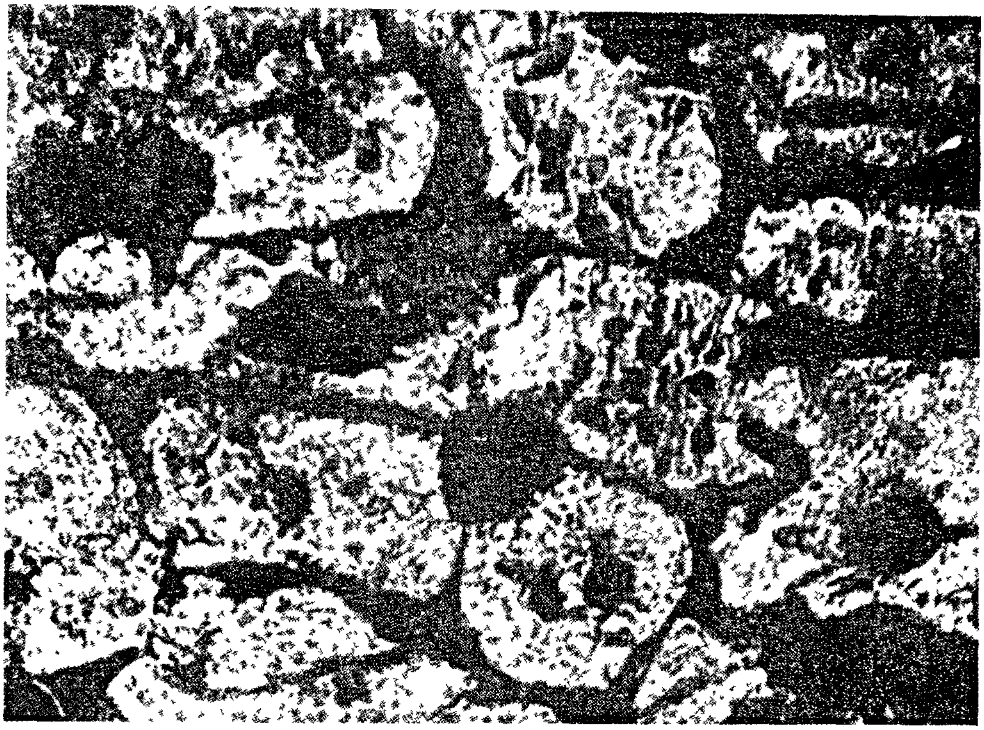

FIGURE 3. *Polymineral structure of portland cement grains.*'
Published by Prof. A. A. Baikov.
Enlargement 350 times.

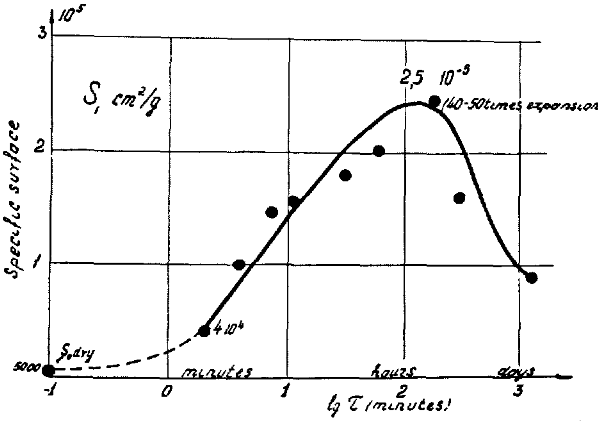

FIGURE 4. *Diagram of cement grain active-surface increase during first hydration period.*

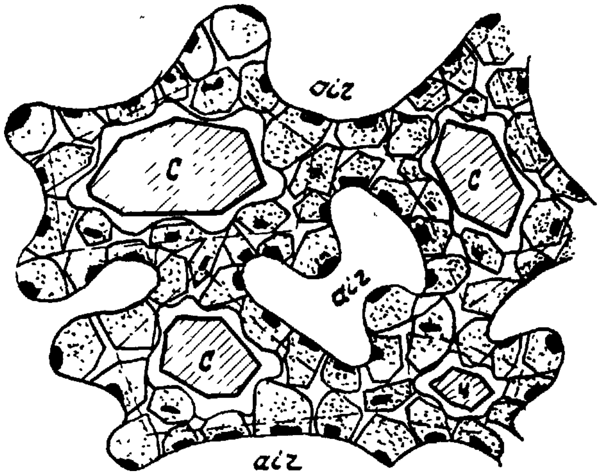

FIGURE 5. *Scheme of gel and air distribution in hardening cement paste.*

deficiency. The more air bubbles, large and small, spread through the structure, the quicker is the development of solution saturation and new crystallization. N. V. Mikhailov [4] has shown in his research on cement hydration the existence of two stages of structure formation:

(a) the stage of formation with predominance of thixotropic coagulation structure, with reversible recovery after mechanical destruction, and

(b) the stage of strengthening, characterized by both crystallization and coagulation structure.

These two stages are definitely distinguished by the change of plastic properties of the cement paste, and are established by continuous and regular tests with a plasto-viscosimeter (method of N. Mikhailov and E. Kalmikova) [4]. For every kind of cement paste there exists one distinctive point (fig. 6) when the plastic strength of structure increases quickly.

In the coagulation structure, soon after its formation, the processes of calcium hydroaluminate crystallization proceed quickly with unusual formation of crystalline needles and chains, which

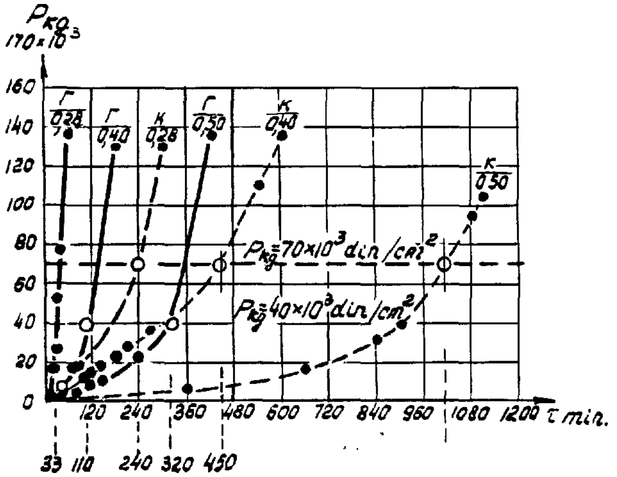

FIGURE 6. *Changes of cement paste plastic strength with time, for different cements and different water contents.*

pierce the coagulation structure of the slow hardening hydrosilicate components like a framework. After the cement paste colloidal phase reaches maximum saturation of new formations, these structures are thickened and completely form such a pseudocrystalline framework.

Maximum saturation is characterized by a breaking point in the diagram (fig. 6), which exactly divides the different states of cement paste structure.

By cement setting and hardening, ions of hydrated clinker salt are ejected to the more distant solution zone, free of hydrated salt influence. Movement of these ions becomes more difficult, the more bubbles, big and small, in this solution (fig. 5). During the first stage, ions of calcium, alumina, and ferroalumina clinker salts predominate, to which later calcium silicate ions are added. Very soon, particularly with low water content in the mixture (hard paste consistency), oversaturation of solution is attained and crystallization begins, giving compounds of new formation, gluelike in appearance, and different in form and configuration. Then the process of crystallization accelerates, following partial water release, with absorption on the new formation surfaces.

As a result of permanent water exhaustion in the direction of nonhydrated clinker kernels, the new formations, in crystallization and coagulation states, are in permanent compression. Particles of these formations draw together (fig. 7), because of molecular attraction in the zones of capillary particle contacts.

Surface capillary tension in these contacts also draws the particles closer. The equilibrium now depends on the capillary forces which attract the structural particles and simultaneously push the particles away. Later these forces not only act spontaneously but also through the thin layer of the water jacket covering the particles.

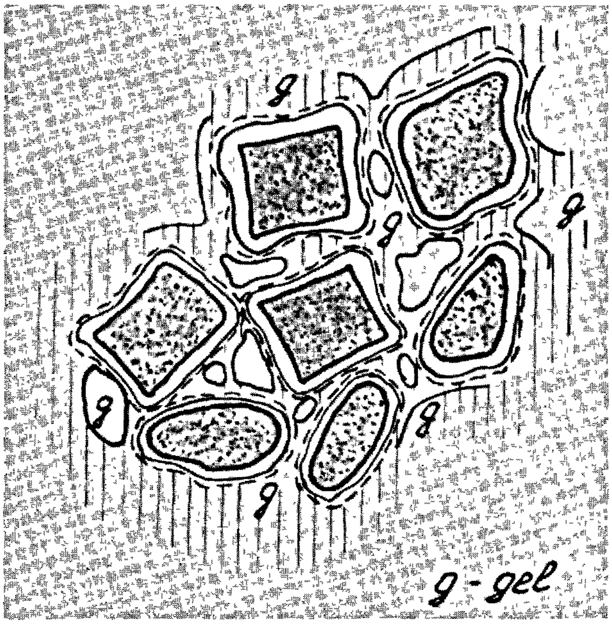

FIGURE 7. *Scheme of hardening cement structure.*

Water molecules which have lost their mobility and are attached to particles by attraction forces due to the tensioning influence between the particles are gradually squeezed out from the contact and packed densely, often replacing by direct molecular interaction new hydrated particle formations. As a result chains, needles, rods, and friable splines of colloidal new particle formations appear and unite or connect by molecular cohesive forces. During C_3S and C_2S hydration, water exhaustion of their kernels causes difficulties, thins the free water layer and finally stops the clinker salt hydration long before expending all the salt reserves. To a certain extent, external water feeding can prolong hydration, but not for a long time. The central zones of C_3S kernels, and especially C_2S, remain as a permanent clinker salt compound, as has been described by Yoong [5].

If the cement paste structure had no air bubbles, each cell between cement grains (generally three) would be filled with water and with hydrated ions of clinker salts, forming only one dimension of crystal, which could freely move in this cell because there is nothing to prevent free transfer in the stream of thermal molecular movement.

If the cement paste cells are air filled (fig. 5), ions may be ejected to the boundary "cement glue—air", and, as a result, along the whole boundary of this cell the possibility exists of forming a great number of crystalline centers, and, in this area, very dense and dispersed cement paste structures arise. These consist of a ramified network of hydrated alumina and ferroalumina compounds, filled (to overflow) with hydrosilica structures. Some scientists [6] affirm that with the hydrosilica formation a crystal of large dimension cannot grow when water content is low, with which we absolutely agree. But this refers only to hardening at temperatures below 100 °C.

When the temperature is over 100 °C, and particularly above 140 °C, even in mixtures with very low water content, calcium hydrosilicate crystallizes in a fibrous network of long lathlike and rodlike crystals known as a tobermorite formation [7], which explains the high mechanical strength of the cement paste in question.

The Soviet method of concrete vibropressing [8, 9] followed by hermetic concrete curing at 140–150 °C in the pressed state, aims to attain strong tobermorite structure quickly. It has already been pointed out that in the state of structure formation, cement glue consists chiefly of alumina and ferroalumina hydrated clinker compounds, which form sufficiently developed fibrous splines and framework.

This structure itself cannot play any important role in cement paste strengthening, but can to a considerable extent insure uniform distribution of hydrated silicate in the whole volume of cement glue, preventing large particles from growing, and providing future high strength of cement paste.

Future cement paste strength can be further increased by repeatedly destroying these cement paste formations by mechanical influences, for example, vibration. In this case there is demolition of many fibrous framework ties which are immediately restored, but in dense structure. During this restoration calcium hydrosilicate crystallization takes place, giving very dispersed and strong cement paste structure. It was on this principle that methods of vibromixing, vibropunching, vibropressing, etc., were developed.

When the alumina and ferroalumina crystalline hydrated formations predominate in cement paste structure, it is possible by varying the amount of water, and by mechanical coercion, vibration and thermal curing to build and rebuild cement paste structure to attain maximum strength.

Shrinkage and Swelling of Cement Paste. Cause of Concrete Watertightness

During the setting and hardening of many known cements, the volume of materials decreases, because of more dense placing of hydrated clinker salts than cement grains plus free water.

Therefore the primary cement paste volume $(C+W+A)$ decreases its volume by hydration to

$$[C+W+A-(1-K)(C_h+W_h)] \tag{1}$$

where C_h=the original volume of the amount of cement that reacted, W_h=water volume for this hydration, A=air volume, K=ratio of the specific volume of the hydrated product to the original specific volume of the mixture of cement and water that reacted.

Equation (1) shows that by hydration the concrete volume undergoes chemical shrinkage, since $K<1$. There is also physical shrinkage by loss of free water, W, in dry air. Chemical shrinkage is large, and it appears chiefly in volume change during setting and during the first hours of cement hardening. For example, the high-alumina cement paste shrinkage in 1 day is 0.7 percent of primary length, and for portland cement paste 1 percent. Shrinkage is also large if cement paste is water-hardened, causing difficulty during hole and cement joint tamping. Later, by dry storage, physical shrinkage develops as cement paste dries. In wet storage, swelling appears and the volume of cement paste increases.

When the liquid phase of hardened cement paste is in equilibrium with air moisture, no volume change in cement paste occurs.

The interaction between the colloidal formations of cement paste is regulated by cohesive forces of capillary contact (fig. 8). The theory of capillary contact, worked out in 1941 [3], shows that this interaction is determined by free water surface curvature in capillary contacts between new cement paste formations and is described as

$$r_1=\sqrt[3]{\frac{3V}{4\pi\alpha}\left(1+\sqrt{1-\frac{\pi x^3}{3\alpha^2V}}\right)-\frac{x^3}{8\alpha^3}}+\sqrt[3]{\frac{3V}{4\pi\alpha}\left(1-\sqrt{1-\frac{\pi x^3}{3\alpha^2V}}\right)-\frac{x^3}{8\alpha^3}}+\frac{x}{2\alpha} \tag{2}$$

and the interaction forces as

$$K=\frac{\pi\gamma}{4}\frac{r_1}{r^2}\left(\frac{1}{\frac{\alpha}{2}+\frac{x}{2r_1}}-1\right) \tag{3}$$

where V=water volume in contact, α=inclination angle of sharp contact side, x=distance between firmly attached colloidal particles, without taking into account water layers, r_1=working diameter of capillary contact, r=average particle dimension, to determine the number of particle contacts in unit surface, γ=surface tension of water.

The cement paste system, under these interaction forces, is always in a state of external compression, constantly changing value when the surrounding air humidity changes. The change of this compression in structure causes cement paste volume changes and shrinkage.

Shrinkage can be calculated by eq (4):

$$\lambda_{sh}=\frac{\pi}{4r^2E_c}=\left[\frac{3}{2}\frac{\gamma^2}{1{,}300\ln\frac{1}{\phi}}-3\gamma\sqrt{\left(\frac{3}{2}\frac{\gamma}{1{,}300\ln\frac{1}{\phi}}\right)^2+r\left(\frac{2\gamma}{1{,}300\ln\frac{1}{\phi}}\right)}+r\left(2\gamma-x\,1{,}300\ln\frac{1}{\phi}\right)\right]+\Delta x \tag{4}$$

where ϕ=relative humidity of the air.

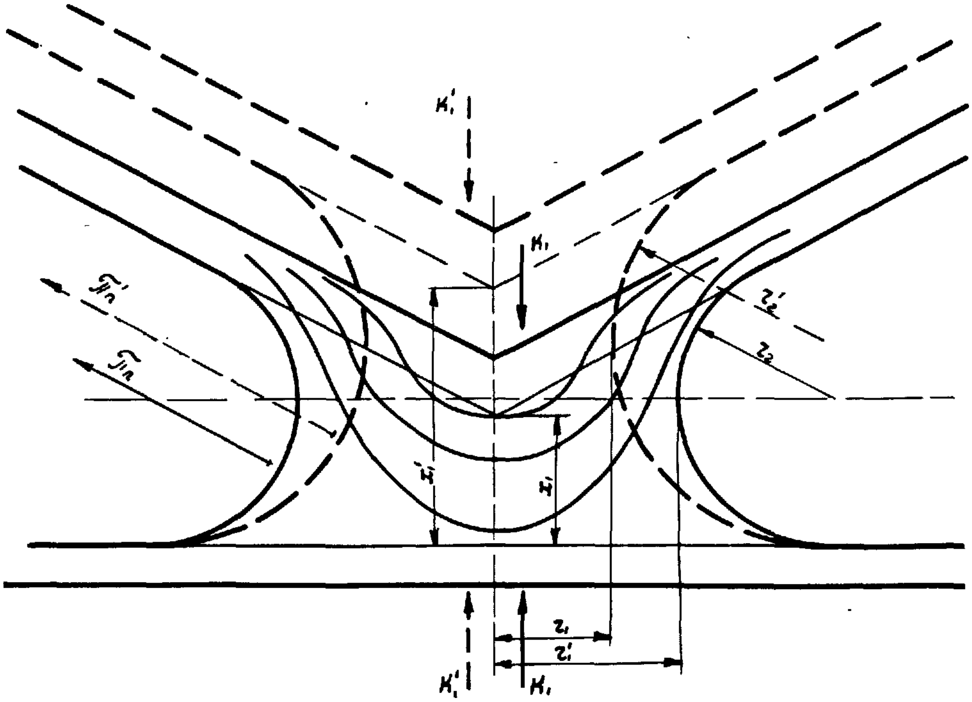

FIGURE 8. *Scheme of coherence of colloidal particles in capillary contact of cement paste.*

Insofar as water exhaustion into diffusion layers and new particle formations and compression by capillary forces develop continuously, in similar manner the average water surface curvature in capillary contacts [3, 10] continuously changes. If at any early moment the humidity of the surrounding air and the water content of the cement paste were in equilibrium, at the next moment, by increasing the humidity, equilibrium disappears and water condensation begins, which relieves the particles' capillary compression, lowering shrinkage. If unlimited humid flow of air is maintained, there is full compensation of shrinkage compression. When hardened cement samples are stored in water, its unlimited ingress produces concrete swelling; but in this case interparticle pores and spaces filled with water increase. If these samples are placed in dry air, cement paste quickly loses water from the large pores, and gives higher shrinkage than in the normal hardening condition. On the other hand, in dry air from the first moment of cement setting and during hardening, equilibrium is absent, and cement paste loses water the more rapidly the larger the pores of the cement structure. As a result high shrinkage appears, connected with water decrease in the capillary contacts. With very dry air and large pores, water loss is so rapid that cement hardening may completely stop. This water loss is accompanied by a high shrinkage (physical factor). The importance of sufficient water retention, especially during the time of setting and first period of hardening, is clear.

TABLE 1. *Technical code for waterproof expansion cement—WEC*

No.	Qualities	Measurement data
1	Stable volume changes	By water setting and warm testing; no volume change.
2	Setting time:	
	(a) Initial set, not before	4 min.
	(b) Final set, not later than	10 min.
3	Grinding fineness:	
	(a) Residue on screen No. 200, not more than	12 percent.
	(b) Passed through screen No. 90, not less than	75 percent.
4	*Compression strength,* not less than:	
	(a) Cubes 20 x 20 x 20 mm made with cement paste of normal plasticity, water-stored 1 hr after mixing:	
	Age:	
	2 hr	...
	6 hr	75 kg/cm².
	3 days	300 kg/cm².
	28 days	500 kg/cm².
	(b) Prisms 31.5 x 31.5 x 100 mm, made with mortar of normal plasticity, 1:2 (by weight), stored 1 hr after mixing:	
	Age:	
	24 hr	120 kg/cm².
	3 months	200 kg/cm².
5	Elongation of 31.5 x 31.5 x 100 mm prisms made with cement paste of normal plasticity:	
	(a) Dry-air-stored and tested at age of 1 day, not less than	0.05 percent.
	(b) In water after 1 hour and tested at age:	
	1 day, not less than	0.2 percent.
	28 days, not more than	1.0 percent.

Cement paste in normal storage after long water storage gives greater shrinkage than cement paste with initial curing in air.

Cements are applied in structures as mortar or concrete. The external effect of shrinkage is less than in pure cement, because of aggregate resistance. But the degree of cement paste shrinkage in the cells between aggregates is the same; therefore in the cement paste structure high tensile stresses arise, which can result in microcracks. Microcracks permit water seepage which penetrates through the concrete, not only by applied pressure, but easily because of its own weight. The consequences of cement shrinkage are seen in cases of cement repair of filtrated cracks and holes when the cement paste cracks, or the cracks appear on the hole edge. Invisible microcracks can easily be seen when filtration begins at once upon application of water pressure.

WEC application provides full shrinkage compensation and sufficient expansion. WEC technical properties are given in table 1 [15].

Lab testing of WEC must be done in definite sequence, differing considerably from the ordinary cement testing. It must be remembered that WEC storage and transportation is permitted only in hermetic packing. WEC technical data must be controlled monthly.

Structure of Products of Combined Hydration of Calcium Aluminate Salts, Lime, and Gypsum. The Conditions of $C_3A(C\bar{S})H_{12}$ Formation. Its Stability and Manner of Recrystallization

Former investigations of calcium silicate and aluminate products of cement hydration have analyzed new cement paste structure formations. But such research gives a picture only of the hydrated system with high water content.

Furthermore, the newest technique of concrete production uses less water in concrete, with the result that the structure formation develops differently.

We can affirm that cement hydration with low water content gives quite new formations hitherto unknown. In this connection, we also worked out new methods that influence structure formation. Finally we were able to externally affect structure-building processes and deliberately conduct and change them.

This rebuilding presents large-scale possibilities, still untouched, to obtain new cement paste structure forms.

Broad research by famous scientists in the direction of studying cement paste structure and the mechanisms of their formation and growth, by petrographic microscope, electron diffraction, and electron microscope give no results. This is because these methods cannot test and study the processes of hydration of cement with low water content.

At times this confuses the researcher since the conditions do not correspond to reality.

Difficulties increase because the influence of cement paste structure formation is operative not only at the time of setting, in the first minutes and hours of cement hardening, but at any other time when the original cement paste structure is sufficiently formed and strengthened.

Defects of all microscope methods of cement paste structure analysis result from the manner of sample preparation with high water content, when the required structure form does not appear, or of sample preparation by paste grinding, rubbing, and surface polishing of hardened cement paste, when the structure studied completely disappears or basically changes. Therefore for microscopic analysis we applied special microphotographic methods with very thin nondisturbed cement paste samples which were hydrated on glass (method of Yoong [5]). The feature of this method is in fine cement grinding, with hydration on a glass plate with a low quantity of water, placing on the glass in a very thin layer and pressing with the glass cover to spread the paste. Some samples are then hermetically isolated by glue or paraffin. Thus we obtain nondisturbed cement paste samples, which are stored in dry air, humid air, and water.

It must be said that this method, though only qualitative, answers the questions: Has the structure the formations we are looking for? When do they appear or disappear? Positive advantages of this method of analysis are the possibility of prolonged and continuous optical study of all changes which occur in structure formation, and the possibility of protecting hydrated compounds from carbonation (by CO_2 in air).

Studies by Danelian on high-alumina cements with various compositions gave the following average chemical content:

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Loss on ignition
12.3	44.3	4.5	35.0	1.4	1.9	0.60

This cement consists chiefly of CA and low quantities of C_2S and C_2AS. Immediately after mixing it gives a hexagonal structure rich in crystalline water—C_5AH_{34}, with index of refraction 1.487–1.480.

Table 2 gives structural formations and strength of high-alumina cement paste hydrated at 0.3–0.4 water cement ratio, and stored in dry air, humid air, and water.

Hexagonal formations of C_5AH_{34} and C_2AH_8 appear in dry storage, but are unstable and soon disappear, recrystallizing into forms of the low-calcium CAH_{10}. The strength does not increase with time, and remains at a low level, about 250–300 kg/cm^2.

Hexagonal forms C_5AH_{34} and C_2AH_8 which are more stable appear in humid and water storage. Here cement paste strength reaches 950 kg/cm^2 at the age of 1 yr.

Specimens hardening in water give a similar picture. Here new forms with 1.480–1.498 light

TABLE 2.—*High-alumina cement*

Cement paste properties	Storage condition	Age, days						
		3	14	28	90	180	270	360
New hydrated cement formation.	Air	C_5AH_{34}	C_2AH_8	C_2AH_8	C_2AH_8 C_5AH_{34}	CAH_{10} C_5AH_{34}	------	1.470–1.498
	Humid air	C_5AH_{34}	C_5AH_{34}	C_5AH_{34}	C_2AH_8 C_5AH_{34}	C_2AH_8 C_5AH_{34}	C_2AH_8 C_5AH_{34}	
	Water	C_5AH_{34}	1.519–1.534	C_2AH_8 C_5AH_{34} C_4AH_{13}	C_2AH_8 C_5AH_{34} C_4AH_{13}	C_2AH_8 1.480–1.498 C_4AH_{13}	C_4AH_{13} 1.477–1.498	C_2AH_8 1.461–1.468 C_4AH_{13}
Compression strength, kg/cm²	Air	256	------	372	370	321	------	250
	Humid air	640	------	810	------	951	------	------
	Water	761	------	941	966	943	------	------

refraction, which can be attributed to C_3AH_{18}, are visible. This structure differs from those of the new formations brought about by alumina cement hydration in suspension, when the products of hydration are C_2AH_8, C_4AH_{13}, and C_3AH_6, depending on lime content.

The hexagonal forms C_2AH_8 and C_4AH_{13} were very definite in investigations of water storage samples. These structures can be described as alternations of hydroxyl layers: C_2AH_8—as $2Ca(OH)_2 \cdot 2Al(OH)_3 \cdot 3H_2O$; C_4AH_{13}—as $2Ca(OH)_2 \cdot Al(OH)_3 \cdot 3H_2O$.

All hexagonal calcium hydroaluminates, as is known from the literature, have a family likeness in electron diffraction. C_2AH_8 has a tendency after a time to dissociate into C_4AH_{13} and AH_3 by the reaction:

$$2Ca(OH)_2 \cdot 2Al(OH)_3 \cdot 3H_2O \rightarrow 2Ca(OH)_2 \cdot Al(OH)_3 \cdot 3H_2O + Al(OH)_3$$

but the layer structure does not break, only one layer of $Al(OH)_3$ attains the amorphous state.

Hydroaluminate attains high lime content formation, C_4AH_{13} in the main, when the lime content is high, which results from alumina cement hydrated together with lime.

All hexagonal calcium hydroaluminate formations become unstable and recrystallize in the cubic form, C_3AH_6. Hexagonal formation in hydration at high temperature has never been seen when gypsum is absent. It is different when cement is hydrated together with gypsum. In this case hexagonal forms are quite stable at normal and high temperature. Gypsum immediately reacts with C_4AH_{13}:

$$C_4AH_{13} + 3(C\bar{S})H_2 + aq = C_3A(C\bar{S})_3H_{32} + CH + aq.$$

By insuring contact with water the formation of $C_3A(C\bar{S})_3H_{32}$ quickly ends. It appears in the form of lathlike rods at low lime concentration and in form of thinnest needles at high lime concentration. Gypsum binding in $C_3A(C\bar{S})_3H_{32}$ is accelerated by adding C_4AH_{13}.

Table 3 gives the structure formation, strength data and volume changes of WNC cement paste samples hydrated at 0.3–0.4 water-cement ratio, and stored in dry air, humid air, and water.

TABLE 3. *Tricomponent waterproof cement WNC*

Alumina cement—75 percent by weight
Gypsum ($CaSO_4$ $0.5H_2O$)—6.25 percent by weight
Artificial hydrocalumite C_4AH_{13}—18.75 percent by weight

Cement paste properties	Storage condition	Age, days						
		3	14	28	90	180	270	360
New hydrated formation.	Air	C_2AH_8	C_2AH_8	C_2AH_8	C_2AH_8 C_4AH_{13} AH_n	1.489–1.504 1.498–1.504	------ ------	1.498–1.504 ------
	Humid air	C_2AH_8	C_2AH_8	C_2AH_8	C_2AH_8	C_2AH_8	C_2AH_8 C_4AH_{13}	------ ------
		$C_3A(C\bar{S})_3H_{32}$	$C_3A(C\bar{S})_3H_{32}$	$C_3A(C\bar{S})_3H_{32}$	$C_3A(C\bar{S})_3H_{32}$	------	$C_3A(C\bar{S})_3H_{32}$	------
	Water	1.510–1.528	1.522–1.537	1.519–1.528	C_2AH_8	C_2AH_8	C_2AH_8	------
		CAH_{10}	1.486–1.195	C_2AH_8	$C_3A(C\bar{S})_3H_{32}$	$C_3A(C\bar{S})_3H_{32}$	$C_3A(C\bar{S})_3H_{32}$	------
Compressive strength kg/cm².	Air	207	------	200	202	235	------	------
	Humid air	210	------	343	340	377	------	------
	Water	210	------	275	380	430	------	------
Elongation (+) or shrinkage (−).	Air	−0.08	−0.16	−0.18	−0.22	−0.22	−0.47	−0.47
	Humid air	−0.05	+0.02	+0.12	------	+0.49	+0.40	------
	Water	+0.08	+0.09	+0.15	+0.33	+0.40	+0.31	------

Cement WNC is a variety of WEC, but with lower gypsum and higher C_4AH_{13} content. It gives little expansion in humid storage and is called waterproof nonshrinking cement.

This cement is characterized by quick setting, quick hardening, and instantaneous watertightness.

Due to this property, WNC is applied for caulking strongly filtrated cracks, holes, cavities, etc.

Table 3 shows that WNC, after mixing, gives hexagonal formations C_2AH_8 and $C_3A(C\bar{S})_3H_{32}$ at once. On the third day of hardening, the high-lime formation C_4AH_{13} does not appear, because of the latter's quick reaction with $C\bar{S}$ with formation of $C_3A(C\bar{S})_3H_{32}$, showing light refraction of 1.464–1.458, but only in the case of humid and water storage. In dry storage no traces of $C_3A(C\bar{S})_3H_{32}$ are found. In long storage (over 360 days) crystals of gypsum were continuously present.

WNC strength is low (a characteristic of this cement). It is 50 percent of normal high-alumina cement strength in humid storage, and only 25 percent in dry storage. But despite this, WNC is indispensible when there is destruction to repair.

The process changes basically by adding lime to high-alumina cement instead of artificial hydrocalumite C_4AH_{13}, when gypsum is present. C_2AH_8 and C_4AH_{13} formations then appear, react with gypsum, and form calcium sulfoaluminate, now as a "low sulfate" structure—$C_3A(C\bar{S})H_{12}$ with light refraction 1.489–1.504 and chain-connected hexagonal plates. When lime is present and the water content limited, at first hydration results only in the "low sulfate" structure, formerly unknown. But this formation is unstable, and with gypsum present and high water content, recrystallizes into the "high sulfate" structure of calcium sulfoaluminate—$C_3A(C\bar{S})_3H_{32}$—with intensive expansion.

$C_3A(C\bar{S})H_{12}$ has plate structure, similar to hexagonal calcium hydroaluminate, and its formation does not lead to expansion.

Table 4 gives new structure forms and light refraction, specimen strength, and volume change for high-alumina cement, gypsum, and lime hydrated together in the proportions 88:4:8 at 0.3–0.4 water content, and stored in dry air, humid air, and water.

At 3 days C_2AH_8 and $C_3A(C\bar{S})H_{12}$ are found in all samples, as well as at 14 days. Later, $C_3A(C\bar{S})H_{12}$ disappears in air-stored samples, but C_2AH_8, C_4AH_{13} and gypsum are present. Test specimens show shrinkage which reaches 0.44 percent at 270 days. C_2AH_8 and $C_3A(C\bar{S})H_{12}$, in humid air and water-stored samples were stable at 3 days, but at 28 days, the water-stored samples showed the high sulfate structure of calcium sulfoaluminate, and expansion was 0.73 percent, causing cracking. Gypsum crystals were also very plainly seen. At 180 days "low sulfate" structures disappear because of complete recrystallization into the "high sulfate" form. Expansion reaches 2.47 percent, cracks open wide, and gypsum disappears completely. Because of large expansion, specimen strength is low, and after 1 yr of water storage is 176 kg/cm².

TABLE 4. *Tricomponent waterproof cement*

Alumina cement—88 percent by weight
Gypsum ($CaSO_4{\cdot}0{\cdot}5H_2O$)—4 percent by weight
Lime (CaO)—8 percent by weight

Cement paste properties	Storage condition	Age, days						
		3	14	28	90	180	270	360
New hydrated cement formation.	Air	1.519–1.528 1.480–1.498 $C_3A(C\bar{S})H_{12}$	C_2AH_8 C_4AH_{13} $C_3A(C\bar{S})H_{12}$	1.480–1.498 1.507–1.528 CAH_{10}	1.480–1.498 1.507–1.528 CAH_{10}	1.480–1.498 C_2AH_8 C_4AH_{13}	---------- ----------	---------- 1.498–1.471
	Humid air	C_2AH_8 $C_3A(C\bar{S})H_{12}$	C_2AH_8 $C_3A(C\bar{S})H_{12}$	C_2AH_8 $C_3A(C\bar{S})H_{12}$	C_2AH_8 $C_3A(C\bar{S})H_{12}$	C_2AH_8 $C_3A(C\bar{S})H_{12}$	C_2AH_8 $C_3A(C\bar{S})H_{12}$	C_2AH_8 $C_3A(C\bar{S})H_{12}$
	Water	C_2AH_8 $C_3A(C\bar{S})H_{12}$	C_2AH_8 $C_3A(C\bar{S})H_{12}$	C_2AH_8 $C_3A(C\bar{S})H_{12}$ $C_3A(C\bar{S})_3H_{32}$	C_2AH_8 $C_3A(C\bar{S})H_{12}$ $C_3A(C\bar{S})_3H_{32}$	C_2AH_8 $C_3A(C\bar{S})_3H_{32}$	C_2AH_8 $C_3A(C\bar{S})_3H_{32}$	----------
Compressive strength kg/cm².	Air	191	----------	277	290	313	----------	304
	Humid air	172	----------	215	220	150	----------	167
	Water	182	----------	247	248	179	----------	176
Elongation (+) or shrinkage (−)	Air	−0.08	−0.07	−0.12	−0.24	−0.30	−0.44	−0.31
	Humid air	+0.01	+0.08	+0.23	+0.73	+2.30	+2.45	+2.60
	Water	+0.06	+0.15	+0.26	+0.70	+2.11	+2.47	+2.63

Stressing Cement—SC, Its Nature and Properties (Strength and Expansion)

The use of gypsum was for a time highly recommended as an additive for portland cement to attain rapid hardening and strength increase.

Naturally, this composition did not achieve good results, as the formation of $C_3A(C\bar{S})H_{12}$ and the following slow recrystallization into $C_3A(C\bar{S})_3H_{32}$ led to a drop in strength and sometimes to concrete destruction. This feature was intensively studied in Germany by the Dyckerhoff firm [12], manufacturers of special brownmillerite sulfate-resistant cement which does not increase the concrete volume and is not destroyed when gypsum is added. It differs in this respect from normal cement with a large tricalcium aluminate content, which together with a low water content gives the "low-sulfate" form of sulfoaluminate of calcium, with subsequent destructive recrystallization into the "high-sulfate" form. Considering in this connection two examples of portland cements (see figs. 1 and 2), attention should be paid to the fact that sufficient iron oxide in the cement to a high degree retards the formation of dangerous forms of calcium sulfoaluminate, even in calcium hydroxide saturated media. Complete absence of C_3A is a characteristic feature of this brownmillerite cement, which is why it is not destroyed in sulfate water.

In other countries, scientific thought seeks to counteract the destructive influence of sulfate water by introducing pozzolan into the concrete during mixing. D'Ans and Eick [13], and Eitel [14] have shown that adding pozzolan does not eliminate the formation of calcium hydrosulfoaluminate. It only retarded ettringite formation for weeks and months.

The formation of the "low-sulfate" form of calcium hydrosulfoaluminate proceeds violently, and subsequent recrystallization into the "high-sulfate" form occurs in mechanical mixtures of portland cement, high alumina cement (or other aluminate compounds) and gypsum powders. Thus, a paste mixture of 65 percent portland cement, 15 percent gypsum, and 20 percent alumina cement of normal consistency, stored in water after hardening 2–3 days to a strength of 200–300 kg/cm², rapidly expands, due to the water absorption and "high-sulfate" formation, until it is finally disintegrated into an adhesive finely dispersed mass. This mixture has no hydraulic properties and would appear to be unfit for use. Yet its expansive power is very great. As explained in detail below, such a hardening cement mixture, not immersed in water, does not cause hydrosulfoaluminate recrystallization.

The cement paste in this case expands somewhat on account of the mix water, but is not destroyed. However, if such a cement paste is immersed in water even after 1–2 yr, the recrystallization process is renewed with great force and the system is completely destroyed, forming an adhesive mass.

It is clear that this type of cement cannot ever be used for construction purposes.

Investigating the hardening processes of portland cement clinker mixed with gypsum in various proportions, we noted that, even for small additions of gypsum reacting with C_3A, the formation and recrystallization of calcium hydrosulfoaluminate took some time, longer when water ingress into the system became more difficult.

It is possible to make up the initial combination of components with low water content so that upon isolated storage of the cement paste (without water admission) the expansion stops at a definite age. However, when water is admitted the process is renewed and leads to expansion, which finally stops without destroying the system.

As an example, cement paste of the proportions 14:20:66 (gypsum, high-alumina cement, portland cement) mixed with 30 percent water (fig. 9) may be used. Along the abscissa, days are plotted and, along the ordinate, relative expansion

14% Gips
20% T-Z
66% PZ
+ 30% H₂O

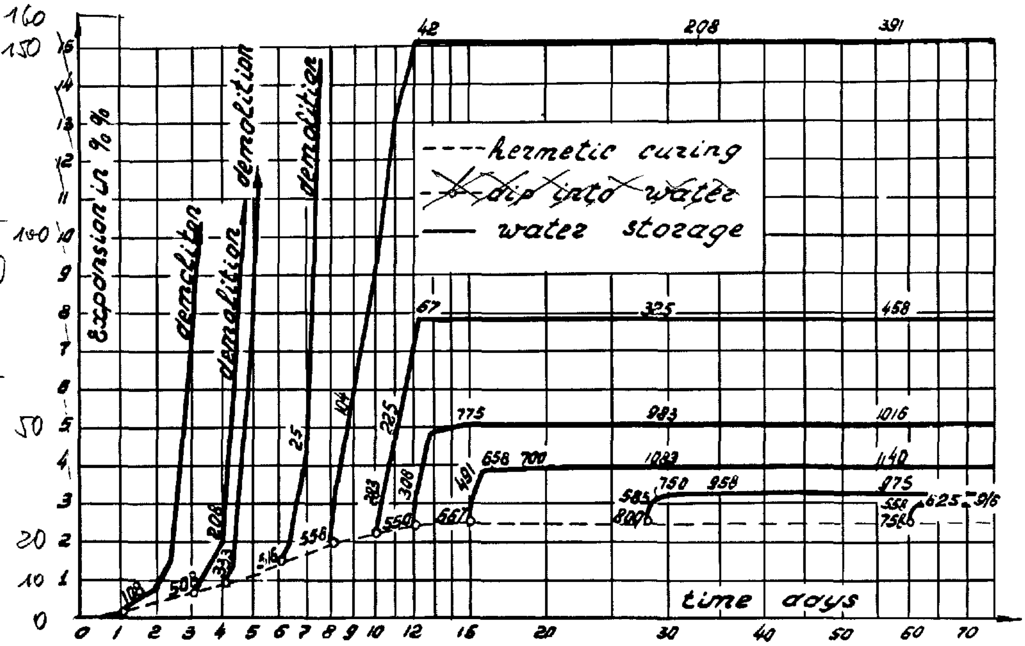

Figure 9. *Expansion-strength diagram of stressing cement paste at ~~200~~°C in the isolated state showing changes with time at which immersed.*

× 20°C

of the sample in percentage. The dotted line shows expansion of sample during isolated storage in paraffin-coated foil. At 15 days, expansion is stabilized at a level of 2½ percent. Cement paste strength at this age equals 667 kg/cm²; after 28 days 800 kg/cm². If such samples are taken from isolation on 1, 3, 4, and 6 days and immersed in water, they expand rapidly and samples are completely disintegrated. Samples immersed after 8 days and having at that time a strength of 558 kg/cm² showed rapid recrystallization to "high-sulfate" formation, but were not destroyed completely and retained their shape without any signs of cracks. At 12 days, i.e., after 4 days of water storage, the samples had expanded 15 percent (fig. 10) and the strength was only 42 kg/cm². However, during further water storage, at 28 days the strength reached 208 kg/cm², and at 60 days, 391 kg/cm². Samples immersed after 10 days, with strength of 560 kg/cm², had expanded 8 percent at 12½ days, and the strength had dropped to 67 kg/cm², but with further water storage a strength of 458 kg/cm² was attained at 60 days.

For samples immersed after 12 days, the strength, which was then 536 kg/cm², dropped temporarily to 308 kg/cm² at 13 days, but at 15 days rose to 775 kg/cm². The expansion was 5 percent, and the strength continuously increased, reaching 1,016 kg/cm² at 60 days.

Similar results were obtained when samples were immersed after 15, 28, and 60 days.

The curve in question shows that, with increase in specimen age at the time when immersion begins, additional recrystallization of the calcium hydrosulfoaluminate occurs by additional water absorption, but in a lower degree and in less destructive form. However, all specimens during the initial water expansion period showed a temporary 30-35 percent drop of strength.

The example mentioned shows that the processes of setting, hardening, and expansion of the tricomponent composition of portland cement, high-alumina cement, and gypsum may be controlled. Later we will show that it is possible to direct these processes by optimum proportioning of components. Henceforth this composition will be called stressing cement SC (see table 5—Technical Code) [16].

Self-stressed cement paste is composed of selected cement paste structure with prearrangement and reorganization of the entire structure during cement, mortar, and concrete setting and hardening processes. Previously, examples of directed interference with cement paste existence and behavior were unknown.

Pure portland cement and high-alumina cement are best applied as clinker, first grinding them for SC preparation. It is advisable that the cement fineness be not less than 3,500 cm²/g. The tricomponent powders are batched in the vibrating mill for 8–10 min, to uniformity.

At low water mixture (25–30 percent by weight), lime, portland cement, and the CA of the alumina cement dissolve rapidly and a large amount of water is absorbed. Ions of hydrated minerals rush toward the zones of lower concentration of the liquid phase and crystallize, and meeting with gypsum grains they react and form lathlike splines of calcium hydrosulfoaluminate on gypsum grain surfaces.

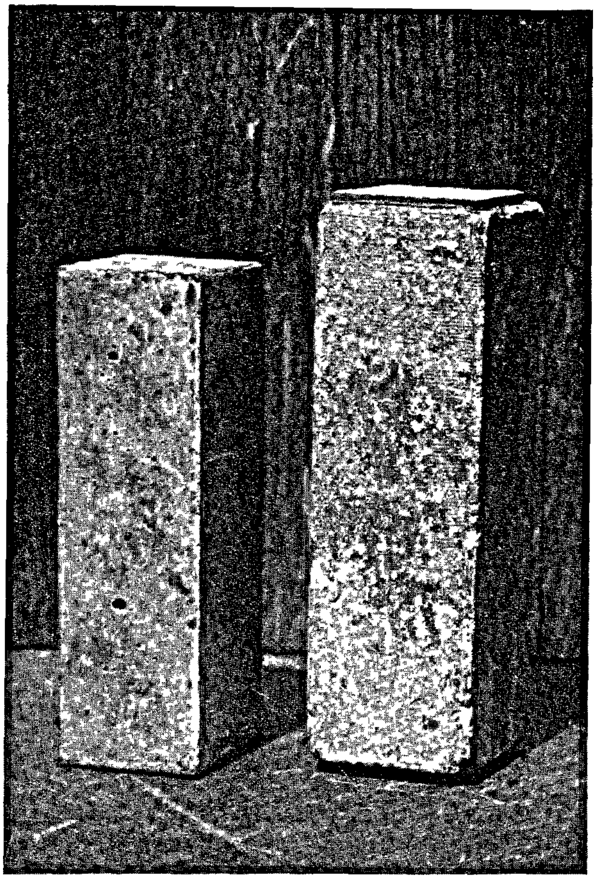

FIGURE 10. *View of SC hydrated specimen with 15 percent elongation, immersed 8 days after isolated storage (see figure 9), in comparison with similar portland cement (nonelongated) specimen.*

The plastic strength of the system rapidly increases, beginning 2–3 min after mixing.

The saturation with calcium hydrate, and the limited water phase, hampers the growth of the "high-sulfate" formation $C_3A(C\overline{S})_3H_{32}$ which is limited by formation of a "low-sulfate" product $C_3A(C\overline{S})H_{12}$.

As a result, a branched framework is formed of $C_3A(C\overline{S})H_{12}$, C_4AH_{13}, and $C_3A(C\overline{S})_3H_{32}$ lathlike splines.

The last two needlelike formations are completely intertwined. The higher the water cement ratio at hydration, the more $C_3A(C\overline{S})_3H_{32}$ and the less $C_3A(C\overline{S})H_{12}$ and pure gypsum.

This intertwining is, during the initial period, rather loose, gradually becoming compacted by

TABLE 5. *Technical code for stressing cement* (SC)

(Specifications)

No.	Qualities	Measurement data
1	Setting time:	
	(a) Initial set, not before	2 min
	(b) Final set, not before	6 min
2	Fineness of grinding:	
	(a) Residue on screen, N 02, not over	1 percent
	(b) Passing through screen N 0085, not less than	80 percent
3	Strength of cubes, size 20 x 20 x 20 mm, made of cement paste of normal consistency, should be as follows:	
	(a) For specimens cast 18–20 hr at 20±2 °C, not less than	200 kg/cm²
	(b) For specimens cast 18–20 hr at 20±2 °C and then 6 hr (without molds) in water at 70° C, not less than	450 kg/cm²
	(c) For specimens given hydrothermic treatment in conformance with § "b" of the given item and then stored in water at 15–20 °C for 24 hr:	
	Not less than	600 kg/cm²
	Not less than	850 kg/cm²
4	Elongation of prism, size 31.5 x 31.5 x 100 mm, made of cement paste of normal consistency, given hydrothermal treatment according to the sequence described in § "b", should be at the end of treatment not less than	2. 2 percent
	Elongation of prism during such treatment, in relation to the elongation value at the end of 6-hr thermal treatment, should be:	
	(a) After 2 hr thermal treatment, in the range	75–85 percent
	(b) After 3 hr thermal treatment, in the range	92–97 percent
	Increase of specimen elongation in water storage, in relation to the elongation value at the end of thermal treatment, should be:	
	After 7 days, not over	12 percent
	After 28 days, not over	15 percent
	NOTE: Conformance with requirement of §§ "a" and "b", item 3, and §§ "a" and "b", item 4, is rapid test of SC.	
5	Strength of cubes, size 30 x 30 x 30 mm, made of normal consistency SC mortar (1:1) by weight, should be:	
	(a) For specimens cast 18–20 hours in molds at 20±2 °C, not less than	150 kg/cm²
	(b) For specimens cast 18–20 hours at 20±2 °C and then 6 hours (without molds) in water at 100 °C, not less than	250 kg/cm²
	(c) For specimens given hydrothermic treatment in conformance with § "b" of given item and then stored in water at 20±2 °C:	
	After 1 day, not less than	300 kg/cm²
	After 3 days, not less than	300 kg/cm²
	After 7 days, not less than	300 kg/cm²
	After 28 days, not less than	500 kg/cm²
6	Elongation of prism, size 31.5 x 31.5 x 100 mm, of normal consistency SC mortar (1:1) by weight, should be:	
	At end of thermal treatment (according to § "b", item 5), not less than	0.2 percent
	During further water storage 15-20 °C:	
	After 1 day, not less than	0.5 percent
	After 3 days, not less than	1.5 percent
	After 7 days, not less than	1.8 percent
7	Samples of cement paste of normal consistency mortar (1:1) by weight, during testing (in disks) at the end of thermal treatment should be entirely impermeable at pressure	20 atm

ions and newly formed silicate compounds, which crystallize in the aluminate and sulfoaluminate framework. A feature of crystalline calcium hydrosilicate formation is that, in media with a small amount of water, development rapidly stops, and the growth does not exceed the limits of colloidal dimensions. There is strong competition between all reacting new formations in the cement paste colloidal zone, which quickly leads to exhaustion of moisture resources and retardation of the hydration of the initial cement materials. After about 24 hr of isolated natural hardening (to prevent carbonation of new formations) the strength of the cement paste reaches 200–300 kg/cm², and the cement paste coagulation-crystallization structure is characterized by the presence of a highly branched framework of intertwining heavy splines of lath, needle, and lattice-like formations of hydrosulfoaluminate structure and chains of calcium hydroaluminate. The space taken up by these compounds is filled with a coagulation structure of hydrated silicate formations, disintegrated nonhydrated cement kernels, and gypsum grains coated with a solid feltlike shell of $C_3A(C\bar{S})H_{12}$.

SC cement, in a high-water-content mixture, forms $C_3A(C\bar{S})_3H_{32}$ quickly and without interference, because the indefinite number of hydrated ions of CA of high alumina cement and the quantity of C_3A and C_4AF in the portland cement, gradually delivered, rapidly react with the gypsum under conditions of relatively low Ca ion concentration. But the reaction of $C_3A(C\bar{S})_3H_{32}$ formation rapidly ends during the early hardening period when the strength of cement paste is low. In this case there is no noticeable expansion of the system.

Thus, SC with low water mixture supplies the best condition for obtaining in the system the maximum quantity of $C_3A(C\bar{S})H_{12}$, ready for recrystallization.

If such a hardened system is immersed, the cement paste greedily absorbs water and the recrystallization process rapidly converts $C_3A(C\bar{S})H_{12}$ into $C_3A(C\bar{S})_3H_{32}$, with simultaneous expansion of the system, for the process occurs on gypsum grain surfaces, and causes structural rearrangement with water absorption. The $C_3A(C\bar{S})_3H_{32}$ structure is formed on the gypsum grain surface like directed thin needles and presses against the adjacent new formations, disturbing their adhesion. As a result of this growth, the structure is completely demolished and breaks into separate small pieces. This behavior was observed in cement paste specimens (fig. 9), immersed in water after 1, 3, 4, and 6 days of isolated storage. Simultaneously, due to $C\bar{S}$, recrystallization of C_4AH_{13} formation into $C_3A(C\bar{S})_3H_{32}$ occurs.

If expansion of the system during recrystallization is limited to 15 percent, total destruction does not occur, but as mentioned above, destruction of mechanical adhesion between colloidal particles of C_2SH_2 and CSH leads to structural weakening, which, after expansion stops, heals as the result of delivery of ions of hydrated silicates of calcium and the development of new connections. For specimens immersed after 15 days, healing proceeds very quickly, and some weakening is observed only in brief loss of strength.

Destruction of structural adhesion as a result of recrystallization to $C_3A(C\bar{S})_3H_{32}$, and the formation of new connections, may also be directed by shifting the destruction and restoration periods, timing them to the accumulation of new high strength silicate formations, and superimposing them for strength stabilization.

Direct Methods of Expansion and Hardening. Optimum Alumina Compound Admixture. Optimum Hydrothermic Hardening Process. Self-Stressing Mechanism

Hydrothermic treatment of the system is effective for such formerly discussed adjustment.

Through heating, the influence of the hydration of the silicate cement components is highly accelerated. Therefore the reproducing processes are performed rapidly and at a certain temperature do not lag behind the processes of structure destruction. During a definite time, as many and even more connections are restored as are destroyed. Because of this, the strength is either maintained at the fixed level, or even increases on expansion.

Heating of the system makes it possible not only to avoid excessive expansion and destruction of the cement paste, but also permits time decrease for all processes, which, according to the curve (fig. 9), take so long to develop.

Investigations have shown that heating cement paste for 2 hr at 70–80 °C when the strength is about 200–300 kg/cm^2 gives expansion sufficient for the system without any signs of strength drop.

Figure 11 shows data on expansion and strength increase of SC specimens heated at 80 °C for 1, 2, 3, 5, and 7 hr when the initial strength was 200 kg/cm^2. All samples heated 2, 3, 5, and 7 hr expanded 2 percent and reached strength of about 500 kg/cm^2. Further water storage of SC samples did not show more expansion, because the gypsum was fully consumed during the first 2 hr of heating, and all $C_3A(C\overline{S})H_{12}$ was recrystallized into $C_3A(C\overline{S})_3H_{32}$.

However, the strength of the cement paste continuously increased owing to the progress of the hydration of the C_3S and C_2S of the portland cement, leading the system to further densification. Cement paste after 28 days reaches a strength of 1,200–1,300 kg/cm^3. Thus, heating the system for more than 2 hr had no effect in any case. It might be assumed that such hydrothermic treatment during hardening would be selected as best for application in structures; however, with mortar, difficulties were met with. The composition of SC paste, which resulted in an increase of strength accompanying 6 percent expansion during heating, showed a much greater strength drop in mortar, sometimes 2–3 times, making this composition of mortar unfit for self-stressing.

Actually, reinforced concrete self-stressing is possible only when the concrete bond with reinforcement exists and concrete acts as a hard body, deforming identically and simultaneously with the steel. For such reinforcement action, concrete should continuously possess the required strength and density. Insufficient strength due to temporary drop causes plastic concrete flow around the reinforcement, without its significant lengthening. Thus, we obtain large reinforced concrete expansion, but without self-stressing, even though, during further hardening in water storage, the strength is not only restored, but significantly exceeded. This may be because, during the rapid process of SC expansion, cracks arise from the retarding action of the aggregates, which do not increase in volume.

All attempts to prevent the drop in SC mortar strength lead to lower expansion power, and in turn to insufficient self-stressing.

Self-stressing technology has therefore been greatly changed.

Investigations showed that $C_3A(C\overline{S})H_{12}$ recrystallization into $C_3A(C\overline{S})_3H_{32}$, in calcium hydrate media, is retarded by further temperature increase; simultaneously, hydration of C_3S and C_2S is considerably accelerated at the higher tem-

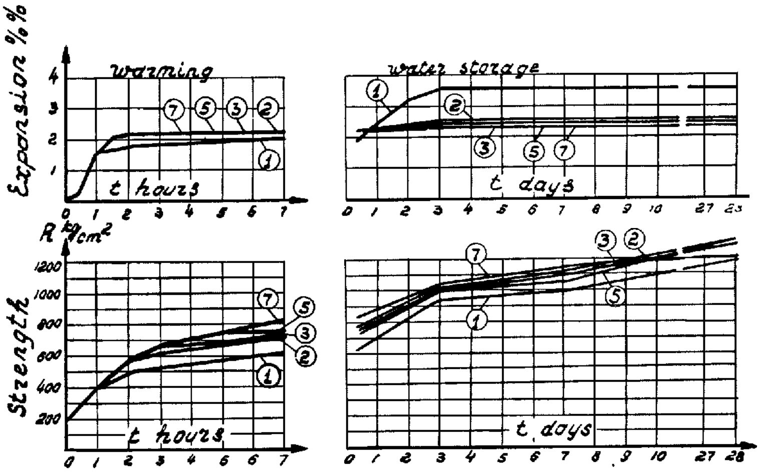

FIGURE 11. *Expansion-strength diagram of stressing cement paste for various durations of water heating, at 80 °C.*

Data in circles show number of hours of heating.

perature. Therefore, the structure destruction period is moved backward, and the period when new connections arise in the process of dissolution and hydration of silicate materials in the cement is moved forward. As a result the following sequence was set for hydrothermic treatment of SC mortar: 6 hr heating in water at 100 °C (boiling water), with initial strength about 160–200 kg/cm^2. Here mortar expanded very little, with specimen strength increasing to 300–400 kg/cm^2. During further water hardening, expansion progressed rather evenly, stopping after 3–10 days of water storage.

During expansion, mortar strength either did not change or slightly increased.

In this case the expansion mechanism generally acts, only the process takes several days, giving the hardening of C_3S and C_2S time to heal the recrystallization ruptures which have appeared.

Further experimental work [17] showed that this self-stressing mechanism is the best available, and it was somewhat improved to make the allowed expansion time less than 3 days. Additional investigations were then undertaken. Equipment was built for self-stressing mechanism investigation (fig. 12), which could reproduce elastic resistance of any amount. Each chosen degree of rigid resistance corresponded with a certain coefficient of linear system reinforcement, i.e., reproduced any required percentage of concrete reinforcement.

Prisms of sizes 100 × 31.5 × 31.5 mm and 300 × 50 × 50 mm, with strips embedded at the faces, were selected as experimental specimens. Cylinders with transverse spiral wire coils were also investigated, whereby limited elastic volume expansion was obtained.

The investigations of self-stressing showed that elastic resistance increase against specimen expansion leading to self-stressing variation may be expressed approximately by the following equation:

$$\sigma_c=\sigma_c'\sqrt[5]{\frac{\mu}{0.24}}$$

where σ_c=unknown reinforced concrete self-stressing, in kg/cm^2 with reinforcement=μ, σ_c'= reinforced concrete self-stressing with $\mu'=0.24$ percent, μ=concrete reinforcement coefficient.

By investigation, a very important and vital feature of SC structure was found, relating both to theory and practice. For very large free stressing-cement expansion, uniaxial elastic resistance of sufficient intensity decreases expansion

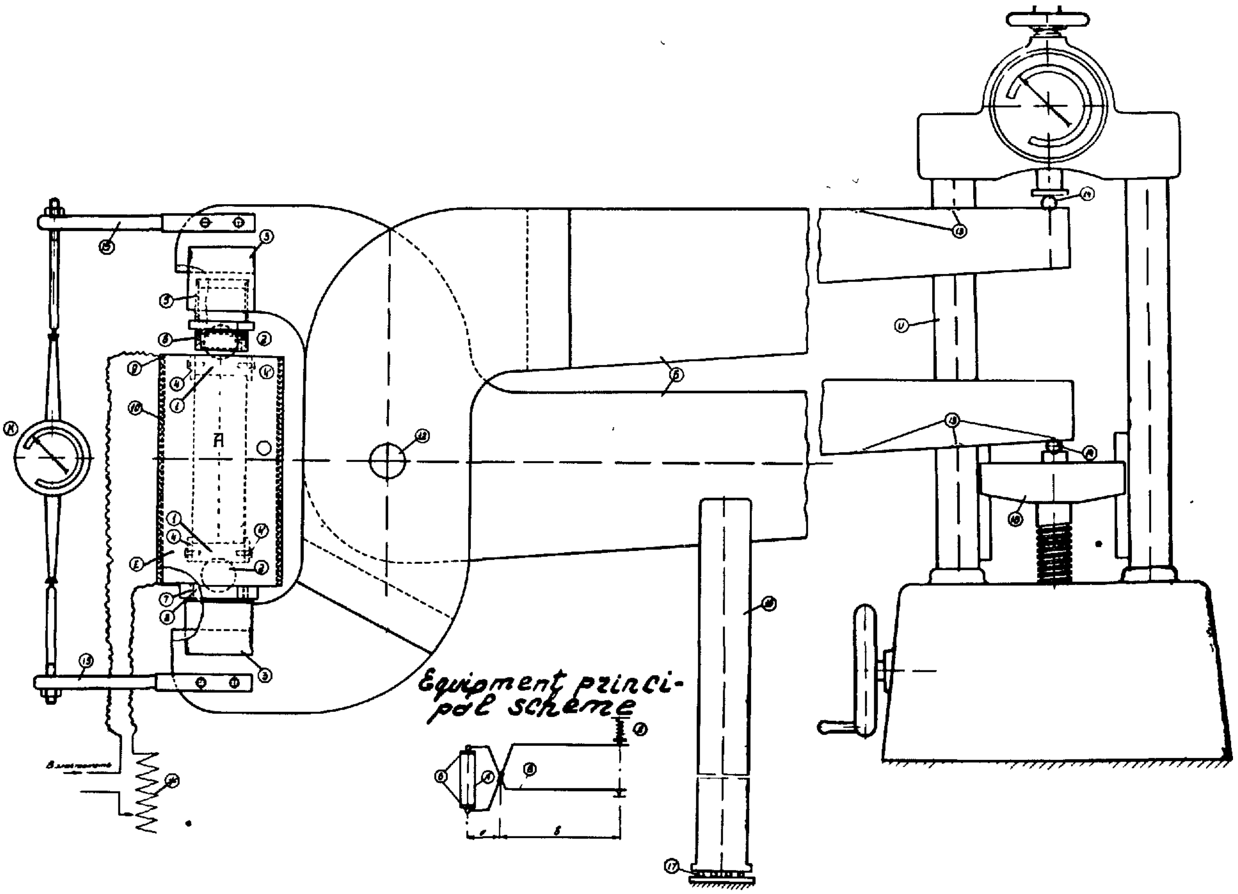

FIGURE 12. *Measuring instrument for testing cement paste expansion force.*

by over 10 times not only in the direction of action of the resistance but crosswise as well.

This is explained by the strength and volume stability of the system resisting transverse plastic deformations, under uniaxial compression, if cement composition and the hydrothermic sequence of treatment are optimal and there is no drop in concrete strength during self-stressing.

Equipment for investigation of self-stressing power is made to imitate every hydrothermic sequence and all conditions of variable moistening and drying of specimens.

Self-stressing investigations [16] have shown that every portland cement may be employed for production of SC by adding high-alumina cement and gypsum. The only problem is to find the optimal proportioning.

1. If high-aluminate portland cement has rich C_3A content, SC from this cement possesses high expansion, but does not stabilize rapidly.

2. If brownmillerite portland cement is used, without C_3A expansion, SC from this cement stabilizes rapidly, but with less expansion value.

Good results in our experiments were obtained with alite portland cement having the following average mineralogical content:

C_3S	C_2S	C_3A	C_4AF	CaO	MgO	KH
47.02	24.44	12.53	10.46	0.50	4.06	0.864

Using this cement, the SC content proportions selected were 14:20:66, which were checked in comparison with the higher activity SC proportions 18:22:60.

Figure 13 shows the curve of SC strength increase at normal temperature, 22 °C, for storage in isolated conditions under a paraffin layer.

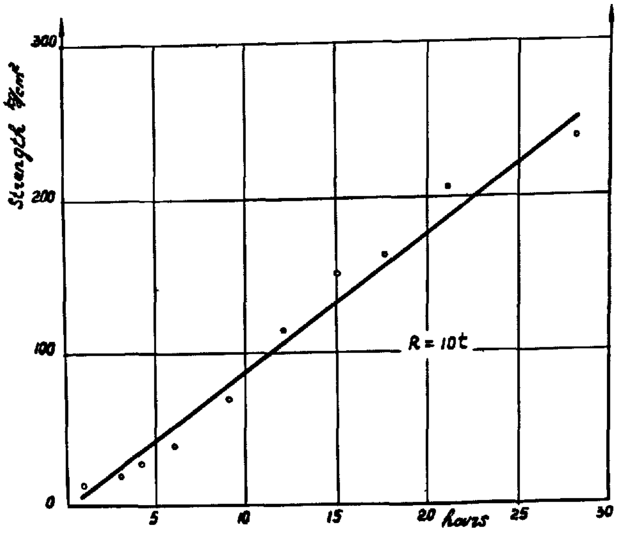

FIGURE 13. *Strength increase of SC mortar isolated in paraffin.*

Essentially the linear law of strength increase is maintained, being expressed by the equation: $R=10t$; the strength required to be attained during isolated hardening, about 200 kg/cm², is reached after 24 hr.

The selected SC components passed systematic and prolonged checking in pastes and 1:1 mortars, to establish the time stability of their mechanical properties.

Investigations were carried out on expansion, water absorption, strength in "free" and restrained conditions, self-stressing value in relation to degree of reinforcement (average for possible use, 1 percent), and other properties.

For selecting the required quantity of high-alumina cement with 14 percent gypsum, many combinations were investigated, by varying high-alumina cement content from 4 to 32 percent.

Results of 28-day investigation of SC mortar are shown in figure 14. Optimal high-alumina cement admixture of 18–20 percent gives the highest strength, 650 kg/cm²; highest expansion, 2.1 percent; and maximum water absorption, 6 percent (by weight).

Investigation of SC mortar properties with respect to time is shown in figure 15. Here during 6-hr heating: strength of "free" specimens increased from 160 kg/cm² to 268 kg/cm², and strength of restrained specimens increased to 310 kg/cm²; expansion and water absorption were low, 0.20 percent and 0.5 percent, respectively; self-stressing equalled 16 kg/cm². In further water storage, at 28 days the strength was 420 kg/cm² for "free" specimens and 450 kg/cm² for

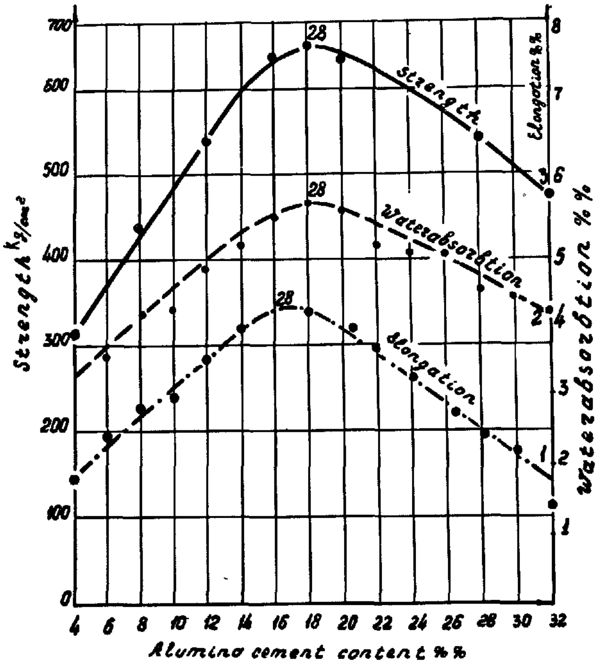

FIGURE 14. *Elongation, strength, and water absorption of SC mortar (1:1) with 14 percent gypsum, versus alumina cement content.*

Heated at 100 °C for 6 hr.

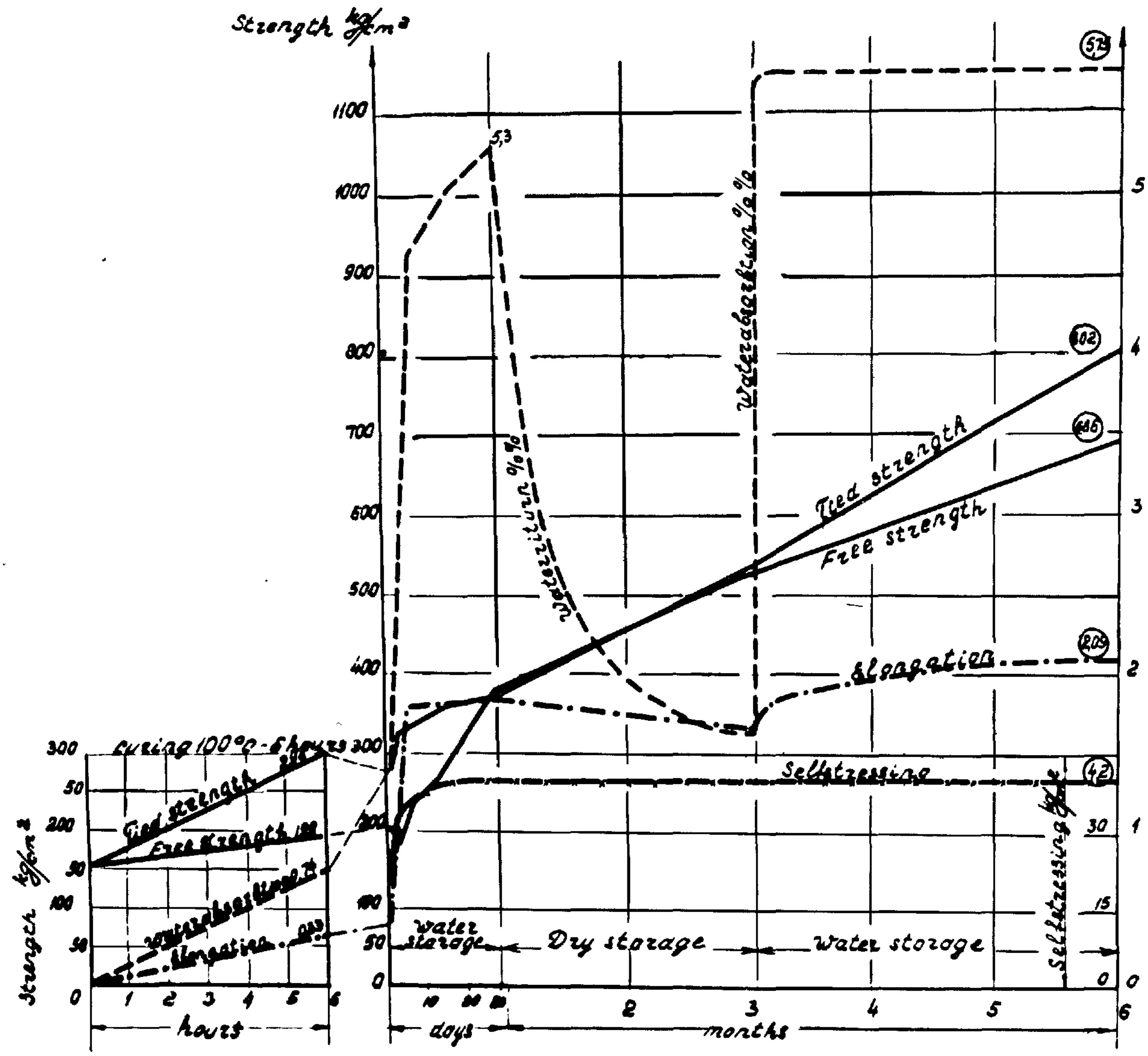

FIGURE 15a. *Elongation, strength, and water absorption of self-stressing SC mortar (1:1), versus storage condition (water-air).*

Proportions 14:20:66.

Heated at 100 °C for 6 hr.

restrained specimens; expansion was stabilized at 3 days (at 2.3 percent) with slight increase to 7 days; water absorption practically ended on the 14th day at 5.6 percent, and on the 28th day was 5.8 percent; self-stressing ended completely within 14 days and was 42 kg/cm².

After 6 months, the following results were obtained: strength of "free" specimens, 614 kg/cm²; restrained specimens, 740 kg/cm²; expansion, no change, i.e., 2.33 percent; water absorption, 6.7 percent; self-stressing, no change, i.e., 42 kg/cm².

It is important that during water storage the strength always continuously increases and reaches a high value, approaching 1,000 kg/cm² in 2–3 yr. We were more interested in the strength of restrained SC samples, as this is the chief characteristic limiting the relatively small deformations of reinforced self-stressed mortar.

At present, data are available on stable strength and the degree of self-stressing of SC mortar samples stored in water for 6 yr, this showing conclusively that all expansion processes are over, after the first several days of mortar existence.

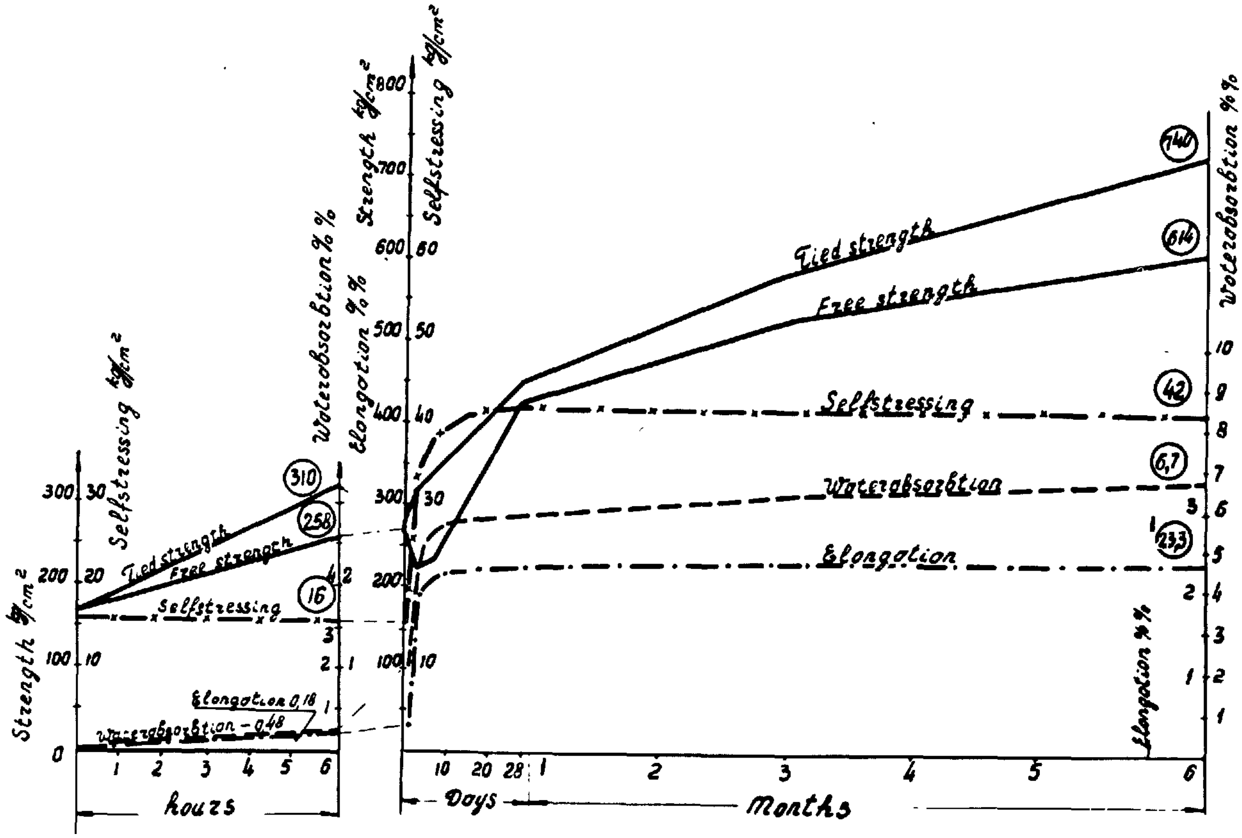

Figure 15b. *Elongation, strength, and water absorption of self-stressing SC mortar (1:1).*

Proportions 14:20:66.

Heated at 100 °C for 6 hr.

Water Absorption and Water Loss of SC Mortar. Influence of Initial Water-Cement Ratio. Influence on Self-Stressing of Premature Destruction of Initial Structure During Formative Period. "Stress Calibration"

Water absorption of SC mortars is of some interest. Water absorption is sufficiently high—for some combinations, 7–8 percent. Naturally, not all water is used for $C_3A(C\overline{S})_3H_{32}$, C_4AH_{13}, and other formations. Apparently up to 70 percent of this water should be considered as hygroscopic moisture. However, it is very characteristic that, during drying, this water leaves the system slowly, but is absorbed again very quickly. Apparently, the capillaries in the structure are widely branched and very fine, this explaining the complete impermeability of SC mortar. SC mortar samples 25 mm thick resist hydrostatic pressure of about 20–25 atm without any signs of sweating.

Absorption and water loss properties are clearly shown in figure 15 for SC mortar (1:1); cement composition 14:20:66 with hydrothermic treatment at 100 °C for 6 hr. Strength of restrained specimens is 802 kg/cm² after 6 months.

Mortar specimens absorb 5.3 percent water in 28 days. Removed from water and exposed to natural drying conditions for 2 months they lost 3.5 percent of the absorbed water and retained only 1.8 percent. Again immersed they reabsorbed the lost amount of water. It should be noted besides that a large variation of the moisture content of SC mortar slightly changes specimen length. Thus, 1.8 percent expansion at 28 days is lowered, as a result of 2 months isolated storage, to 1.6 percent, i.e., by 0.2 percent. Further moist storage not only restores initial expansion, but exceeds it.

For combinations of optimum high-alumina cement content, water absorption is higher, some water remaining in the system no matter how long the specimens are stored in air.

Figure 16 shows data on water absorption and water loss of the 1:1 mortar for SC with 11 percent gypsum, and variable high-alumina cement content, 4–32 percent. Combinations containing 16, 18, 20, and 22 percent of the high-alumina cement absorb about 6.1 percent water and lose

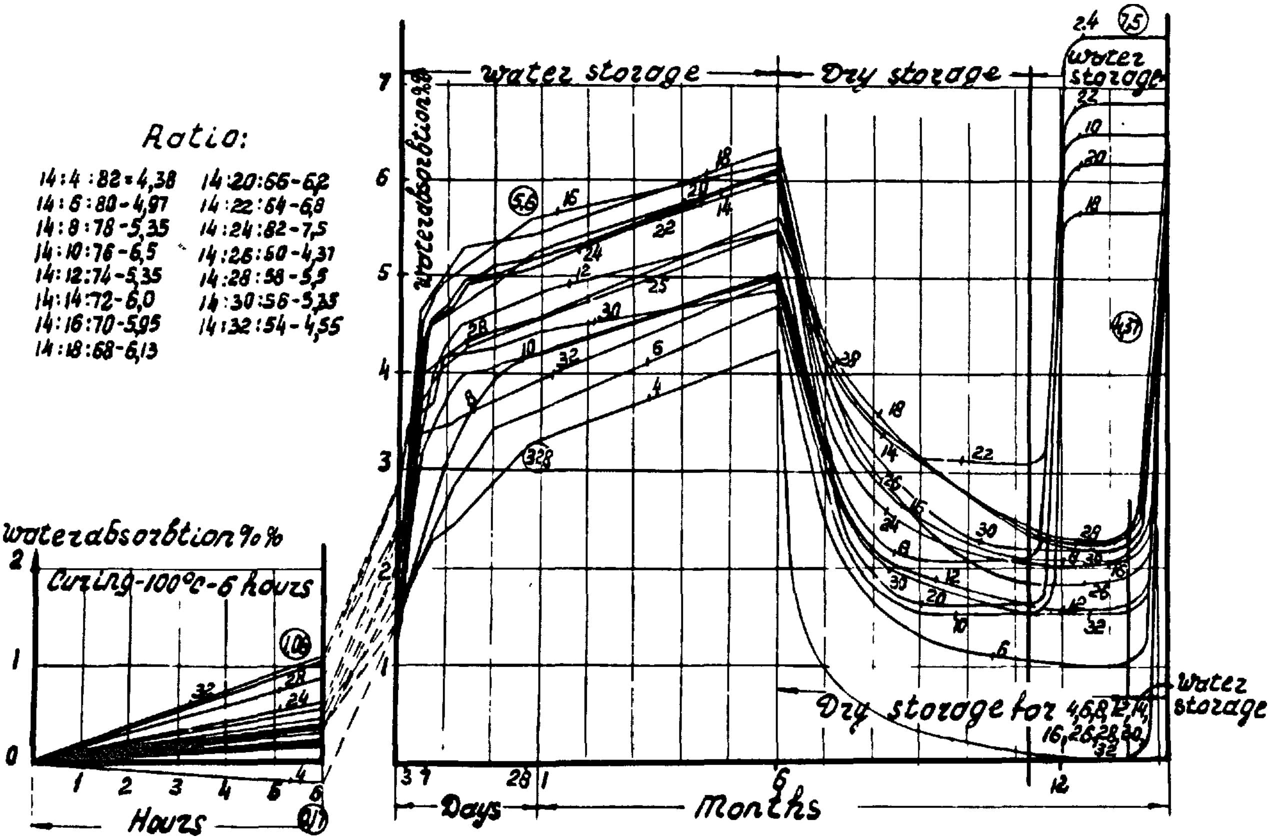

FIGURE 16. *Water absorption and water loss depending on storage condition (water-air-water).*

on the average 3.5 percent, retaining 2.6 percent. Combinations with 4 percent, i.e., almost without any high-alumina cement, absorb 4.2 percent and lose the same amount. As noted above, water loss during 6 and even 8 months is slow, while absorption is rapid.

Of some importance is the influence of the degree of repeated drying and absorption on self-stressing value. Does self-stressing disappear completely after some time? For determining this, expansive power measurements (fig. 17) have been made on 5 series of specimens differing only in hydrothermal treatment period: 1, 2, 3, 4, and 6 hr (see graphs from top to bottom). The sequence for all samples: water—20 days; air—15 days; water—20 days; air—20 days; water—25 days; air—35 days.

The investigations have shown that during drying about half of the initial self-stressing value is lost. Repeated moistening restores almost the entire self-stressing value. During these investigations it was determined that samples heated 6 hr lose practically nothing, i.e., during moistening they completely restore the initial self-stressing. The samples heated 2 hr irrevocably lose up to 15 percent of the initial self-stressing after several drying and moistening cycles.

Consequently, 6-hr hydrothermic treatment has several advantages over 2-hr treatment and it should be recommended for production of self-stressed structures.

Figure 18 shows investigations of strength and expansion of 1:1 mortar made with SC proportioned 14:12:74. In one case it received normal hydrothermic treatment at 100 °C for 6 hr and then water storage, in another case it underwent natural hardening in the paraffin-isolated condition. The specimens hardened in paraffin isolation for 14 months.

The mortar (1:1) that received normal hydrothermic treatment reached after 14 months of water storage a strength of 900 kg/cm^2, and expanded 1.9 percent at 10 days. Isolated dry-stored mortar had a very low strength—155 kg/cm^2; apparently, the calcium hydrates and hydrosulfoaluminates during formation and partial recrystallization absorbed the entire mixing water reserve (30 percent); there was not enough water for C_3S and C_2S hardening, and hydration stopped. In this case, specimen expansion was 3 percent, thus higher than for the first group. When, after 14 months, samples were immersed, water absorption was so rapid and the forces caused by calcium hydrosulfoaluminate recrystallization so large that the samples were rapidly and completely demolished.

The behavior of SC mortar specimens that had received hydrothermic treatment shows that SC

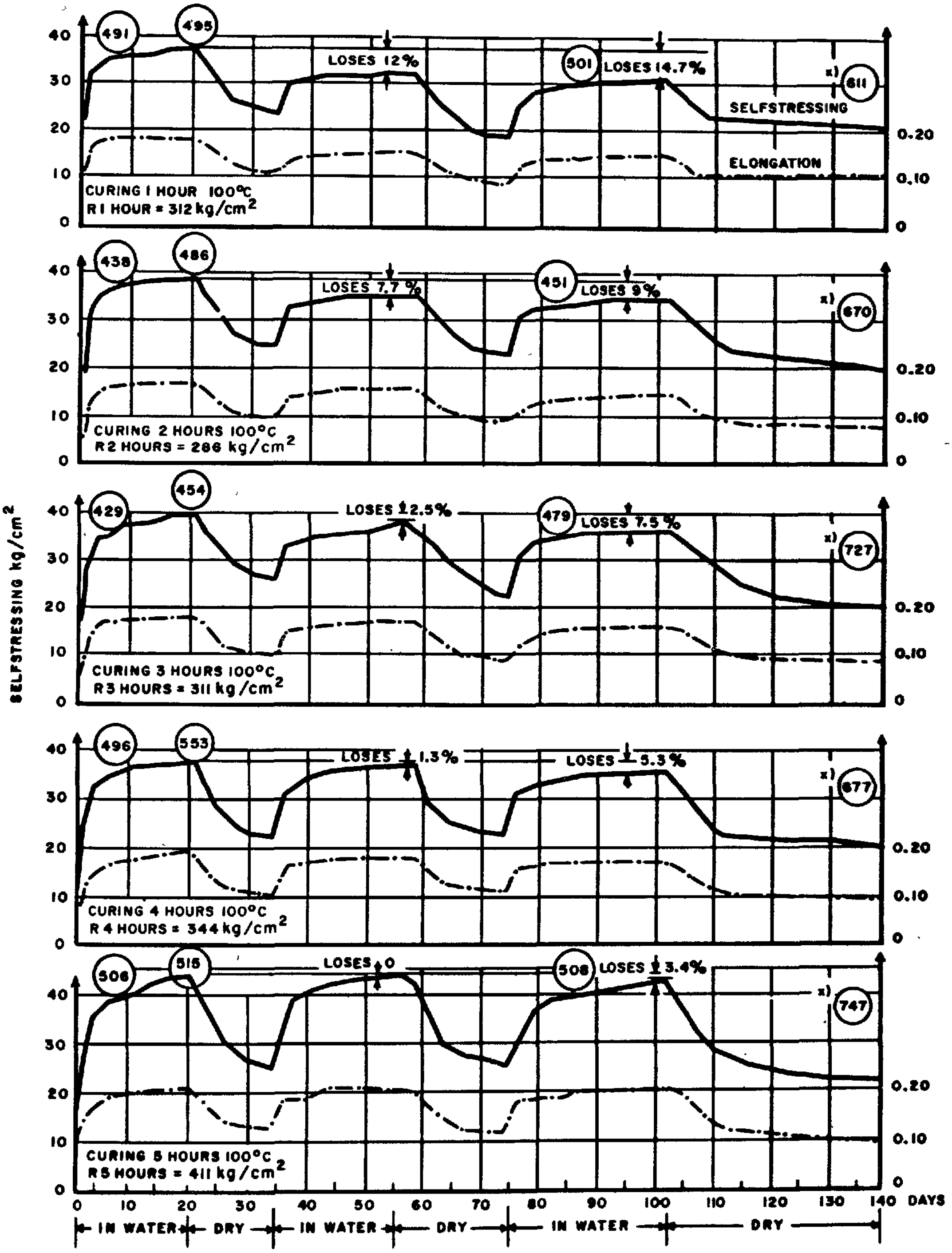

FIGURE 17. *Wetting and drying condition of self-stressing SC mortar (1:1).*

Proportions 14:20:66.

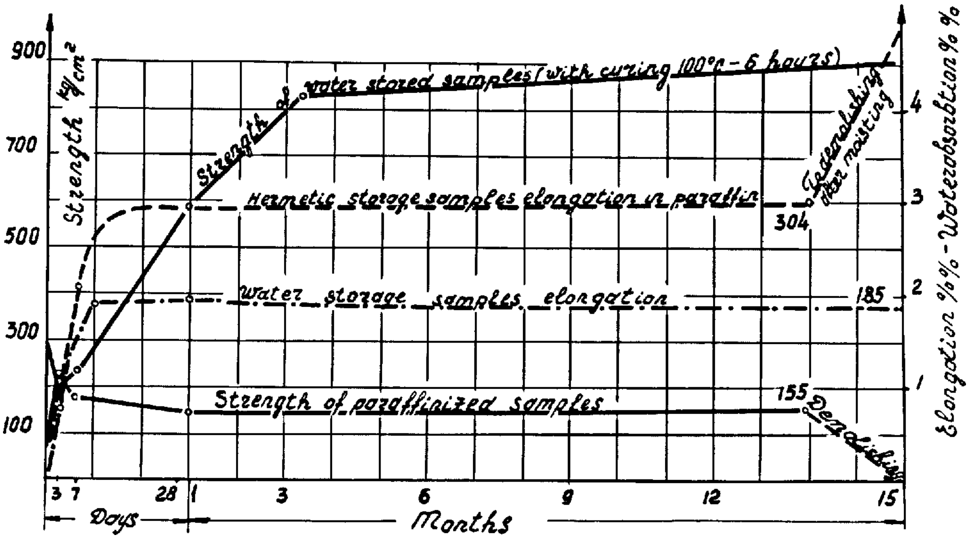

FIGURE 18. *Influence of water storage on elongation and strength of SC mortar (1:1) after heating at 100 °C for 6 hr in comparison with paraffin-isolated SC mortar (1:1) hydrated without heating.*

Proportions 14:12:74.

is a full-value hydraulic cement because of its hydrothermic treatment and its maximum strength reached during long-term moist storage. Therefore it should be employed for structures under pressure, in pressure pipes, tanks, in underground structures, and in highly moist conditions.

//C

During investigations of SC mortars (1:1) it was found that the lower the water-cement ratio, the higher the self-stressing and strength. Very short SC mortar setting period, 2 min, hampered mortar batching and placing in molds. Vibratory mixing and vibratory casting, and cement retarding agents like lignosulfonates, were therefore necessary (½ percent sulfate-alcohol waste additive or tartaric acid, ⅒ percent technical). These setting-retarding methods are effective, but in both cases the degree of expansion is lowered and self-stressing is about 30 percent less. This is caused by the fact that in both cases there is destruction of the initial, rather friable, but very convenient frame structure of self-stressed SC, owing to which the frame structure, an essential part in expansion, is without strength in the spaces free of cement glue.

waste

The self-stressing of 1:1 stressing mortar makes it possible to obtain an average concrete self-compression value in the range 20 to 50 kg/cm². This self-compression is the result of the structural reinforcement's elastic resistance to expansion, there being stressing to different degree, depending on reinforcement dimensions, over the range of 14,000 kg/cm² to 3,000 kg/cm², for 0.15 to 1.5 percent of reinforcement. For many structures such a prestressing value gives a satisfactory effect. With reinforcement higher than 1.5 percent, the concrete self-stressing intensity remains almost unchanged. However, the self-stressing value in the member sections may be changed as a result of a technological action, which we call "stress calibration". By special methods of stress application, both before and after hydrothermic treatment, it is possible to redistribute reaction forces in a member to any limit, and then the degree of fiber stresses in concrete may reach at least 150 kg/cm².

It should be noted that investigations have been made in the USSR in the coal mining industry when designing structures for reinforced concrete mine propping. The main requirements for propping members are low weight and high load capacity (about 10 tons/m²). During investigation of self-stressed vibrated bracings (channel type) with 0.75 percent reinforcing of the bracing section and 1.8 percent in the bracing tensile zone reinforced with high strength wires, the following stressed bracing conditions were obtained, by hydrothermic treatment for 6 hr at 100 °C and then 3 days water storage. High (6,000 kg/cm²) stresses in the upper reinforcement and comparatively low (1,500 kg/cm²) stresses in the lower reinforcement resulted in uniform compression of the concrete bracing, intensity 22 kg/cm².

The "stress calibration" [16] employed for bracings at stresses of 8,200 kg/cm² of the lower reinforcement made it possible to redistribute the stresses. Then the lower reinforcement in the middle part of bracings received a stress of 6,900 kg/cm² and the upper a stress of 800 kg/cm². The diagram of concrete stress distribution of the bracing section now shows the following fiber stresses: at bottom 200 kg/cm² and at top —47 kg/cm² (tensile). The method of "stress calibration" is still new and practical application will be possible, after much testing.

All above-mentioned SC mortar investigations refer to vibration during mixing and placing, owing to which the average self-stressing value obtained—40 kg/cm²—is lower than the actual

SC mortar self-stressing value, about 60 kg/cm², not yet reached for vibrated samples. The actual self-stressing values, corresponding to the SC chemical possibilities, were obtained with SC mortar by shotcreting. The dry mixture, delivered from the cement gun by compressed air at a pressure of 3–5 atm through a hose to the nozzle, was moistened at that point by water under pressure, and then thrown with high speed against the surface of the cast article. From the moment of moistening to placement by the gun, only hundredths of a second passed. Therefore, mortar placed by shotcreting is very dense, with minimum water content (about 0.20–0.22) and it is placed long before SC setting begins.

The advantages obtained by shotcreting technology can be enumerated: self-stressing reaches 50–60 kg/cm², and the strength at mature age is 80–1,000 kg/cm².

Self-Stressing of SC Pressure Pipes. Production Technology of Pressure Pipes and Their Testing

In the USSR the technology and equipment are simultaneously being worked out for three methods of manufacturing self-stressed pipes: shotcreting, centrifuging, and vibrosqueezing. Each of these methods provides for manufacture of pipe of specific diameters: shotcreting for pipes of dia. 600 to 1,000 mm, centrifuging for pipes of dia. 300 to 500 mm, vibrating-squeezing for pipes of dia. 150 to 250 mm.

The pipes manufactured by these technological methods retain internal pressure, without sweating, up to 15–20 atm, and may be used for operations under working pressures of 6 and 10 atm.

A special two-seat automatic machine (fig. 19) has been designed for making pipe by shotcreting. The automatic machine is equipped with a slowly rotating core (4), with foldable mechanism to make clearance between the shotcreted pipe and core. Besides, the machine has a rotating coil and wire reel (8), which may either be held by an electromagnet (7) and moved up and down with a platform (3), winding wire around the pipe, or may turn together with the core, remaining in the bottom no-work position (as shown in fig. 19). A set of nozzles is installed through which the SC mortar is shotcreted on the core to form the pipe. While the pipe is being manufactured in one station (LH), the other (RH) is used for preparatory operations. During rotation of core and motion of the platform (3) up and down, shotcreted layers are placed at the same time as the reinforcement coils. When the last layer is being placed, the surface is smoothed with a mechanical knife. After the first pipe casting (in the LH station), the set of nozzles is turned 180° and shotcretes the next pipe (in the other station), and so on. In the first station, the core is retracted and the pipe is removed by lifting it onto a round support and is transferred for further technological treatment, while the core is prepared for new shotcreting.

Figure 20 shows the technology worked out for self-stressed pipe manufacture. The shotcreted pipe, already hardened due to the quick setting of SC, is lowered for 1 min into a pit filled with melted paraffin to make a thin isolation layer, and is then stored for 18–24 hr at normal temperature, which gives the pipe a concrete strength of 200 kg/cm². Then the pipe is placed for 6 hr in boiling water, and into a cold water tank for 5–6 days storage. Finished pipe receives face leveling and hydraulic testing, and is transfered to the warehouse, where it is kept for 21–28 days.

The centrifugal technology of self-stressed pressure pipes has been checked at a Moscow pipe factory. Self-stressed pipes of 400-mm diameter, 50-mm walls, and 4 m long are manufactured there, whereas open channel pipes were previously made in solid molds using paraffin. Difficulties of the short setting time of SC were eliminated by use of a mixer equipped with a vibrating device. Ten min vibromixing destroyed the initial structure to a degree, so that the mixture retained plastic consistency for 30 min, sufficient for centrifuge casting. Pipe manufactured in this way with reinforced frame of stressing mortar was held in paraffin coating 24 hr during which the concrete strength reached 160 kg/cm². The pipe was next heated in a bath 6 hr at 100 °C, and then delivered for water storage. Internal pressure testing of these pipes showed that pipes with weak reinforcement resist internal pressure to 11–12 atm. Wound with prestressed design spiral reinforcement the pipe resists 25–28 atm pressure without leakage. Pipes without stressed coils can be used for pressure piping under 6 atm pressure, with winding for piping water at heads of 10 atm and above.

40 cm
5 cm
4 m

The technology of pressure pipe vibrocasting of small diameter pipe—150–200 mm, 2 m long, and with 25–30-mm walls—has been mastered on a vertical vibrosqueezed pipe casting machine, now industrially used (fig. 21). These pipes are equipped with spigots and are for use in water distribution lines and in pipings for water supply in rural areas with a working head of 4–6 atm. The pipes have cold-drawn wire reinforcement, diameter 4–5 mm.

The vibrosqueezing method of manufacture consists of a vertical vibrating mold slowly filled from the top with SC mortar mixture. A simultaneously vibrating core, introduced from the mold bottom, moves up and down rotating from one side to the other repeatedly, and distributes and tamps the mortar into pipe body and spigot. The simultaneous vibration of core and mold aids in compacting stiff mortar and in casting pipe. When the vibrating core is removed from the mold

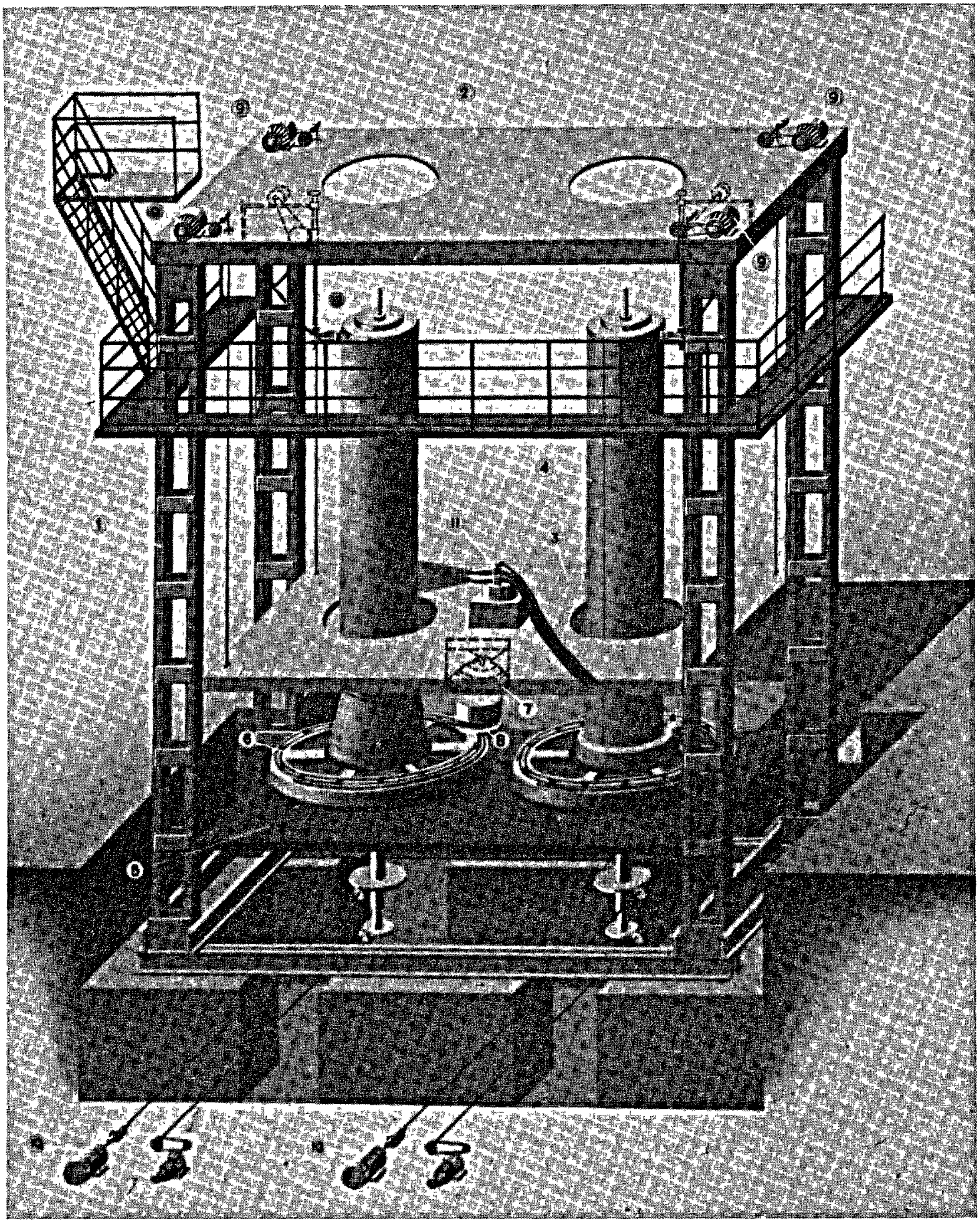

Figure 19. *Scheme of industrial automatic shotcreting machine for large-diameter, high-pressure pipe production.*

1. Stand
2. Upper platform
3. Movable platform
4. Collapsible metal core
5. Lower platform
6. Revolving table
7. Magnetic chuck (or clutch)
8. Spool with wire
9. Elevating motor
10. Motor for rotating table
11. Nozzles
12. End-forming device

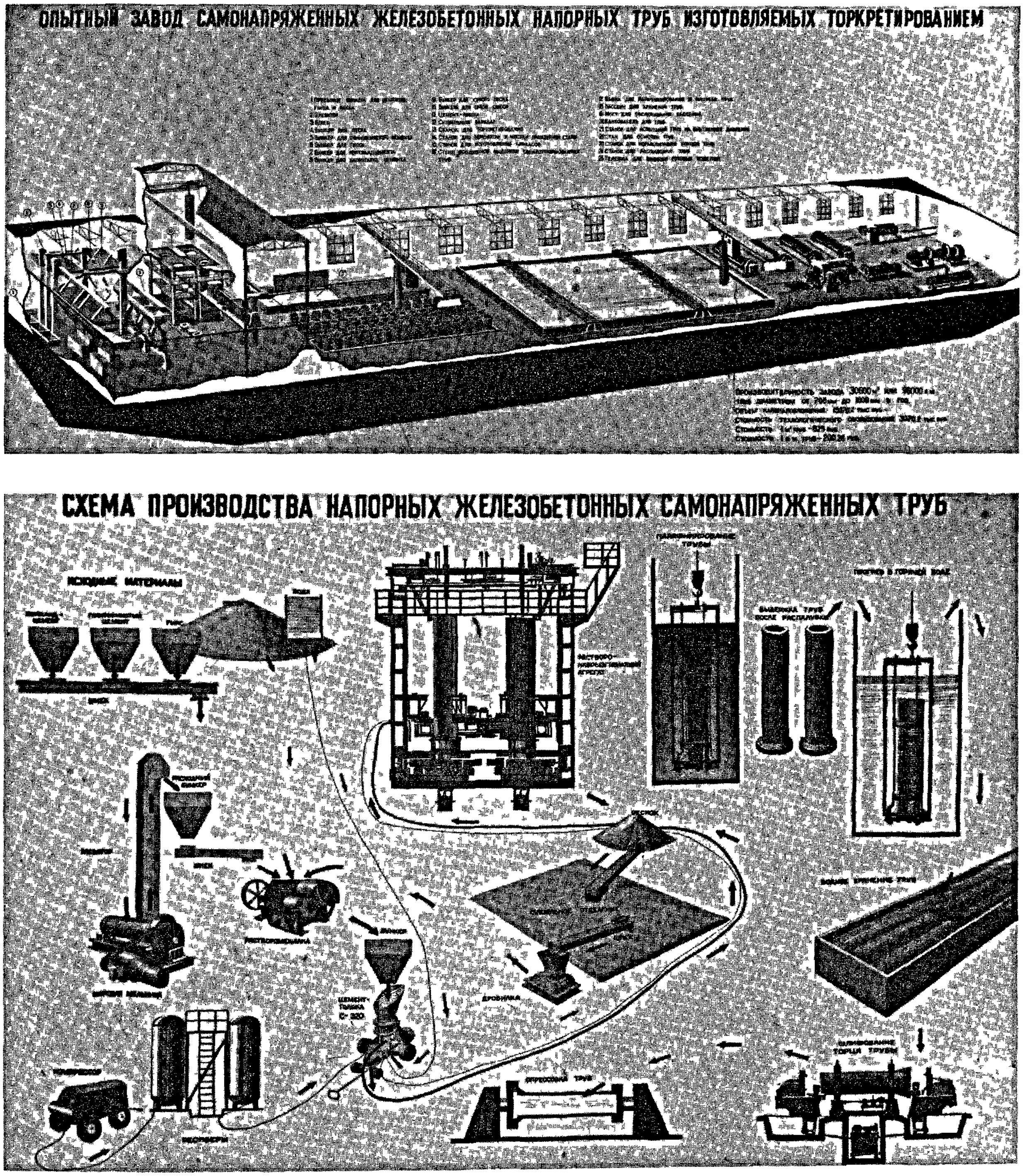

FIGURE 20. *Technology sequence of high-pressure pipe production by shotcreting.*

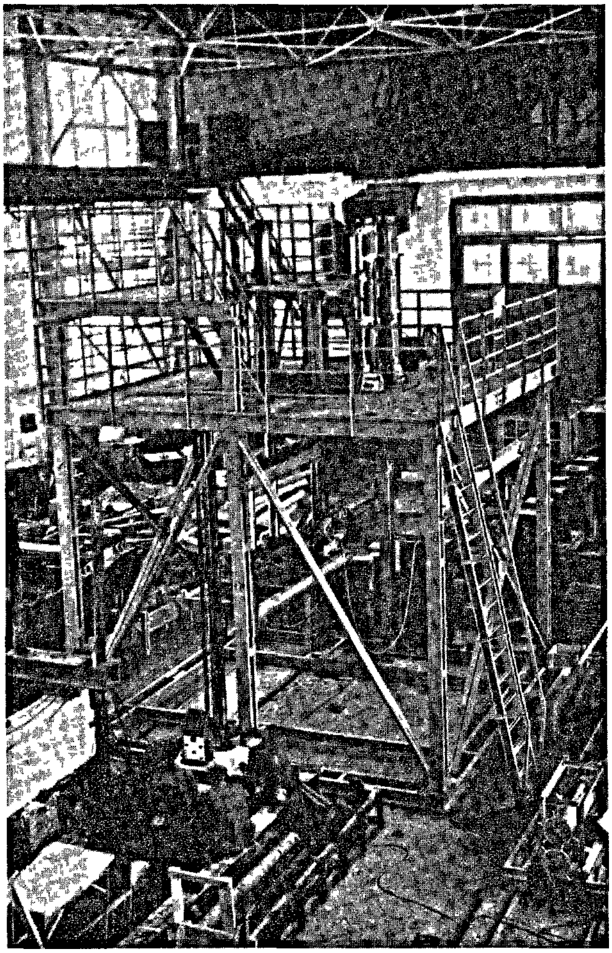

FIGURE 21. *Research vibrosqueezing machine for small-diameter, high-pressure pipe production.*

at the top end it pushes out excess mortar (if there is any) from the pipe. At this time vibration is switched off, and the core, while turning toward one and the other side, is pushed down, sliding along the internal pipe surface and smoothing it. The machine simultaneously casts two pipes over two cores. After the pipe casting process is finished, the molds are removed from the machine and are stored 12–18 hr, during which the concrete reaches a strength of 200 kg/cm². Then delivered pipes are heated 6 hr in a bath at 100 °C, when the pipe mortar reaches a strength of about 300 kg/cm². During subsequent water storage for 3–5 days, the mortar expands and pipe concrete and reinforcement are self-stressed. Here, as well as when centrifuging, vibrated mixing of the mortar occurs before and during the filling of the molds, due to which a significant part of the self-stressing is lost.

Testing of such pipes by internal pressure has shown that they have high impermeability. Even though 20–25 mm thickness of the wall is small, the pipes resist an internal pressure of 17 and even 25 atm without sweating.

A similar sequence is employed for manufacturing and testing pressure pipes by shotcrete casting. A horizontal spraying machine is used for shotcrete casting (fig. 22). In 1958 this machine was redesigned and is now equipped with mechanism for winding spiral reinforcement at the same time as shotcreting. It must be pointed out that previously whenever frame reinforcement was put on the shotcreting process had to be stopped, and it was necessary to remove the pipe with the core from the machine, to tighten the next reinforcement frame, and then to reinstall the pipe on the machine for further shotcreting. If the pipe had more than two reinforcement frames, shotcreting had to be stopped twice. This complicated the casting process and worsened the

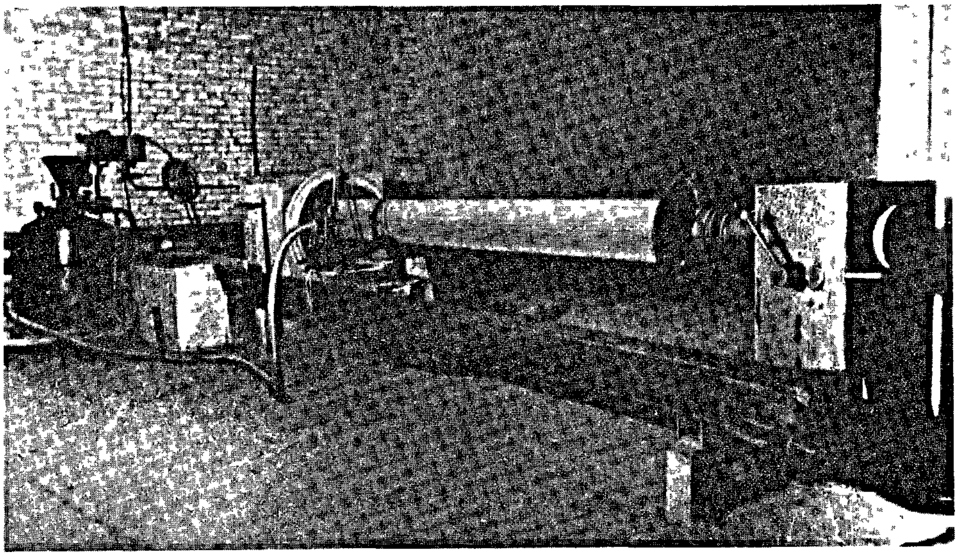

FIGURE 22. *Experimental shotcrete machine for casting high-pressure pipe simultaneously with wire winding.*

density of mortar under the spiral frame. Simultaneous winding of spiral reinforcement during the shotcreting process results in marked lowering in casting time, permits winding many rows with a wide pitch, reliably coats mortar around spiral wire, and may eliminate the need for longitudinal reinforcement.

As a result of shotcrete casting, with simultaneous entire pipe-body winding (throughout the entire wall depth) the spiral reinforcement with interwinding coils of adjacent rows is distributed uniformly in the concrete. In this condition mortar deformations during expansion are slight, thus insuring better use of mortar expansive power and corresponding maximum pipe self-stressing. During the mastery of new type shotcrete casting, it was found that simultaneous winding is the best method of reinforcing self-stressed pipes. Shotcreting needs a nonretarding admixture. Under these conditions the structure formed cannot later be destroyed. Due to the very low water-cement ratio, 0.16–0.22, the maximum quantity of "low-sulfate" hydrosulfoaluminate of calcium is formed and, consequently, maximum power is released for expansion and self-stressing during recrystallization into the "high-sulfate" form. This has been entirely verified by tests. In all cases shotcrete mortar specimens had high expansive force, and produced mortar self-stress of about 40–50 kg/cm^2. These results permit us to consider shotcrete casting as the chief method for manufacture of large diameter pressure pipes. Self-stressed shotcrete concrete has high stability in aggressive media, sea water in particular.

Conclusion

The idea of self-stressed structures, on which many Soviet scientists have worked (Mikhailov, Popov, Litver, Berdichevsky, Karasiev, and Potashnikov) is new in the field of prestressed reinforced concrete. The present level of development of the self-stressing method is progressive in character and has wide perspective for construction use, but also indicates need for further study to improve cement composition and retarding admixture for setting, and need for investigation of more effective self-stressing methods, including water hydration without heating and the method of "stress calibration," in order that one may progress from mortars to concrete with less binding material.

In the USSR, besides the explanation of self-stressing already discussed, G. N. Sivertzev holds another opinion, completely denying the possibility of calcium hydrosulfoaluminate formation in cement media and giving a different explanation for causes of expansion and self-stressing. Sivertzev considers that expansion may develop independently of formation or lack of calcium hydrosulfoaluminate, and that the contradictory phenomena occasionally observed during SC hardening are explained only by colloidal chemistry. Expansion is considered by him to be determined by the unstable dynamic equilibrium of two mutually contradictory processes, namely SC setting and hardening, and solvation processes of SC particles retarding coagulation. SC is marked by the presence of certain antagonistic suspensions (portland cement, high-alumina cement, gypsum, etc.). Here each type of solvate shell of the particles is formed separately, without disorientation of water dipoles, preventing adhering of particles. As the solvate shells cause cement paste expansion, the structure densifies and strength increases. Solvation and expansion develop with unavoidable structure friability and strength drop. During the hydration of ordinary nonexpansive cements, in dense pastes, the solvate shells invariably interfere, causing disorientation of the water dipoles and solvate shells. The solvate shells in this case lose their stable function and aid the direct cohesion of hardened cement paste particles. Sivertzev is conducting very interesting investigations to corroborate and broaden his veiws on SC expansion and self-stressing processes.

In France much work in the field of expansive cement has been done by the French scientist H. Lossier [18], who has produced his own expansive cement. This cement is composed of portland cement, sulfoaluminate cement, and slag, dry-ground in the proper proportions. Fifteen-day hardening in moist condition causes complete expansion and densifies the structure. According to Lossier, resistance should give self-stressing.

The theoretical conclusions of Lossier clearly show the established order and views on cement, and also show that scientists experimenting in this field must find the best mineralogical cement composition, the necessary additives, and the appropriate water content. The view is that the structural synthesis during cement setting and hardening takes place by itself, and forms the cement paste of required characteristics. This is beyond human influence. At best, the required structural formation processes may be accelerated by normal heating or high pressure. This considerably handicaps the designer, when it comes to the mixed cement passing through the required stages (fig. 7) of structural formation and strengthening.

P. S. Rehbinder and N. V. Mikhailov proposed intervention in the processes during the first stage. When preparing very fine cement, ground sand, and active mixture they recommend the use of mechanical influence like vibratory mixing of concrete and multifrequency vibration in all technological stages of mixture processing. This destroys the formed structure, to obtain denser packing of concrete and cement paste particles and development of hydration processes deeper in the cement grains. As a result there is a significant increase of concrete strength and density.

Our aims are broader: we prepare a binder so that the stage of structure formation passes quickly and setting is also rapid. We assume that the cement structure has entered far into the setting stage to form a sufficiently strong and hard cement paste body. With any absorption of water into this structure, even though it is very strong, expansion of cement paste completely destroys the structure, turning it into a jellified substance. Thus, the created structure conceals possibilities of self-demolition. In this respect SC is completely useless as a binding agent. But here the researcher intervenes in cement paste structure building and by definite processes (moistening, heating, mechanical force) rearranges the system, destroying certain cement paste structures, while others arise rapidly in the combinations and sequence required for the hard body to remain unchanged, so that strength is maintained and even increased, while the cement paste volume increases, able in case of resistance to convert deformation power into the work of reinforced concrete stressing.

Thus, cement acquires new qualities, previously not only not used, but even objectionable and in every way undesirable.

The possibility to direct the expansion of hardening binders, and freely to design them, is a new advanced undertaking in cement chemistry, opening wide technical horizons.

The work performed by Soviet scientists in this field is a first step towards using the chemical power of hardening binders, and must be continued in order to find the best way to release and make use of chemical forces inherent in the binders for advantageous work in self-stressing. The efforts of scientists and engineers of many countries should be directed towards this end. It seems to us that maximum results are assured if producers will participate in this work and introduce new achievements in their experimental plants.

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Discussion

Levi S. Brown

The advent and rapid development of prestressed concrete design and construction has opened a new field of broad application. Among the more intriguing variations is that of an expanding concrete member, essentially an expanding cement, whereby the desired prestress is self-effected. It is evident in the wealth of data presented in this paper that the concept, both of the cement and of its effective use, has developed into an established art. While the accomplishment merits high compliment, there are two or three facets of the report that may merit more extended discussion.

The unstable or expanding component of the cement (or concrete) is identified as low sulfoaluminate, proportioned about 35 to 65 percent portland cement. It is put into the cement as the two substances calcium aluminate and gypsum, properly proportioned. It is preserved in the low form by limited quantity of mix water. After thorough set, the hardened member is immersed in water. The availability of the extra water promotes alteration of the low sulfoaluminate to the high sulfoaluminate. The expansion is accomplished by this inversion. The expansion tends to disintegrate the formerly hardened member, which action of course is minimized by restricting the potential expansion, i.e., the low sulfoaluminate, to smaller proportions. If the expansion-curing is augmented and accelerated by heat, it is found that strength is maintained by autogenous healing. Thus a member may expand 3 percent or more, and the concrete still show a strength equal to or greater than that of the initial material. Test data, offered in some abundance, show this to be the eventual effect.

In practical application, a fixed principle of such expansion is that it is triaxial and that interior voids or discontinuities tend to increase in diameter. That is, the envelope of concrete about a prestressing wire tends to enlarge and thereby weaken bond and the desired composite action. Incidentally, elongation of the prestressing wire reduces its diameter and tends further to weaken the bond. This tendency is inherent in the process and should ever be kept in mind. That is to say, the adverse tendency does not necessarily vitiate the objective. It only means that one should be aware of corrective countermeasures. It may be that the autogenous healing automatically restores the bond. Then again, it is noted in the paper that uniaxial restraint tends to transverse compression, an explanation that is subject to serious challenge.

Many properties of the eventual concretes are investigated and described. Among others, a high resistance to sea water or sulfate exposure is noted. That probably is to be expected, since the aluminate is already in the stable high sulfate form. The concept offers intriguing possibilities in respect to endurance of ordinary concrete.

Nothing is said of one property that could be of wide interest. That is resistance to frost action. It is noted that before expansion the concrete is very dense and that it dries out very slowly. When put in water, however, it takes up water very rapidly. This anomalous behavior is quite different from that of conventional concrete. One may well suspect thereby that resistance to frost action could be poor, but no freezing and thawing tests were noted.

Much of the first part of the paper is made a dissertation on the processes of hydration and set of ordinary cement. While it is evident that intensive petrographic studies have been made, the concepts derived do not appear in full accord with conventional thought. For example, it is stated that the original cement particles shatter into much smaller colloids. Our petrographic studies do not support this view. Present purpose however is not to criticize the concept. It is only to note that the dissertation is not essential to discussion of the mechanism of expansion and self-stressing. The discussion suffers somewhat from this earlier and lengthy consideration.

Paper VIII–2. Blast-Furnace Slags and Slag Cements*

W. Kramer

Synopsis

The chemical process, temperature, and viscosity are important factors in the use of slag in blast furnaces. The MgO and Al_2O_3 content of the slag plays an essential role as well as the CaO/SiO_2 ratio. The chemical process and the physical state are decisive for the development of the hydraulic properties of granulated slag. The vitreous state of granulated slag is regulated by the temperature and viscosity of the molten slag and by the cooling conditions. Comparative tests of the action of the chemical composition of granulated slags on their hydraulic characteristics are possible only if the temperature of the melts prior to granulating is above the liquefying point.

Various investigations have revealed the interrelations existing between the tapping temperature, the CaO/SiO_2 ratio of the blast furnace slag, and its strength development under alkaline activation. They also have indicated the influence of a higher MgO or Al_2O_3 content on the hydraulic properties of the granulated slags. Contrary to MgO, a concentration of alumina will improve the reactivity of granulated slags. Cements made thereof, will, under alkaline as well as sulfate activation, experience an increase of strength. There are definite areas of preferred strength development under both activating methods. The interrelations between the hydraulic properties of blast furnace slags and the thermal equilibrium of paragenesis at the crystalline state offer a satisfactory assessing method for slags, the tapping temperature of which is higher than the melting temperature. However, in practical operation, this condition is not always fulfilled. For that reason, special attention should be paid to the glass content of granulated slag in addition to its chemical composition.

A method particularly suitable for practical operation because of its ease of application is the test under ultraviolet light. A quantitative analysis of the red colors of granulated slags is obtained by microscopic examination of fluorescence which, combined with the chemical data is a sufficient basis for assessing the hydraulic value.

The interrelations existing in the development of the technical properties of slag cements give evidence of the prevailing characteristics of the clinker in high-clinker types. In the low-clinker slag cements, the granulated slag is decisive for the hydration process and the strength development. For slag cements rich in granulated blast-furnace slag, the latent hydraulic setting power is released only by the alkalinity imparted to the fluid cement phase. The mineral structure of the clinker appears to be of influence on the strength development of this type of cement.

The processes occurring in the hydration of slag cements are dealt with in reference to the literature available. The possibility of forming links between different Si atoms by both oxygen and oxygen-hydrogen bridges, shown by H. O'Daniel, seems to merit particular attention in view of the importance for the stability of cements against attacking chemicals.

Résumé

La nature du procédé chimique, la température, et la viscosité sont des facteurs importants pour l'utilization du laitier dans le haut-fourneau. Comme le rapport CaO/SiO_2, la teneur du laitier en MgO et en Al_2O_3 joue un rôle important. La nature du procédé chimique et l'état physique sont décisifs pour le développement des propriétés hydrauliques du laitier granulé. La température et la viscosité du laitier fondu et les conditions de refroidissement ordonnent l'état vitreux du laitier granulé. Des essais comparatifs de l'influence de la composition chimique de laitiers granulés sur leurs propriétés hydrauliques ne sont possibles que lorsque la température des fontes avant la granulation est au-dessus du point de fusion.

Des différentes investigations ont découvert les relations qui existent entre la température de coulée, le rapport CaO/SiO_2 du laitier du haut-fourneau, et son développement de résistance sous l'activation alcaline. Elles ont montré aussi l'influence d'une teneur plus forte en MgO ou en Al_2O_3 sur les propriétés hydrauliques des laitiers granulés. Par contraste au MgO, une concentration de l'alumine améliorera la réactivité des laitiers granulés. Si l'on utilise ceux-ci pour la fabrication de ciments, on trouvera une accroissement de résistance sous l'activation alcaline et sulfatée. Des régions definies du développement de résistance maximale existent avec les deux méthodes activantes. Les rapports entre les propriétés hydrauliques des laitiers du haut-fourneau et l'équilibre thermique de la paragenèse à l'état cristalline offrent une méthode convenable d'évaluation des laitiers dont la température de coulée est au-dessus de la température de fusion. Néanmoins, cette condition n'est past toujours encontrée dans l'opération pratique. Ainsi, on doit faire attention spéciale à la teneur vitreuse du laitier granulé aussi bien qu'à sa composition chimique. A cause de son opération facile, une méthode particulièrement convenable à l'opération pratique est l'essai aux rayons ultra-violets. On obtient une analyse quantitative des couleurs rouges de laitiers granulés à l'aide d'une examination microscopique de fluorescence. Ceci donne, en combinaison aux données chimiques, une base suffisante pour l'estimation de la valeur hydraulique.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from Forschungsinstitut für Hochofenschlacke, Rheinhausen, Germany. (This paper was presented at the Symposium by H.-G. Smolczyk.)

Les relations qui existent dans le développement des propriétés techniques des ciments à laitier montrent à l'évidence les caractéristiques prédominantes du clinker dans les types de forte teneur en clinker. Dans les ciments à laitier de faible teneur en clinker, le laitier granulé est décisif pour le processus d'hydratation et le développement de résistance. Dans les ciments à laitier de forte teneur en laitier granulé du haut-fourneau, la tendance latente à prise hydraulique n'est libérée que par l'alcalinité conférée par la phase fluide du ciment. Il semble que la structure minéralogique du clinker influence le développement de résistance de ce type de ciment.

Les processus se présentants dans l'hydratation des ciments à laitier sont discutés en relation à la littérature disponible. La possibilité, montrée par H. O'Daniel, de former des liaisons entre différents atomes de Si pontés de liaisons d'atomes d'oxygène et d'atomes d'oxygène et d'hydrogène, semble à mériter l'attention spéciàle à cause de son importance pour la stabilité de ciments contre les composés chimiques agressifs.

Zusammenfassung

Chemismus, Temperatur und Viskosität sind die für die Schlackenführung im Hochofen bedeutsamen Faktoren. Der MgO- und Al_2O_3-Gehalt der Schlacken spielen hierbei neben dem CaO/SiO_2-Verhältnis eine bedeutsame Rolle. Für die Ausbildung der hydraulischen Eigenschaften der Hüttensande sind Chemismus und physikalischer Formzustand die bestimmenden Größen. Der glasige Formzustand der Hüttensande wird einerseits eingestellt durch die im Zeitpunkt der Granulation vorhandene Temperatur und Viskosität der Schlackenschmelze und andererseits durch die Abkühlungsbedingungen.

Vergleichende Untersuchungen über den Einfluß der chemischen Zusammensetzung der Hüttensande auf ihr hydraulisches Verhalten sind nur dann durchführbar, wenn die Temperatur der Schmelzen vor ihrer Granulation über der Liquidustemperatur liegt. Die in der Berichtszeit durchgeführten Arbeiten haben die zwischen der Abstichtemperatur, dem CaO/SiO_2 Verhältnis der Hochofenschlacke und ihrer Festigkeitsausbildung bei alkalischer Anregung vorhandenen Gesetzmäßigkeiten dargelegt. Sie haben weiterhin den Einfluß höherer MgO- bzw. Al_2O_3-Gehalte auf die hydraulischen Eigenschaften der Sande aufgezeigt. Im Gegensatz zum MgO bewirkt eine Tonerdeanreicherung eine Verbesserung der Reaktionsfähigkeit der Hüttensande. Die aus derartigen Sanden hergestellten Zemente erfahren dadurch sowohl bei alkalischer als auch sulfatischer Anregung eine Anhebung der Festigkeiten. Für die Hüttenzemente bestehen bei den beiden Anregungsarten bestimmte Bereiche mit bevorzugter Festigkeitsausbildung. Die sich dabei ergebenden Zusammenhänge zwischen dem hydraulischen Verhalten der Hochofenschlacken und ihren thermischen Gleichgewichtsparagenesen im kristallinen Zustand geben bei Schlacken, deren Abstichtemperatur über der der Liquidustemperatur liegt, eine gute Beurteilungsmöglichkeit ab. In der Praxis ist diese Voraussetzung jedoch nicht immer erfüllt. Aus dem Grunde ist dem Glasgehalt der Hüttensande neben ihrem chemischen Aufbau besondere Beachtung zu schenken. Einen guten Aussagewert, der insbesondere wegen seiner Einfachheit und schnellen Durchführbarkeit für die Praxis besonders geeignet ist, besitzt die Prüfung im ultravioletten Licht. Bei Einsatz der Fluoreszenzmikroskopie lassen sich quantitative Aussagen über den "Rotgehalt" der Hüttensande als dem hydraulisch wirksamen Bestandteil machen, der zusammen mit den chemischen Daten des Hüttensandes eine gute Beurteilungsgrundlage für ihren hydraulischen Wert bildet.

Die in der Entwicklung der zementtechnischen Eigenschaften im Feld der Hüttenzemente vorhandenen Gesetzmäßigkeiten lassen den vorherrschenden Einfluß der Klinkerkomponente bei den klinkerreichen Hüttenzementen erkennen. Bei den klinkerarmen Hochofenzementen ist dagegen der Hüttensand die den Hydratationsablauf und die Festigkeitsentwicklung bestimmende Größe. Da bei den hüttensandreichen Hochofenzementen das latent hydraulische Erhärtungsvermögen erst durch die Alkalität, welche der Klinker der flüssigen Zementleimphase verleiht, ausgelöst wird, scheint der mineralische Aufbau der Klinker für die Entwicklung der Festigkeit dieser Zementart—insbesondere bei frühen Prüfterminen—von Einfluß zu sein.

Die sich bei der Hydratation der Hüttenzemente abspielenden Vorgänge werden abschließend anhand der vorliegenden Literatur behandelt. Die von H. O'Daniel aufgezeigte Möglichkeit der Brückenbildung zwischen einzelnen Si-Atomen sowohl über Sauerstoff- als auch über Sauerstoff/Wasserstoff-Brücken scheint im Hinblick auf ihre Bedeutung für die Beständigkeit der Zemente gegenüber chemisch angreifenden Stoffen besondere Beachtung zu verdienen.

Preface

At the Cement Chemistry Symposium held in 1952, F. Keil [1] [1] gave a comprehensive survey of the nature and value of the chemical characteristics and data as well as of the physical processes and technological methods elaborated for assessing the hydraulic properties of granulated blast-furnace slags. Since that time, literature on the subject of blast-furnace slags, their hydraulic properties, and the slag cements made thereof, has been enlarged by a series of research and test works.

The present report is intended to point out to what extent these works have helped to define and classify the manifold interrelations existing between the various factors that determine the different specific properties of granulated blast-furnace slags.

Test reports from the Soviet Union and the remaining Slavic-speaking countries could be taken

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[1] Figures in brackets indicate the literature references at the end of this paper.

into consideration only as far as translations or treatises contained in relevant trade journals, e.g., from the German Democratic Republic, have been available for evaluation.

The test results published prior to the Third Symposium will be referred to only at those points where it is found necessary for a better understanding of the recent works. The statements are completed by some provisional information on tests carried out by the Research Institute for Blast-Furnace Slags at Rheinhausen.

For some decades, blast-furnace slag has been of particular importance in the European countries for the manufacture of hydraulic binding agents. The specific properties this material imparts to the cements made thereof have led to an increased interest in its use as granulated slag in the manufacture of slag cements.

Influence of Blast-Furnace Slag on the Furnace Operation

In the blast-furnace process, the slag is deemed to play a purely metallurgical role. It will create the operating conditions required for obtaining a smooth working of the furnace and, at the same time, the quality of pig iron wanted. The interrelations taking place between the iron bath and the molten slag are regulated and determined by the chemical composition, the temperature, and the viscosity of the slag.

On the other hand, these factors are also of decisive importance for the development of the latent hydraulic properties of the blast-furnace slag as well as for the creation of the most favorable conditions for the conversion of the molten fluid into the vitreous state of granulated slag. Hence, a survey of the progress made and of the present situation in the field of slag cements should also take into account those works and researches dealing with the composing of slag in blast furnaces and the conditions of converting molten blast-furnace slag into granulated slag.

Among the great number of scientists studying, during the twenties and thirties, the natural laws of the blast furnace process with regard to the slag in connection with practical experience, C. H. Herty [2] and H. Schenck [3] should be mentioned first. By physico-chemical research, they contributed to an explanation of the processes taking place in the stack and the hearth of the blast furnace. In this way, the influence of slag regulation on the composition of the pig iron and the working of the furnace could be determined on a scientific basis. Experiments with the same or a similar purpose, considering some further factors of influence, have been carried out during the last 15 years by F. Koerber and W. Oelsen [4] as well as by W. Oelsen and other collaborators [5].

The investigations led to the finding that the development of both the pig iron and the slag in blast furnaces is the result of a long chain of consecutive, partly overlapping reactions. They set in shortly after the ore, coke, and fluxes are charged. Passing through intermediate reactions occurring in the shaft partly in the solid state, partly in the fluid stage, the process concludes by reactions taking place in the hearth between the metal melt and the slag bath. By properly selecting the composition of the slag and appropriately regulating the temperature, it is possible to influence the content of accompanying elements in the metal within broad limits to comply with the metallurgical requirements of the steel-making process, as well as to improve the quality of the slag products for conversion.

Without taking into account some special slags, lime and silica are the main components of blast-furnace slags as far as quantity is concerned. The *p*-value, i.e., the ratio of their oxides, constitutes one of the relative values which are used to characterize the blast-furnace slag by its chemical aspect.

Information on the reactions taking place between the CaO/SiO_2 basicity of the slag and the conditions of temperature and viscosity of the slags is given by the phase diagram of the three-component system $CaO–Al_2O_3–SiO_2$ by G. A. Rankin and F. E. Wright [6] as well as by the viscosity examinations of the four-component system $CaO–Al_2O_3–MgO–SiO_2$ by R. S. McCaffery and collaborators [7] which were recently completed by works of T. Saito and Y. Kawai [8] and further of J. S. Machin and T. B. Yee [9]. Changes of the CaO/SiO_2 ratio may therefore occur in acid slags within large ranges without strongly affecting the conditions of temperature and viscosity. However, for basic blast-furnace slags which are of particular interest for use as granulated material in the production of cements, a proportionate interdependence is given between these three values in conformity with the practical realities of blast-furnace operation. For basic ore and fluxes, the slag basicity and the hearth temperature, therefore, will be of decisive importance for the quality of pig iron produced. It is a general rule that an increase of the CaO/SiO_2 ratio will correspond to an increase of the content of C, Si, Mn, and P, and, at the same time, to a reduction of the content of S and N. As to slag cements, an increase of the slag basicity will generally result in a higher hydraulic value of the cements.

However, with basic slags, it will be possible only to a certain extent to raise the basicity by adding a larger quantity of lime to the fluxes. An increase of the lime content at unchanged conditions makes the slag quickly turn highly viscous. Trouble in the working of the furnace and changes of the reduction ratios can thereby only be avoided by substantially increasing the hearth temperature which will strongly affect the efficiency of the process.

The disadvantage of a higher lime content, however, may, to a certain extent, be eliminated by changes of the MgO and Al_2O_3 content of the slags.

An improvement of the flowing properties of high-CaO slags by adding larger amounts of MgO has been demonstrated by practical experiments on a large scale by A. J. Burgess and B. G. Baldwin [10]. The same fact was concluded from the results obtained by Soviet metallurgists such as J. P. Ssjemik [11]. An interesting and valuable survey of experiments at blast furnaces, particularly in the USSR, is presented by M. A. Pawlow [12].

A change of the Al_2O_3 content in blast-furnace slags causes an effect inverse to that of the CaO/SiO_2 ratio. Contrary to the CaO/SiO_2 ratio which, in acid blast-furnace slags, can be varied within a relatively far-reaching range without perceptibly affecting the temperature and the viscosity of the slag, changes of the Al_2O_3 content will be of considerable influence on the slags. The increased viscosity at a higher Al_2O_3 content will impede the use of high-aluminous blast-furnace slags for operating an acid furnace.

Yet, with basic blast-furnace slags, for which a small increase of the basicity results in higher melting temperatures and reduced viscosity, the metallurgical conditions of the furnace process will be improved by adding a larger quantity of alumina.

The favorable effect of such blast-furnace slags normally containing up to 20 percent of Al_2O_3 is known, according to O. Vorwerk and W. Kramer [13], for both the self-fluxing and the composed mixtures to which special alumina vehicles are added for regulating the alumina content. This feature was recently confirmed by F. Schrader [14]. He succeeded further in proving by practical experiments with Indian ores that an increase of the alumina content in slags up to 25 to 28 percent made the working conditions difficult in consequence of the resulting increase of viscosity. On a certain scale, a possibility of influencing the working of the furnace and the quality of the pig iron is offered by adding larger quantities of alumina to the blast-furnace slags.

As evidenced by the results of the investigations carried out by P. Huettemann [15] concerning the manufacture of basic steel and steel pig, it will be possible to convert a slag of high basicity without any reduction of efficiency only upon an increase of the Al_2O_3-content.

The above-explained effects of magnesia and alumina on the viscosity of blast-furnace slags refer to the circumstance of only one of the two components being variable. According to the studies made by E. F. Osborn, R. C. De Vries, K. H. Gee, and H. M. Kraner [16], this condition must be given, since the effects of magnesia and alumina on the viscosity of slags may not be summed up. To obtain an optimum viscosity by adding alumina, a normal MgO content of the slags will be required, whereas, on the other hand, the effect of an increased MgO content can be observed at a low Al_2O_3 content. The results of these research works have been confirmed by the above-treated operating experiments.

By way of laboratory tests, W. Oelsen, E. Schuermann, and S. Osman [17] investigated the effects of additions of alumina and magnesia in interaction with the iron melt and the slag bath. They came to an important finding for assessing the working of slag, viz, they found out that for calculating the basicity of a CaO–MgO–Al_2O_3–silicate slag, the value of MgO cannot be simply added to that of CaO, as the sulfur content of pig iron is largely determined by the CaO/SiO_2 ratio. With regard to desulfuring, the MgO must consequently not be rated as a complete lime substitute. For the same reason, alumina may not be looked upon as a lime substitute. It follows that the advantages of the MgO or Al_2O_3 content in basic slags lie in their effects of reducing the melting point or of improving the viscosity. Since alumina acts mainly as a liquefying agent in basic CaO slags, it would not be correct to add its value to the acids for calculating the basicity. In other words, the Al ion of basic melts may only be considered as a network-changing element at temperatures above the melting point. As known, the Al ion can act both as network-changing and network-forming agent. As blast-furnace slags should be granulated in such a way as to be largely frozen at the state of melting, the Al ion is maintained in such cases as a network-changing element of granulated slags.

The above studies should give rise to submitting the empirical formulae based on chemical analysis data to a critical examination. All measures referred to by the foregoing to contribute to improving the working of the furnace and the quality of pig iron will exert also a favorable influence on the hydraulic properties of granulated slags. The interrelations given between the chemical process, the temperature, and viscosity on the one side, and the hydraulic properties of the granulated slags on the other hand, have been explained by F. Keil by means of a survey of a series of former research works.

Operating Tests of Blast-Furnace Slags

Influence of Chemical Composition

For the last decade, large-scale practical tests have been carried out in blast furnaces, by which the effects of such measures on the quality of the pig iron, the working of the furnace, and the operating of the slag as well as on the hydraulic properties of the granulated slags produced were examined. O. Vorwerk and W. Kramer added as much aluminous iron vehicle (red mud) to high-basic ores and fluxes as proved necessary to obtain slags of a certain composition and of low viscosity.

The most favorable range of viscosity of these slags at relatively low furnace temperatures was deduced from the phase diagram of the three-component system $CaO-Al_2O_3-SiO_2$ given by G. A. Rankin and F. E. Wright and from the viscosity tests made on this system by R. S. McCaffery and collaborators. Simultaneously, these large-scale tests of practical blast-furnace operation confirmed partial results of the research done by E. F. Osborn, R. C. De Vries, K. H. Gee and H. M. Kraner on the optimum composition of blast furnace slag of the four-component system $CaO-MgO-Al_2O_3-SiO_2$.

The resulting slags were converted into slag cements after being granulated. The favorable action of increased alumina content on the hydraulic properties of basic granulated slags, either alkali- or sulfate-accelerated, could be proved in this way. The practical value of the tests is demonstrated by the evidence of a regulated slag composition leading by the resulting uniform and favorable working conditions to an improvement of the quality of the pig iron produced as well as of the blast-furnace slag.

P. Huettemann evaluated the operating results obtained in the manufacture of basic steel and steel pig with regard to both metallurgical and cement technical aspects. He succeeded in determining the essential values having influence on the reduction process and completed the study by an analysis based on a large number of operating data covering several years. According to his findings, the influence of increased alumina content on the strength development of cements is independent of the basicity of the slag, as far as the initial strength is concerned. For the strength obtained after a period of 28 days, however, such a dependence is evident. At low basicity, its effect will then be greater than at a high CaO/SiO_2 ratio.

Both these research works have promoted in Western Germany the manufacture of highly hydraulic granulated slags from slag solutions of composed ore and fluxes for the production of low-clinker blast-furnace and sulfate-slag cements exhibiting high initial and final strengths.

The dependence of the hydraulic properties of granulated slags on the slag composition and the furnace temperature was further thoroughly investigated by J. Roquejoffre [18]. The slag samples taken by him over an extended period, considering simultaneously the operating conditions, were examined with regard to their hydraulic characteristics. He found that among others there are interrelations between the tapping temperature and the CaO/SiO_2 ratio on the one hand, and between the CaO/SiO_2 ratio and the compressive strength on the other. Comparative tests of the hydraulic properties of four species of granulated and one species of crystalline blast-furnace slag were carried out by T. Tanaka and K. Takemoto [19] with the purpose of investigating the strength development of the cements made thereof by considering the chemical composition of the slags. A clear relation between the various characteristic values referred to for the hydraulic properties of granulated slags and the strength values of the cements made thereof could not be discovered. This lack of correlation is due to the fact that not only the properties of the slag melt will be of importance for the quality of a granulated blast-furnace slag, but also the conditions under which the slag is converted into the vitreous state.

Influence of Granulation

At an earlier date, G. Mussgnug [20] pointed out the influence exerted by the slag temperature on the development of the hydraulic properties of granulated blast-furnace slags.

By experimental examination of 150 slags derived from the blast-furnace tests carried out by A. J. Burgess and B. G. Baldwin, B. G. Baldwin [21] found that all slags could be completely converted into the vitreous state, if, prior to chilling, the temperature of the melt was some degrees above the liquefying point.

L. Blondiau [22] reported on the effects that substantial reduction of the temperature prior to granulating the slags will cause in the cements made thereof. He found out that, for example, a lowering of the granulation temperature from 1,538 to 1,479 °C will reduce the strength values of sulfate slag cements by 10 to 40 percent.

The influence of granulation is dealt with by W. Kramer [23]. Two species of granulated blast-furnace slags—produced from the same melt by different granulating conditions—were tested by him. The strength development of the cements made thereof differed, particularly among the low-clinker mixtures. The strength of cements made of granulated slag of low gravity and of foamed structure was 30 to 45 percent higher than that of cements made with slag of a compact vitreous structure. The influence of granulation was particularly great on the initial strength of the cements. By properly regulating the conditions of granulation, the hydraulic hardening of granulated blast furnace slags can be improved.

Test results of the influence of these cooling conditions on the hydraulic properties of hematite slags were reported by P. Bornatsch [24]. Three species of hematite slags of slightly varying chemical composition were subjected to different cooling conditions. The glass content of the resulting granulates was determined by microscope and brought in relation to the compressive strength of the slag cements made thereof.

By this method, the compressive strength could be determined from the glass content of the slags. Slight variations of the chemical composition of the slags tested were of no essential importance to the strength of the cement.

Examination of Synthetic Glass

For clarification of the influence exerted by the chemical composition on the development of the latent hydraulic properties of the granulated blast-furnace slags, a series of extended experimental examinations of laboratory slags and synthetic glasses have been carried out during the period under report.

E. F. Osborn, R. C. De Vries, and K. H. Gee determined the optimum composition of blast-furnace slags with regard to synthetic glass having a fixed alumina content, but varying amounts of CaO, MgO, and SiO_2.

Optimum compositions of slags were found to be as follows (percent by weight):

Al_2O_3	SiO_2	CaO	MgO
5.0	36.0	43.0	16.0
10.0	32.0	44.0	14.0
15.0	28.5	44.0	12.5
20.0	24.0	45.0	11.0
25.0	19.0	48.0	8.0
	(12.0) [a]	(57.0) [a]	(6.0) [a]
30.0	9.0	56.0	5.0
35.0	7.0	54.0	4.0

[a] The values in parentheses indicate a second optimum slag at the 25-percent level of the four-component system.

Further compositions closely ranging near the main points of the four-component system CaO–MgO–Al_2O_3–SiO_2 became completely fluid below 1,500 °C, and exhibited a maximum absorbing power for sulfur. The authors mention further that the optimum slag compositions will require a smaller amount of melting heat and will be of low viscosity. Slight variations of their chemical structure will, consequently, neither cause a sudden increase of viscosity, nor trouble the working of the furnace.

B. G. Baldwin examined the results of E. F. Osborn and collaborators by experimental tests of samples of blast-furnace slag he had taken from a working test (A. J. Burgess and B. G. Baldwin). The melting temperature and the viscosity conditions of about 150 slag samples were determined in a nitrogen atmosphere. An increase of the melting temperatures in consequence of the oxidation of FeO and MnO could thereby be avoided, but not the volatilization of part of the sulfur contained in the slags. It appears from the examination that the liquefying temperatures of blast-furnace slags deviate only slightly from the melting temperatures of the corresponding mixtures—based on the four oxides CaO, MgO, Al_2O_3, and SiO_2.

This relation was also found by E. E. Hofmann [25] by tests of blast-furnace slags under working conditions, by which the great variations of the results of measuring could be eliminated by the application of statistical analysis.

The diagrams published by E. F. Osborn and collaborators, therefore, are reliable for the determination of optimum compositions at 1,500 °C. Lower temperatures, due, e.g., to the operation of the furnace, or which could be caused by the material remaining too long in the ladle between tapping and granulating, will, at a constant Al_2O_3 content, lead to a separation of crystals and thereby to a lowering of the fluidity of the slag. The elimination of these effects which would be of disadvantage to the development of the hydraulic properties of granulated blast-furnace slags can be achieved via the chemical process by reducing the CaO content or increasing the SiO_2 and MgO contents of the slags.

The separation of crystals is connected with a change of the chemical composition of the melt. The resulting slag minerals, particularly the melilites and orthosilicates, are of greater basicity than the average composition of the remaining solution. This acid residual slag solution will not exert such favorable effects on the reactions wanted in the hearth of the blast furnace, as those obtained with the original slag after the latter has been converted into a homogeneous fluid solution by decomposition of the crystals. Such incorrect coordinations of slag composition and temperature leading to a separation of crystals, are of disadvantage to the quality of the pig iron produced as well as to the hydraulic properties of the granulated slag. These authors lay stress on the particular value of a regulated composition of the slag being in the interest of both the blast-furnace operator and the user of the blast-furnace slag.

F. Keil and F. W. Locher [26] manufactured more than 45 glasses of the three-component system CaO–Al_2O_3–SiO_2, of which about 15 glasses were melted with an addition of 5 percent of MgO. They examined the hydraulic setting properties caused by activation by means of clinker, anhydrite, and calcium hydroxide. The results of the strength tests were shown in the diagram of the three-component system.

In activating the glasses free from MgO by clinker, two ranges of high compressive strength could be observed, situated at 18 percent of SiO_2 and at 30 percent of SiO_2. The same glasses showed, however, only one range of high compressive strength, when activated by means of $CaSO_4$ and $Ca(OH)_2$, respectively.

The optimum strength of these glasses with any of the three activating agents was restricted to a small area of the three-component diagram and nearly concentrated to an approximate composition of 50 percent of CaO, 19 percent of Al_2O_3 and 31 percent of SiO_2.

An addition of 5 percent of MgO, making the glasses similar in composition to the blast-furnace slags produced in Europe, partly resulted in higher strength values under activation both by clinker and $CaSO_4$. The comparative strength development of four technical blast-furnace slags is quite in conformity with the results obtained with synthetic glasses.

The range of optimum compressive strength values of MgO-glasses under clinker activation, obtained after 28 days, is shown by figure 1 in the field of a 5-percent MgO content of the four-component system CaO–MgO–Al_2O_3–SiO_2.

When activating these glasses by means of $CaSO_4$, a narrow restricted area of high compressive strength will develop, approximately at

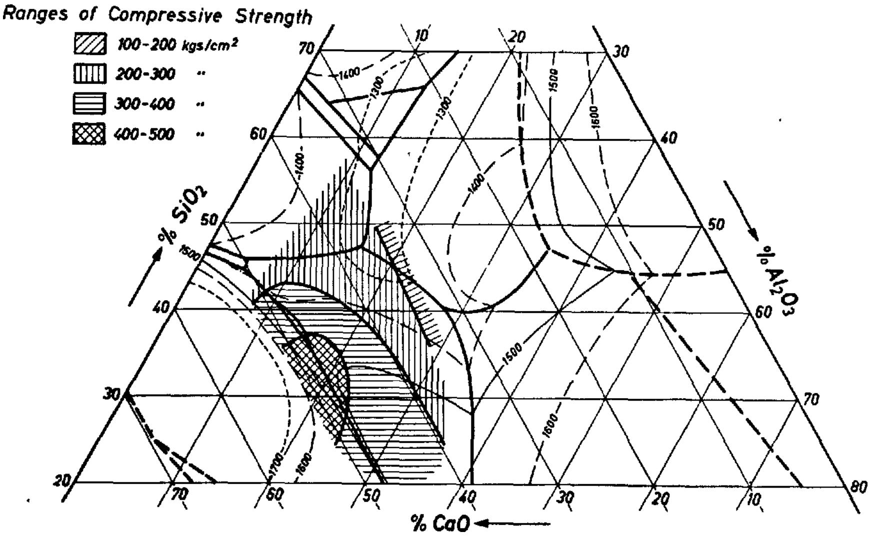


FIGURE 1. *Compressive-strength values, obtained after 28 days, of glasses of the* CaO—Al_2O_3—SiO_2—MgO *system stimulated by means of portland-cement clinker.*

Data referring to a 5-percent MgO level.
(According to Keil and Locher, 1958)

a glass composition of 48 percent of CaO, 5 percent of MgO, 18.5 percent of Al_2O_3 and 28.5 percent of SiO_2. When using $Ca(OH)_2$ for activation, the addition of MgO will not cause any increase of strength.

Generally speaking, the authors conclude from the results obtained that the hydraulic properties of the glasses depend on their solubility as well as on the rate of solubility measured in the solutions of the activating agents and on the type of hydrates produced. As to the solubility, they consider the location of the Al ion (whether as a network-forming or a network-changing element) within the glass structure as the decisive factor. The activating action of clinker and lime is traced back to an increase of the lime concentration in the cement solution which will favor a quick decomposition of the glasses and a formation of dicalcium silicate hydrate.

T. Tanaka, T. Sakai, and J. Yamane [27] examined 34 different glasses covering a range of about 26 to 40 percent of SiO_2, 14 to 30 percent of Al_2O_3 and 40 to 52 percent of CaO. The mixing ratio between slag and anhydrite remained constant at 85 to 15. The clinker content amounted to 2.4 and 6 percent.

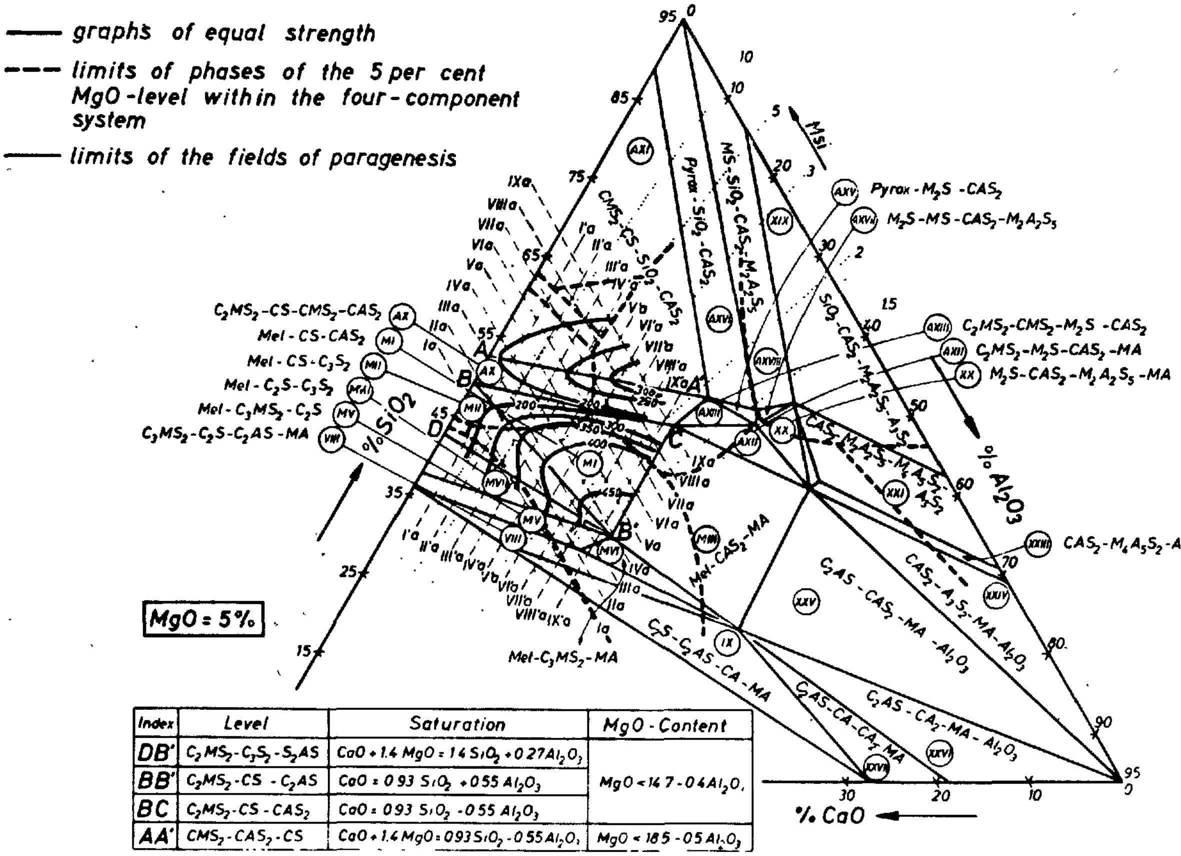
Sulfate-slag cements based on synthetic slags of a composition of 28 to 34 percent of SiO_2, 16 to 20 percent of Al_2O_3 and 46 to 50 percent of CaO delivered strength values more than 80 percent higher than those of conventional portlant cement. The greatest strengths were obtained at the following slag composition: 18 to 20 percent of Al_2O_3, 50 percent of CaO and 30 to 32 percent of SiO_2. At this composition, the sulfate-slag cement produced greater strength than portland cement. The composition of the glass of maximum strength with anhydrite activation was as follows: 18 percent of Al_2O_3, 32 percent of SiO_2 and 50 percent of CaO. For clinker activation, the formula was: 15.5 percent of Al_2O_3, 33 percent of SiO_2, and 51.5 percent of CaO. The field of particularly low strength remained nearly constant for either activating method.

Carrying out similar series of tests, L. Santarelli and G. Goggi [28] tried to determine, in addition to the influence of fluxes such as CaF_2, MnO, FeO, and others, the action of the glass content of the granulates. The favorable influence of a higher glass content as well as of an increased alumina content was confirmed. The flow characteristics of high-aluminous slags and the hydraulic setting power could be improved by small additions of CaF_2.

The most interesting approach to interpreting and explaining the hydraulic properties of the vitreous blast-furnace slags by deductions on the basis of solution theory as well as of confirming the foundations based on the results of the strength development of synthetic slags, was made by S. Solacolu [29]. In view of the finding that the hydraulic properties of the slags will not change proportionately to the oxide composition, he rejects the method of determining the granulated slag by the data and characteristics obtained by chemical analysis as being unsuitable. He believes further the assessing of the energy content of slags on the grounds of structural observation to be incorrect. He considers the difference of energy existing between the unstable glasses and their crystalline devitrification products as being small and unimportant among the factors decisive for the setting power. However, S. Solacolu finds a close connection between the hydraulic activity of vitreous slags and the paragenesis of thermal equilibrium in the crystalline condition. According to the tests, the hydraulic properties are subject to a uniform change within the same paragenesis, whereas in transition to another paragenesis, this change takes place in an inconstant way. S. Solacolu, therefore, regards a heterogeneous constitution of the slag as the basis for assessment of the setting power, supposing the vitreous slags to possess a "quasi-crystalline structure," in which the phases of the crystalline equilibrium are largely preformed according to the rules of a thermal-equilibrium crystallization. Formulae are indicated for calculating the concentration of active and inactive phases on the basis of the oxide compositions. The assessment of the slags is then made according to the hydraulic value of the type of paragenesis determined.

From the eutectics possible in the 20 forms of paragenesis of the four-component system CaO–MgO–Al_2O_3–SiO_2 according to T. W. Parker [30], only such types are taken into account that are of interest for blast-furnace slags of hydraulic characteristics. For explanation, figure 7 by S. Solacolu is included here as figure 2. It shows the fields of paragenesis of the thermal-equilibrium phases within the range of the compositions of blast furnace slags (circled points) and the graphs of equal strength values. On the average, slags of the system MgO–CaO–Al_2O_3–SiO_2 (MgO = 5 percent) tested as shown by the figure are located in the fields of paragenesis M I (melilite-wollastonite-rankinite), M II (melilite-wollastonite-anorthite), A X (akermanite-diopside-wollastonite-anorthite) and A XI (diopside-wollastonite-quartz-anorthite). The graphs of same-strength values (S-indices) clearly indicate two maximum points, viz, in the fields of the basic slags along the line *BB'* corresponding to the cleavage plane between M I and M II, and in the fields of the acid slags along *AA'*, the cleavage plane between A X and A XI. The basic slags are separated from the acid ones by a marked minimum. Within the various fields, the strength of the slags changes uniformly, whereas this change takes place inconstantly at the transition from one field of paragenesis to another.

Though a direct comparison is not possible, the diagram drawn by S. Solacolu was compared with the diagram of F. Keil and F. W. Locher, corresponding to the same compositions of slags. In the range of optimum strength, a coincidence is given between the two diagrams. The highest values (Solacolu) and the greatest compressive strengths after 28 days (F. Keil and F. W. Locher) in both diagrams are to be found in the phase of gehlenite (melilite). The examinations by F. Keil and F. W. Locher as well as by S. Solacolu offer suitable possibilities of comparative scientific research for determining the hydraulic character-



Index	Level	Saturation	MgO-Content
DB'	C_2MS_2-C_3S_2-S_2AS	$CaO + 1.4\,MgO = 1.4\,SiO_2 + 0.27\,Al_2O_3$	$MgO < 14.7 - 0.4\,Al_2O_3$
BB'	C_2MS_2-CS-C_2AS	$CaO = 0.93\,SiO_2 + 0.55\,Al_2O_3$	
BC	C_2MS_2-CS-CAS_2	$CaO = 0.93\,SiO_2 - 0.55\,Al_2O_3$	
AA'	CMS_2-CAS_2-CS	$CaO + 1.4\,MgO = 0.93\,SiO_2 - 0.55\,Al_2O_3$	$MgO < 18.5 - 0.5\,Al_2O_3$

FIGURE 2. *Graphs of equal strength in a section within the fields of paragenesis of the* CaO—Al_2O_3—SiO_2—MgO *system at the 5-percent* MgO *level.*

(According to Solacolu, 1958)

istics of such melts. These are pure glasses which were melted from the initial components until the state of equilibrium was reached. Although clear data are not contained in the works on this point, it must be supposed that the temperature exceeded the liquefying point by a considerable extent. The conversion of the melts into the vitreous state is therefore effected from a condition of equilibrium. The variations from this rule observed by other authors may be traced to different slag temperatures.

It follows from Baldwin's work that with a reduction of temperature, possible variations in this connection will require respective changes of the chemical composition of the slag to maintain a constant viscosity. An application of the interrelations determined for the chemical process of glass manufacture will only be possible in the field of granulated slag under the condition that the temperature of the melt is above the melting point. This takes for granted that the state of equilibrium of the slag solutions has nearly been reached in practical operation and maintained until the moment of granulation. In the manufacture of pig iron, this condition is obtained rather with self-fluxing material than with composed fluxes.

In the latter case the molten slag will not remain in the hearth of the blast furnace long enough to effect homogeneity. By the continuous confluence of differently composed primary melts, the final melt will contain parts of varying chemical composition, which, on granulating, are transferred into the solid state. This feature also explains why previous efforts to draw conclusions from the over-all chemical analysis as to the hydraulic properties of granulated blast-furnace slag made evident certain interrelations, but did not permit one to establish generally accepted rules.

Particular attention must, therefore, be paid to the state of the granulated blast-furnace slag, which virtually characterizes the physical properties of the slag for operation purposes in the manufacture of cement, especially in the production of low-clinker cements (blast-furnace and sulfate-slag cements). The chemical process must be observed additionally.

Importance of the Physical State for Assessing the Hydraulic Properties of Granulated Blast-Furnace Slag

In the report entitled "Slag Cements" which F. Keil gave on occasion of the Cement Chemistry Symposium held in 1952, he subjected every method of assessing the hydraulic properties of granulated blast-furnace slag, which was not based on a chemical analysis, to a critical examination.

During the period under report, A. Lommatzsch [31] has tried to obtain by means of differential thermal analysis a clear understanding of the binding and setting process of granulated blast-furnace slags under sulfate activation. In view of the results of his examinations, he thought them to be of a certain indicative value, attributing the thermal effects observed in the range of 800 to 900 °C to modifications and new formations typical for the hydraulic properties of basic blast-furnace slags.

P. Bornatsch further tried to use calorimetric graphs of heat capacity for assessing different blast-furnace slags. The results of his test, however, are of only limited use, since, despite its low heat conductivity, blast-furnace slag will cool very quickly, and the melting loss conditions prevailing in the coal crucibles cannot be defined. For that reason, the temperatures measured by him are about 100 °C too low. Characteristic conversion points could not be detected. Both works consequently did not contribute to a substantial enlargement of the previous knowledge in the field of blast-furnace slags.

Particular interest is still paid to the method developed in the metallurgical plant of Cockerill at Ougree-Marihaye by R. Feron [32] to classify granulated blast-furnace slags according to the luminous colors they will emit on exposure to ultraviolet rays. The granulated slags glow differently depending on their physical state. Bright red and pink shades are emitted by granulated slags of normal vitreous structure. Granulated slags of high-crystalline structure emit blue and violet colors. Their presence in the granulated slag is evidence that the slag has been melted under unfavorable conditions in the blast furnace or that bad granulating conditions have led to a moderate development of the vitreous state. The strength development of granulated slags, therefore, differs according to the luminous rays emitted.

Based on these observations, the method developed by Féron was found suitable for plant control and has been accepted. His examinations have been confirmed by J. Cleret De Langavant [33]. The importance of the ultraviolet test, also affirmed by him, is restricted by F. Pirotte [34] to granulated slag of the same origin. J. Roquejoffre proved by his tests as well that granulated slags glowing in the range of pink to bright pink exhibit better setting properties, but he believes the method of luminescence is not an exact criterion for assessing the hydraulic properties of granulated blast-furnace slag.

In evaluating the results obtained by Roquejoffre, it must, however, be considered that his examinations differ in principle from those of other observers. Whilst in general dry samples of granulated blast-furnace slags as delivered are tested, Roquejoffre ground the samples into a cement state before analyzing. As his own tests confirmed, the method would hereby lose a great part of its value, as beyond a certain grain size, the particles individually glowing in different colors will no longer be separately perceptible to the eye. Only weak luminescence is then produced, being shifted to brighter, whitish shades.

Considering the different opinions the various observers have had about the method of fluorescence, this method has not met with the widespread adoption hoped for. Its advantage, however, is to be seen in the ease of its application.

The luminous colors appearing on the grains of granulated slag are dependent not only on the incorporation of color centers, but presumably also on the type of prevailing ions, ion compounds, and lattice complexes as well as on their coordinating system. On the other hand, the more-or-less vitreous state of granulated blast-furnace slags reveals the condition exhibited by the solution at the point of solidification by fast cooling prior to granulating.

Our own experiments in the Research Institute for Blast-Furnace Slag at Rheinhausen showed that the differently fluorescing grains of granulated slag are not only dependent on different chemical and mineral compositions, but that they also exhibit various structures and inclusions which are due to varying temperatures and viscosity conditions during the formation of the individual particles of the melt and are, at the same time, indicative of the degree of reduction reached.

The radiographic and microscopic examination of the fluorescence of the differently glowing particles of granulated blast-furnace slag led to a subdivision into a high-aluminous and a high CaO and MgO group (see figure 3).

The granulated slags of hydraulic value with a high-aluminous component emit yellowish-red colors, and those of the lime-and-magnesia series exhibit a pink fluorescence. Between them and the clearly violet or brightly blue glowing crystalline particles exist manifold transitions. The mineral content and the state of aggregation of these transitions as well as of the imperfectly reduced grains glowing dark violet to black violet or blue to black can be seen from the table.

The main components of the high-aluminous group are high-aluminous melilites and wollastonites in addition to small quantities of merwinite. The CaO-MgO group is characterized by orthosilicates (merwinite, dicalcium silicate, monticellite) and high-magnesia melilites. Thus, the pink and blue glowing particles of granulated slag possess a predirected arrangement of ions

High Al_2O_3-content (as per chemical analysis)		Granulated Slags	High CaO (MgO)-content (as per chemical analysis)	
Mineral composition of the fluorescent particles microscopically and radiographically determined	Luminescent color Microscopic analysis of fluorescence	States of aggregate (microscopic examination)	Luminescent color Microscopic analysis of fluorescence	Mineral composition of the fluorescent particles microscopically and radiographically determined
$2CaO \cdot Al_2O_3 \cdot SiO_2$ $+ 2CaO \cdot MgO \cdot 2SiO_2$ Melilites (high-gehlenite mixing links)	pure violet	completely crystalline crystals >1μ (partly little glass)	pure blue (strongly glowing)	Orthosilicates: $3CaO \cdot MgO \cdot 2SiO_2$ merwinite ± monticellite $CaO \cdot MgO \cdot SiO_2$
beside: Ca(Mg) orthosilicates CaS, some wollastonite occasionally rankinite	bright violet to lilac white	many crystal separations<1μ of much or less glass	bright blue to bluish white	beside: high-åkermanite melilites, little glass, rankinite and wollastonite
↑ SiO_2 increasing Al_2O_3 increasing ↓ Melilites (high-gehlenite) beside orthosilicates and some pseudowollastonite, occasionally rankinite CaS preferably dissolved in glass	red violet[x] red (carmine) yellowish red red yellowish brown - red brown to brown[xx]	vitreous with many or less inclosures of single crystals, crystal aggregates, crystal cells and dispersed Fe (Mn)-oxides	marine blue[+] bluish grey grey pink pink bright reddish grey brown[xx] brown pink to brown	↑ Increasing C_2S Orthosilicates + CaS (merwinite prevailing) beside high-åkermanite melilites, little rankinite and pseudo-wollastonite CaS preferably crystalline separated ↑ SiO_2 increasing CaO increasing ↓
as above plus C (coke) residues, however, Fe-Mn-oxides finely dispersed and oxidated	black brown	vitreous metal oxides strong oxidation	velvet black	as above plus C (coke) residues, however, Fe-Mn-oxides finely dispersed and oxidated
	brownish black violet	additional crystal inclusions	grey blue black	

[x] Violet shade due to crystal cells not clearly perceptible by microscopic and radiographical examination

[+] Percentage increases with storing

[xx] Brown or grey brown shade due to a stronger absorbing power of the glass in consequence of finely dispersed metal oxides and carbon

FIGURE 3. *Determinable characteristics and mineral separations of luminescent particles of granulated blast-furnace slag.*

indicative of insular silicates. In the particles glowing in the range of yellowish-red to violet, there are, additionally, some weak networks of anion complexes.

As demonstrated by microscopic examination, the transitions observed at each series are to be traced back to the luminescence of crystal centers, which, however, are no longer perceptible radiographically. Further variations of the intensity of the luminescent colors depend on the state of the grains of the granulated slag. Highly porous and finely foamed grains emit colors of bright shades, whereas solid compact ones will glow darkly. Bright luminescent colors may also be changed into dark and black shades by incorporation of carbon pigments, finely dispersed iron particles, or ferrous and manganic oxides. Thus, the luminescence of granulated blast-furnace slags reveals not only their vitreous content, but simultaneously the degree of reduction of the slag solutions reached in the melting process.

The distribution of the crystal inclusions as well as the crystal aggregates of the bright fluorescent grains of granulated slag depends on whether they had already precipitated before granulating or whether they were formed only in the process of granulating. In this way, the microscopic observation of the fluorescence of ground particles of granulated slag permits further an evaluation of the method of granulating.

For determining the hydraulic value of differently glowing particles of granulated blast-furnace slag, a granulated slag was analyzed by its various parts of luminescence, and slag of each luminescent color was separately ground together with 30 parts of clinker and 5 parts of calcium sulfate to form an experimental cement of a specific surface area of 2,900±50 cm^2/g (according to Blaine). For comparison, a mixture composed of clinker and quartz sand was prepared. The strength test of miniature prisms (1×1×6 cm) according to Keil gave the following values:

Neutral test and experimental cements of the fractions of luminescence	Bending tensile strength in kg/cm^2				Compressive strength in kg/cm^2			
	after a period of . . . days							
	2	3	7	28	2	3	7	28
65 percent quartz sand 30 percent clinker 5 percent calcium sulfate	6	8	10	15	34	41	48	63
Violet	5	8	11	18	35	45	60	95
Blue	9	9	19	45	49	56	93	200
Dark pink (gray-brownish pink)	15	29	50	83	82	134	242	414
Yellowish red (brick red)	15	25	54	83	80	126	231	430
Bright pink	16	26	50	80	97	144	266	437

The experimental cements are arranged according to the development of the 28-day compressive strength. As can be gathered from the table, the hydraulic components of value in the granulated blast-furnace slags are represented by the brightly glowing particles, whereas the blue and violet glowing grain fractions are scarcely of any influence on the strength development, particularly of the initial strength.

As the determination of the cement strength must still be regarded as the most reliable method of assessing the hydraulic value of granulated blast-furnace slag, the ultraviolet test suggested by Feron figures as a suitable rapid way of examination for assessing and classifying granulated blast-furnace slags. However, for quantitative indications, the determination of the percentages of the different fractions of luminescent colors of granulated slags will be required.

Such particles of granulated blast-furnace slags, separated by screens of 0.09 and 0.06 mm according to their fractions, were microscopically counted as to their fluorescence. The determined percentages by volume of the particles of granulated slags glowing in the range of pinkish red-reddish brown, being glasses, were put in comparison with the strength values of slag cements according to DIN 1164, since the vitreous content of granulated blast-furnace slag has always been considered as a coefficient of quality. As, from experience, the hydraulic value of the dark brown glowing particles of granulated slag is lower than that of the brightly glowing grains, the former were only evaluated by half of their percentage for the sum of the vitreous components. The existing interrelations are graphically shown by figure 4.

The reproduction at the left compares the development of compressive strength of the cements made of granulated blast-furnace slags with the CaO/SiO_2 ratio of the granulated slag. An evident relation between these two values does not exist.

The figure reproduced at the center shows the dependence of the strength development of cements on the percentage of red colors under exposure to ultraviolet rays. The red colors contain the luminescent fractions pink, yellowish red, and half of the dark brown. The points indicating the individual granulated blast-furnace slags are further characterized in the figure by their CaO/SiO_2 ratios.

It appears from the drawing that the red colors of granulated slags emitted under exposure to ultraviolet rays, as well as the chemical composition characterized by the CaO/SiO_2 ratio, have a special bearing on the strength development, i.e., on the hydraulic setting power of granulated slags. Assessing the granulated blast-furnace slags by one of these two factors only will not furnish a clear result. The combination of the physical factors with the chemical data, as indicated by the right-hand section of figure 4, however, gives an excellent picture of the inherent natural laws.

Thus, the hydraulic characteristics of granulated blast-furnace slags are dependent on both the chemical composition and the physical properties of the slags. Most frequently, the CaO/SiO_2 ratio is chosen as representative of the chemical composition. The indicative value of the physical properties is represented by the glass content of the granulated slags, which results from temperature, viscosity, and conditions of granulating.

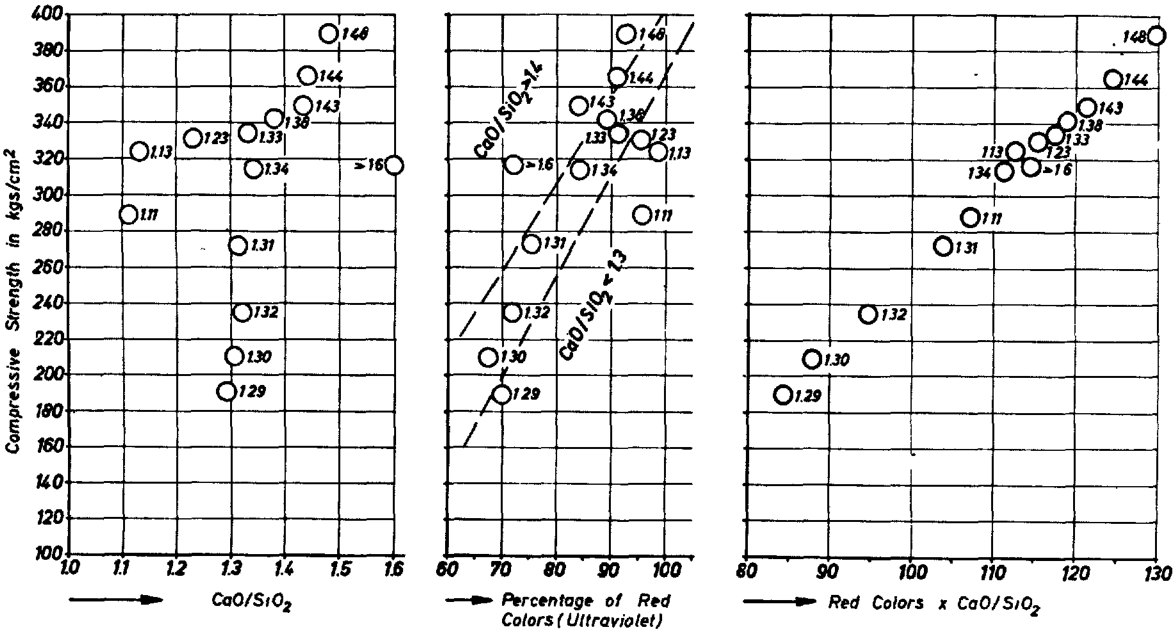


FIGURE 4. *Interrelations between* CaO/SiO₂ *ratio, fluorescence, and compressive strength.*

It can be gathered from the microscopic examination of fluorescence that the glass content should preferably be replaced by the content of red-glowing color fractions contained in the granulated slags. Contrary to the glass content determined by microscope, the microscopic analysis of the fluorescence makes it possible to identify glass portions of different hydraulic action. For granulated slags melted from composed blast-furnace ores and fluxes, the red colors found by analysis of the fluorescence give a clearer picture and may consequently be regarded as the hydraulically effective glass content of the granulated blast-furnace slags. Thus, a clear determination of the hydraulic behavior of granulated blast-furnace slags will be possible at the present state of knowledge, if both the physical conditions and the chemical composition of the granulated slags are taken into account.

Manufacture and Characteristics of Slag Cements

Slag cements are classed among mixed cements. They are made by grinding the components clinker, granulated slag, and gypsum.

Common and Separate Grinding

In the decades past, collective grinding generally prevailed due to the mixing methods not being so far advanced. It was then only the question of an interrupted or a closed cycle. General data on the advantages of one system against the other cannot be established, as either system has its own advantages.

The combination mill, as mainly used in former times, proved quite satisfactory for grinding materials of uniform grinding characteristics. It is, however, too rigid for working components of different grinding hardness and will tend to an overgrinding of the light components, which may be of disadvantage, decreasing both the mill output and the quality of cement. For such raw materials, a superiority of the separator mill is given over the combination mill.

Dealing with this question, Boerner [35] succeeded in proving that, due to its selective method of working, the separator mill will grind the denser clinker species more finely than the less dense granulated slags. In addition to a satisfactory grinding capacity, an improvement of the quality of the resulting cements can also be recorded. This grinding method further offers the advantage of a greater invulnerability against an incorrect mixing of the material to be ground or against varying operating conditions.

In the manufacture of cements consisting of several components, as is the case with slag cements, it is the question, in recent times, of first grinding the individual components separately and then mixing them intimately. The advantage of separate grinding lies in the fact that each component can be ground to the most efficient grain size required for obtaining the optimum hydraulic properties. This system appears useful for the manufacture of cements derived from components of different grinding properties as well as in such cases when, owing to its chemical composition or to its granulating conditions, the granulated slag exhibits only a low hydraulic setting power.

By research on high-magnesian slags, N. Stutterheim [36] succeeded in proving the particular value of separate grinding for the manufacture of slag cements. The resistance to grinding is stronger for granulated slags containing MgO than for the clinker used for activating.

By collectively grinding the clinker and the granulated slag in the proportion of 1:1, the concrete made of this slag cement exhibits a slower initial setting rate than a corresponding concrete prepared with portland cement. The resulting decreased development of heat renders the slag cement particularly suitable for the construction of dams. Two dams have already been built with satisfactory results in South Africa by means of such slag cement containing high-magnesian granulated slag.

His examinations of separate grinding of the components proved that, with high-magnesian granulated slag containing between 13 and 20 percent of MgO and between 38 and 28 prcent of lime, the effect of magnesia on the hydraulic setting power of the granulated slag was not as strong as that of corresponding CaO and alumina contents. Such MgO-containing granulated slags will, even at a finer grain of the slags, influence in a positive way only the final strength of cements. However, an increase of the specific surface of the clinker component from 3,200 to 5,000 cm^2/g will result in a substantial improvement of the initial strength of slag cements. The examinations carried out by Stutterheim thereby demonstrate that, with the purpose of developing most favorable strength values, a separate grinding should be preferred to a collective one for slag cements of such a composition.

The advantages of a separate grinding are further enlarged by L. Blondiau [37], who states that slag cements manufactured by separate grinding will, on long storage, normally be less sensitive to moisture than collectively ground slag cements.

Separate grinding is therefore of particular interest for the manufacture of mixed cements, the more so as, according to Horn [38], a reduction of the grinding cost may also be counted on.

Considering the rapid progress of technique, particularly in the field of homogenizing, it may be expected that the greatest attention, also from the standardization aspect, will be paid to the problem of separate grinding in the years to come. The advantages of pneumatic homogenizing have already been utilized in Germany and some other countries for the regulation of constant qualities of cement.

Composition and Characteristics of Slag Cements

The considerable progress experienced in the field of mechanical engineering, combined with an enlargement of knowledge of the factors acting on the hydraulic properties of slag cements has contributed to an increase in quality of slag cements. The special properties the granulated slag will impart to cements made thereof, as well as the strength formation, were improved. Both an increase of the percentage of granulated slag in cements and an improvement of their hydraulic properties resulted in a more favorable development of the relation between bending tensile strength and compressive strength, a reinforcing of the setting, a decrease of heat formation, and an increase of the resistance to chemicals. In contrast a similar uniform development of the strength formation depending on the content of granulated slag could not be established.

The interrelations existing in the system clinker-granulated slag-gypsum have been examined by W. Kramer [39] in the restricted field of slag cements. It was found out that a proportional relation between the percentage of granulated slag and the strength development of cements must not necessarily be given. As to the compressive strength after 7 days, the same values were obtained with low-clinker cement mixtures (about 20 to 30 percent clinker) as with high-clinker cements (clinker content exceeding 60 percent).

By tests of the latent setting power of granulated slag, R. Stumper and W. Schumacher [40] found as well, that at a constant grain size the characteristics of slag cements will not be subject to change at clinker contents varying from 30 to 70 percent. They stress that the fine grain size is of essential influence on the strength development of slag cements. They further conclude that the mechanical strength of a slag cement, the material composition of which is known, may be regarded as the sum of the individual strength values of the base components, clinker and granulated slag.

W. Kramer and F. Schroeder [41] point to the special influence exerted by the mineral composition of the clinker on the strength formation of low-clinker slag cements. They emphasize that, for an efficient development of the hydraulic properties of low-clinker slag cements, it will be necessary to adjust the composition of the clinker to that of the granulated slag.

The influence of the material structure of the clinker on the characteristics of slag cements has further been examined by L. Blondiau [42] and H. Sopora [43].

In agreement with the tests made by Stumper and Schumacher, Sopora demonstrated that the strength formation of high-clinker slag cements will be dependent on the strength of the clinker, whereas the compressive strength is almost proportional to both the C_3S content and the C_3S/C_2S ratio of the clinker. Yet, Blondiau could not prove with certainty such an unequivocal interdependence by his tests.

For converting magnesium granulated slag, the examinations carried out by N. Stutterheim and R. W. Nurse [44] are of particular interest.

They showed that at a MgO content up to 18 percent, the magnesia does not appear as a free compound, but as a silicate compound which will not affect the constancy of volume of the slag cements made thereof. The strength formation, however, experiences lower values at early tests as compared with that obtained with portland cement, because the effect of the MgO content does not match the action of CaO and Al_2O_3. The special advantages of separate grinding for the development of the initial strength of cements made of high-MgO slags have already been referred to.

Particular importance is attributed to the Al_2O_3 content of the granulated slag for the development of the initial strength of slag cement, as already known from previous tests made among others by R. Grün and F. Keil [45]. Such high-aluminous slags are further characterized by a sulfate activation sensitivity. They form the basis of sulfate-slag cements.

W. Kramer [46] reported on the technological characteristics of sulfate-slag cements, as manufactured in Germany. The point detected by him referring to the high resistance of this species of cement to aggressive water—especially sulfate water—was confirmed by L. Blondiau [47] on the grounds of practical experience. Contrary to concrete tubes made of high-CaO cements, concrete tubes manufactured of sulfate-slag cement did not experience any corrosion despite a flow for many years of waste water having a high content of SO_3 and SO_4 ions and notwithstanding the concentrating of H_2S above the waste-water level.

W. Ruopp and T. Kohlhof [48] reported an extremely favorable experience while building a dam in Germany. Concrete made of sulfate-slag cement in combination with coarse aggregates exhibits a particularly low heat generation, a small shrinkage, and high initial strength, which render it most suitable for the use of inclined-plane boarding.

B. Wentz [49], L. Blondiau [50], Th. Alix [51], and S. Haerig [52] give reports of satisfactory results obtained with slag cements in practical building, among others in the field of road and airport construction.

Some of these works particularly emphasize the good results obtained by using blast-furnace lump slag as an additive. Since blast-furnace slag acts as a supplier of CaO to the aqueous stage of the cement solution, it seems to have a favorable bearing on the strength of the concrete made thereof and of slag cement.

Hydration Processes

The process of hydration of granulated slag is by far not as clear as that of portland-cement clinker. Nevertheless, several works dealing with a restricted section, produced a series of revealing results.

At the contact with water, slag releases Ca ions. At the surface of the grains of slag, acid hydrate layers will separate, according to J. D'Ans and H. Eick [53] and also swollen, water-impermeable aluminum oxyhydrate gels as found by S. Chatterji and D. Lahiri [54]. These impermeable hydrates dissolve as soon as the CaO concentration reaches a sufficiently high level. The delivery of calcium ions by the granulated slag to the solution may then continue.

According to S. Chatterji and D. Lahiri, mixtures of calcium aluminate hydrate and hydrogarnet will form upon the hydration of grains of basic slag, whereas gehlenite hydrate will form with low-calcium slags for which the Al_2O_3/SiO_2 ratio is less than one. On the whole, the formation of hydrogarnets appears to be dependent on high-calcium and calcium-supersaturated solutions. (F. H. Dörr [55] and C. H. Schmitt [56].)

For calcium silicates, the calcium oxide concentration of the solution is decisive for the kind of product formed. If the CaO content exceeds 0.020 mole/l, formation of CSH–II (according to Taylor)$=1.7$–$2.0\,CaO{\cdot}SiO_2{\cdot}aq.$ will be the rule. At a lower concentration, CSH–I (according to Taylor)$=0.8-1.5CaO{\cdot}SiO_2{\cdot}aq.$ is in equilibrium with the solution. This CSH–I approaches tobermorite in its structure. It is the function of the lime-supplying agent to always maintain in suspension as much lime as is required for the hydration process to develop without interruption. The fact that blast-furnace slag delivers Ca ions when agitated in water, whereas it absorbs Ca ions from lime water, is thereby also explained.

In the former case, the CSH–I is in equilibrium with the aqueous phase. Delivery of Ca ions to the solution will not be sufficient to bind the silicate hydrate of higher calcium content. In the presence of lime water, however, these conditions exist, and for that reason, the CSH–II will now be in equilibrium with the aqueous phase.

As to the process occurring in the activation of blast-furnace slags by means of anhydrite and clinker, H. Kuehl [57] has supplied a plausible explanation. The products resulting by this process are ettringite, ettringite monosulfate, aluminum hydroxide, and secondary calcium silicate hydrates.

In the hydration of silicate glass, the hydrates formed will be very similar in their crystalline structure to zeolites, e.g., the three-dimensional combination of SiO_4 tetrahedrons with AlO_4 tetrahedrons. It must be considered in this connection that the zeolites represent pure hydrates, whereas the designation of "hydrates" for the other products is not quite correct. In the former case, H_2O appears as a molecule, whilst in calcium silicate hydrates, this type of bond occurs only in part. As reported by H. O'Daniel [58], it was found on the analysis of afwillite, hillebrandite, and tobermorite, that the hydroxide is not quite without a tetrahedron bond in these compounds. Upon his judgment, bridges may, in theory, thereby be given from Si to Si by both an oxygen and oxygen-hydrogen way.

These types of bonds are of particular importance to the formation of the structure of the binding agent. The silicon-oxygen groups constitute components of higher resistance to chemical influences than hydroxide bridges, which may easily be separated in the presence of concrete-affecting anions of corrosive waters. The stability depends on the frequency of incorporation of such Si-O groups.

Tests made to this effect by the Research Institute for Blast-Furnace Slags at Rheinhausen have shown that, with slag cements, the quantity of OH groups to be incorporated is dependent on the composition. At a lower clinker content, the quantity of OH ions in cement solutions is substantially reduced. This explains the satisfactory stability of cements rich in blast-furnace slag against the influence of chemically aggressive materials.

Summary

The chemical process, temperature, and viscosity are important factors in the use of slag in blast furnaces. Interrelations exist between them, rendering it possible to regulate the reactions taking place in the stack and hearth of the furnace by changing the chemical composition of the blast-furnace slag for the most favorable working conditions. The MgO and Al_2O_3 content of the slag plays an essential role, as well as the CaO/SiO_2 ratio.

The chemical process and the physical state are decisive for the development of the hydraulic properties of granulated slag. For that reason, a regulated working of the slag is of advantage not only to the metallurgical processes taking place in the blast furnace, but also to cement manufacture. The chemical activity is already determined by the slag melting. The vitreous state of granulated slag is regulated by the temperature and viscosity of the molten slag at the granulating process on the one hand, and by the cooling conditions, on the other, depending on the granulating installation.

Comparative tests of the action of the chemical composition of granulated slags on their hydraulic characteristics are only possible if the temperature of the melts prior to granulating is above the liquefying point. Differences of results may be due to non-observation of this precaution in some tests.

The works carried out during the period under report revealed the interrelations existing between the tapping temperature, the CaO/SiO_2 ratio of the blast-furnace slag, and its strength development under alkaline activation. They further indicated the influence of a higher MgO or Al_2O_3 content on the hydraulic properties of the granulated slags. Contrary to the action of MgO, an increased concentration of alumina will improve the reactivity of granulated slags. The cements made thereof will, under alkaline as well as sulfate activation, experience an increase of strength, particularly at the initial stage.

As to slag cements, there are determined areas of preferred strength development under both activating methods. The existence and the location of strength maxima strongly suggest a heterogeneous phase constitution of blast-furnace slags. The interrelations between the hydraulic properties of blast-furnace slags and the thermal equilibrium of paragenesis at the crystalline state offer a satisfactory assessing method for slags, the tapping temperature of which is higher than the melting temperature.

However, in practical operation, this condition is not always fulfilled. For that reason, special attention should be paid to the glass content of granulated slag in addition to its chemical composition. The methods examined in the period under report are explained. A preferable indicative value which is particularly suitable for practical operation, because of its ease of application, is attributed to the test under ultraviolet light. A quantitative analysis of the red colors of granulated slags as components of the hydraulic effect is obtained by means of a microscopic examination of fluorescence which, combined with the chemical data of granulated slags, is a sufficient basis for assessing the hydraulic value.

The interrelations existing in the development of the technical properties of cement—particularly of the strength values—in the field of slag cements give evidence of the prevailing characteristics of the clinker in high-clinker types. In the low-clinker slag cements, the granulated slag is decisive for the hydration process and the strength development. The action exerted by the mineral structure of clinker on the strength development of slag cements may be demonstrated. A completely clear answer to this question, however, has not been given so far.

As for slag cements rich in granulated blast-furnace slag, the latent hydraulic setting power is released only by the alkalinity imparted to the fluid cement phase. The mineral structure of the clinker appears to be of influence on the strength development of this type of cement, particularly at the initial tests. A definite clarification of the interrelations, however, could not yet be obtained during the period under report.

Based on the work under consideration, mention is made of the technical properties of slag cements—especially of low-clinker blast-furnace cements and of sulfate-slag cements—in connection with their use for various constructions.

Concluding, the processes occurring in the hydration of slag cements are dealt with in reference to the literature available. The possibility of forming links between different Si atoms by both oxygen and oxygen-hydrogen bridges, shown by H. O'Daniel, seems to merit particular attention in view of its importance for the stability of cements against attacking chemicals.

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Discussion

Renichi Kondo

The paper by W. Kramer entitled "Blast Furnace Slags and Slag Cements" is particularly interesting to me, as I have been studying mainly in this field. Allow me to bring up some questions on problems that arose during reading the paper.

On the Structure of High-Lime Glass

In his paper, he wrote that "the Al ion of basic melts may only be considered as a network-changing element at temperatures above the melting point," and consequently "the Al ion is maintained as a network-changing element of granulated slag." I understand that his term "network-changing element" coincides with the term "network modifier" generally used in glass study.

My experiments have manifested several indications, however, that the Al ion tended to take fourfold coordination, i.e., to act as a network former [1].[1]

From the determination of the glass-forming range in the CaO–Al_2O_3–SiO_2 system, the limit was found close to Zachariasen's number $n=0.29$, and MgO extended it a little. The n-value is an indication, in the expression A_mB_nO, where A is the network modifier such as Ca^{2+}, and Mg^{2+}, B is the network former such as Si^{4+} and Al^{3+}, while O is O^{2-}.

It seemed possible to substitute Al^{3+} ion for SiO_2 in the form of a tetrahedron. In the CaO–Al_2O_3 system, glass formation occurred only at around $Ca_{12}Al_{14}O_{33}$ where Al^{3+} ion could take fourfold coordination. The melilite series of solid solutions is known as the main component of blast-furnace slag, and in this mineral Al^{3+} and Mg^{2+} ions take fourfold coordination.

Moreover, the thermal behavior of high-lime glass revealed that the replacement of SiO_2 by Al_2O_3 tightened the structure [2]. Figure 1 illustrates the temperatures of the endothermic and exothermic effects in DTA measurements of samples on the join CaO·SiO_2—CaO·Al_2O_3.

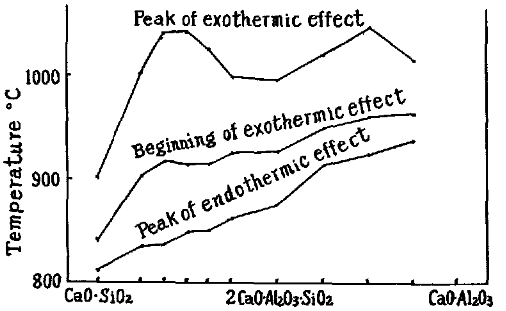

FIGURE 1. *Thermal behavior of glasses in the* CaO·SiO_2–CaO·Al_2O_3 *system.*

The effect of the chemical composition may be such that the introduction of CaO breaks the chain of covalent bonds and somewhat lowers these temperatures, while the replacement of SiO_2 by Al_2O_3 produces unsaturated O in $[AlO_4]$ tetrahedra, tightening the structure and raising these temperatures.

There is a test for evaluating cement slag by means of DTA, as mentioned by Dr. Kramer, and the basis for this procedure may partly be explained by the above behavior.

Optimum Composition of Slag for Cement

The results obtained by S. Solacolu are of special interest. He found two peaks of strength in three- or four-component systems and proposed "the quasi-crystalline structure theory" in order to explain this fact. I rather prefer to think from my experimental results mentioned below that the larger peak of strength appearing in the high-CaO region is based on the latent hydraulic property, while the smaller peak in the lower CaO region is due to the other causes, probably pozzolanic action.

The latent hydraulic properties of systematically prepared glasses were already examined in 1952 [1, 3] by us, with special regard to the effect of interaction between the composition of glassy samples and the sort of exciters. This interaction was very significant. For an example, C_2AS glass was evaluated as low in activity in cases such as portland blast-furnace cement, especially that low in clinker, and common sulfated slag cement. It was evaluated, however, as the most desirable glass to use to obtain maximum strength in lime-slag cement or lime-gypsum-slag cement containing much lime as the alkaline exciter. The higher the alumina content in slag, the greater is the hydraulic activity, but at the same time greater

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[1] Figures in brackets indicate the literature references at the end of this paper.

amounts of exciters are required. In such a condition, the exciters seem to assist the pozzolanic action of glass instead of acting as catalysts.

Evaluating Methods for Slag

The potential mineral composition of granulated blast-furnace slag may now be estimated by X-ray analysis. Such a study is in progress, mainly by X-ray diffractometer, in cooperation with the members of Committee No. 111 of the Japan Society for the Promotion of Science.

Granulated slag gives a broad halo, the diffraction angle of which changes approximately with its basicity, while with samples devitrified by heat treatment there appear sharp diffraction lines of melilite of various compositions and of other silicates.

This method seemed to be the most promising for the evaluation of slag, because of its swiftness and accuracy. The application of an X-ray spectrometer such as the Autrometer is also under consideration for the rapid chemical analysis of slags.

Grinding Process

It is suggested in Dr. Kramer's paper that "the advantage of separate grinding lies in the fact that each component can be ground to the most efficient grain size required for obtaining the optimum hydraulic properties."

I have tried the substitution of coarsely ground granulated blast-furnace slag for a part of the sand and portland cement with the purpose of improving the characteristics of mortar [4].

It was necessary that the grain size of this additional slag fall between those of sand and cement. The addition of some type of calcium sulfate was also desirable for its action of accelerating the hydration of slag.

The application of this admixture improved the characteristics of mortar such as workability, strength, chemical resistivity, drying shrinkage, efflorescence, etc., and also allowed a reduction in the quantity of cement.

From the experiments described above or made previously, the size distribution of portland blast-furnace cement is desired to be such that the portland cement clinker is in the medium size range with its distribution as narrow as possible and the slag part is divided to extend on either size.

The hydration of cement proceeds chemically much more easily with increasing fineness, but the suitable grain-size distribution tends to act not only for the development of increased strength but also for improving the workability and for decreasing the bleeding and shrinkage.

New Types of Slag Cement

The utilization of slag cements is expected to be enlarged in the near future by the improvement of their characteristics suitable for various usages.

First, I studied methods to determine the optimum content of alkaline and sulfate exciters for the development of strength in sulfated slag cement, and found that the conduction calorimeter [5] and the chemical determination of SO_3 in the extracted liquid [6] are effectively applicable for the purpose. Sulfated slag cement showed a heat-liberation peak of 1.1–1.2 cal/g-hr., having gentle slopes to both sides at about 18 hr as illustrated in figure 2, and the optimum quantity of alkaline exciter might be inferred from the minimum quantity necessary for giving a peak of this definite height and shape. At the optimum value of SO_3 content in the sulfated slag cement, the concentration of SO_3 in the extracted liquid remained approximately constant at 500–600 ppm after 3 days.

The very early 3-day strength of the low-clinker type of portland blast-furnace cement produced in Japan was only about half that of normal portland cement, but it could be improved to be of the same order by further addition of anhydrite up to 5 to 10 percent, without decreasing the long-time strength [4]. The drying shrinkage of the original cement was rather low, but the addition of anhydrite increased the expansion due to hydration by such an amount as to compensate for the drying shrinkage, yet there was no sign of a risk of excessive expansion. K. Okada found that the portland blast-furnace cement revealed a tendency toward lower creep in comparison with the several types of cement, a desirable characteristic in its application for prestressed concrete.

The specimens containing blast-furnace cement sometimes caused remarkable expansion in contact with sulfate solution, but the further addition of calcium sulfate to the original cement remarkably improved the chemical resistivity by the formation of a dense and inactive texture [7].

Sulfated slag cement is expected to be advantageous for the development of the strength of soil cement and lean mortar, both having high

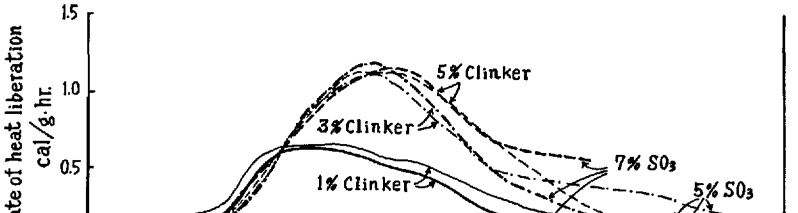

FIGURE 2. *Rate of hydration of sulfated slag cements of various compositions.*

water-cement ratios, as its hydrated products retain much combined water. The optimum content of alkaline exciter in sulfated slag cement increased along with the water-cement ratio and also with the clay content in the mixture. The expansion due to hydration, even with the expansive cement, generally declined together with the water-cement ratio. It would be very desirable if the clay in soil could take part in sustaining the strength as a part of the cement. Possibility of this action was confirmed, provided the quantity of alkaline exciter and calcium sulfate in the cement was greatly increased.

Accordingly, the addition of about 20 percent or more of calcium sulfate appears to make portland blast-furnace cement suitable for soil stabilization. The mixture of lime and calcium sulfate is one of the most desirable additives for the stabilization of clayey soil [8].

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Discussion

H.-G. Smolczyk

First we want to thank Mr. Kondo for the interest he has taken in our paper and for his most interesting contribution to the discussion. I am going to make the following comments:

The modal mineral composition of granulated blast-furnace slag has been determined at the Research Institute for Blast-Furnace Slags for many years by means of X-ray analysis. But aside from the nature and quantity of the slag minerals one obtains only the total content of the entire vitreous phase.

As this method can neither give indications about the different glasses nor about their structure in vitreous slags—and we consider this structure to be the most important measure of assessment for the latent hydraulic capacity—it has not yet been applied for determining the quality of granulated slags. The only usefulness consists in ascertaining to what extent the vitreous constituents have been replaced by more or less hydraulic inert slag minerals as melilite, wollastonite, merwinite (and stablilized dicalcium silicate, if any).

The vitreous part of a commonly used granulated blast-furnace slag is composed of various glasses with different hydraulic values. This fact was first suggested by F. Schröder [1],[1] who deduced it from the wide dispersion of the refractive indices of many samples investigated in the Research Institute for Blast-Furnace Slags at Rheinhausen, Germany.

As it is impossible to separate the various glasses by means of another method, he applied the ultraviolet test for this purpose. He gave instructions to select the different luminescent glasses and to manufacture test cements and determine their strength properties on mortar prisms 1×1×6 cm.

It was thereby possible to prove that granulated blast-furnace slags are composed of vitreous grains with different hydraulic properties.

Further, F. Schröder found that an increase in the concentration of activator particles or an incorporation of minor components (metals or oxides) may reduce or extinguish the emitted luminescence colors. Taking into consideration this kind of change in the luminescent colors he pointed out that, independently from the different melting processes, to a first approximation a number of granulated slags radiate on exposure to ultraviolet light within the same regions of wavelengths (pink, salmon-colored, reddish-brown, dark-brown, blue, and violet).

On the basis of these results he recommended the ultraviolet test suggested by R. Féron [2], J. Cleret de Langavant [3] and P. Pirotte [4], and developed the evaluating method as described by W. Kramer in the paper under discussion.

As far as can be judged from experience available, a granulated blast-furnace slag with normal chemical composition radiates intensively, in the case of a good and rapid granulation, emitting pure red colors. "Pink" is the prevailing color in granulates with Al_2O_3 content <14 to 15 percent and a minor MgO content. The "salmon-colored" portion increases with Al_2O_3 >14 to 15 percent and a greater MgO content. Slag glasses, obtained from relatively cold-blown Thomas pig-iron slags radiate less intensively and the "red" colors change to "grey-brown", "yellowish-brown", "reddish-brown" and "dark-brown". A deficient granulation changes the luminescence colors in the same way.

F. Schröder extended his investigations also on blast-furnace slags high in magnesia. They emit luminescent colors within the same regions of the visible spectrum. Due to the small bivalent

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[1] Figures in brackets indicate the literature references at the end of this paper.

Fe-like ionic-radius (MgO^{++} 0.78 A and Fe^{++} 0.83 A), the emitted colors will be weakened or extinguished in the same way by increasing percentages of MgO.

An X-ray-analytical examination of the minerals incorporated showed different proportions for the "pink" and the "salmon-colored" fractions of the luminescence colors. The ratio of orthosilicates/melilites (+ wollastonite), (i.e., nesosilicates/soro-silicates) is generally >1 for the "pink" and <1 for the "salmon-colored" fraction.

F. Schröder concluded, therefore, that the [SiO_4]-network of the "pink" luminescent glasses is extensively dispersed in isolated tetrahedrons of [SiO_4] ([AlO_4]), while in the "salmon-colored" luminescent glasses small complexes of tetrahedrons are predominant (double tetrahedrons in melilites and short chains in wollastonite), which means that a first condensation has taken place. Consequently it seems to be possible to obtain indications about the structure of the vitreous constituents of a blast-furnace slag at the moment of their quenching, by means of their luminescence.

As to the question of the type of bond of Al_2O_3 in slag glass, we should like to give the following comment: before being fixed either as a network former or as a network modifier in the crystal lattice, the Al^{3+} ion will take a balanced position between these two possibilities which is then kept frozen in the glass by the rapid cooling.

AlO_4 groups are spots of weakness in the SiO_4 network. With rising temperature the network will break off at these points, due to the different deformation of the coordination polyhedrons.

In addition to the Ca^{++} ions, the temperature acts as a network modifier too. There is no reason to connect this action with any alteration of the coordination number of the Al ions from 4 to 6. It is preferable to assume that within a definite temperature range the actuation of covalence forces can be avoided by the mutual deformation degree of the Si- and Al-coordination polyhedrons, and that in the melt both exist parallel, as isolated groups or small polyhedron complexes. Within definite temperature ranges and up to certain concentrations, one sort acts against another as a sofetening agent or reversely (as in the case of high polymeric substances).

In consequence we come to the conclusion that the luminescence is an important property of a granulated blast-furnace slag concerning the critical examination of the hydraulic capacity.

A number of factors are co-acting to form this property: temperature of the slag, chemical composition, viscosity, and granulation conditions. Their different influence can be demonstrated, and aside from this, the luminescence enables us to obtain information about the structure of the slag glass, which is very important for the latent hydraulic capacity.

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Discussion

G. Malquori, R. Sersale, and P. Giordano-Orsini

While investigating hydration products of basic granulated slags in the presence of activators, we have treated slags with lime solutions and have systematically followed the morphological evolution of hydration products by means of optical and electronic observations. It is impossible to report here in full the results of our researches, but they have already been published in Italian journals [1].[1] We should like, however, to show here some of the micrographs that appear to be of interest.

Table 1 shows the chemical composition of the slags we have employed.

TABLE 1. *Analyses of slags*

Chemical composition (percent of substance dried at 105 °C)

Slags	SiO_2	Al_2O_3 $+TiO_2$	CaO	MgO	FeO	MnO	S (from sulfides)	Na_2O	K_2O
No. 1	34.95	10.53	46.27	4.07	0.45	1.97	1.68	0.46	0.44
No. 2	35.27	10.86	42.81	4.63	.60	3.47	1.61	.70	.50
No. 3 [a]	34.05	18.27	42.69	4.99	------	------	---------	------	------

[a] Synthetic slag sample prepared in laboratory.

Electron micrograph 1 shows slag sample No. 1 (table 1) after treatment with initially saturated lime solution. The observation was made after shaking slag and lime solution for 24 hr. Feltlike masses covering the surface of an original grain and some aggregates of lime crystals showing rhombic section, lying at the boundaries of other grains, are to be seen. The above mentioned feltlike masses are probably to be identified with tobermorite.

As has already been stated [2], at low temperatures (below 100 °C), tobermorite has been recognized in two crystal shapes: large crystal sheets and fibrous or needlelike crystals. In saturated lime solutions—which are in general used in our experiments—fibrous or needlelike growth seems to be promoted.

The role of ettringite in the rapid growth of needlelike crystals has not yet been entirely clarified even for portland cement [3], because of the abundance of these structures in comparison with the normal content of SO_3, amounting to about 2 percent for commercial portland cements.

With regard to blast-furnace slags hydrated in the presence of saturated lime solution, it is to be noted that we have found needlelike crystals,

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[1] Figures in brackets refer to the literature references at the end of this paper.

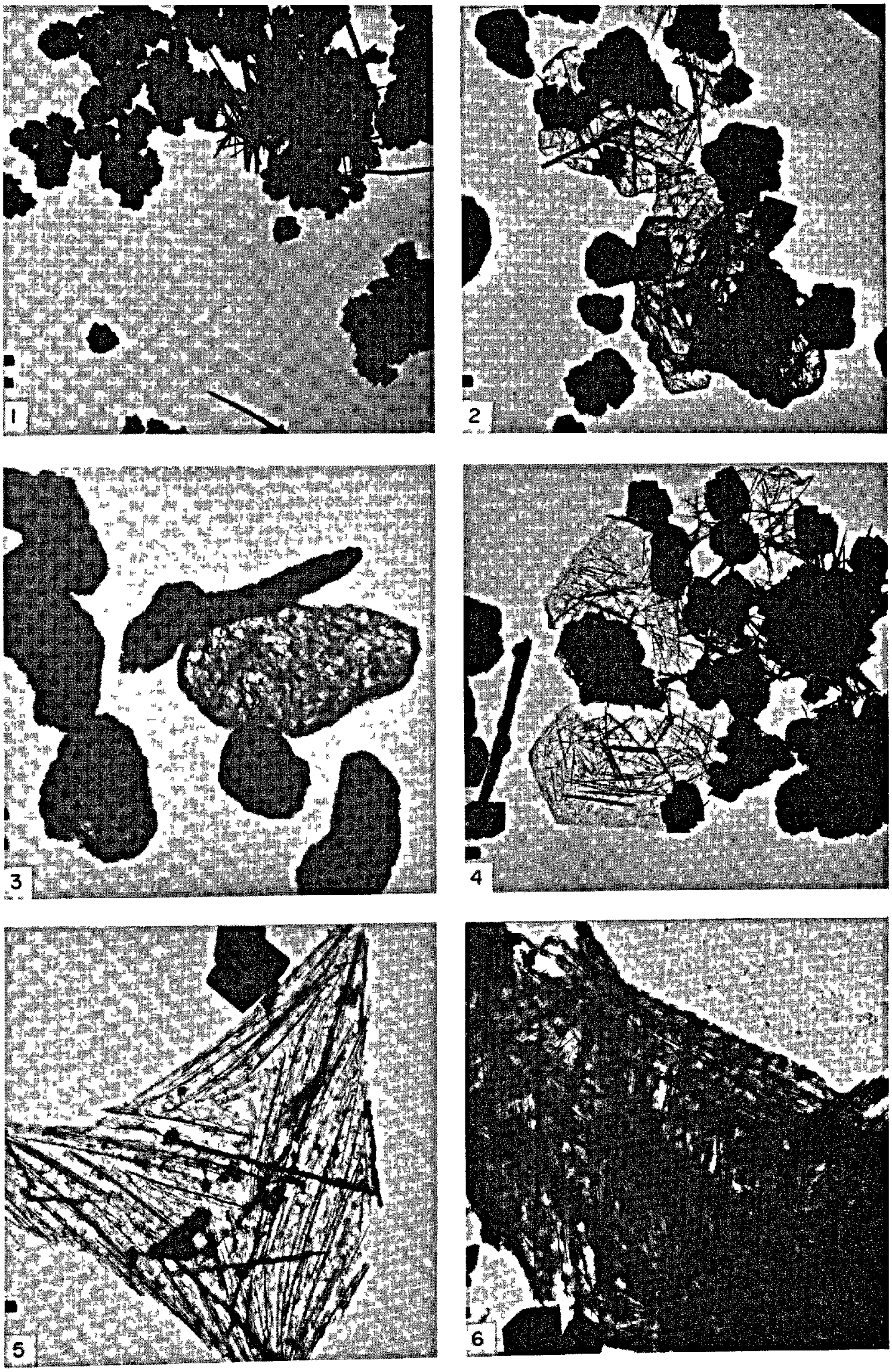

FIGURE 1. *Electron micrographs showing the morphological evolution of hydration products.*

t = time elapsed between sample preparation and the microscopic observation.
T = CaO content of contact solution while preparing sample (mM/liter).

(1) t=24 hr ; T=~17	(4) t=24 hr , T=~21
(2) t= 5 days, T=~12	(5) t= 5 days, T=~21
(3) t=60 days; T=~ 6	(6) t=60 days, T=~16

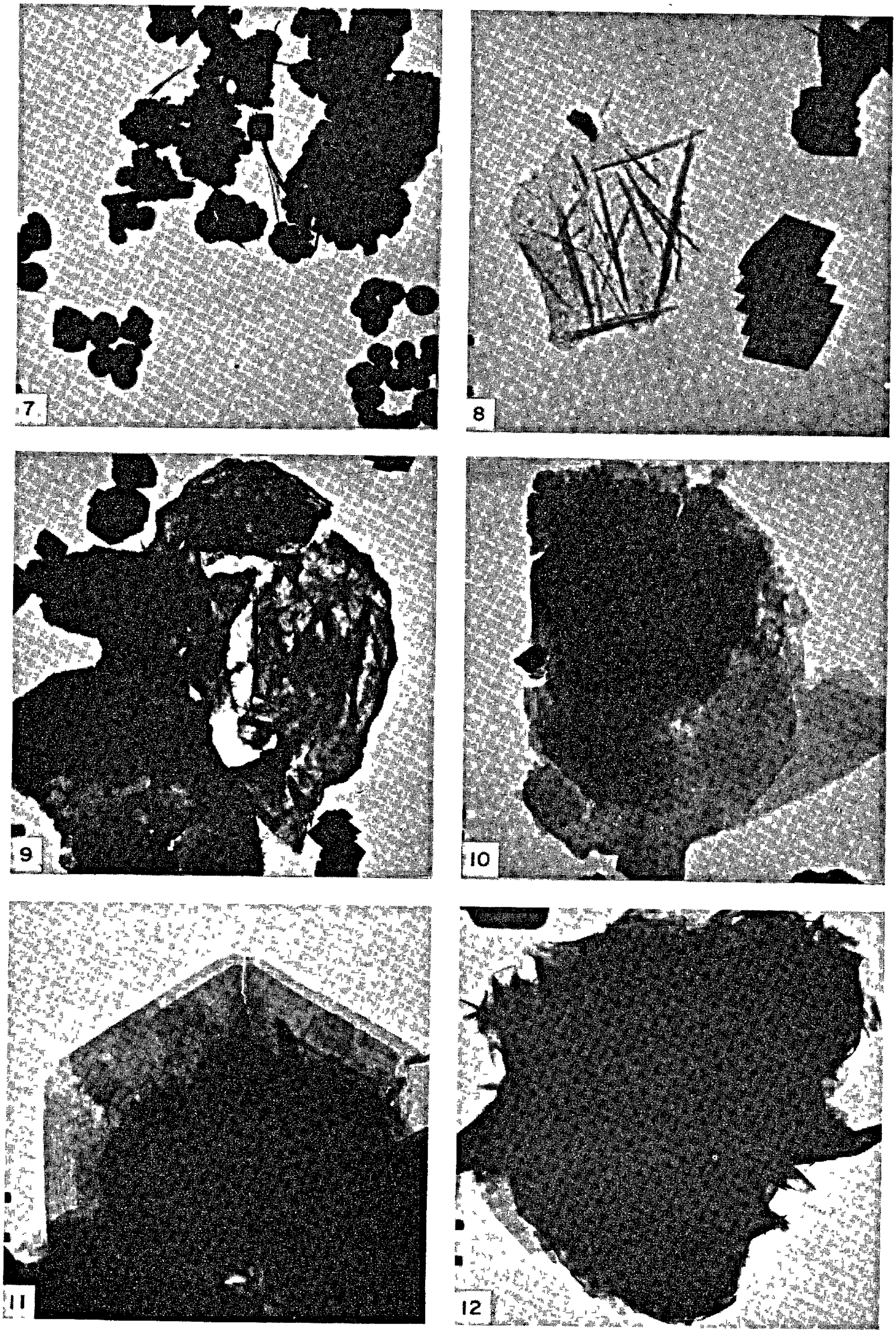

FIGURE 1. *Electron micrographs showing the morphological evolution of hydration products*—Continued

t=time elapsed between sample preparation and the microscopic observation.
T=CaO content of contact solution while preparing sample (mM/liter).

(7) t=24 hr ; T=~21
(8) t= 5 days; T=~19
(9) t=60 days; T=~16
(10) t=24 hr ; T=~21
(11) t= 5 days; T=~19
(12) t=60 days; T=~16

covering the surface of glassy slag grains, for sulfur-free slags as well. This very interesting question will be thoroughly investigated in a following paper.

Electron micrograph 2 shows, after five days' shaking, the same feltlike masses we have observed in micrograph 1, lying on not yet well-contoured thin hexagonal plates.

Micrograph 3, after 60 days, shows only a thickening of the structures in micrograph 2. It is to be noted that the evolution from picture 2 to 3 occurs in an unsaturated lime solution.

Micrographs 4, 5, and 6 refer to the same slag sample No. 1 (table 1). The initial lime-slag ratio is higher (10 percent) than it was in the former case (3.3 percent). Observations were made, as usual, after 24 hr, 5 days, and 60 days.

Micrograph 4 shows the same feltlike masses (tobermorite) as micrograph 2, lying, this time too, on thin, well-contoured hexagonal plates. Micrograph 5 clearly shows the above mentioned feltlike masses (micrographs 2 and 4).

Micrograph 6 shows the thickening of the structures of 5. The evolution from micrograph 4 to 6 occurs this time in a constantly saturated lime solution.

Micrographs 7, 8, and 9 refer to slag sample No. 2 (table 1), after treatment with lime solution. The initial lime-slag ratio equals 6.6 percent. Micrographs have been made, as usual, after 24 hr, 5 days, and 60 days shaking.

Micrograph 7 shows the beginning of formation of feltlike masses (but not so advanced as for sample 1 under the same experimental conditions (micrograph 1)) and the presence, too, of $Ca(OH)_2$ either as spherulites or as crystals showing rhombic section. Micrograph 8 shows tobermorite that, initially a feltlike mass, exhibits now a needlelike structure. This time, too, hexagonal plates of calcium aluminate hydrates support these needles. Lime crystals, as well as residual feltlike masses are still present. Micrograph 9 shows the thickening of the structure in micrograph 8. Hexagonally contoured plates supporting needles are now well shaped. The evolution from micrograph 8 to 9 occurs partly in a saturated lime solution and partly in a solution below saturation. Small lime crystals, as micrograph 9 shows, are to be attributed to lime deposit during specimen preparation.

Micrographs 10, 11, and 12 refer to sample 3 (table 1) after treatment with lime solution. The initial lime-slag ratio equals 6.6 percent. Observations were made after 24 hr, 5 days, and 38 days.

Micrograph 10 shows a semi-transparent contour, lying at the boundaries of a slag grain, which is to be identified with hexagonal calcium aluminate hydrates. Micrograph 11 shows very well-grown ordinary hexagonal plates.

Micrograph 12 shows feltlike masses, which are to be identified with tobermorite, and hexagonal plates of calcium aluminate hydrates. The last observation refers to bottom materials in contact with no longer saturated lime solution. The abundance of hexagonal aluminate plates is to be attributed to the high alumina content of this slag sample (No. 3, table 1).

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Discussion

H. Williams and S. K. Chopra

Indian slags are characterized by low CaO/SiO_2 and SiO_2/Al_2O_3 ratios and as such are not considered good for making supersulfated or slag-sulfate cement (references 26 and 27 of the above paper). While determining the composition of the glass of maximum strength, Tanaka (reference 27) and his co-workers kept the mixing ratio between slag and anhydrite constant at 85 to 15. Many other workers have employed more or less similar ratios for the activation of synthetic glasses and industrial slags. However, the data given below show that by carefully working out the optimum conditions of activation in the light of observations made by Keil and Locher (reference 26) and by Blondiau [1][1] regarding the quantity and solubility of $CaSO_4$ in relation to the contents of lime and soluble alumina, strengths can be raised substantially so as to make the slags acceptable for industrial exploitation.

The slag found most suitable for making portland blast-furnace cement in an earlier investigation [2], and having the ratios of CaO/SiO_2 and SiO_2/Al_2O_3 as 1.11 and 1.47, respectively, also proved best for sulfate activation. The trial cements prepared by mixing slag, burnt gypsum (optimum temperature 750 °C) and clinker in the proportions usually employed in the manufacture of supersulfated cement did not show good strength development in 1-in. cubes prepared from the cement pastes of normal consistency. The determination [3] of unreacted $CaSO_4$ in the set cement showed practically complete depletion of $CaSO_4$ in three days time. In view of these results and the high alumina content (22.6 percent) of the slag, the effect of increased amounts of $CaSO_4$ on the development of strengths was studied, and the results are shown in figure 1. There was a general increase in strengths and the optimum amount of $CaSO_4$ appeared to be 20 to 25 percent. The trial mix K55 having proportions 70/25/5 was considered best for

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[1] Figures in brackets indicate the literature references at the end of this paper.

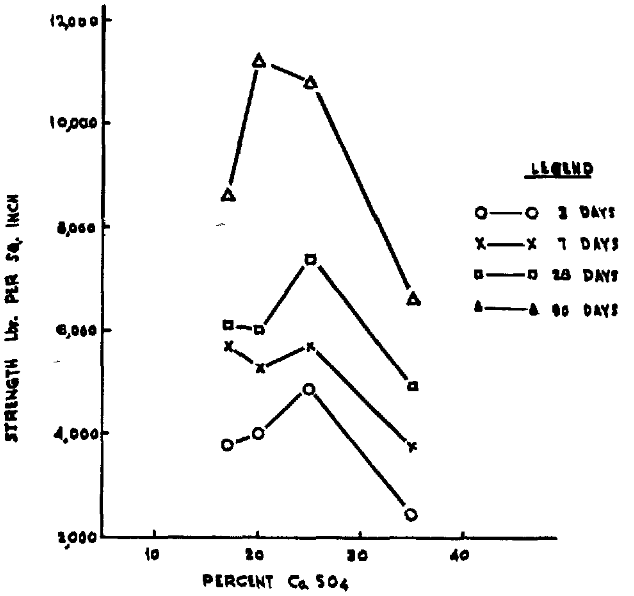

FIGURE 1. *Effect of calcium sulfate content on the development of strength.*

making supersulfated cement (the optimum amount of clinker was found to be 5 percent). The physical properties of the cement (4,000 cm^2/g) compare favorably with some of the cements being produced elsewhere [4]. For example, the strengths of 1:3 mortar cubes (vibrated) were found to be 2,400, 3,500, 6,330, and 11,600 lb/in.^{2} at 3, 7, 28, and 90 days, respectively. A 1:2:4 concrete with W/C ratio of 0.6 showed a strength of 6,500 lb./in.^{2} at 28 days. Grinding the cement finer is likely to result in still better early strengths. There was practically no expansion in 1:3 mortar bars on storage in water for 9 months, and examination of the set cement products by chemical methods, DTA, and X-ray spectrometer analysis (2 θ from 5 to 50 °) have shown that there is no likelihood of any delayed expansion.

That the optimum amount of activator is 20 to 25 percent is also borne out by comparing the hydration products of the cement K55 with those of the cement K44 containing an insufficient quantity of $CaSO_4$ (i.e., 17 percent.)

DTA of the cement K55 showed the formation of high sulfate form of sulfoaluminate (ettringite) at all ages from 3 to 90 days. The magnitude of the endothermic peak at 160 °C showed that ettringite was present in the largest quantity at 28 days. Very good agreement of the X-ray powder data of the 28-day-old sample (table 1a) with the published data [5], indicates that the composition of the cementitious phase is almost $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$. At all other ages the ettringite phase seems to have a lower SO_3/Al_2O_3 ratio. The longest spacing at these ages occurs at 9.71 A, and according to Midgley and Rosaman (paper III–S2, this symposium) the phase has an SO_3/Al_2O_3 ratio of more than 2.58. Since complete X-ray data is not available, it is difficult to discount the existence of $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot aq.$ in solid solution with $3CaO \cdot Al_2O_3 \cdot 3Ca(OH)_2 \cdot aq.$, which has been reported by Nurse [6] as the cementing solid in set pastes of supersulfated cement prepared from slags of relatively low CaO/SiO_2 ratios. The lines at 5.02A, 2.86A, 2.55A and 1.82A in the 7-day-old sample probably show the presence of dicalcium aluminate hydrate.

The differential thermal analysis of the set trial cement K44 showed only one endothermic peak at 150 °C both at 3 and 7 days. A very large endothermic peak at 170 °C and a small inflection at 240 °C at 28 days show [7] the presence of cementing solids of the ettringite type having a molar ratio of $CaSO_4/Al_2O_3$ of about 2.5. The X-ray data (table 1b) shows that this phase was also present at 90 days, in addition to the low form of sulfoaluminate which was also evident from a second endothermic peak at 195 °C in a 90-day-old sample. The presence of Strätling's compound, or gehlenite hydrate, in the 7-day-old sample is also indicated by the appearance of the lines at 4.20A, 2.65A, 2.52A, and 2.42A.

The composition of the ettringite phase seems to be related to the quantity of $CaSO_4$ used (table 1c). The development of strength in the trial cements could be related qualitatively to the quantity of ettringite formed up to 28 days only, because afterwards, while there was a great increase in strength, there was no increase in the quantity of ettringite. Obviously the gain in strength at later ages is mostly due to other phases such as calcium silicate hydrate and alumina gel which may be present in amorphous or poorly crystalline state. D'Ans and Eick [8] have suggested that at a later stage in hydration some of the ettringite decomposes again to form the low sulfate compound. However, Lea [9] doubts if a change between two compounds of such different molecular volume could occur without some marked effect on the strength of the set cement. Perhaps this explains why the gain in strength from 28 to 90 days for the cement K44 was half of that for the cement K55.

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TABLE 1. *X-ray diffraction data*

a

Cement K55 (25 percent $CaSO_4$)								Cement K54 (20 percent $CaSO_4$)	
3 days		7 days		28 days		90 days		90 days	
d(A)	I/I_0	*d*(A)	I/I_0	*d*(A)	I/I_0	*d*(A)	I/I_0	*d*(A)	I/I_0
9.71	VVS	9.71	VVS	9.82	VWW	9.71	VVS	9.60	VVS
5.60	W	5.60	MS	5.68	VWW	5.60	WM	5.60	WM
4.69	VWW	5.02	VW	4.67	VVW	4.69	VVW	4.64	VVW
3.88	VWW	4.69	VW	3.91	VW	3.88	VWW	3.85	VW
3.49	W	3.88	WM	3.52	VW	3.49	VW	3.48	VW
3.34	VW	3.49	W	2.79	VWW	3.34	WM	3.34	VWW
3.02	VW	3.34	W	2.33	VVS	3.02	VW	2.77	VW
2.55	VW	3.02	VWW	2.20	VVW	2.55	VW	2.55	VWW
2.20	VW	2.86	VWW	2.02	S	2.20	VVW	2.20	VW
		2.55	VW			1.82	S		
		2.28	VVW						
		2.20	VWW						
		1.82	MS						

b

Cement K 44
(17 percent $CaSO_4$)

3 days		7 days		28 days		90 days	
d(A)	I/I_0	*d*(A)	I/I_0	*d*(A)	I/I_0	*d*(A)	I/I_0
12.1	MS	9.5	VVS	9.50	VVS	9.50	VVS
9.5	VVS	5.50	WM	5.60	VWW	8.85	VVW
5.50	W	4.62	VW	4.69	VW	5.60	VWW
4.65	VW	4.20	M	3.87	S	4.69	W
3.85	WM	3.85	WM	3.35	VVW	4.43	WW
3.45	VWW	3.27	VWW	2.57	VW	3.87	VW
3.32	WM	2.65	VVW	2.20	VW	3.35	VWW
2.54	W	2.52	VVW			2.84	VW
2.15	VWW	2.42	VVW			2.70	VW
		2.28	VVW			2.57	VWW
						2.29	VVW
						2.20	VW

c

$CaSO_4$	Longest spacing at 90 days
Percent	*d*(A)
17	9.50
20	9.60
25	9.71
35	9.60

[a] Al used as an internal standard.
[b] Intensities in relation to the strongest line of Al at 2.33A.

Discussion

J. H. Welch

There are two points in Dr. Kramer's paper on which I should like to comment. The first concerns the importance of the physical state of the slag after granulation in its influence on latent hydraulicity. However efficient the granulation process adopted, a slag which is tapped at a temperature below the liquidus will already be partly crystalline and will tend to crystallize further during granulation. Providing a chemical analysis of the slag is available, a fairly reliable estimate of the liquidus temperature can be interpolated from the data of Osborn et al [16],[1] and if the slag temperature lies above the liquidus it is theoretically possible to obtain 100 percent efficiency of granulation.

The point I want to emphasize is that some years ago I demonstrated the feasibility of very rapid slag liquidus determinations by direct high-temperature microscopy, and this led to the comprehensive investigation by Baldwin [21], who used high-temperature microscopy to study slag behavior. Dr. Baldwin and I made direct comparisons of liquidus determinations on several slags both by high-temperature microscopy and standard quenching procedures, and we obtained agreement which was generally better than 5 °C. The technique is such that the liquidus of an actual slag composition can be determined without resort to chemical analysis and the use of phase diagrams within a matter of minutes. Moreover, Baldwin was able to determine the relative ease of granulation of different slag compositions and the potential crystal growth during granulation of slags which were not fully molten. He was also able to assess quantitatively the viscosity of the slags at various temperatures by direct observation of crystal movement within the melt. The viscosity-temperature relation is important in determining the probable efficiency of granulation of a particular slag composition.

The second point I wish to raise concerns the use of the factor CaO/SiO_2 ratio multiplied by the number of red-fluorescing slag particles as determined under the microscope, which has been used as an index of slag hydraulicity. Our experience at the Building Research Station of fluorescence measurements as a criterion of slag performance is that slags produced by one particular furnace or process may be usefully compared in this way, but that this does not apply to slags of varying origin. I would like to know, therefore, whether Dr. Kramer has found that the CaO/SiO_2 ratio combined with a fluorescence count can be used as a reliable index of slag behavior whatever the origin of the slag.

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[1] Figures in brackets indicate the literature references at the end of Kramer's paper, pp. 972–973.

Paper VIII-3. Portland-Pozzolan Cement*

Giovanni Malquori

Synopsis

The writer presents a general outline of the nature and trend of the results obtained by the researches that in the space of the last ten years have been carried out on pozzolanic materials and on their employment when mixed with hydrated lime or with portland cement.

In the first part, attention is paid to the differences between the peculiar constitutional characteristics of the various materials showing pozzolanic activity, and it is pointed out that in the case of the true pozzolanas the ability of their silica and alumina contents to combine with lime is principally related to the structural instability of the volcanic glass; on the other hand, for compact or semicompact volcanic tuffs—which have resulted from a transformation (autometamorphism), followed by cementation, of the incoherent products (pozzolanas) by reason of hydrothermal or pneumatolitic reactions—the above mentioned ability is to be attributed to the reactivity of the zeolitic structure.

The nature of the pozzolanic activity is next examined. The different investigational methods—differential thermal analysis, optical examination, and X-ray diffraction—when applied to investigation of the nature of the cementing compounds that result from the reaction between calcium hydroxide and the active part of the pozzolana, clearly show that these compounds are of the same type as those derived from portland-cement clinker hydration.

The determination of the activity of pozzolanas is discussed from two standpoints: the strength of mortars and concretes obtained by using as the binder the mixture hydrated lime-pozzolana or pozzolanic cement, and the ability of the pozzolanic materials to combine with lime.

Factors that increase the general resistance to corrosion are the absence of free mobile calcium hydroxide in the hardened cement, the particular texture of the latter resulting from pseudo-gelatinous bodies formed during the hardening, and their waterproofing and protective action towards more vulnerable compounds such as calcium hydroxide and aluminates.

Brief mention is made of the addition of pozzolanic materials in order to prevent expansion and cracking due to reaction between alkalies of the cement and aggregates, the heat of hydration of pozzolanic cements and its evaluation, the attempts that have been made to activate pozzolanic properties, and finally the role of pozzolanic cements in actual construction.

Résumé

L'auteur esquisse en général la nature et la tendance des résultats obtenus par les recherches qui, au cours des dix dernières années, ont été poursuivies sur les matériaux pouzzolaniques et sur leur utilisation quand on les mélange à la chaux hydratée ou au ciment portland.

Dans la première partie l'attention est attirée sur les différences entre les caractéristiques de constitution particulières des divers matériaux qui présentent une activité pouzzolanique. Il est signalé que dans le cas de pouzzolanes véritables l'aptitude de leur teneur en silice et en alumine à se combiner à la chaux est liée principalement à l'instabilité de structure du verre volcanique. D'autre part, pour les tufs volcaniques compactes ou semi-compactes—résultat d'une transformation (autométamorphisme), suivie d'une cémentation, des produits incohérents (pouzzolanes) à cause de réactions hydrothermiques ou pneumatolithiques—l'aptitude susdite doit être attribuée à la réactivité de la structure zéolitique.

La nature de l'activité pouzzolanique est ensuite examinée. Les différentes méthodes d'investigation: analyse thermique différentielle, examen optique et diffraction des rayons X, appliquées à la recherche sur la nature des composés liants qui proviennent de la réaction entre l'hydroxyde de calcium et la partie active de la pouzzolane, indiquent nettement que ces composés sont du même genre que ceux qui dérivent de l'hydratation du clinker de ciment portland.

La détermination de l'activité des pouzzolanes est discutée de deux points de vue: la résistance des mortiers et bétons obtenus en utilisant comme liant le mélange: chaux hydratée et pouzzolane ou ciment pouzzolanique, et l'aptitude des matériaux pouzzolaniques à se combiner à la chaux.

Les facteurs qui augmentent la résistance à la corrosion générale sont l'absence d'hydroxyde de calcium libre mobile dans le ciment durci, la texture particulière de ce dernier résultant de corps pseudo-gélatineux formés pendant la prise, et leur étanchéité à l'eau et leur action protectrice envers des composés plus vulnérables tels que l'hydroxyde de calcium et les aluminates.

On mentionne rapidement l'addition de matériaux pouzzolaniques pour empêcher l'expansion et la fissuration dues à la réaction entre les alcalis du ciment et des aggrégats, la chaleur d'hydratation des ciments pouzzolaniques et son évaluation, les efforts qui ont été poursuivis pour activer les propriétés pouzzolaniques, et finalement le rôle des ciments pouzzolaniques dans les constructions actuelles.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Institute of Industrial Chemistry, University of Naples, Italy.

Zusammenfassung

Der Verfasser gibt eine allgemeine Übersicht über die Natur und die Tendenz der Ergebnisse, die während den letzten zehn Jahren in der Pozzolanforschung gezeitigt worden sind, und er spricht auch über die Ergebnisse, die man mit Mischungen der Pozzolane mit gelöschtem Kalk oder Portlandzement erhalten hat.

Im ersten Teil werden die Verschiedenheiten zwischen den speziellen Struktureigentümlichkeiten der verschiedenen Materialien, die ein pozzolanartiges Verhalten zeigen, angedeutet, und es wird darauf hingewiesen, dass im Falle wirklicher Pozzolane die Fähigkeit der darin enthaltenden Silizium- und Aluminiumoxyde, sich mit Kalk zu verbinden, hauptsächlich durch die strukturelle Unbeständigkeit des vulkanischen Glases hervorgerufen wird. Im Gegenteil dazu muss bei den kompakten oder halbkompakten Tuffsteinen, welche durch eine Transformation (eine sogenannte Autometamorphose), mit folgender Zementation aus dem zusammenhangslosen Material (den Pozzolanen) durch hydrothermale oder pneumatolithische Reaktionen entstanden sind, die vorerwähnte Eigenschaft durch die Reaktionsfähigkeit der Zeolithstruktur hervorgerufen werden.

Im zweiten Teil wird die Natur des Pozzolanverhaltens besprochen. Die verschiedenen Methoden, wie die differentielle Thermalanalyse, die optische Betrachtung und das Röntgenbeugungsdiagramm, haben für die zementierenden Bestandteile, die durch eine Reaktion zwischen Kalziumhydroxyd und dem aktiven Teil des Pozzolans hervorgerufen werden, bewiesen, dass man es mit denselben Verbindungen zu tun hat, die auch bei der Hydratation der Portlandzementklinker entstehen.

Die Bestimmung der Pozzolanaktivität wird unter zwei Gesichtspunkten behandelt: Die Festigkeit der Mörtel und des Betons, die man erhält, wenn das Bindungsmittel gelöschter Kalk mit Pozzolan oder Pozzolanzement ist, ist ein Gesichtspunkt, und die Fähigkeit der Pozzolanmaterialien, sich mit Kalk zu verbinden, ist der andere.

Faktoren, die die allgemeine Korrosionswiderstandsfähigkeit erhöhen werden danach besprochen, namentlich, die Abwesenheit freien, beweglichen Kalziumhydroxyds im ausgehärteten Zement, die Spezialtextur eines solchen Zements, welche auf pseudogelatinöse Verbindungen zurückzuführen ist, die während des Härtens sich gebildet haben, auch ihre Wasserfestigkeit und ihr Schutz gegen den Angriff durch Kalziumhydroxyd und Aluminate.

Danach wird die Beimischung der Pozzolanmaterialien die die Ausdehnung und die Rissbildung verhindern, die als Folge der Reaktion zwischen Alkalien des Zements und der Aggregate entstehen, kurz besprochen, sowie die Erhitzung bei der Hydratation (Hydratationswärme) der Pozzolanzemente und ihre Auswertung, die Versuche, die gemacht worden sind, um Pozzolaneigenschaften zu aktivieren, und zum Schlusse die Rolle, die die Pozzolanzemente in Konstruktionsarbeiten spielen.

Introduction

The subject of this report was thoroughly treated by F. M. Lea at the Symposium on the Chemistry of Cements, held at Stockholm in 1938 [1].[1] Later, the subject of pozzolana and pozzolanic cements was widely reviewed and discussed at the Symposium on the Use of Pozzolanic Materials in Mortars and Concretes, held at San Francisco in 1949 [2], and subsequently at the Meeting for the Study and Application of Pozzolanas, organized in Rome in 1953 [3].

Moreover, a special chapter was given over to pozzolanas and pozzolanic cements in the latest edition of Lea and Desch's work, "The Chemistry of Cement and Concrete" [4]. The same subjects were also referred to in the second edition of "The Chemistry of Portland Cement" by R. H. Bogue [5].

Other publications, the original texts of which we have been unable to obtain, have appeared in recent years in the Soviet Union and in Japan, in both of which countries it has long been the practice to mix pozzolanic materials with portland cement. Indeed, the Japanese were among the first to use pozzolanic materials added to portland cement in preparing concrete for marine works, and as early as about 1930 the production of cements in the Soviet Union made increasingly large use of materials having "pozzolanic activity" when mixed with portland cement.

However, several of the problems, on which is based the interpretation of the behavior of the pozzolanic addition in cements of this type, have not yet been fully and satisfactorily cleared up, nor has decisive progress been made in this direction.

The opinion on the chemistry of pozzolanic action as a whole that R. H. Bogue expressed in his treatise is therefore still valid today: "The chemistry of pozzolanas is still not solved. . . . And only when the chemical action is completely understood will it be possible to design a 'pozzolan' of ideal composition for any particular purpose."

In the following pages we propose coordinating and setting forth briefly the data that have been obtained in recent years, to supplement those contained in the literature referred to above.

Pozzolanic Materials

The definition given by F. M. Lea [4] is quite unimpeachable: "Pozzolanas are usually defined as materials which will combine with lime at ordinary temperature, in the presence of water, to form stable insoluble compounds possessing cementing properties."

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[1] Figures in brackets indicate the literature references at the end of this paper.

The same may be said of that given by the ASTM Standard on Cement, Designation C340–58 T, which states: "Pozzolan shall be a siliceous or siliceous aluminous material, which in itself possesses little or no cementitious value, but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties."

Neither of the foregoing definitions makes reference to the type of material but only to its ability to combine with calcium hydroxide, in the presence of water, to form compounds possessing cementitious properties.

Pozzolanic activity therefore depends on the fixative property of the material in respect of calcium hydroxide and its ability to harden under water as a consequence of the changes the above reaction produces. These characteristics may be separate one from the other, and it may happen that while large quantities of lime are fixed by the material having pozzolanic activity the accompanying cementitious properties are quite moderate.

Materials having pozzolanic activity are therefore defined, in respect of their use, as cementitious materials, quite apart from the interpretation of the chemical and chemico-physical phenomena which are responsible for the hardening of the hydraulic binder.

There are many materials that possess this reactivity with calcium hydroxide (pozzolanic activity) and differ greatly from one another in their origin, composition, mineralogical constitution, etc. First of all, they can be divided into natural and artificial materials.

Natural Materials having Pozzolanic Activity

First place is due, for historical reasons and for their wide, well-known range of application, to the Italian volcanic pozzolanas from the Phlegraean (Pozzuoli) and the Latium (Rome) regions.

These true natural pozzolans are pyroclastic, incoherent materials that originated from prevailingly explosive types of volcanic eruption. The particles of pulverized magma entrained by the gases thus went through a strong quenching process which made them rich in glassy substance or in any case left them in a state of special instability, hence of special reactivity, also, to attack by calcium hydroxide.

The instability of volcanic glass made it vulnerable both to endogenous actions (for instance, zeolitization and cementation) and to exogenous actions (for instance, argillization).

It should be remarked that while zeolitization generally enhances pozzolanic activity, any alteration of the original volcanic glass towards the clay minerals is usually unfavorable, and indeed, diminishes this property [6, 7, 8, 9].

The intrinsic reactivity of volcanic glass in true pozzolanas is enhanced by the peculiar physical conformation of this material, because during the rapid cooling the gases originally dissolved in the liquid magma are quickly released, generating a system of small "ducts" in the solidified material and considerably increasing its surface for attack [6, 8].

The chemical composition of these pozzolanas depends on the magma from which they come. For example, the typical Phlegraean pozzolanas belong to the alkalitrachytic type, more acid, less reactive and hence less altered than the Roman pozzolanas which are instead of the leucititic type, i.e., more basic.

B. Tavasci [10, 11] examined several samples of Latian and Phlegraean pozzolanas under the microscope, observing that while the Segni pozzolana—which belongs to the Latian leucititic type—consists essentially of leucite dendrites and some parts of augite, cemented by a groundmass of considerably altered glass, the Bacoli pozzolana (Phlegraean) is, instead, made essentially of bubbled glass, with a few inclusions of sanidine crystals, and still more seldom of plagioclases and pyroxenes [12].

Tavasci [10] appears, moreover, to have noted the presence of zeolites in the Latian pozzolana, that is, of the crystalline formations that can be classified as of the chabazite and phillipsite group.

Nothing of this kind has been observed by other experimentalists in the Phlegraean pozzolanas [13] which, as already stated, appear far less altered than the Latian ones.

Besides the Latian and Phlegraean pozzolanas mentioned above, other volcanic regions of the Italian peninsula supply natural pozzolanas. No true pozzolanas are found in the volcanic system of Mount Etna (Catania), but only volcanic ashes, incoherent, mainly crystalline, and very little altered, owing to the lack of prevailingly explosive eruptions. The volcanic ashes thrown out by Vesuvius subsequent to the explosive type of eruption described by Pliny the Younger are also mostly crystalline (leucotephritic), hence with little or no pozzolanic activity.

Ashes and lavas of identical mineralogical composition, originating from alkalitrachytic, leucititic, leucotephritic and haüynophyric types of magma, forced to solidify as a glass by melting and subsequent quenching, acquire pozzolanic properties.

The glass obtained is highly reactive towards calcium hydroxide solution.

Volcanic, pyroclastic, incoherent materials with pozzolanic properties have been reported in various parts of the world, and some of them, like Santorin Earth (Grecian isle of Santorin), have been widely used for practical purposes.

In conclusion it can be stated that the action of true natural pozzolanas is determined by the type of original magma, and principally the origin and history of the pyroclastic material, on which depends the quantity of glassy fraction and its extent of alteration. Metamorphic or diagenetic alterations may have a favorable or unfavorable influence on the material's pozzolanic activity.

Compact volcanic tuffs, which are used in the pulverized state as pozzolanic material, are quite different from the true natural pozzolanas described above. They originate from the same pyroclastic materials but involve a transformation process.

The best known example is the Rhenish "trass," obtained by grinding the very soft tufaceous rock from the Eifel quarries, and especially from those in the Nette and Brohl valleys, close to Neuwied and Andernach.

The original tufaceous rock is found together with an incoherent, mainly pumice-like material, likewise of volcanic origin. An intervening stratum of weakly coherent material divides the compact tuff from the incoherent pyroclastic material mentioned above.

The beds therefore lie in a very similar way to those of Neapolitan yellow tuff [9] which is constitutionally similar to the Rhenish volcanic tuff [14, 15]. Both are of the alkalitrachytic type, with almost the same chemical composition, and thin sections viewed under the microscope present an apparently isotropic groundmass, incorporating fragments of pumices and crystals of the minerals found in the original pyroclastic materials: sanidine, augite, hornblende, biotite, etc.

The cementing groundmass appears markedly altered; it is essentially zeolitic, its main constituent being herschelite, which comes from the alteration (autometamorphism) of the glass in the original pyroclastic materials owing to hydrothermal or pneumatolytic action.

The zeolitization of artificial obsidians (glasses) of the rhyolitic, alkalitrachytic [16], leucititic, leucotephritic [17], haüynophyric [18], and basaltic [19] types has been reproduced in the laboratories of the Institute of Industrial Chemistry, University of Naples. It has thus been possible to reproduce some examples of compact volcanic tuff starting from natural, essentially glassy pyroclastic materials, such as the Phlegraean pozzolanas [9], and in this way to throw light on the origin of these tuffs which, as already mentioned, is assumed to lie in the alteration occurring in volcanic glass as a result of hydrothermal or pneumatolytic action.

Like the Rhenish "trass," the Neapolitan yellow tuff, when pulverized, reveals considerable pozzolanic activity, both in fixing calcium hydroxide and in its general behavior when mixed with portland cement to produce pozzolanic cement.

Constitutional characteristics very closely similar to those of Neapolitan yellow tuff and Rhenish tuff from the Eifel district are to be found in an alkalitrachytic, light yellow, compact tuff from the Grand Canary, recently examined by us [20]. In the apparently isotropic groundmass, which cements inclusions of various types among which sanidine crystals and pumices predominate, phillipsite can be detected.

The tuffs from the Latian volcanic region, of the leucititic type, are highly zeolitized, and the zeolites that we were able to find both as cementing groundmass constituents and as well-formed crystals lining the cavities in the material were: chabazite, phillipsite and herschelite [21, 22, 23].

Comments on the presence of zeolites in the cementing groundmass of volcanic tuffs are given in the literature [24, 25, 26, 27].

Altered rhyolitic volcanic tuffs, no longer containing glass because they are deeply zeolitized to clinoptilolite (high-calcium heulandite) and to analcite, have been mentioned by R. C. Mielenz, L. P. Witte, and O. J. Glantz as having pozzolanic activity [28].

Tufaceous compact rocks which can be ground to produce "trass" have been reported and utilized in other parts of the world—for instance, in Bavaria, Rumania [29], and Crimea.

Evidently there exists between the true pozzolanas, incoherent and rich in glass component, and the compact tuffs which originated from the cementation of pyroclastic materials, a series with intermediate characteristics according to the type and extent of alteration that has occurred. All these materials possess varying degrees of pozzolanic activity.

In the tuffs mentioned, the alteration (autometamorphism) of the original natural glass by hydrothermal or pneumatolytic action, which induced cementation of the pyroclastic, incoherent, original material, caused zeolitization. Consequent upon this change the final product, i.e., the tuff, was found in our research to be more reactive to calcium hydroxide than was the starting material (pozzolana).

In the light of the foregoing, true pozzolanas can be distinguished from "trass," as there is a fundamental constitutional difference between these two materials both possessing pozzolanic properties. The term "trass" therefore should be applied only to the product obtained by grinding tufaceous rocks formed by zeolitization of the glassy portion of primary pyroclastic materials.

It is known that the water stably retained by the material when dried at 100–105 °C is considered as a quality indication for "trass" [30]. This factor is actually indicative of its degree of zeolitization. The water in question is given up in a regular way by heating at rising temperatures.

That this difference has not been elucidated explains why some researchers have found that the true pozzolanas, Latian and Phlegraean, have only a very weak [25, 31] aptitude for base-exchange, whereas this is appreciable in "trass" and volcanic tuffs constitutionally similar thereto, precisely because of their characteristic degree of zeolitization.

Besides the true, incoherent pozzolanas, the pumices, and compact volcanic tuffs, several other natural materials have pozzolanic activity. Examples are lavas containing a fair percent of glassy component; products of various kinds deriving from extensive alteration of different types of volcanic rock by numerous causes; opaline silica; diatomaceous earths; clays which have been naturally roasted by incandescent lava flowing over them, etc.

Among others may be mentioned the Danish "moler," the French "gaize," the "tripel" from Briansk, consisting of amorphous silica which, in conjunction with another material already mentioned—liparitic tuff from Karadagh (Crimea)—is used in the Soviet Union for making pozzolanic cement.

Artificial Material Showing Pozzolanic Activity

First place must today be given to "fly ash," a residue from the combustion of solid pulverized fuels in big thermoelectric power plants. Its essentially vitreous physical state, provided it is accompanied by an appropriate composition and admissible content of unburnt carbon matter, suits it for use in pozzolanic materials, and Europe is following the example of the United States in extending its use for this purpose.

Fly ash usually has a low alkali content, because of its origin, lower than that of the true Italian pozzolanas and the volcanic tuffs employed for their pozzolanic properties ("trass").

Next in importance are the roasted clays, which are dehydrated at suitable temperature, this varying according to the type of silico-aluminous constituents (kaolinite, montmorillonite, illite groups). Heat treatment endows the clay with pozzolanic properties in that, apart from any interpretation as to the nature of the change induced by dehydration, the elimination of water brings out silica and alumina which readily react with calcium hydroxide in the presence of water·

Other natural materials that are activated by heat treatment are the "moler" and "gaize" already referred to. Dehydration essentially activates the clay fraction that they originally contain. There are also some entirely artificial materials, consisting of certain waste matters from the chemical industry, for instance: "Si-stoff." These, however, have a narrow range of use and are therefore not of general interest.

Blast-furnace slags cannot be classified as pozzolanic materials since they differ from these both in composition and in the manner of their hydraulic action.

Actually, while the pozzolanas, irrespective of their origin and composition, turn into compounds with cementitious properties only through fixation of calcium hydroxide, granulated blast-furnace slags, i.e., glassy slags, with hydraulic properties, are in themselves sufficiently basic and therefore have but a weak pozzolanic activity, in the sense of their ability to combine with lime coming from the saturated contact solution.

Pozzolanic Activity

The materials referred to in the previous section are of widely differing types according to their origin, composition, constitution and structure. But all possess, according to the definition, the property of reacting with calcium hydroxide in the presence of water to form compounds possessing cementitious properties; which will presumably be the same, or very similar, irrespective of the initial system, i.e., of the type of pozzolanic material made to react with lime.

In appraising the pozzolanic activity of any given material, in the sense of its ability to combine with lime, account must be taken of the chemical components, of their chemical bonds, and of the physical state.

Silica and alumina are, in effect, vulnerable to calcium hydroxide when their structural bonds are weak and unstable in the original material, as is the case with volcanic glass, or the zeolitic structure deriving from the alteration thereof. The same applies to clay materials when, through total dehydration by heat treatment, the bonds between silica and alumina are relaxed or annihilated.

If, instead, Si, Al, and O are bound in the lattices of the individual minerals formed by crystallization of the magma, or in those of the silico-aluminous materials which constitute natural clays, the calcium hydroxide acts far more slowly or not at all.

From the standpoint of cementitious action, that is, the hardening process, the parts played by silica and alumina cannot be considered separate one from the other. It has already been said that there are siliceous materials with no, or very little, alumina, which while rapidly fixing noteworthy quantities of calcium hydroxide from its saturated solution, do not offer such a satisfactory performance from the standpoint of hardening, and produce low mechanical resistance when mixed with lime to make mortars and concretes.

According to F. Murakami [32] the presence of reactive alumina considerably enhances the mechanical strength of pozzolanic cements, particularly for brief curing.

Practically nothing has yet been learned of the part played by the minor components of pozzolanic materials, i.e., iron and alkalis. It may be assumed that when the original structural arrangement of the starting material is destroyed by the attack of calcium hydroxide, the iron undergoes changes similar to those occurring in alumina though far slower and that the alkali remains partly fixed by the newly formed pseudogelatinous products. There should not, however, be a very appreciable effect on the final arrangement of the final system.

The results of our investigations have shown [14, 33] that the zeolitic structures that we found in the volcanic tuffs examined—chabazite, herschelite, and phillipsite—are attacked more quickly by calcium hydroxide than are the true, practically entirely glassy pozzolanas, the cementation of which produced these tuffs.

Both the zeolitized tuffs and the single zeolites tested in a constantly saturated solution of calcium hydroxide revealed a strong capacity for fixation, considerably higher than that corresponding to a mere base exchange [34]. At the same time, the performance of these materials from the standpoint of cementitious properties was good [35].

This observation confirms what F. M. Lea [1, 3] has asserted for some time, that the pozzolanic activity of "trass" is not correlated with its ability for base exchange.

The single zeolites and zeolitized tuffs that we examined revealed a normal base-exchange capacity, more or less in the ratio of the equivalents, but the quantity of calcium hydroxide involved in the mere base exchange is far smaller than that fixed by the material kept in contact with a constantly saturated solution of calcium hydroxide. The calcium hydroxide does not, therefore, act on the zeolitized material merely by base exchange with the alkalis, but by breaking down the zeolitic structure, after which the silica and alumina are enabled to combine with the calcium hydroxide to form cementitious compounds.

In other words, the quantities of calcium hydroxide involved in an ion-exchange process are small and do not explain the far-reaching radical change that is responsible for the hardening of the material when it is mixed with hydrated lime to form mortars and concretes.

It is the zeolitic structure and its instability that make the zeolitized material more highly reactive to calcium hydroxide than are the eminently glassy pozzolanas.

In handling the question of the chemistry of pozzolanic cements it is obviously necessary to interpret and elucidate all aspects of the phenomena which play a part in the hydraulic action of materials having a pozzolanic effect, whatever their origins and composition may be.

Unfortunately no final elucidation has yet been forthcoming on the series of changes through which these materials perform their role of hydraulic binders. The main reason lies in the difficulties of testing and interpreting the very nature of these systems, which make it extremely arduous, not to say impossible, to distinguish real from apparent equilibrium, stable from transient arrangements.

Once having identified, in the reaction between calcium hydroxide and materials with pozzolanic activity, the chemical phenomenon responsible for their hydraulic behavior, it was obvious that one might attempt to throw further light thereon not only by studying the nature of the reaction solids with a view to identifying the final, stable structure of the system, but also by studying the evolution towards the hypothethical condition of stability.

One calls it hypothetical, because diagnosis is a difficult and complex task. The pozzolana grain is attacked from outside and is gradually coated with newly formed products which protect the kernel in a manner that prevents any estimation or time-wise evaluation of the products originating from the calcium hydroxide attack on the pozzolanic material.

However, apart from an interpretation of the process by which calcium hydroxide attacks material, at the outset of our investigations we concerned ourselves with two aspects which we considered of interest: the extent and the velocity of fixation of calcium hydroxide by pozzolanic materials kept in contact with constantly saturated solutions [7].

The extent varies according to the type of pozzolanic material in question, its composition, constitution, and content of minerals weakly, or not at all, susceptible to attack. The velocity is perhaps the most useful indication; for if it is true that the various pozzolanas, mixed with hydrated line or portland cement and tested in mortar or concrete, reveal little difference in strength over long periods of wet storage, there is a definite difference over short periods.

At all events, an interpretation of pozzolanic activity as a whole cannot be given only on the basis of these two characteristics. There is a third far more complex aspect which concerns the nature of the transformations, i.e., the chemical and physical phenomena that occur as a result of the attack by the lime.

It has been stated, in principle, that materials with a high reactive silica content will, if kept constantly in contact with a saturated solution, speedily bind large quantities of calcium hydroxide, yet when used in mortar or concrete they reveal mechanical strength decidedly below that obtained when using true natural pozzolanas in the very same way, although the latter give a less satisfactory response [36] from the standpoint of the characteristics referred to above, particularly velocity.

Quite some time ago we developed a very simple method for testing the ability of pozzolanic material to combine with lime, which furnished a sufficiently close evaluation [7, 36]. The test, currently in use, consists of adding separately greater and greater amounts of CaO to equal quantities of the pozzolanic material that is being tested, which is ground to a given fineness and placed in sealed bottles, with a constant volume of water free from CO_2. The bottles are continually agitated, and the lime content of the contact solution is determined at regular intervals, as well as the amount of alkalis that may be given up by the pozzolanic material as the lime attack proceeds, until the percent of CaO (gravimetric) drops and remains below that of the saturated solution at the test temperature and for the alkali content that is separately determined. The alkali is inferred from measuring the solution alkalinity or by direct spectrophotometric assay [37].

This procedure gives the time required for a given weight of material tested to fix an amount of lime equal to the weight of CaO present in the system on commencement of the test, less the amount removed with the single titrations and the lime still in solution in the residual liquid. The different times taken for fixation of the varying quantities of CaO made to react with the initial system enables one to draw the curves showing the speed of attack.

There is every reason to assume that, at the end of the transformation that they undergo by the action of lime, pozzolanic materials must have produced cementitious compounds that are probably of the same type as those constituting the final system obtained by hydration of the anhydrous components of portland cement clinker.

In the case of materials with pozzolanic activity, which must combine with lime to reach conditions of stability in the Al_2O_3–SiO_2–CaO–H_2O system (ignoring the minor components), the course of the transformation must perforce differ from those occurring in the hydration of clinker, and it is not easy to follow this, mainly because of the difficulty in distinguishing transient from permanent arrangements.

The test referred to has shown that pozzolanas are, at ordinary temperature, able to fix large amounts of calcium hydroxide from constantly saturated solutions; and that these amounts are greater by far than those ascertainable using the various modifications of Vicat's test, the results of which lead to a wrong evaluation of pozzolana lime-retaining capacity.

In investigating the effect of lime on both Latian and Phlegraean pozzolanas, we found [38] by X-ray examination that materials that had fixed between 40 and 70 g of CaO per 100 g of pozzolana—by contact with constantly saturated calcium hydroxide solution—showed quite distinguishable lines characteristic of the solids in the SiO_2–CaO–H_2O system for CaO-SiO_2 ratios between 1 and 1.5; and that when observed in transmitted light through the microscope they revealed a nonresolvable, amorphous groundmass embodying thin, hexagonal contour lamellae very similar in appearance to the hexagonal crystals of calcium aluminate hydrates and to the lamellae perceivable among the products of the reaction between calcium hydroxide solution and dehydrated kaolin.

It was not possible to obtain any evidence of the presence of Strätling's compound, C_2SAH_x in the groundmass.

Attempts to follow the development of the solid in contact with the constantly saturated lime solution by means of chemical attack of various kinds were unsuccessful, nor was any type of fractionation efficient or suitable for the purpose.

Later, R. Turriziani was able, with more efficient experimental facilities [39] to improve the first investigations referred to above, and using differential thermal analysis and X-ray methods he studied the solids that form when Segni pozzolana (Latium, leucititic type) remains for a long time in contact with a constantly saturated lime solution. He remarked that the differential-thermal-analysis (DTA) curves revealed a first endothermic effect at low temperature (140 °C) which can be ascribed to the presence of Taylor's silicate: $C_{0.8\text{-}1.5}SH(I)$, and a second effect (220 °C) which can be attributed to the presence of C_4AH_{13}. This finding was corroborated by the X-ray diffraction data. Nevertheless, the presence of small quantities of C_2SAH_x cannot definitely be ruled out.

In addition, R. Turriziani [40] examined the products of the reaction of Segni pozzolana and calcium hydroxide mixed in varying proportions (the tests being performed in a different manner from that indicated above—that is, by keeping the mixtures in a fluid state up to the end of the investigations) and also true mortars prepared with currently employed proportions and kept in water. The DTA and X-ray examination of the solids confirmed the presence of calcium silicate of tobermoritic type. Alumina is found in the mortars in the form of C_4AH_{13}; in other preparations the compounds C_2SAH_x prevails instead.

According to J. Chapelle [41] the action of lime on materials having pozzolanic properties produces calcium silicate CSH_x and tetracalcium aluminate C_4AH_x. The latter transforms to cubic C_3AH_6 if the reaction between pozzolana and saturated lime solution takes place at the boiling point. This researcher was unable to identify silicoaluminate, C_2SAH_x.

The reaction between pozzolana and calcium hydroxide has also been studied by R. Turriziani, at a temperature of 45 °C [40]. This study confirmed the presence of C_3AH_6 (cubic) already reported by G. Malquori and V. Cirilli [38] in the solids of the dehydrated kaolin-lime-water system at a temperature of 70–80 °C.

Kaolin dehydrated at between 600 °C and 700 °C, if kept at ordinary temperature in contact with a constantly saturated calcium hydroxide solution, will fix considerable quantities, tending to a saturation point represented by the ratio $3CaO{:}2SiO_2{\cdot}Al_2O_3$ [38].

In following the development of the groundmass under the microscope it was possible to note, embodied in a mass consisting partly of nonresolvable material and partly of small birefringent scales, hexagonally contoured laminae, looking very much like those of the hexagonally shaped calcium aluminate scales, but with a slightly lower refractive index than the latter.

On heating the solids at 70–80 °C in the presence of their equilibrium solution, crystals of the cubic system were seen to appear (trapezohedra, hexakisoctahedra), outwardly similar to cubic aluminate C_3AH_6 crystals. At the same time it was found that the above change is greater in velocity and intensity the higher the CaO content of the solution.

In X-ray diffraction patterns of the various groundmasses having different CaO contents and obtained by keeping the system at ordinary temperature, besides the lines characteristic of the solids of the SiO_2–CaO–H_2O system, for CaO/SiO_2 ratios between 1.5 and 1 there appeared new lines that did not belong to the patterns of any of the calcium aluminate hydrates. The diffraction patterns were like those obtained by Strätling and ascribed by him to the compound C_2SAH_x [42, 43].

The presence of the tobermoritic type of calcium silicate, as well as of C_2SAH_x, was confirmed by R. Turriziani and G. Schippa [44] by means of X-ray investigation and DTA.

V. Cirilli [45] saturated kaolin, dehydrated at 630–700 °C, with lime, by contact with a constantly saturated calcium hydroxide solution. Subsequently he processed the solid thus obtained by progressive hydrolysis, the course of which appears to rule out the presence of free calcium aluminates.

Likewise, according to R. Turriziani and G. Schippa [46], the solid cubic phase containing alumina, found among the products of reaction of calcium hydroxide and dehydrated kaolin in the presence of water at 50 °C, appears to be a hydrogarnet of the C_3AH_6–C_3S_3A series containing 0.3 to 0.4 molecules of silica.

Results obtained by observing lime-pozzolana motars under the microscope are no more promising.

G. Gallo [47] had formerly examined mortars consisting of three parts (by volume) of pozzolana to one of hydrated lime, and in the nonresolvable, amorphous groundmass of the newly formed products had identified hexagonal crystals which he ascribed to the aluminate C_3AH_{10}.

Later, B. Tavasci [11, 48, 49], examined both thin sections and polished sections of lime-pozzolana mortars, cured in water for about five years, and having a lower lime content than the above specimens. Among the newly formed products he was able to identify lamellar crystals whose appearance and optical characteristics led him to classify them as calcium aluminate hydrates.

The groundmass is isotropic and when magnified appears to have a granular structure. It was impossible to establish its nature merely by optical examination; however, while the possible presence of C_2SAH_x cannot be excluded, it is probable that the principal component of the mass is a low-lime silicate hydrate of the okenite type CS_2H_2.

On the whole, the optical investigations carried out by numerous researchers on the solids resulting from reaction of pozzolana with calcium hydroxide, and on pozzolana mortars, have not produced more than approximate data on the nature of the solids that are formed by this reaction.

The identification of newly formed solids, viz, of the cementitious compounds present in the materials examined, has been greatly aided by DTA and roentgenographic techniques which, while not in themselves decisive, are reciprocally complementary and, considered in conjunction with optical findings, contribute to the final diagnosis, which may be summarized as follows:

(a) The presence of calcium silicate hydrate of the tobermoritic type has been ascertained as an apparently amorphous groundmass, in the form of a gel and in any case having a low degree of crystallization.

Since the tobermorite highest in lime is stable in a calcium hydroxide solution having a near-saturation titer, while the lower-lime forms are stable in weaker solutions (0.28 g/liter of CaO), the composition of the calcium silicate hydrate in hardened pozzolana mortars, although remaining within the tobermorite range, must vary.

In hardened high-pozzolana mortars, the tobermorite present should correspond to the low-lime form.

(b) The presence of calcium aluminate hydrate, probably C_4AH_{13}, was ascertained.

(c) The presence of C_2SAH_x was not sufficiently established.

The whole collective data seem to warrant the opinion that the cementitious compounds formed by pozzolanic action are of the same type as those formed by hydration of portland cement.

Material having pozzolanic activity, if kept in contact with a constantly saturated calcium hydroxide solution, is more quickly attacked if calcium sulfate is present at the same time.

Likewise, if calcium hydroxide is added to the pozzolana-calcium sulfate-water system (the solution being always saturated with $CaSO_4 \cdot 2H_2O$), the lime is fixed by the pozzolana far more quickly than when calcium sulfate is absent [50].

This behavior is characteristic of materials containing alumina, and not only of pozzolanic materials. By sulfo-calcic attack alumina can be made to react in minerals that at ordinary temperature withstand attack by calcium hydroxide alone [50].

G. Malquori and A. Spadano [50] noted furthermore that when pozzolanic materials are attacked by calcium sulfate in the presence of excess quantities of calcium hydroxide, the solid swells markedly, and in direct proportion to the quantity of sulfate retained by the material.

Observation under the microscope has in each case revealed the characteristic needle-shaped crystals of the high-sulfate form of calcium sulfoaluminate: $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$.

The results summarized in the foregoing proved that sulfo-calcic attack was more vigorous than attack by calcium hydroxide alone, that the alumina in the pozzolana was quickly and entirely attacked by the combined action of calcium hydroxide and sulfate, and that in every case the high-sulfate sulfoaluminate was formed.

More recently R. Turriziani and G. Schippa [51, 52] studied the behavior of mixtures of pozzolana, hydrated lime, gypsum, and water using various proportions, and employing DTA and X-ray techniques in their investigations. They obtained evidence of the presence of $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ and, under certain conditions, of $3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$. They rule out all possibility of C_2ASH_x being present at the same time.

J. Chapelle [41] supports the previous findings of G. Malquori and A. Spadano on the behavior of pozzolanic materials containing alumina in connection with the combined action of calcium hydroxide and sulfate, and confirms that the alumina is exclusively taken up in the sulfoaluminate.

To corroborate the foregoing observations on the vulnerability of the alumina contained in pozzolanic materials when attacked by calcium sulfate, F. Parissi [53] and G. Malquori and F. Sasso [54] had shown that pozzolanic cements prepared with Italian pozzolanas—which are silico-aluminous—do not withstand the Anstett test, especially if this is performed after short periods of water curing; moreover, if gypsum is added to the hydrated lime-pozzolana (silico-aluminous) mortar this causes marked expansion, approximately proportional to the percent of gypsum added to the initial mixture (for the same ratio of pozzolana to hydrated lime).

The swelling is so marked as to crack the test specimens, and occurs all the more rapidly the higher the percent of gypsum initially present. The compressive strength of test specimens of mortar prepared from the ternary mixtures likewise drops quickly when the proportion of gypsum is increased. The expansion of the test specimens is always accompanied by the formation of high-sulfate sulfoaluminate.

R. Turriziani and G. Schippa [40, 51, 52], also investigated the compressive strength of mortars obtained by mixing Latian pozzolana, hydrated lime and varying quantities of gypsum, and found a slight increase in strength up to 6 percent of gypsum added. Above 10 percent, however, with even short periods of storage, the test specimens became swollen and disintegrated, hence more or less without mechanical strength.

These researchers also believe that the decrease in mechanical strength noted in their pozzolanic-mortar test specimens is due to the formation of expansive sulfoaluminate, which takes place more quickly than fixation of lime by the pozzolana [50].

There is every reason to assume that the change occurring in pozzolana when it is mixed with hydrated lime to form pozzolanic mortar proceeds more or less in the same way as in the case of mixtures of pozzolana and portland cement.

R. Turriziani [40] recently succeeded in corroborating this assumption by examining portland cement and pozzolanic cement pastes made by mixing the former with Italian pozzolana (Segni). The pastes were wet cured at 18 °C for one year, and throughout the transformation of the material to its final arrangement, followed over a period of one year, samples were taken at given intervals, appropriately conditioned and examined by DTA and roentgenographic methods. In the portland-cement pastes it was possible to identify calcium silicate hydrate of the tobermoritic type, tetracalcium aluminate hydrate, free calcium hydroxide resulting from hydrolysis, and high-sulfate sulfoaluminate. Neither the compound C_2ASH_x nor low-sulfate sulfoaluminate could be identified. With pozzolanic cement, the components of the hardened pastes appear the same. However, as was to be expected, the calcium hydroxide content was markedly less (fig. 1).

B. Tavasci [55] examined hardened pastes of both portland and pozzolanic cements under the microscope, observing that the pozzolanic cement-paste structure seems intermediate between that of portland cement and of hydrated lime-pozzolana mortars. In pozzolanic cement pastes the free calcium hydroxide produced by hydrolysis of the clinker constituents is still visible, although obviously considerably less than in portland-cement pastes. B. Tavasci remarks that the larger pozzolana granules appear strongly attacked and surrounded by a thick layer of newly formed products.

R. Turriziani and A. Rio [56] attempted to determine the free calcium hydroxide present in pozzolanic cement pastes wet-cured for different lengths of time; they made use both of Franke's solubilization method and DTA, and concluded that apart from quantitative accuracy it was an ascertained fact that the hardened pozzolanic cement pastes examined, even those prepared with a high pozzolana content and given the longest wet-curing, always contained free calcium hydroxide produced by hydrolysis of the clinker constituents, although to a much smaller extent than observed in portland-cement pastes.

Altogether the foregoing considerations prove that pozzolanic cements are potentially susceptible to attack by aggressive agents.

Little is known of the behavior of the minor constituents in the hardening process of mortars of hydrated lime and pozzolana and of pozzolanic cements.

For Fe_2O_3 the methods of research employed so far have not succeeded in distinguishing the ternary combinations $CaO–Fe_2O_3–H_2O$ from the corresponding ones containing alumina. The diffraction pattern of tetracalcium ferrite hydrate is similar to that of tetracalcium aluminate hydrate, at least in the zone of the more intense lines, and the same thing is true of the complex salts with the sulfuric radical. However, bearing in mind that the gel of ferric hydroxide fixes calcium hydroxide only very slowly, it must be concluded that even assuming part of the ferric oxide contained in the pozzolana to be reactive, it can play but a minor part in the fixation of the lime and in the setting and hardening process.

The classical natural pozzolanas, for instance the Italian leucititic and alkalitrachytic pozzolanas, contain noteworthy percentages of alkalis which are freed during the transformation caused by lime attack. A. Rio, for example [57], has tested pozzolanic cement pastes, made with the same clinker and varying percentages of Segni and of Bacoli pozzolanas, at different periods of cur-

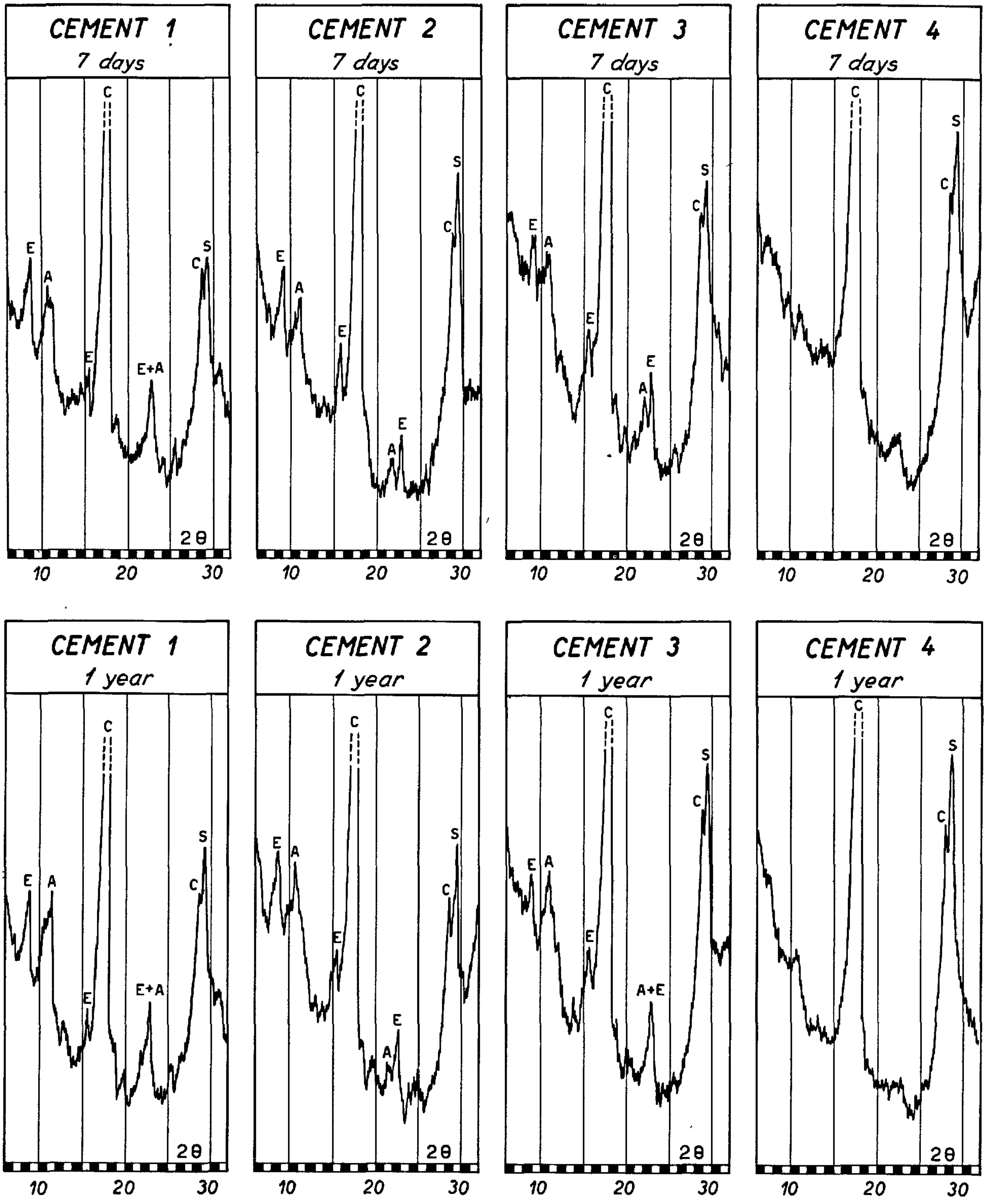

FIGURE 1a. *X-ray diffractograms of portland cement pastes.*

w/c=0.30; E=ettringite; A=tetracalcium aluminate; C=calcium hydroxide; S=calcium silicate. From R. Turriziani [40].

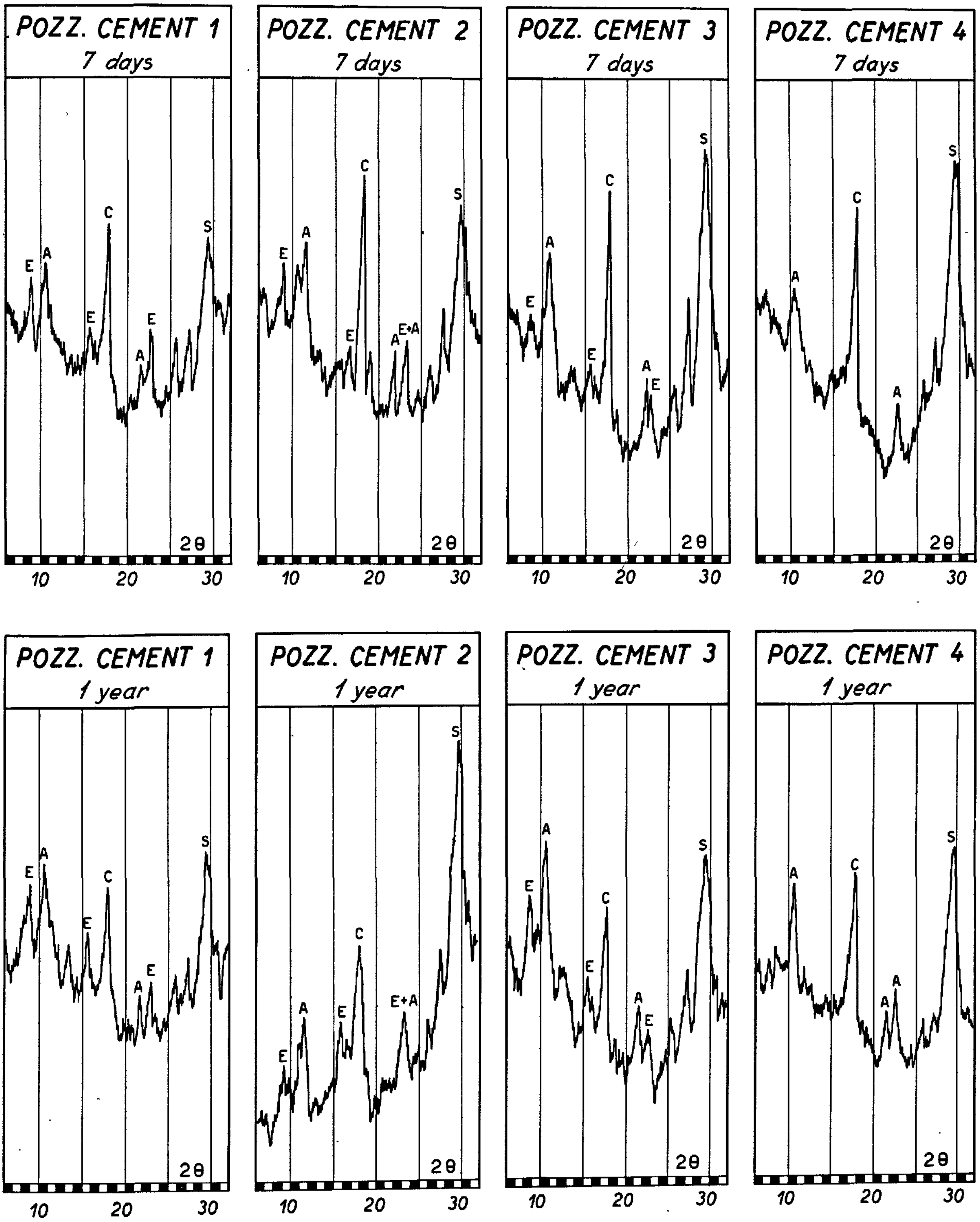

FIGURE 1b. *X-ray diffractograms of portland-pozzolan cement pastes.*

w/c=0.35; E=ettringite; A=tetracalcium aluminate; C=calcium hydroxide; S=calcium silicate. From R. Turriziani [40].

ing, and found that after one year the Segni pozzolana gave up 85 percent of its initial alkali content, and the Bacoli pozzolana 55 percent.

Alkalies not only decrease calcium hydroxide solubility, but probably become fixed on the pseudogelatinous newly formed compounds.

Unfortunately very little is known about the systems SiO_2–Al_2O_3–CaO–K_2O–H_2O and SiO_2–Al_2O_3–CaO–Na_2O–H_2O, and it is hoped that in the near future these fields will be appropriately investigated. It should be repeated, nevertheless, that the research so far carried out on the constituents of hydrated lime and pozzolana mortars and on hardened pozzolanic cements, has shown that the products of the reaction between calcium hydroxide and silica and reactive alumina in the pozzolana, are the same as those indicated when hardened portland cements are investigated in the same way.

It is therefore a justifiable conclusion that the presence of alkali has no substantial influence either on the way in which the transformation proceeds or on the nature of the end products, except, perhaps, from the standpoint of kinetics, considering that, among other things, the solubility of calcium hydroxide drops.

Evaluation of the Pozzolanic Activity

According to the definition, the constituents of pozzolanic material must have the ability to combine with calcium hydroxide to form compounds possessing cementitious properties.

It is evidently desirable for this action to take place as rapidly and intensely as possible.

There are as yet no sufficiently reliable tests for predicting *a priori* how pozzolanic material mixed with hydrated lime or portland cement in mortar or concrete will behave, either from the standpoint of mechanical-strength performance or from that of reduction of free calcium hydroxide in the hardened binder. Nor does ability to fix calcium hydroxide from a constantly saturated solution arrange the different materials according to the order in which they are rated if tested in mortars or in concrete in association with hydrated lime or portland cement.

Reactivity tests, viz, solubilization by chemical acid-basic attack of both the original pozzolanic material and the same material after reaction with lime, have proved equally unsatisfactory.

It thus follows that an evaluation of pozzolanic material for purposes of its addition to portland cement must be based on two factors: the mechanical strength of mortars and concretes made up with a portland-pozzolana mixture, and the disappearance, or anyway the reduction, of free calcium hydroxide in the hardened pozzolanic cement.

These two factors must be considered and rated separately, observing the behavior of the mortar or concrete under conditions that are as nearly as possible those of current practice.

This requirement means determining under standard conditions both the mechanical strength of the mortars or concretes [58, 59] and the extent to which free calcium hydroxide is reduced, or the characteristics of the mixture (mortar and concrete) that are correlated with the lack or scarcity of free calcium hydroxide.

These tests must be designed with a view to their practical purpose, hence speed is required when the test is proposed for acceptance or rejection of pozzolanic material.

With regard to mechanical strength, especially that of hydrated lime-pozzolan mortars, it was suggested long ago that the hardening time be speeded up by curing the test specimens at higher than normal temperature. The ASTM C340–58T test, for instance, specifies curing the test specimens at 55 ± 1.7 °C.

An evaluation of the second factor in pozzolanic activity, namely, the material's ability to combine with calcium hydroxide, based on determination of the free calcium hydroxide in the pastes, mortars, or concretes after reasonably short periods of curing, is inaccurate, whether this test is performed by dissolving or by extraction with chemical reagents, or whether DTA and thermogravimetric analysis are used. Not only that, but in this evaluation it must be borne in mind that when pozzolanic binders harden, a portion of the calcium hydroxide remains embodied and protected by the newly formed pseudogelatinous products, which impede its passage into solution. This immobilized calcium hydroxide will be again found to a great extent as free hydroxide in the pulverized material which is tested as mentioned above.

N. Fratini [60], for instance, found that one week after preparation a portland-cement paste gives up so much calcium hydroxide during wet curing that it saturates the contact solution. But he found that this is not the case with a pozzolanic cement paste made from a mixture of portland cement and Italian pozzolana in the ratio: $\frac{SiO_2+R_2O_3}{CaO} \geq 1$, despite the fact that the mass, i.e., the cement paste, contains free calcium hydroxide identifiable both with solubilizing reagents and with DTA.

This behavior corroborates the suggestion advanced that part of the calcium hydroxide released by hydrolysis of the clinker constituents is enclosed, protected and thus immobilized. It would seem that protective films of newly formed products passivate the crystals.

N. Fratini [61] also proposed an accelerated test [62, 63, 64], for determining, apart from the composition ratio: $\frac{SiO_2+R_2O_3}{CaO}$, or the portland-pozzolana ratio of the mixture, whether a cement claimed to be "pozzolanic" will not, when tested in paste form by standard methods, give up enough calcium hydroxide to the contact solution to saturate it. The method consists of determining the total alkalinity and the calcium hydroxide content of the solution in which the tested paste is steeped during curing under predetermined conditions. Having ascertained the solubility of calcium hydroxide in the presence of alkalies at the test temperature, it is possible to determine whether the solution is saturated or oversaturated with calcium hydroxide (as in the case of portland cement alone) or not saturated. In the diagram in figure 2, therefore, the points representing the composition of the contact solutions for hardened cements containing no free, easily removable calcium hydroxide must be located below the solubility isotherm.

The test proposed by N. Fratini is designed to determine whether the material with pozzolanic activity added to the portland cement, whatever its nature may be and whatever may be the mixture ratio, will actually fix the calcium hydroxide freed by hydrolysis of the portland cement. In practice the test is carried out at a temperature of 40 °C. The cement (20 g) and distilled water (100 ml) mixture, placed in glass bottles, waxed and sealed, is kept at the above temperature for varying periods in a thermostat. At predetermined times the contact solution is removed to determine the total alkalinity and the calcium hydroxide content (gravimetrically). The type of pozzolanic material mixed with the portland cement, and the mixture ratio, are satisfactory if the point representing the analyzed solution comes below the solubility curve shown in figure 2.

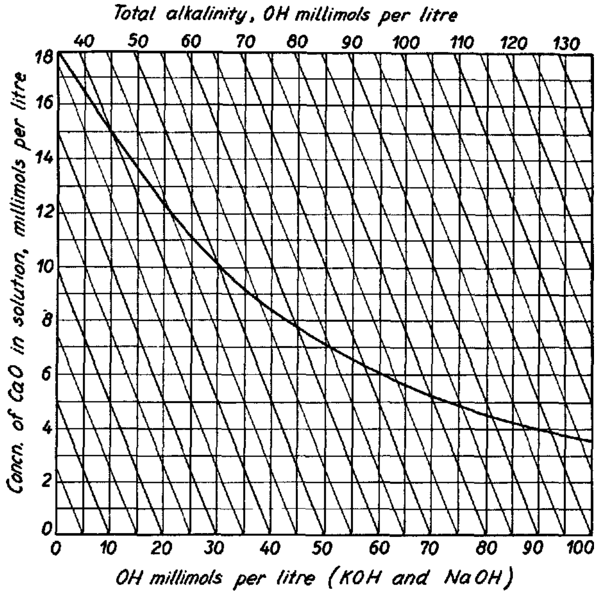

FIGURE 2. *Solubility isotherm (40 °C) for* Ca(OH)$_2$, *in the presence of alkalies.*

Pozzolanic Cements and Corrosion Resistance

It has been shown that from the qualitative aspect, the final compounds found in hardened pozzolanic cement are of the same type as those produced by hydration of portland clinker constituents.

Free calcium hydroxide is, however, contained in hardened pozzolanic cement in much reduced measure, and is protected and isolated by the newly formed pseudogelatinous products surrounding the crystallites, which prevent their passing into solution and hindering ionic diffusion.

For this reason the tobermoritic phase of hardened pozzolanic cements must have a lower lime content than that obtainable by hydration of portland cement.

Moreover, even if the end products of hardening are qualitatively the same, there must be a considerable difference in the development of the process and in the final arrangement, because while the cementitious compounds originate in portland cement exclusively from hydration of the clinker constituents, with pozzolanic cement they originate partly from the reaction between lime from hydrolysis and the active constituents of the pozzolanic material that is mixed with the portland cement.

In reacting with the free calcium hydroxide and supplementing it with low-basic, more stable compounds, the pozzolana does away with an important cause of vulnerability in hardened cement.

The newly formed, pseudogelatinous, expanded products tend to fill up the spaces between the original grains of portland cement and pozzolana, and to fill the micropores of the mortar and concrete, thus aiding in reducing permeability, and enhancing corrosion resistance.

This particular texture, in conjunction with elimination of potentially attackable calcium hydroxide, may account for the improved resistance attained by mixing pozzolanic materials with portland cement.

That the nature of the products of the reaction between pozzolanic constituents and the lime liberated during clinker hydration does produce a difference in the texture of the two types of hardened cement, i.e., pure portland and pozzolanic cement, is confirmed by the results of a systematic series of percolation tests made by F. Arredi [65] with concrete made up in the same way, the only difference being in the type of cement; and by L. Santarelli and C. Cesareni [66] with mortars prepared from different cements, including pozzolanic types.

The protective action of the tobermoritic, low-crystallized phase, with respect to more vulnerable constituents in hardened pozzolanic cement has been confirmed by observations made by

B. Tavasci and A. Rio [67, 68], who emphasize the greater resistance of pozzolanic cement (which is less basic than portland and above all contains far less free calcium hydroxide) in withstanding decalcification due to leaching conditions.

It has already been repeatedly stated that pozzolanic cements do not possess any intrinsic, specific, chemical resistance to attack by sulfates. The reactive alumina of pozzolana is, in fact, found in hardened cement, in the form of potentially vulnerable calcium aluminate.

Nevertheless, as calcium hydroxide gradually disappears with the development of the pozzolanic action, the conditions set up may be unfavorable to the formation and stability of expansive sulfoaluminate.

The cement's reduced basicity and low content of free calcium hydroxide, as well as the protective and waterproofing action of the newly formed compounds—a protection which undoubtedly hinders and slows down ionic diffusion, i.e., exchange with the contact solution—are likewise factors in support of probable higher resistance to sulfate attack, which can be achieved by mixing pozzolana with portland cement [69].

It may likewise be expected that the improvement of corrosion resistance will be enhanced according to the length of wet curing given the pozzolanic cement, because the pseudogelatinous compounds, which are not stable forms, evolve as time passes, gradually acquiring their final arrangement and probably becoming an increasingly efficient barrier to ionic diffusion.

In the light of the foregoing considerations, to improve the resistance of pozzolanic cements to sulfate attack the following points should be borne in mind:

(a) the advisability of using a pozzolanic material having very little, or no, reactive alumina;

(b) the advisability of using a clinker with a low C_3A content in portland-pozzolana mixture.

To determine the mixture ratio, useful data can be obtained with the test suggested by N. Fratini.

Pozzolanas as Additives to Prevent Expansion Caused by the Alkali-Aggregate Reaction

Additions of pozzolanic material to portland cement are today advised as a suitable means for preventing expansion, and the cracking caused thereby, that result from reaction of the reactive silica contained in certain aggregates with the alkalies present in the cement.

When pozzolanic materials having little or no alkali are added to the cement, such as, for instance, diatomaceous earths, certain burnt clays, certain types of fly ash, etc., the pozzolana will have the effect of inhibiting reaction between the alkali of the cement and the reactive aggregate by retaining at least a good part of the alkalies, so as to diminish the quantity thereof in the contact solution, and hence the extent and rate of attack on the surface of such aggregates as may be susceptible to alkali attack. More precisely, the alkalies will be partly dissolved in the contact solution and partly retained by the products of the reaction of the calcium hydroxide with the pozzolana, more particularly by the calcium silicate hydrate, forming weakly soluble compounds.

Natural pozzolanas and volcanic tuffs contain considerable percentages of alkali which are released by the transformation occurring in the material during the hardening process of pozzolanic cement, and it has already been seen that the quantities thus freed are conspicuous. If the pozzolanic cement has been prepared with materials like the Italian pozzolanas and "trass", for instance, which in reacting with calcium hydroxide give up a large part of their alkalies, the protection afforded by the reactive aggregates suggested in the foregoing interpretation appears doubtful, the more so in that the conspicuous quantity of alkalies in the pozzolana has to be added to those in the portland cement.

However, the fact remains that in Italy, where pozzolanic materials have been used for more than two thousand years, in mortar and concrete, and have been mixed with portland cement for the past fifty years, no trouble has yet developed which could be ascribed to the reactivity of aggregates with alkalies, not even when the pozzolanic cement was mixed with aggregates like lavas, for instance, presumably containing alkali-reactive glass.

This is a field still open to further investigation.

Heat of Hydration of Pozzolanic Cements

The estimation of heats of hydration of pozzolanic cement by determining the heat of solution of anhydrous cement and of hydrated cement is not as accurate as with portland cements, because pozzolanic material is not completely soluble [70, 71, 72, 73]. Nevertheless, since both anhydrous and hydrated pozzolanic cement have about the same rate of solution, an approximate estimate of the heat of hydration can be made even without waiting until the sample has entirely dissolved. It can be assumed that the fraction of pozzolana that offers resistance to dissolution in the acid solvent, will likewise resist reaction with calcium hydroxide while the cement is hardening, and will therefore have been altered very little or not at all in the hardened cement.

A proposal was recently made [74] to evaluate the heat of hydration of pozzolanic cements by performing the hydration under conditions of no heat loss (adiabatic calorimeter). The adiabatic calorimeter used is based on the principle of keeping the sample being hydrated (a block of concrete) in surroundings automatically maintained at the same temperature as that of the sample.

The heat of hydration of pozzolanic cement depends principally on the ratio of clinker and pozzolana in the mixture and on the type of clinker.

Low heat of hydration clinkers, brownmilleritic clinkers for instance, are mixed with pozzolana to produce a cement that is used on a wide scale in Italy, especially in building dams.

Activation of Pozzolanic Materials

Proposals have been made from many sources for increasing the activity of pozzolanic materials by appropriate treatment—generally heat processes. With natural, typical pozzolanas, unless they are altered materials particularly rich in clay matter, heat treatment is ineffective; actually at temperatures about 650–700 °C the effect is definitely deleterious to pozzolanic properties.

Experiments made by Q. Sestini and L. Santarelli [75] and by R. C. Mielenz, L. P. Witte, and O. J. Glantz [28] confirm that heat treatment is useful only in the presence of clay materials which acquire pozzolanic properties pursuant to dehydration.

R. Turriziani and G. Schippa [76] have studied the thermal behavior of Roman pozzolanas (leucititic) treated up to 750 °C for varying periods. They investigated the density, calcium-fixing ability, and setting times of mortars made up with treated pozzolanas, finding that while treatment up to about 400 °C did not change the activity of Roman pozzolanas, higher temperatures had a detrimental effect in that they notably diminished the rate at which calcium hydroxide was fixed and the reactivity to acid-basic attack, while the density appeared to be augmented. These effects are all the more marked the higher the temperature and the longer the time of heat treatment.

K. M. Alexander [77] has proposed strong acid treatment to activate materials having weak pozzolanic activity or none at all. The acid attack on decomposable silicates releases gelatinous silica, which is responsible for the pozzolanic activity of the material thus treated. However, for practical and economic reasons, this treatment does not seem to have much prospect of success beyond the laboratory.

Pozzolanic Cements in Practical Applications

Low heat of hydration and enhanced resistance to corrosion relative to ordinary portland cements are the two characteristics which distinguish pozzolanic cement and account for its wide-scale use in the bigger types of concrete constructions like dams and marine works.

The particular texture of the hardened cement, viz, the presence of pseudo-gelatinous formations which tend to fill the empty spaces, gives better waterproofing action than standard-mixture concretes, a quality that is especially valuable in works which have to withstand continual contact with water. In Italy, impressive amounts of pozzolanic cement have been employed over the past fifty years precisely for the above uses, and results have always been entirely satisfactory.

However, as compared with portland cement, the portland-pozzolana mixture also has its drawbacks. Slightly more water is needed in the mixtures; drying shrinkage is greater, likewise the expansion of submerged mortars and concretes. From the standpoint of mechanical strength, not only in tamped mortar but equally in plastic mortar and concrete, pozzolanic cement is slower to harden than pure portland. Strength after short curing—more particularly in the case of plastic mortars and concrete than with tamped mortar—is decidedly less than that of the same portland cement used alone.

As hardening proceeds for further periods of time, and if the hardening is aided by storing the mortar or concrete in water, the discrepancy diminishes, then disappears, and subsequently the strength of the pozzolanic material is greater than that of mortars and concretes made with pure portland cement, all other conditions being equal. Increases in tensile strength are generally greater than those in compressive strength.

If, on the other hand, the mortar or concrete remains in the open air, the pozzolanic cement will have lower strength than pure portland, even after long curing. When used in construction exposed to the air, the pozzolanic addition should not be considered completely inert and therefore purely a diluent of the cement, because the concrete, and in particular the cement in it, retains some free water which is the vehicle by which the lime hydrolysis of the clinker is able to attack the pozzolana grain.

The newly formed, pseudogelatinous products which envelop the grain and, expanding, fill the empty spaces, are in turn both the cause and the site of the phenomena of adherence about which we know nothing, so we are unable to assess their undoubtedly considerable influence on the strength of the hardened cement. For example, it is well known that by using clinker as an aggregate extremely strong concretes are obtained [78, 79].

It may further be recalled that with pozzolanic additions such as diatomaceous earths, the workability of the pastes can be improved and the tendency of the aggregates to segregate reduced, at the same water-cement ratio [80].

With regard to frost resistance, concretes made from pozzolanic cements and air cured are considered more sensitive than those made of pure portland cement, although this undesirable characteristic can be repressed by the use of air-entraining agents.

The physico-mechanical properties of portland-pozzolana mixtures obviously depend on both the type of clinker and the type of pozzolanic material, as well as on the mixture ratio.

Undoubtedly the lack of reliable criteria for predicting the behavior of pozzolana when mixed with portland clinker has in the past limited and still inhibits wider use of pozzolanic cements beyond specific applications like marine works and the larger types of cast concrete constructions.

It must be admitted that with our present knowledge it is still impossible to estimate accurately the most suitable mixture ratio for a given clinker and a particular type of pozzolana in order to obtain optimum cementitious properties.

This ratio has to vary not only with the type of the two materials mixed, clinker and pozzolana, but also in accordance with the end purpose of the cement, which may call for enhancement of one, or a limited number, of quality characteristics.

Actually, the technology of the production of cement has forged ahead of its application so that only in special cases like thin, light prestressed structures, which so far do not constitute the greater part of the total, is quick-hardening cement with high initial strength called for. In the majority of end uses, the advantages accruing from very high strength would be questionable if they were to give rise in practice to an unduly low cement content in the concrete, or inappropriate reduction in the size of the structures, with the same concrete mixture ratios [81].

In endeavoring to augment concrete strength by means of the cement factor only, it should be considered that as a rule the initial strength of portland cements with high hydraulic value is accompanied by negative characteristics, such as high heat of hydration with its ensuing thermal effects, increased drying shrinkage, and diminished corrosion and frost resistance, all factors which are closely related to the life of the construction.

In Italy, pozzolanic cements, which are classified under proper standard specifications demanding a composition ratio (portland-pozzolana mixture) with a high pozzolana content, have for many years been widely employed not only for the specific end-uses referred to in the foregoing, but also for all kinds of air-cured constructions.

In other words, this cement stands on the same footing as portland in satisfying the demands of a considerable part of the cement uses contemplated by current building techniques.

However, developments in these techniques, and the ensuing demand for higher strengths, may, and probably will at some future time, lead to a further quality differentiation between pure portlands and pozzolanic cements.

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Discussion

W. C. Hansen

The statement by the author that pozzolans produce "pseudogelatinous formations which tend to fill the empty spaces" suggested the idea of calculating the porosities of hardened cement pastes made without and with pozzolans. In these calculations, it was assumed that SiO_2 forms $C_3S_2H_3$ and that Al_2O_3 forms either C_3AH_6 or C_4AH_{13}. It was also assumed that SiO_2 and Al_2O_3 in glasses, altered tuffs, and activated clays have somewhat lower densities than those of quartz and corundum. The values used for the densities of the various compounds are as follows:

Compound	*Density*	*Compound*	*Density*
$Ca(OH)_2$	2.23	C_4AH_{13}	2.08
C_3S	3.15	S	2.31
$C_3S_2H_3$	2.44	A	3.50
C_3AH_6	2.52		

The first four were taken from Lea [1],[1] the fifth from Roberts [2] and the others from a chemical handbook [3].

The calculations were made on the basis that the cement was pure C_3S, that clays have the composition AS_2, that the water content of the cement paste was 40 percent by weight of solids (cement plus pozzolan), and that the decrease in the volumes of the reactants upon combination exists as void spaces in the hardened paste. In other words, it is assumed that the volume of the undried hardened paste equals the sum of the volumes of the reactants (solids plus water) and consists of solid reaction products, uncombined water, and void space with the sum of the last two representing the porosity.

Calculations were made for six reactions as follows:

$$\begin{array}{ll}
 & 2(C_3S)+6H=C_3S_2H_3+3CH \\
\text{Weights} & 456+108=342+222 \\
\text{Volumes} & 144.7+108 \quad 140.2+99.5 \\
\multicolumn{2}{l}{\text{Void Space}=(144.7+108)-(140.2+99.5)=13.0}
\end{array} \qquad (1)$$

$$\begin{array}{ll}
 & 2(C_3S)+2S+6H=2(C_3S_2H_3) \\
\text{Weights} & 456+120+108=684 \\
\text{Volumes} & 144.7+52+108 \quad 280.4 \\
\multicolumn{2}{l}{\text{Void Space}=(144.7+52+108)-280.4=24.3}
\end{array} \qquad (2)$$

$$\begin{array}{ll}
 & 2(C_3S)+A+9H=C_3S_2H_3+C_3AH_6 \\
\text{Weights} & 456+102+162=342+378 \\
\text{Volumes} & 144.7+29.1+162 \quad 140.2+150 \\
\multicolumn{2}{l}{\text{Void Space}=(144.7+29.1+162)-(140.2+150)=45.6}
\end{array} \qquad (3)$$

$$\begin{array}{ll}
 & 8(C_3S)+3A+51H=3(C_4AH_{13})+4(C_3S_2H_3) \\
\text{Weights} & 1824+306+918=1680+1368 \\
\text{Volumes} & 478.8+87.4+918 \quad 807.7+560.8 \\
\multicolumn{2}{l}{\text{Void Space}=(478.8+87.4+918)-(807.7+560.8)=115.7}
\end{array} \qquad (4)$$

$$\begin{array}{ll}
 & 14(C_3S)+3(AS_2)+69H=3(C_4AH_{13})+10(C_3S_2H_3) \\
\text{Weights} & 3192+306+360+1242=1680+3420 \\
\text{Volumes} & 1013.3+87.4+155.8+1242 \quad 807.7+1401.6 \\
\multicolumn{2}{l}{\text{Void Space}=(1013.3+84.7+155.8+1242)-(807.7+1401.6)=289.2}
\end{array} \qquad (5)$$

$$\begin{array}{ll}
 & 4(C_3S)+AS_2+15H=3(C_3S_2H_3)+C_3AH_6 \\
\text{Weights} & 912+222+270=1026+378 \\
\text{Volumes} & 289.4+81.0+270 \quad 420.6+150 \\
\multicolumn{2}{l}{\text{Void Space}=(289.4+81.0+270)-(420.6+150)=69.8}
\end{array} \qquad (6)$$

TABLE 1.

Reaction No.	Weight of solids	Volume of water [a]	Volume of reactants	Volume of combined water	Volume of free water	Volume of voids	Volume of total pores	Percent [b] porosity by volume
1	456	182.4	252.7	108	74.4	13.0	87.4	34.5
2	576	230.4	304.7	108	122.4	24.3	146.7	48.1
3	558	223.2	335.8	162	61.6	45.6	107.2	31.9
4	2,130	852.0	1,484.2	918	−66.0	115.7	(c)	(c)
5	3,858	1,543.2	2,498.5	1,242	301.2	289.2	590.4	25.2
6	1,134	453.6	640.4	270	183.6	69.8	253.4	39.5

[a] 40 percent by weight of solid reactants.

[b] Volume of voids plus volume of free water as percent of volume of reactants (solids plus water).

[c] 40 percent water is insufficient for complete reaction.

The data from the calculations give rise to table 1.

From these calculations, one might draw the following conclusions regarding the influence of pozzolans in producing hardened pastes with porosities below those of hardened pastes of portland cements:

(1) A highly siliceous pozzolan is harmful.

(2) A highly aluminous pozzolan is beneficial if the reaction product of the alumina is C_4AH_{13} and only slightly beneficial if the product is C_3AH_6.

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[1] Figures in brackets indicate the literature references at the end of this paper.

(3) An aluminous product with an A/S ratio of 1:2 is beneficial if the reaction product of the alumina is C_4AH_{13} but harmful if the product is C_3AH_6.

The author points out that, compared to portland cements, the portland-pozzolan cements require more water, have greater drying shrinkage and greater expansion when submerged in water. Some investigators have visualized this expansion as filling void space. Lea [4], following a theory by Lafuma, pictured the solid grain of pozzolan reacting in the hardened paste with dissolved $Ca(OH)_2$ to form solid products *in situ* which, upon crystallizing, exert a thrust against the surrounding solids. This mechanism of the reaction appears to be correct, but it is difficult to see how this expansion would have much, if any, effect in decreasing the space classed as voids and the space occupied by uncombined water in the hardened paste.

It seems that the results for porosities obtained from these calculations should indicate approximately what is to be expected from pozzolans of different compositions. If this is true, then the influence of a given material on such properties as strength, resistance to leaching by water, resistance to attack by sulfates, and resistance to freezing and thawing might be predicted in a general way from information regarding the amounts of reactive SiO_2 and Al_2O_3 in the product. Any material that tended to increase the porosity of the hardened paste would be expected to be harmful with respect to those properties. These calculations have not taken into account the effects of any inert materials that might be present in commercial pozzolans.

The author points out that the alkali content of the pozzolan may play a substantial role in the kinetics of the reaction with $Ca(OH)_2$. It seems that this might be particularly true for glasses and that the alkali content of the cement may also have a marked effect upon the rates at which glasses are converted to calcium compounds. Alkalies in the cement that are released to the water will increase the OH^- ion concentration in the liquid phase and make it more aggressive toward the glass. They will also decrease the Ca^{2+} ion concentration, which would tend to retard the rate of conversion to calcium compounds. However, the increase in OH^- ion concentration probably has a greater effect than the decrease in the Ca^{2+} ion concentration.

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Discussion

N. R. Srinivasan

I will confine my remarks mainly to the following three points:

(1) Certain aspects of the structure of pozzolanic materials.

(2) The relationship between pozzolanic action and cement hydration.

(3) The resistance to sulfate attack as offered by the pozzolanas.

In the course of a past investigation [1, 2][1] at the Central Road Research Institute, New Delhi, on the pozzolanic properties of burnt clay powder (Surkhi), many of the earlier findings of Mielenz and others [3] regarding the relationship between the structural collapse of the clay and its pozzolanic activity were confirmed. In addition, it was pointed out that the structural defects, including the strain in the bonds that accompany the dehydration of clays, greatly influence pozzolanic activity. Thus it was suggested that the conditions governing pozzolanic reactions are the same as those that govern the solid-state reactions.

Experiments on different samples of the individual oxides, viz, silica, alumina, and iron oxides showed, as expected, widely differing reactivity for the different samples of the same oxide. This variation was attributed to the different structural and surface conditions which are greatly interrelated. Among these oxides, silica from silicic acid gels showed by far the greatest reactivity. Alumina and iron oxides of certain forms exhibited a limited degree of reactivity. Some natural aluminosilicates like kaolin showed, after burning at optimum temperature, the highest reactivity. This is in line with the evidence presented in this paper wherein the presence of "reactive alumina" (which could reasonably be taken as the low-temperature form of gamma alumina and related forms) is said to enhance the reactivity of the pozzolana. The reactivity in all these cases was measured by determining the compressive strengths of lime-pozzolana mixtures.

At present some work is being done to study certain parallels that seem to exist between the required structural conditions for an effective silica-alumina cracking catalyst and an effective pozzolana. It is true that catalytic and pozzolanic reactions are entirely different from each other. The catalyst is a foreign body which without any apparent change presents a surface with 'active spots' where reactions between the components can take place more rapidly. The pozzolan on the other hand is part of the reacting system that undergoes permanent changes through new chemical bonding with hydrated lime. But part of their mechanisms may have something in common as is indicated by the following.

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[1] Figures in brackets refer to the literature references at the end of this paper.

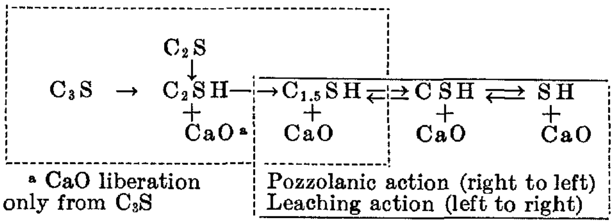
It is known that neither silica nor alumina by itself is as good a catalyst as a proper combination of both. The silica-alumina catalysts obtained through coprecipitation have in them the $>\mathrm{Si{-}O{-}Al}<$ bonds, which could not be formed if both or either of the oxides were anhydrous to begin with. In the case of clay catalysts, their modes of preparation are strikingly similar to those of clay pozzolans, both of which need acid treatment and/or dehydration. In all the preparations, the Al ion is said to occupy a tetrahedral position, which is held to be an essential condition for catalytic reaction [4]. This structural defect has been shown to involve the movement of the O ions by a few tenths of an angstrom and consequent strain in the bonds [5]. The AlO_4 part also needs a H ion to balance the electrical charge, and this ion imparts the 'acid' character to the catalyst [4]. This H ion plays an important part in the reactions. Many of the said factors may also facilitate chemical bonding of the molecules with the surfaces, and thus affect both pozzolanic and catalytic reactivity. It appears that the mode of bonding will be explained in due course by the principles of the solid state and semi-conductors.

If it is accepted that the reactivity is mainly controlled by structural defects, it is possible to explain some anomalies regarding pozzolans and cements. It explains, for instance, the apparent difference between the different types of pozzolans. The reactivity of the natural pozzolans of volcanic origin could mainly be attributed to the high degree of structural disorder that is known to exist in the glassy phase. Thermal treatment of these products may often result in the release of the excess strain in bonds and a somewhat more orderly structural arrangement as happens during the process of annealing, and may thus adversely affect reactivity. The present paper shows that such reduction in reactivity does take place. Pozzolanas like opal, chalcedony, diatomaceous earth, etc., are mainly composed of hydrated silica and may thus behave similar to silica gels. Dehydration of these brings about special surface conditions with defective structure conducive to enhanced reactivity. Those like clays, bauxite, etc., also need dehydration accompanied by complete or partial collapse of the structure, so that highly reactive forms of silica, alumina, or a complex remnant structure of the alumino-ferro-silicate, all characterized by a highly defective structure, could be left behind.

In the case of cement compounds, the varied structural investigations have more or less established that structural defects, such as the irregular coordination of ions which leave structural "holes" and bond strains, and the tetrahedral coordination of Al in certain structures, are effective in promoting hydration reactivity. Similar defects seem to affect pozzolanic reactivity as well.

The final products of both cement hydration and pozzolanic reaction appear to be the same, as has been pointed out in this paper, even though the course of their formation is different. A combined picture of the two reactions could be given as below:

Cement Hydration (left to right)



Sulfate resistance. Till now it was held that use of burnt clay in concrete was one of the measures to counteract sulfate attack. An extensive investigation at the Central Road Research Institute [6] has shown that clays calcined at 600–800 °C were not as effective in preventing sulfate attack as those burnt at 1,000 °C. In fact, with certain clays like kaolins burnt at 600–800 °C, the concrete suffered greater damage than in the case of plain concrete. The following explanation appears to be close enough to the one indicated in this paper.

At 1,000 °C, the alumina released from any clay after structural disintegration is in the high-temperature gamma form or alpha form, both with a comparatively better crystallinity, ordered structure and reduced reactivity. Thus the alumina in clays calcined at 1,000 °C is not able to combine effectively with the CaO and SO_3 to form the expansive sulfoaluminate. At lower temperatures, the alumina is in the highly reactive, microcrystalline, low-temperature form of gamma alumina with defective spinel structure. In the system $CaO{-}Al_2O_3{-}CaSO_4{-}H_2O$, it is reasonable to expect marked reaction, leading to ettringite formation, only with the reactive form of gamma alumina as obtained from clays calcined at a lower temperature.

With the above explanation it appears as if the dehydrated clay structure, despite its complex nature, is so highly strained that the bonds get broken and the individual oxides get separated easily, thus giving the components for the $CaO{-}Al_2O_3{-}CaSO_4{-}H_2O$ system.

Other reasons may include the type of sulfoaluminate formed (ettringite or the low-sulfate type) depending upon the concentration of the lime solution in the vicinity of the reaction.

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Discussion

L. Santarelli

Prof. Malquori's paper refers to the methods used to measure the heat of hydration of pozzolan cements and dwells on the difficulty accompanying the solution method, due to the incomplete solubility of these cements.

Malquori points out a weak point in the determination of the heat of hydration of pozzolan cements and it seems, therefore, opportune to return to the subject, due to the undeniable importance that the measurement of the heat of hydration has on the use of pozzolan cements in the construction of dams.

Two studies [1,2] [1] on the subject appeared after Malquori's paper had been presented to this Symposium, and I wish to refer to them in this discussion. They propose a modification of the ASTM method and present a new thermometric method known as the "Controlled dispersion thermometric method."

The main modification of the ASTM method consists in maintaining constant the temperature of the surroundings of the reaction vessel, extending the solution period to two hours so as to reduce to a minimum the insoluble residue due to the pozzolan (this extension is rendered possible by the thermostatic bath which facilitates the correction system), and adopting a special device for the introduction of the sample in the acid mix.

The adoption of these modifications permitted the substantial reduction of the strong variations which occur in the measurement of the heat of hydration by the solution method.

The table 1 shows the dispersion coefficients observed with two pozzolan cements (prepared with the same clinker and two different pozzolans), compared with those of portland cement (prepared with the same clinker used in the pozzolan cements).

It is worth remarking that in the previous tests with the solution method (not modified) by the same operator, the average dispersion for pozzolan cements was 10 times as high.

The second study concerns the elaboration of a method which would not require particular chemical operations as does the solution method and which also would permit the following of the evolution of heat during the initial stage.

With the apparatus shown in figure 1, it is possible to follow the thermal process of hydration from 15 minutes to 28 days.

Adopting spherical Dewar vessels, it was possible to obtain very low dispersion coefficient values K (8–10 cal/deg/hr) permitting the making of measurements up to 28 days.

TABLE 1. *Standard deviation (σ) and coefficient of variation (σ%) values (modified solution method)*

Sample	Heat of solution (average figures for anhydrous cement and hydrated cement at 7 and 28 days)		Heat of hydration (average figures at 7 and 28 days)	
	σ	σ%	σ	σ%
Pozzolan Cement L	1.37	0.26	1.57	2.73
Pozzolan Cement F	1.03	0.19	2.11	3.52
Portland Cement	0.79	0.14	1.12	1.44

The thermal capacity of the Dewar vessels is determined by the cold water plus hot water mix method: with this calibration method the dispersions obtained calculating thermal capacities are <0.2 percent.

Table 2 shows the statistical data obtained in two series of tests run with this method on one portland and one pozzolan cement.

A noticeable decrease of the σ percentage value for pozzolan cements in comparison with the solution method may be seen, while for the portland cement practically the same values are obtained (the increase of 0.33 can not be considered a significant difference).

TABLE 2. *Heat of hydration and σ and σ% values (thermometric method)*

Cement	Days	Calorimetric vessel					Average σ	σ %
		1	2	3	4	5		
		cal/g	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	
Portland	3	61.96	62.17	61.94	60.42	60.29	61.36±0.92	1.50
	7	70.10	69.52	69.52	69.79	67.24	67.14±1.45	2.11
	14	73.22	72.86	73.37	70.61	71.13	72.24±1.27	1.75
	21	74.61	74.10	75.14	72.01	72.96	73.76±1.27	1.72
	28	75.99	74.98	76.16	72.84	74.35	74.86±1.35	1.80
								$\overline{X}$=1.77
Pozzolan	3	36.58	36.90	36.22	37.00	36.61	36.66±0.31	0.84
	7	45.99	46.90	45.39	46.76	46.90	46.39±0.67	1.44
	14	52.66	53.50	51.75	53.53	53.95	53.08±0.88	1.65
	21	55.31	56.06	54.34	56.12	56.65	55.70±0.89	1.60
	38	56.21	57.13	55.50	57.28	57.80	56.78±0.96	1.69
								$\overline{X}$=1.44

Comparing the results obtained with this and the solution method we may see the influence of the higher temperature reached by the cementitious paste with the thermometric method (maximum temperature 30–32°) and of the initial period of 15 minutes, during which the cementitious paste remains outside the Dewar vessels (which in reality takes place also in practice). Studies to examine thoroughly the influence of these variables with the aim of rendering comparable the two methods are in progress.

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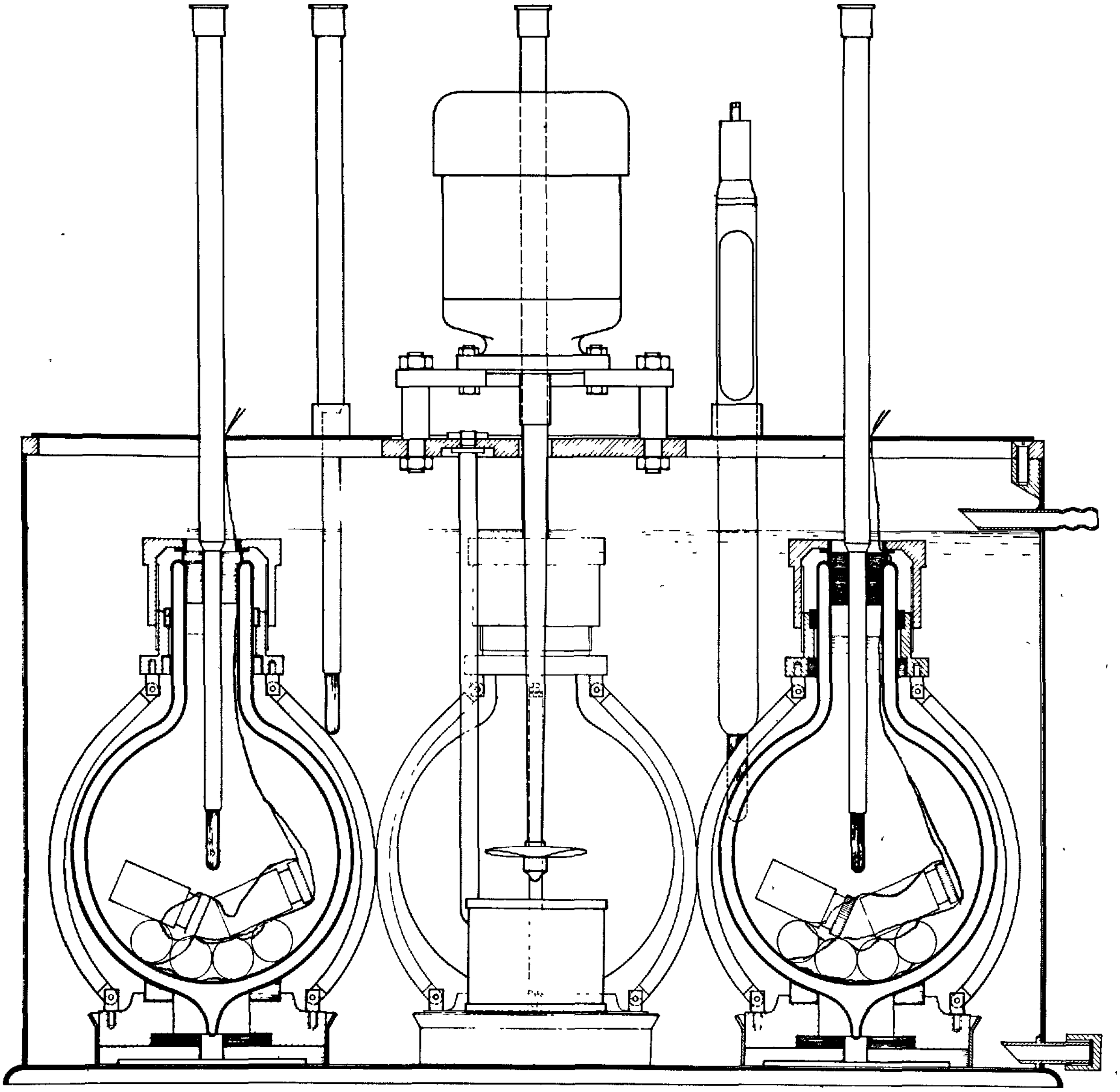

FIGURE 1. *Cross section of thermostat showing the details of the thermos bottles with containers for the cementitious paste.*

Discussion

H.-G. Smolczyk

Professor Malquori's excellent paper is of high interest to us, especially with regard to a comparison between pozzolan cements and blast-furnace slag cements. In his paper Professor Malquori states ". . . glassy (blast-furnace) slags with hydraulic properties are in themselves sufficiently basic and therefore have but a weak pozzolanic activity, in the sense of their ability to combine with lime coming from the saturated contact solution." We are also of the opinion opinion that, in general, basic blast-furnace slags show less ability to combine with lime than do highly active natural pozzolans. But well-composed, highly hydraulic blast-furnace slags do bind CaO, too, while hydrating, and this particular property can lead to the fact that mortars made of low-clinkered blast-furnace slag cements with a high percentage of well granulated slag contain but a very small amount of $Ca(OH)_2$.

The well-known capacity of good blast-furnace cements to resist various aggressive fluids can to a certain extent be explained by this property.

In figure 1 the results of some experiments are represented by graphs. A good hydraulic granulated slag, with varying admixtures of the same clinker and the same gypsum content, was ground, and the free $Ca(OH)_2$ was measured after 3, 7, and 28 days of water storage and plotted

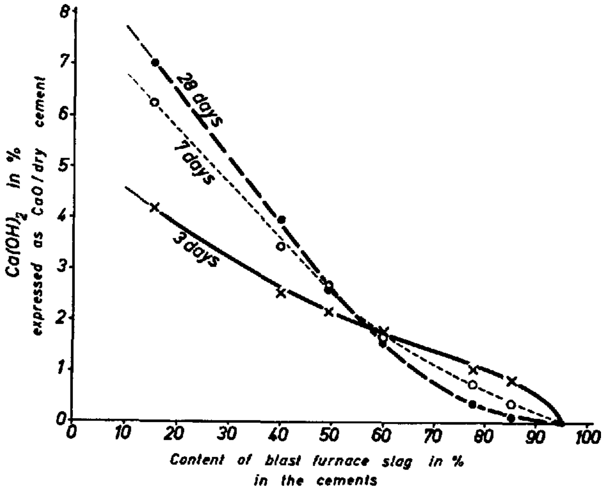

FIGURE 1. *Pozzolanic activity of a granulated-base blast-furnace slag with high activity.*

against the slag content. The graphs show the double influence of hydraulic blast-furnace slags: First, the content of newly formed soluble lime decreases in any of the three test periods in relation to the lower clinker content of the cements. If, on the other hand, reference is made to the change of the Ca(OH)$_2$ content with increase in the period of storage, the high-clinker slag cements exhibit a continuous increase of Ca(OH)$_2$, whereas low-clinker blast-furnace slag cements suffer a reduction, and, in the most extreme case, may approach zero.

Discussion

E. Burke

I should like to emphasize the importance of the author's statement that two factors must be measured in the evaluation of a pozzolanic cement; namely, the pozzolanicity which can be measured by the method described and which has been accepted by the International Standards Organization, and the mechanical strength.

In evaluating the mechanical strength attention needs to be directed to practical manufacturing conditions. In assessing the value of a pozzolana it is usual to test it by grinding or mixing it with a portland cement clinker or cement and comparing it with the same cement without pozzolana. Pozzolanas vary very greatly in their grindability so that a specific surface test is not of great value and even a sieve test is not without difficulties. The method we have used is to standardize the amount of energy used in the grinding; e.g., in a laboratory mill the total number of revolutions is the same for both the control portland cement and for the pozzolana cement.

A useful test to determine when the pozzolana contributes to the mechanical strength is to calculate or determine the strength of the control portland cement at the water/cement ratio used with the pozzolana cement, assuming that the pozzolana is part of the aggregate, i.e., the water/cement ratio is calculated on the portland cement portion only. In many of the pozzolanic materials we have tested so far we have found that no strength is contributed by the pozzolana until after 7 days but in the case of the very reactive Italian pozzolanas there is distinct contribution to strength even at three days.

The author's statement that the compounds formed on the hydration of pozzolana cements are essentially the same as those in the case of portland cement can be confirmed. One would, therefore, expect that, if the portland cement portion is a sulfate resisting type, much improved resistance would be obtained. The higher resistance of pozzolana cements made with ordinary portland cement must be attributed largely to the smaller amount of free calcium hydroxide. However, we have found that cements of this type are not as resistant as the Type V cement, especially when its C$_3$A content is very low. It would also be interesting to know if the more reactive pozzolanas give cements less resistant to sulfates than the less reactive pozzolanas. One might expect this in the light of Srinivasan's contribution, where it was stated that clays burned at 600–800 °C gave less resistant pozzolana cements than those burned at 1,000 °C.

Closure

Giovanni Malquori

Let me thank first of all Dr. Hansen for his remark, which is of particular interest as a proposal for further investigations. He suggests the usefulness of taking into account the variation in porosity of portland-pozzolan cement pastes and concretes, as a function of the lime attack on pozzolana, in view of the fact that the "absolute volume" of the final system, which consists of the pozzolanic reaction products, is somewhat smaller than the initial one, i.e., from the sum of the starting materials' "absolute volumes."

The interpretation of the problem is rather complicated. To make, indeed, a precise distinction among the different variables affecting it, is, in practice, not easy, taking into account that the systems we are dealing with are of the greatest complexity because of the following factors: structural disorder, presence of minor constituents, and possible solid state associations. Furthermore, distinguishing stable from transient structures is likewise difficult.

Early dilatometric investigations [1] carried out in order to evaluate the "absolute volume" variation (shrinkage) during hardening of pozzolanic materials–lime pastes (ratio: 1:1), kept in excess

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[1] G. Malquori and F. Sasso, Volume changes during the hardening of the system: materials showing pozzolanic activity-lime-water, Ricerca Sci. 8, (II), 440 (1937).

water, showed that the shrinkage is related to the amount of reactive Al_2O_3 in the starting pozzolanic material, as well as to the water stably bound (above 105 °C) in the hardened paste, exception being, of course, made of the water bound to free $Ca(OH)_2$.

Dr. Hansen's remark suggests the opportunity of further investigation in the field of the physical properties of pozzolana-lime and portland-pozzolan cement pastes with regard both to the kind of pozzolana and to the mixture ratio.

I agree with Mr. Srinivasan that all transformations which determine or increase disorder and structural instability—reticular deformation, defects, and so on—increase the solid reactivity.

I also agree with Mr. Burke that the decrease, and still more the elimination, of free and mobile lime in the hardened pozzolanic cement which has been kept in water, is the main factor in the interpretation of its resistance to chemical attack by the dangerous constituents of the immersing water.

I would like to add to what has been said by Mr. Smolczyk that the problem of the behavior of granulated basic slag toward lime solution has been studied a long time at our Institute in Naples, and that our results confirm Mr. Smolczyk's indications.[2]

Finally, I thank Professor Santarelli for his remark.

I conclude by apologizing for possible omissions, and for probably not having duly emphasized the importance of some topics. This is due to the amplitude of the subject dealt with.

It should also be clear that the chief aim of this report is to emphasize that the subjects which have been briefly outlined, far from being exhausted, may well be the ground of further investigation. Personally I will consider that this aim has been satisfactorily fulfilled if the report will push further researches, the results of which I hope will be presented at the next "International Symposium."

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[2] R. Sersale and P. Giordano Orsini, Hydration and transformation of blast-furnace slags by contact with calcium hydroxide solution, Atti Accad. Sci. Fis. e Mat. [III], 1, (1960); Ricerca Sci. 30, 1230, (1960).

Paper VIII-4. Calcium Aluminates and High-Alumina Cements*

P. Lhopitallier

Synopsis

During the past 10 yr, new studies have been made concerning calcium aluminates. Anhydrous aluminates have not been the subject of important research: however, it seems that the reality of the compound C_6A_4fS, the formula of which had been proposed by Parker, is dubious.

Hydrated aluminates, on the contrary, have been widely studied. Researches concerned especially: The equilibrium diagrams; the reality of the compound C_3AH_n (hexagonal); the dehydration of aluminates.

Concerning the equilibrium diagram in the system $CaO-Al_2O_3-H_2O$, at various temperatures, we recall that it had been studied, during the previous years, at 21 and 90 °C only. During the period between 1950 and 1959, its construction at lower temperatures was attempted. Generally, all the results confirm, roughly, the observations made previously by Bessey and Wells. However, the picture of the equilibria, first at 1 and 5 °C, then at 21 °C, permitted a definition of the region of existence of the compound CAH_{10}, the reality of which had not previously been established.

Furthermore, it appears as established now that in normal conditions of use and at ambient temperature, the hexagonal compound that is formed is CAH_{10}, the compound C_2AH_8 being only an intermediary phase of very brief existence, except in the presence of a great excess of hydration water.

As for the C_3AH_n, it is known that its existence is debated. Schippa and Turriziani have brought new data into the discussion. According to these writers, C_3AH_{12} would be in fact the monocarboaluminate $C_3A{\cdot}CaCO_3{\cdot}H_n$, whose formation cannot be avoided, the hexagonal aluminates being especially responsive to the action of CO_2 in damp atmosphere. This fact justifies the interest that would be offered by the study of the quaternary system $Al_2O_3-CaO-CO_2-H_2O$.

The same aluminates are equally sensitive to the humidity of atmospheric air. The molecules of water in the hydrates seem in effect to be bound to the molecules in a very loose manner. The loss of this crystallization water, when great enough, corresponds to a change in the crystal unit, a change which can be seen in the X-ray diffraction spectra.

The identification of the hexagonal aluminates, by the method of X-ray diffraction, is therefore somewhat tricky. It is really important that the spectrum corresponding to a definite number of molecules of water may be known with sufficient precision.

Résumé

Au cours de ces dix dernières années, de nouvelles recherches ont été entreprises sur les aluminates de calcium. Les aluminates anhydres n'ont pas été l'objet de travaux importants: cependant, il semble que l'existence du composé C_6A_4fS, dont la formule fut proposée par Parker, soit sujette à caution.

Les aluminates hydratés par contre, ont été très étudiés. Les recherches ont, en particulier, porté sur: Les diagrammes d'équilibre; l'existence du C_3AH_n; la déshydratation.

En ce qui concerne les diagrammes d'équilibre du système $CaO-Al_2O_3-H_2O$ à différentes températures, rappelons que celui-ci n'avait été étudié en effet, jusqu'alors, qu'à 21 et 90 °C. Au cours de la dernière décade, son tracé a été tenté à plus basse température. D'une façon générale, tous les résultats obtenus confirment, dans leurs grandes lignes, les observations faites antérieurement par Bessey et Wells, entre autres. Toutefois, le tracé des courbes d'equilibre, à 1 et 5 °C d'abord, à 21 °C ensuite, a permis de définir le domaine d'existence du CAH_{10}, composé dont le comportement n'avait pas auparavant été examiné.

Il semble d'ailleurs établi maintenant qu'à la température ambiante et dans les conditions habituelles d'emploi des ciments alumineux, l'aluminate hexagonal qui se forme est précisément CAH_{10}, C_2AH_8 n'ayant qu'une très brève existence, sauf si la quantité d'eau d'hydratation est importante.

Pour le C_3AH_n, on sait que son existence est controversée. L'équipe italienne de Schippa et Turriziani a apporté un élément nouveau dans le débat. D'après ces auteurs, le C_3AH_{12} serait en réalité le monocarboaluminate $C_3A{\cdot}CaCO_3{\cdot}H_n$, dont la formation apparaît comme inévitable, les aluminates hexagonaux étant particulièrement sensibles à l'action du CO_2 en milieu humide, d'où l'intérêt que présenterait l'étude du système quaternaire $Al_2O_3—CaO—CO_2—H_2O$.

Ces mêmes aluminates sont également sensibles à l'influence de l'hygrométrie de l'ambiance. Les molécules d'eau des hydrates semblent, en effet, liées de façon lâche à la molécule. Le départ de cette eau de cristallisation, lorsqu'il devient important, s'accompagne d'une modification des dimensions de la maille cristalline, modification qui se répercute sur les spectres de rayons X.

Il en résulte que l'identification des aluminates hexagonaux à l'aide des spectres de diffraction X devient plus délicate. Il est donc important que les spectres correspondant aux différentes proportions de molécules d'eau soient connus avec précision.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the laboratories of Ciments Lafarge, France. (This paper was presented at the Symposium by R. Rabot.)

Zusammenfassung

In den letzten zehn Jahren sind die Kalziumaluminate wiederholt untersucht worden. Es ist nicht viel über wasserfreie Aluminate gearbeitet worden, aber man hat doch herausgefunden, daß die Verbindung C_6A_4fS, deren Formel von Parker vorgeschlagen worden ist, vielleicht garnicht existiert.

Aber die hydratisierten Aluminate sind sehr oft untersucht worden, und man hat hier vor allen Dingen die Zustandsschaubilder, die Existenzfähigkeit der Verbindung C_3AH_n (hexagonal), und die Entwässerung der Aluminate untersucht.

Das Zustandsdiagramm des Systems CaO–Al_2O_3–H_2O war früher nur bei 21 und 90 °C untersucht worden, aber man hatte doch zwischen 1950 und 1959 versucht, es für niedere Temperaturen zu konstruiren. Die Ergebnisse können so zusammengefaßt werden, daß die Beobachtungen von Bessey und Wells im allgemeinen bestätigt worden sind. Aber die Gleichgewichte, die bei 1, 5° und später auch bei 21 °C erhalten wurden, haben erlaubt, das Gebiet der Existenzfähigkeit der Verbindung CAH_{10}, dessen Existenz früher zweifelhaft war, zu begrenzen.

Es ist nun auch festgestellt worden, daß unter den gewöhnlichen Gebrauchsbedingungen und den vorherrschenden Außentemperaturen, die hexagonale Verbindung CAH_{10} gebildet wird; die Verbindung C_2AH_8 ist nur eine Zwischenphase, die eine sehr beschränkte Lebensdauer hat, sei es denn, daß Hydratationswasser im großen Überschuß vorhanden ist.

In Beziehung zu C_3AH_n muß gesagt werden, daß man schon immer die Existenz dieser Verbindung angezweifelt hat. Schippa und Turriziani haben neue Messungen, die etwas zur Diskussion beitragen können, unternommen. Diese Forscher behaupten, daß das sogenannte C_3AH_{12} mit der Verbindung der Formel $C_3A{\cdot}CaCO_3{\cdot}H_n$ vollig identisch sei, da man dessen Bildung ja nie vermeiden kann, weil besonders die hexagonalen Aluminate in einer feuchten Atmosphäre sehr schnell mit CO_2 reagieren. Das deutet an, daß eine Untersuchung des quaternären Systems Al_2O_3–CaO–CO_2–H_2O doch sehr wünschenswert wäre.

Diese Aluminate sind auch gegen die Feuchtigkeit der atmosphärischen Luft sehr empfindlich. Es sieht so aus, als ob die Wassermoleküle in den Hydraten an die Aluminatmoleküle nur schwach gebunden sind. Wenn das Krystallisationswasser in genügendem Maße verloren geht, verändert sich die Raumgruppe, was im Röntgendiagramm erkannt werden kann.

Das hat nun zur Folge, daß das Identifizieren der hexagonalen Aluminate durch Röntgendiagramme mit Vorsicht vorgenommen werden muß. Von grosser Wichtigkeit ist hier die Bedingung, daß das Spectrum einer bestimmten Anzahl von Wassermolekülen genau identifiziert ist.

Introduction

Since 1951, in which year Steinour [53][1] published a very complete study of our knowledge of calcium aluminates and high-alumina cements, much work has been done on the subject.

We have tried to complete the study by Steinour for the period between 1950 and 1960, and the present communication was written for this purpose. We have thus attempted to assemble and to summarize the most important available data of the latter period on the following topics:

Aluminates and anhydrous cements,

Phase relations in the system CaO–Al_2O_3–H_2O,

Hydration process of aluminates and high-alumina cement,

Opposing views concerning the reality of a hydrated hexagonal tricalcium aluminate,

Dehydration of some hydrated aluminates and resulting effects on their structure.

We emphasize the fact that this communication is mainly a bibliographical study. In addition, we often refer to the important general publications by Kühl [29] and Lea [32] who gave, in 1952 and 1956 respectively, most useful accounts of the question at the time.

We apologize for any omission from our list of references.

Anhydrous Calcium Aluminates and High-Alumina Cements

We would only remember here the principal points of the question as they were stated by Lea in his book in 1956. In fact, very little new data has appeared since 1952—in which year Parker [42], in London, published his general study—until 1959, except perhaps those concerning the compound C_6A_4fS:[2] however, for this last, the research is not finished and the results are not yet published.

Aluminum and calcium oxides are present in roughly equal proportions, e.g., 35–40 percent, in the composition of high-alumina cements made industrially from bauxite, and limestone. Besides these principal constitutents, another important one is iron, in the form of FeO or Fe_2O_3, in the proportion of about 15 percent (expressed as Fe_2O_3). The condition of iron in high-alumina cements is determined by the nature of the atmosphere in the furnace in which the cement has been calcined. These cements also contain silica (3–7 percent) and some minor constituents as titania, magnesia, and alkalis, these in much smaller proportions than in portland cement (always under 1 percent).

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[1] Figures in brackets indicate the literature references at the end of this paper.

[2] The symbol f is used herein for FeO.

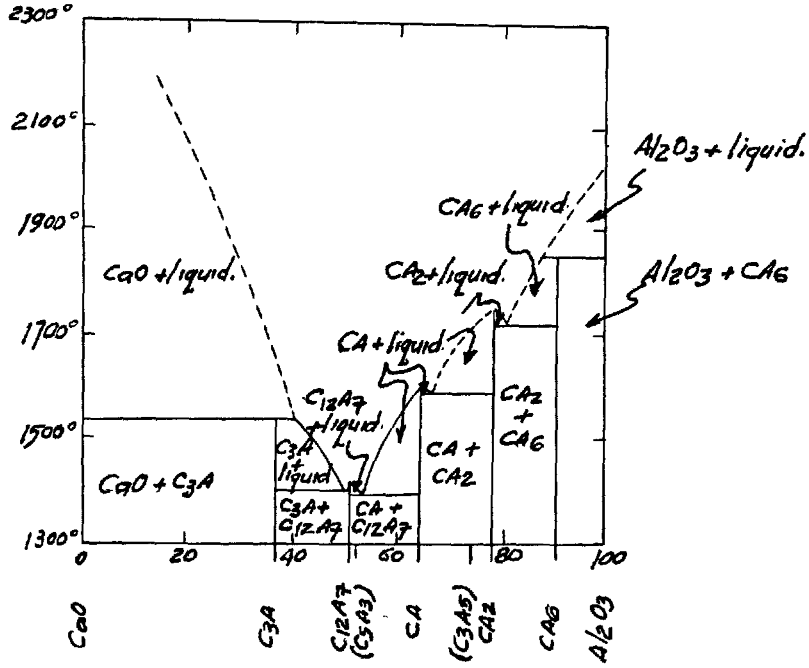

FIGURE 1. *The system* CaO—Al_2O_3.
After Lea [32].

Thus, the potential constituents of high-alumina cements concern not only the binary system CaO–Al_2O_3, but also more complex systems, of which the following have been especially studied: CaO–Fe_2O_3, CaO–Al_2O_3–SiO_2, CaO–Al_2O_3–Fe_2O_3, and, of course, CaO–Al_2O_3–SiO_2–Fe_2O_3 (these systems are illustrated in figs. 1, 2, 3, 4, 5).

Five compounds are formed in the system CaO–Al_2O_3, among which only four are found in high-alumina cements: $C_{12}A_7$ (formerly C_5A_3), CA, CA_2 (or C_3A_5), CA_6. The fifth, C_3A is met only in portland cements.

There is no longer any doubt about the existence of the compound $C_{12}A_7$, and the C_5A_3 formula is only retained as more convenient and because many people are accustomed to it: however, the difference between the two formulations is very little, as Lea pointed out.

"Unstable C_5A_3", resulting from the annealing of the glassy phase of clinker, was for a while confused with a pleochroic prismatic compound which may be found in high-alumina cements. Nurse and Welch show that the two compounds are, in fact, very different: "unstable C_5A_3" actually exists, but Parker, in 1952, considered the prismatic phase, already mentioned, as a solid solution which he formulated: C_6A_4(f,M)S. We shall consider it further.

Further, fused mixtures of composition $C_{12}A_7$ may represent a metastable equilibrium between C_3A and CA, and, under specified conditions, these two compounds may crystallize separately.

It was thought, formerly, that there exists a definite compound C_3A_5, which was then considered one of the main hydraulic constituents of high-alumina cement. It is thought now that C_3A_5 is, in fact, a mixture of CA and CA_2. Although this mixture may give high strengths, CA_2 as an isolated compound is practically inactive. The compound CA_6 has been described and studied by Filonenko and Lavrov [20].

The system CaO–Al_2O_3–SiO_2 gives the compound C_2AS (gehlenite) which hydrates slowly and which can be found in some high-alumina cements.

In the same way, the system CaO–Al_2O_3–Fe_2O_3 presents a compound C_4AF (brownmillerite) which enters the composition of high-alumina cements, as well as portland cements. It was

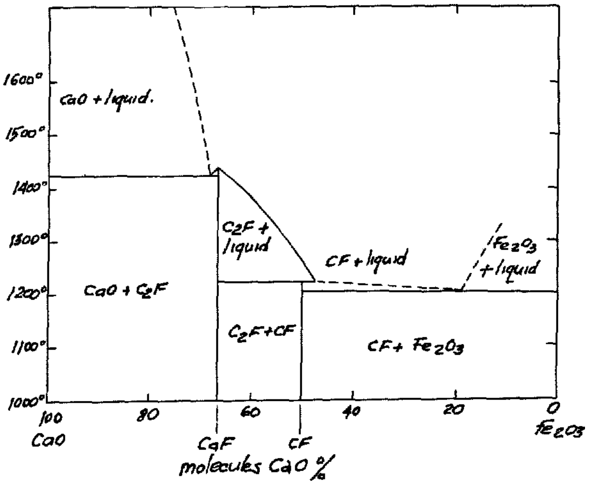

FIGURE 2. *The system* CaO—Fe_2O_3.
After Lea [32].

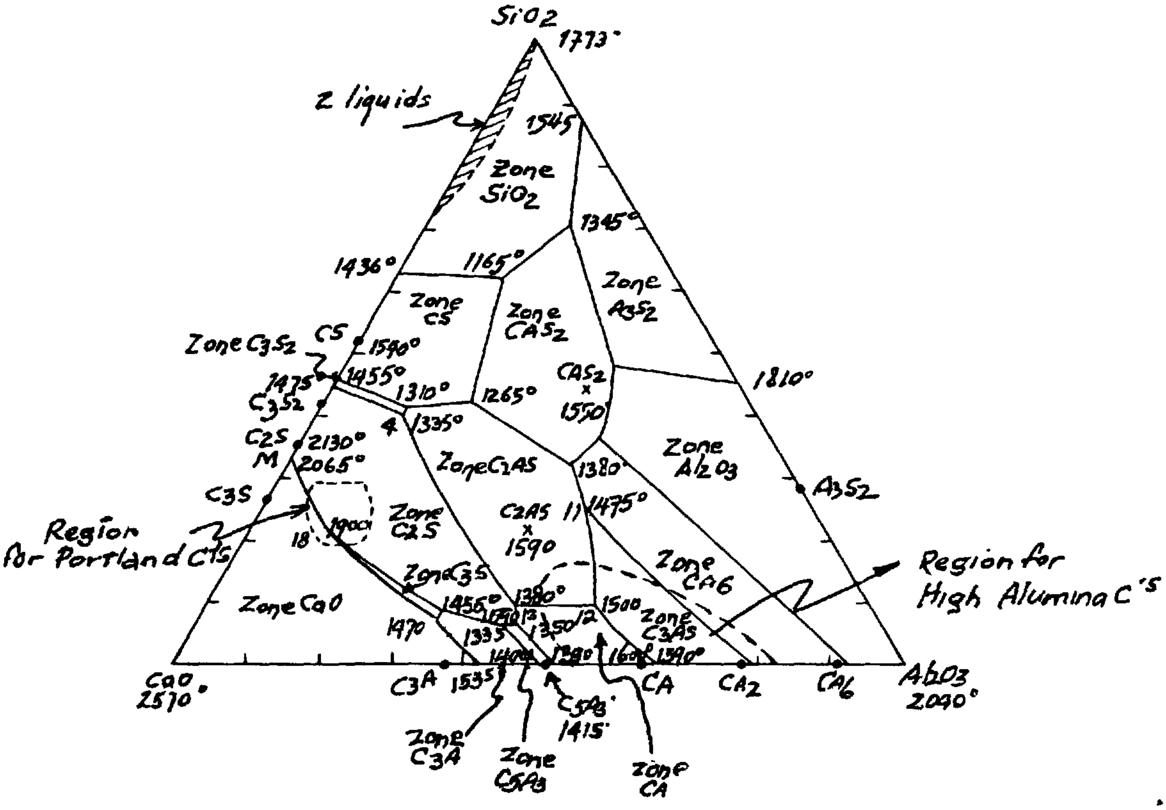

FIGURE 3. *The system* CaO—Al_2O_3—SiO_2.

After Lea [32].

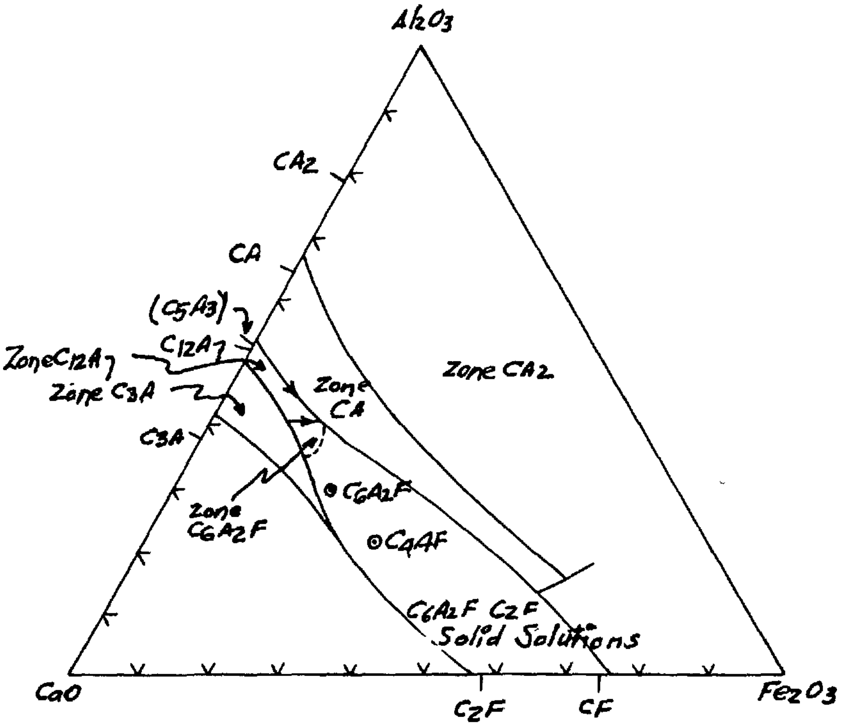

FIGURE 4. *The system* CaO—Al_2O_3—Fe_2O_3.

After Lea [32].

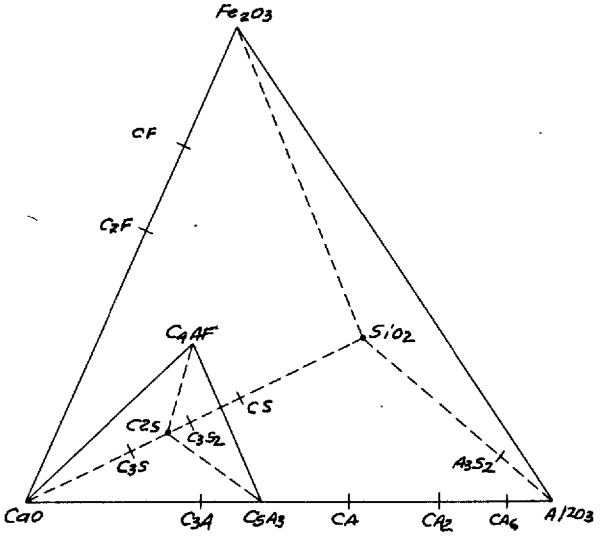

FIGURE 5. *Relation of the system* CaO—C_2S—C_5A_3—C_4AF *to the greater system* CaO—Al_2O_3—SiO_2—Fe_2O_3.

After Lea [32].

first considered a definite compound, but it is thought now to be in fact an intermediate composition which occurs in a series of solid solutions between C_2F and a composition C_6A_2F.

The region of the system CaO–Al_2O_3–SiO_2–Fe_2O_3 of interest in portland cements has been extensively studied, but this is not the case for the region concerning high-alumina cement (see figs. 5 and 6). Parker, in 1952, determined the nature of the minerals present in high-alumina cement and has grouped them as follows: CA—C_6A_4fS—$C_{12}A_7$—C_2S, CA—C_6A_4fS—C_2S—C_2AS, CA—C_6A_4fS—$C_{12}A_7$—FeO, C_6A_4fS—$C_{12}A_7$—C_2S—FeO, CA—C_6A_4fS—C_2AS—FeO.

At the time, these compositions had not been accepted without reserve or divergence (see Lhopitallier and Assaud [35]).

According to Parker, the reality of a compound formulated C_6A_4fS was most probable, because of the existence of an analogous compound C_6A_4MS, TiO_2 being able to replace a part of SiO_2 in both compositions.

However, a not yet published work by Welch makes doubtful the reality of C_6A_4fS, whose formula had not been absolutely established (Robson [47]). For Welch, "unstable C_5A_3," as it has been described formerly by Rankin and Wright, is a reality as a metastable phase in the system CaO–Al_2O_3, and does not depend for its formation on the presence of secondary oxides. The author has not recognized the existence of solid solutions with MgO and (or) SiO_2. Solid crystals of "unstable C_5A_3" have been easily prepared on a heating-plate microscope, and optical characteristics as well as dimensions of the crystal unit have been recently published by Aruja [1].

As for the compound to which the formula C_6A_4(f,M)S was given, it could not be a homogeneous compound, in spite of the fact that it contains the main part of the "fibrous constituent." Welch, however, has described a compound possibly formulated C_7A_5M, very similar to the "fibrous material" in its optical properties and, as to X-ray diagrams, presenting some similarity with C_6A_4MS. The region of stable existence for C_7A_5M would be enlarged because of the existence of a solid solution between this compound and gehlenite, C_2AS. It is thus possible to suppose that the quaternary compound is a solid solution between C_7A_5M and C_2AS.

This possibility of a solid solution is firmly supported by the following facts, according to Welch: Progressive change, observed by optical methods, of the crystalline form of the fibrous mineral along the line C_7A_5M—C_2AS; progressive elevation of the melting point of the mineral along this same line; progressive change of the reticular

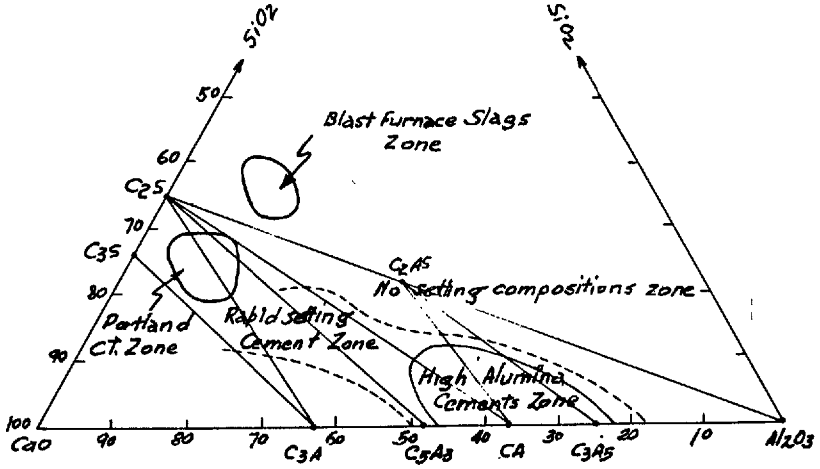

FIGURE 6. *Cement zones in the system* CaO—Al_2O_3—SiO_2.

After Lea [32].

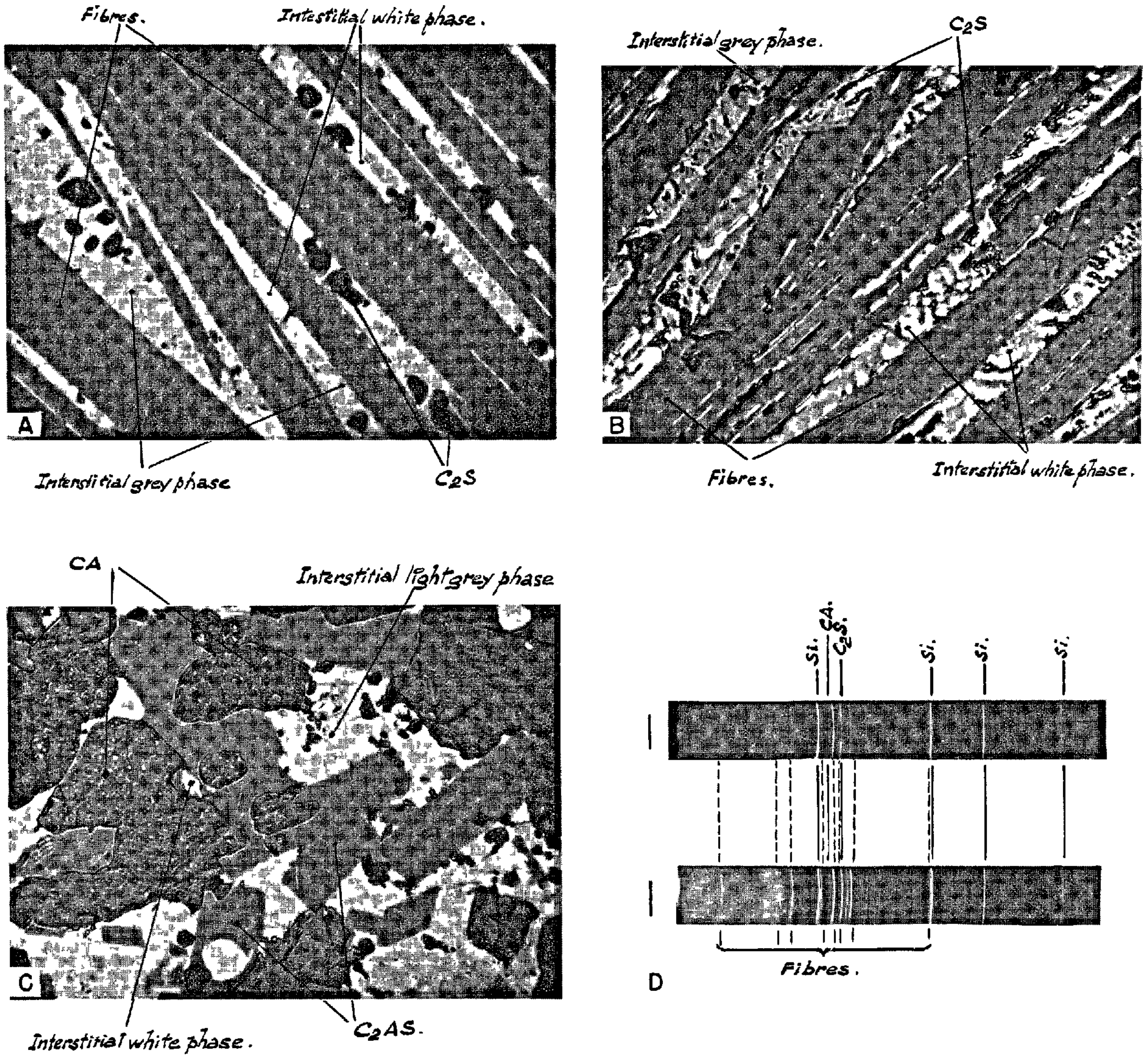

PLATE 1. *Fused high-alumina cement after oxidizing.*

A. FeO=9.6%.
B. Annealing: 550 °C during 240 hr. FeO=0.05%.
C. Annealing: 1,300 °C during 240 hr. FeO=0.20%.
D. X-ray diagrams: Upper—fused high-alumina cement; lower—the same after annealing at 550 °C.

lengths on the X-ray diagrams of the compositions situated along the same line C_7A_5M—C_2AS.

The composition: $2(C_2AS)$, C_7A_5M (or $C_{5.5}A_{3.5}M_{0.5}S$) is not very far from the formula, adopted formerly for the compound C_6A_4MS, but, as opposed to the latter, it seems to be homogeneous and has a higher melting point, although incongruent. The X-ray diagrams of both compounds, the former and the new one, are similar if it is considered that some lines are due to the presence of impurities in C_6A_4MS.

It seems probable, too, that there exists a compound C_3A_2M, whose region of precipitation is situated between those of $C_{12}A_7$, CA, and MgO in the system CaO–Al_2O_3–MgO. Its crystalline form and its optical characteristics do not allow it to be distinguished from C_7A_5M, but the distinction can be made by X-ray examination.

Welch thinks that many compounds, analogous to C_7A_5M and C_3A_2M, resulting from the replacement of MgO by FeO, and Al_2O_3 by Fe_2O_3, are possible and that the structure of these solid solutions is extremely complex.

It must be kept in mind that all those results are only provisional: the existence of C_6A_4MS was doubtful (also that of C_6A_4fS) because the formula could not be arranged in the crystal unit determined for the fibrous material. However, the compositions proposed by Welch do not enter more easily into this same crystal unit. The last word has not been said on the subject.

It is not very satisfying to observe that the commercial high-alumina cements contain some 16 percent of iron oxides, and that it has not been possible, so far, to determine the structural distribution of these oxides. Concerning the question of the compound C_6A_4fS, the formula proposed by Parker does not appear as a real solution.

We have been able, effectively, to observe that a high-alumina cement, made in a non-oxidizing atmosphere and presenting a fibrous structure under the microscope, shows, after oxidizing annealing at temperatures over 1,000 °C, a progressive change of the fibers, and, finally, their disappearance (plate 1). In their place appears a ferrite or an aluminoferrite and CA or C_2AS, according to the conditions of experiment.

On the contrary, if annealing is done below 1,000 °C, always in an oxidizing atmosphere, and for periods long enough to reach the total oxidation of FeO to Fe_2O_3 (with verification by chemical analysis) the fibers are not altered and the X-ray diagram of the annealed compound is practically the same as for the starting compound (plate 1–D).

In conclusion, these results place in doubt the initially proposed formula for the fibrous constituent.

The System $CaO–Al_2O_3–H_2O$ at Different Temperatures. Equilibria Diagrams

Work of Bessey [4]

As far back as 1938, Bessey proposed a representation of the system $CaO–Al_2O_3–H_2O$, based on the work by Lea and Bessey, at 25 °C; in this diagram is represented the stable equilibrium curve[3] of the cubic aluminate C_3AH_6 and, related to this curve, a zone in which are found the metastable equilibrium curves of hexagonal aluminates (curve AB and region BDE, fig. 7).

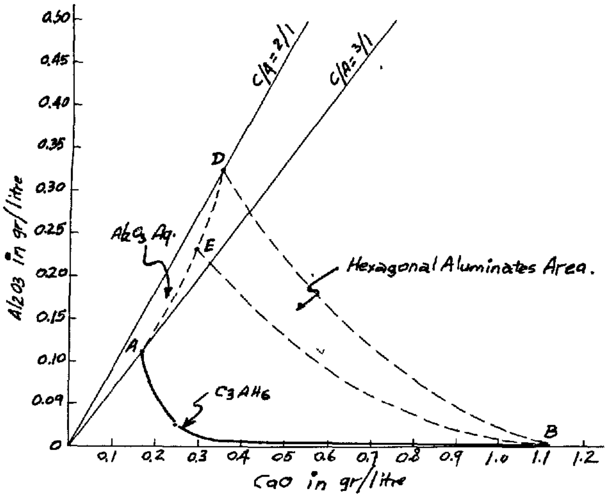

FIGURE 7. *The system* $CaO—Al_2O_3—H_2O$ *at 25 °C.*

After Bessey, 1938 [4].

Work of Wells, Clarke, and McMurdie [59]

In 1943, Wells, Clarke, and McMurdie published a more detailed drawing of the diagram, giving, for temperatures 21 and 90 °C, the equilibrium curves for stable and metastable forms of aluminates, lime, and alumina.

The experimental process chosen by these authors, and adopted afterwards by various investigators for this type of research was the following:

Solutions of monocalcium aluminates are prepared by dissolution of anhydrous CA or high-alumina cement in water, and are mixed with exact quantities of lime water of known concentration. The solution composition is determined at the beginning of the experiments, and the modifications occurring with time are determined by analysis. The precipitates thus obtained from supersaturated solutions are chemically analyzed and studied by various modern investigation processes (such as optical microscopy, electron microscopy, roentgenography, and differential thermal analysis).

Figure 8 indicates a metastable equilibrium curve for hexagonal aluminates, as determined by Wells, Clarke, and McMurdie. On this diagram, the crosses give the starting compositions of solutions, the circles giving the compositions at equilibrium. The dotted lines joining a cross to the corresponding circle give, at any point of the curve, the solution composition at a certain instant. The figures on each line represent the value of the C/A ratio in the precipitate, when in equilibrium with the solution. Wells, Clarke, and McMurdie so determined the curve KRB, which is the metastable equilibrium curve of hexagonal aluminates.

It can be easily seen on the diagram that the increase of CaO concentration in solution is followed by a general decrease of the Al_2O_3 concentration, indicating a progressive increase of the C/A ratio which rises from 2 to 4.

It must be noted that this curve KRB does not present any step for C/A ratios of 2, 3, and 4; this indicates that separate solubility curves for di-, tri-, and tetracalcium aluminates do not exist. The progressive increase can be considered from two different points of view: Either the curve KRB is constituted by the mean solubility values of a series of hydrated aluminates, or the same curve is representative of the solubility of a series of solid solutions, for which the C/A ratio varies. After complementary studies, Wells, Clarke, and McMurdie considered the first hypothesis to be correct.

The same metastable equilibrium curve KRB can be attained by starting from undersaturated

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[3] The expressions "equilibrium curve" or "solubility curve" are indiscriminately used in this text. They always mean that the curves so represented give the composition of the solution at equilibrium with the precipitated phases.

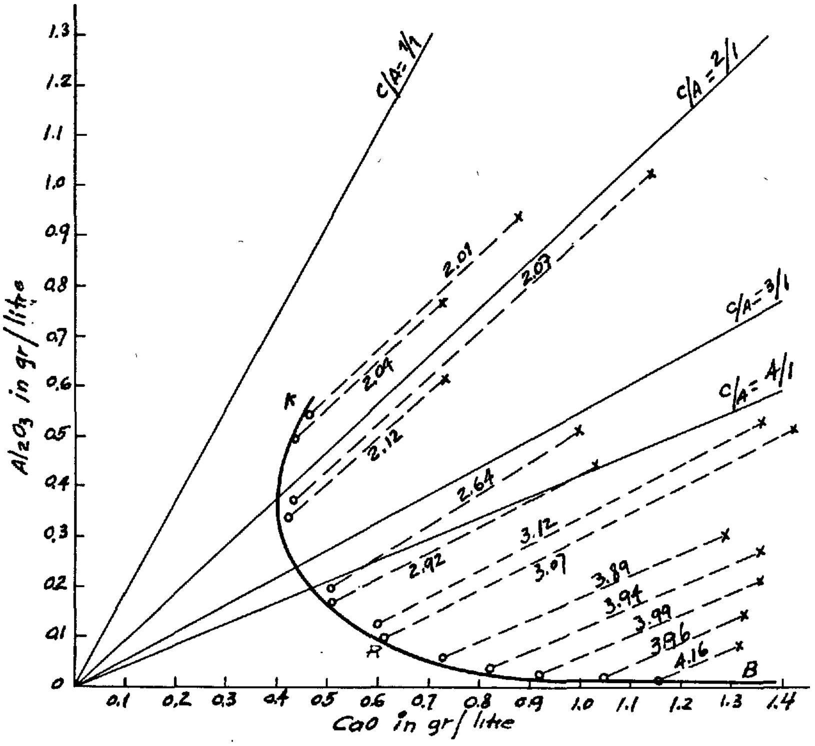

FIGURE 8. *The system* $CaO—Al_2O_3—H_2O$ *at 21 °C.*

Approach to metastable equilibrium for hexagona aluminates (Wells and co-workers [59]).

solutions, instead of supersaturated ones, slowly dissolving pure crystallized aluminates in lime solutions of rising concentrations.

The study, by chemical analysis, of the precipitates formed, and particularly the determination of the H_2O/Al_2O_3 ratio, shows that this ratio rises, generally, with the C/A ratio and that the limits of composition of the hydrated hexagonal aluminates are: $2CaO{\cdot}Al_2O_3{\cdot}5–9H_2O$ and $4CaO{\cdot}Al_2O_3{\cdot}12–14H_2O{\cdot}$

Wells has shown that these hexagonal aluminates are metastable and above 21 °C change more or less rapidly into C_3AH_6. The cubic crystals of C_3AH_6 can be obtained by keeping solutions, whose compositions are the same as the ones already described, for longer times than those allowing the formation of the hexagonal alumi nates. Then, the C/A ratio in the precipitates is very near 3/1 and the equilibrium curve is nearer the coordinates axes. The same curve can be obtained by dissolving C_3AH_6 in lime water.

This solubility curve for C_3AH_6 (A′FB) is represented in figure 9, as well as the mean metastable curve of the hexagonal aluminates. On the diagram are traced the representative lines of the solutions studied, similar to the lines drawn on figure 8, but corresponding only to precipitates in which the C/A ratio is 3/1.

The complete diagram of the equilibria in the system $CaO–Al_2O_3–H_2O$, at 21 °C, as established by Wells, Clarke, and McMurdie, is represented in figure 10. In this system, there are only two stable phases: crystalline gibbsite (AH_3),[4] whose stable equilibrium curve is OF, and cubic tricalcium aluminate (C_3AH_6), whose stable equilibrium curve is BF.

Point F is an invariant stable point for AH_3—C_3AH_6—solution, situated, according to investigators, at Al_2O_3=0.02 g/l and CaO=0.25 to 0.35 g/l. For lime concentrations less than these figures (mean value=0.33 g/l), gibbsite is the stable phase, while C_3AH_6 is stable for values above the same figures.

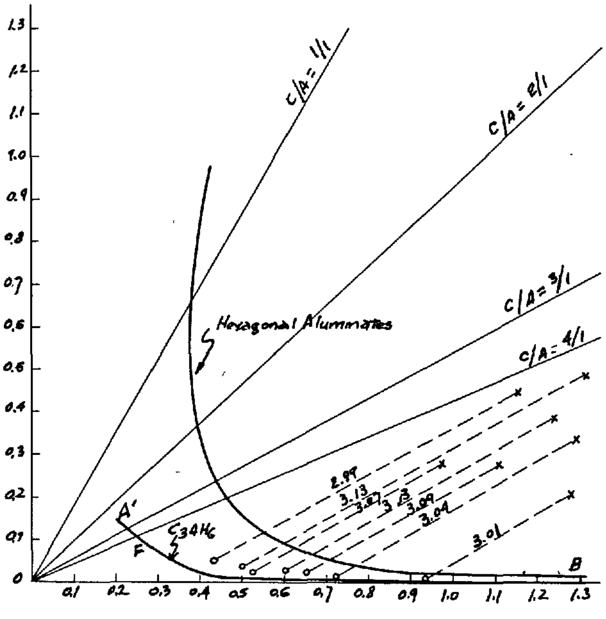

FIGURE 9. *The system* $CaO—Al_2O_3—H_2O$ *at 21 °C.*

Approach to stable equilibrium for C_3AH_6.

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[4] In this text, AH_3 corresponds to perfectly crystallized gibbsite, while $Al_2O_3{\cdot}aq.$ is a more or less crystalline form of hydrated alumina.

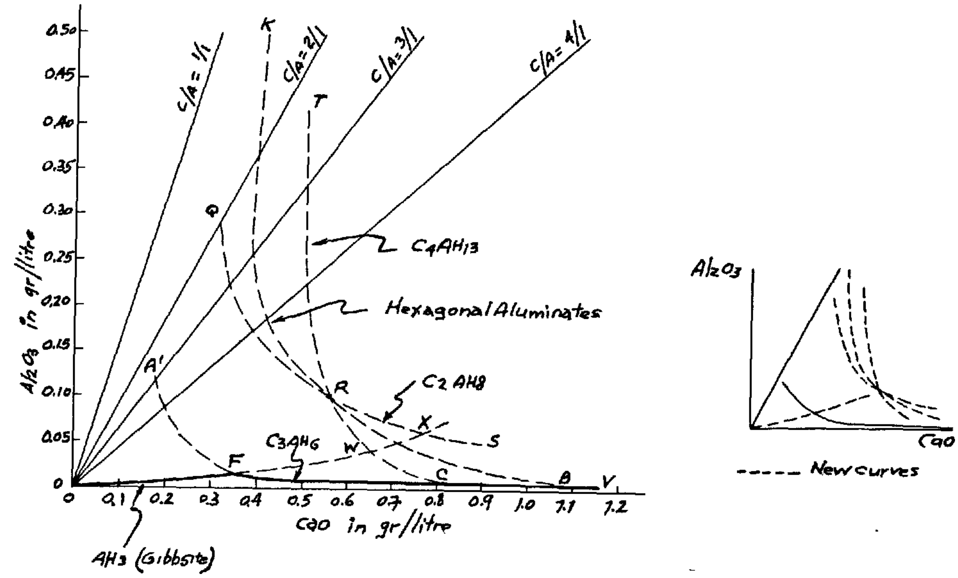

FIGURE 10. *The system* $CaO—Al_2O_3—H_2O$ *at 21 °C.*

After Wells, Clarke, and McMurdie, 1943 [59].

Line FA′ is the metastable prolongation of the curve for C_3AH_6; A′ gives the solubility of gibbsite, as traced by Bessey. It is also the invariant point for Al_2O_3·aq.—C_3AH_6—solution. Normally, in this region of the system, the dissolution of C_3AH_6 should be incongruent, accompanied by precipitation of gibbsite. In fact, it is possible to obtain a congruent dissolution of the cubic aluminate because of the considerable delay observed in the crystallization of alumina gel, the soluble form of this oxide. When looking at the diagram as established by Bessey, it may be seen, indeed, that the curve for Al_2O_3·aq. (OAED) is for its main part metastable towards C_3AH_6.

In figure 10, the curve KRB represents the metastable equilibria of the hexagonal forms of the hydrated calcium aluminates. It was already shown that along this curve, the C/A ratio of precipitates in equilibrium with solution, varies from 2, point K, to 4, point B: this curve has been experimentally established, as shown in the already studied figure 8. For its main part at least, this curve is situated in area BDE, defined by Bessey [4] as the region of existence of the metastable hydrated aluminates, and gives the mean solubility of these compounds.

Although these aluminates seem to be homogeneous, this is only apparent, as shown by X-ray examination. In fact, it seems that there are only two hexagonal compounds, which are able to crystallize together. The examination of the C/A ratios of the precipitates given in figure 8, the values of which vary from 2 to 4, suggests this conclusion.

However, it will be seen further that some investigators think there is a hexagonal tricalcium aluminate, while others suppose that the compound observed is the carboaluminate $C_3A·CaCO_3·H_n$, whose X-ray diagram is practically the same as that for C_3AH_{12}.

Whatever be the truth, Wells, Clarke, and McMurdie have drawn two metastable equilibrium curves for C_2AH_8 and C_4AH_{13}, respectively QRS and TRV,[5] which envelop the curve KRB.

The point R is the metastable invariant point for C_2AH_8, C_4AH_{13}, and solution. Both hexagonal aluminates coexist at this point, whose coordinates are at 21 °C, CaO=0.53 g/l, Al_2O_3=0.11 g/l.

The point Q indicates the solubility of C_2AH_8 in water, as determined by Bessey.

The solubility curve of C_2AH_8, for rising concentration of CaO, goes from R, invariant point for C_2AH_8—C_4AH_{13}—solution, to point S beyond which C_4AH_{13} is the only relatively stable phase: between R and S, C_2AH_8 is metastable towards C_4AH_{13}.

Curve TRV, the metastable equilibrium curve for C_4AH_n, terminates at point V, the metastable invariant point for C_4AH_n—$Ca(OH)_2$—solution (CaO=1.15 g/l, Al_2O_3=0.0005 g/l).

Those two curves are crossed by the metastable prolongation of curve OF for gibbsite, at two points W and X, hypothetical points which should be, consequently, the two metastable invariant points for AH_3—C_4AH_{13}—solution and AH_3—C_2AH_8—solution, respectively.

Figure 11 illustrates modifications which occur in the system $CaO–Al_2O_3–H_2O$, when changing temperature from 21 to 90 °C. The only curves concerned are those for C_3AH_6, Al_2O_3·aq. and $Ca(OH)_2$. The curves for hexagonal aluminates are not represented, being very little modified.

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[5] These curves, only theoretical, represent the metastable equilibria of the hexagonal aluminates crystallizing in a pure state.

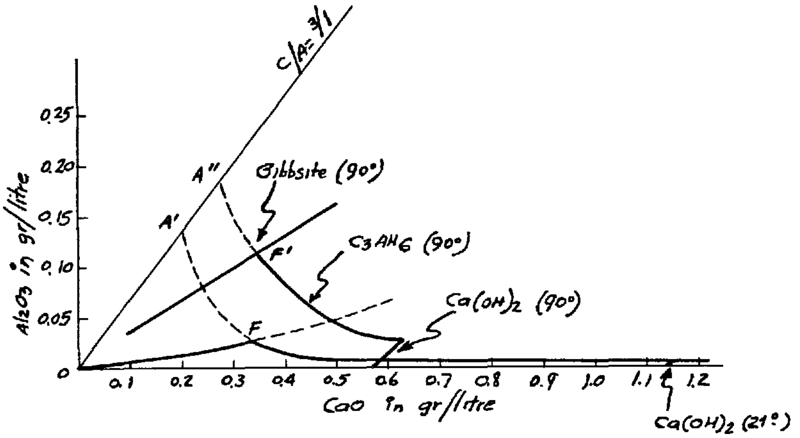

FIGURE 11. *The system* CaO—Al_2O_3—H_2O *at 21 and 90 °C.*

After Wells and collaborators, 1943 [59].

Invariant point F, for C_3AH_6—AH_3—solution, which, at 21 °C, has as coordinates $Al_2O_3=0.02$ g/l, CaO=0.25–0.35 g/l, is situated, at 90 °C, at $Al_2O_3=0.11$ g/l, CaO=0.33 g/l. The curve for AH_3 goes through the origin, but the slope is sharply increased. It will be seen later that stable equilibrium curves for AH_3 are assembled in the form of a sheaf of lines passing through the origin. The stable equilibrium curve for $Ca(OH)_2$ is much nearer the zero and is much longer than at 21 °C.

Work of D'Ans and Eick [17]

More recently, in 1953, the system CaO–Al_2O_3–H_2O was studied again, at 20 °C, by D'Ans and Eick who traced, as did Wells, Clarke, and McMurdie, two distinct metastable equilibrium curves for the two hexagonal aluminates C_2AH_n and C_4AH_n. The diagram (fig. 12) was divided into several crystallization zones, delimited by the different solubility curves.

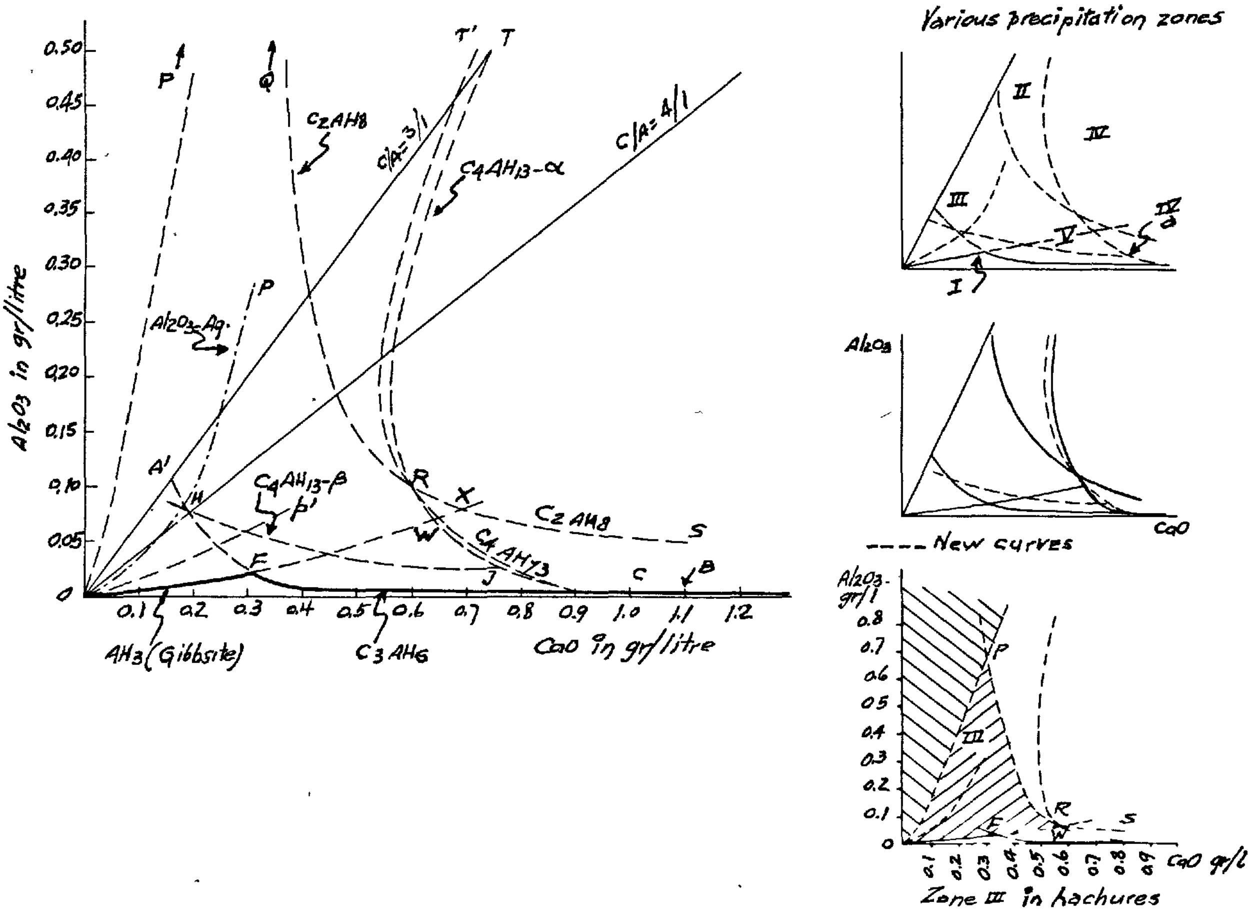

FIGURE 12. *The system* CaO—Al_2O_3—H_2O *at 20 °C.*

After d'Ans and Eick, 1953 [17].

The study made by these authors proceeded quite in the same way as the one by Wells, Clarke, and McMurdie [59], that is to say: Preparation of crystallized precipitates from filtered supersaturated solutions; progressive dissolution of anhydrous or hydrated aluminates in water or in lime solutions of various concentrations; study of the transformation of metastable phases into stable ones by analysis of mother solutions.

Region I is limited by the three stable solubility curves of C_3AH_6, AH_3 (gibbsite), and $Ca(OH)_2$. The solutions whose compositions are situated in this region cannot precipitate, for they are undersaturated towards stable phases in the system.

On the limiting curves of this region, two stable invariant points can be formed. These are F (C_3AH_6—AH_3—solution; $Al_2O_3=0.025$ g/l, $CaO=0.315$ g/l); and B (C_3AH_6—CH—solution; $Al_2O_3=0.00325$ g/l, $CaO=1.172$ g/l).

The stable equilibrium curve C_3AH_6, like the one for gibbsite, was defined by dissolving the pure compound in lime solutions of various concentrations, that is, starting from undersaturation. At ambient temperature, C_3A is dissolved extremely rapidly, while C_3AH_6 is often very slow to precipitate. The supersaturation, in this case, is such that it is possible to enter a region where the supersaturation is very strong towards hexagonal aluminates; then these compounds precipitate first.

Region IV is entirely situated at the right of the limit TRS. Solutions can be obtained whose compositions lie in this zone, by dissolving anhydrous CA or high-alumina cement in water. The filtered solutions when mixed with such quantities of lime water that their C/A ratios lie between 3/2 and the quasi-supersaturation in CaO, precipitate a crystalline phase. The solid composition is not homogeneous. It is a mixture of C_2AH_8, C_3AH_{12}, and for the most part α-C_4AH_{13}, all of them crystallizing as hexagonal plates. It is not possible to distinguish one compound from another except by their refractive indices. The pure compounds, however, are seldom found because of their strong tendency to give mixed crystals.

D'Ans and Eick think that concerning C_3AH_{12}, it is possible to consider this compound as a mixture of C_2AH_8 and α-C_4AH_{13} or C_2AH_8 and lime.

The fact that there is a transition point R ($Al_2O_3=0.095$ g/l, $CaO=0.610$ g/l) makes the hexagonal aluminates of higher lime content than C_2AH_8 metastable towards this last compound for the section of the curve which is above R. On the contrary, compounds corresponding to the portion RS are metastable toward α-C_4AH_{13}.

Besides, although one might expect to see C_2AH_8 precipitate in the region at the right of R, before any other compound, only small quantities of it are observed, and they transform progressively into α-C_4AH_{13}. The formation of this tetracalcium compound and of its mixed crystals with other compounds containing a lower proportion of lime, is consequently faster than formation of C_2AH_8.

Because of the composition variations of hexagonal phases, the tracing of the maximum solubility curve of C_4AH_{13} is somewhat dubious. For this reason, it has been doubled by a curve T′RC which represents the true compositions experimentally obtained at equilibrium. This curve goes through regions II and IVa and is representative of hexagonal aluminates containing a high proportion of α-C_4AH_{13}, and not only the metastable equilibrium curve for this compound. From a practical point of view, T′RC is more significant than TRC.

Region II is situated between the two curves for hexagonal aluminates C_2AH_8 and C_4AH_{13}, and is limited in its lower part by the portion of curve WX, which is situated between the crossing points of both preceding curves with the metastable prolongation of the curve of gibbsite beyond point F. (W:$Al_2O_3=0.065$ g/l, $CaO=0.660$ g/l, and X:$Al_2O_3=0.072$ g/l, $CaO=0.700$ g/l).

It is in this region that the solubility curves for C_3AH_{12} and C_3AH_{18} would be found. The latter crystallizes in the form of needles, mainly from solutions containing little lime. This compound probably would not crystallize in pure form, but would always coprecipitate with other types of solids.

The solutions whose compositions lie in the part of the region II, which is the richest in Al_2O_3, give, in addition to the less metastable aluminates, Al_2O_3·aq. In this region II, it is equally possible to maintain for a while solutions which are undersaturated towards C_4AH_{13}, without precipitation of solid phases. The term undersaturated solution must be understood to mean a solution supersaturated towards a stable phase, but not towards a metastable phase.

The change in composition of the solutions of high Al_2O_3 content occurs, as for solutions poorer in Al_2O_3, in the direction of point R, attaining finally the point W. At the same time, a large quantity of gibbsite precipitates. For this reason the solubility of the most soluble elements may be disturbed in such a way that the solution compositions are displaced, through region III, along the metastable curve for Al_2O_3·aq.

The curve QRX, a limit of region II, is representative of the solubility of pure C_2AH_8.

Region IVa is limited by the portions of curves SX, XW, WC. Starting from supersaturated solutions in the region IV, the precipitate is mainly α-C_4AH_{13}, or more precisely, mixed crystals a little less rich in lime, whose compositions are on the curve T′RC. Thus the region IVa is rapidly crossed.

The case is not the same when starting by dissolution of C_2AH_8 in a lime solution. In this case, a metastable equilibrium is first established between the solution and C_2AH_8, and simultaneously there occurs a fixation of the lime in solution, with as a consequence, a slow change of C_2AH_8 to α-C_4AH_{13}.

The solutions of region IV (WFC) are characterized by a supersaturation towards stable C_3AH_6. However, at 20 °C, this formation of C_3AH_6 is not very abundant. It is necessary to operate at temperatures higher than 30 °C to observe a rapid transformation.

Region III, limited between points P, R, W, F, O, and the ordinate for Al_2O_3 concentrations, contains all the alumina hydrates that are metastable towards gibbsite; the crystallization of this compound has never been completed, either from supersaturated solutions, or by aging of other hydrates in the system.

The curve PRW must be considered consequently as the equilibrium curve of the various alumina hydrates with C_2AH_8, above point R, and with C_4AH_{13} below the same point. The solubility curve for freshly precipitated hydrated alumina is an almost straight line running from the origin to the point P. This last point is the invariant metastable point for $Al_2O_3{\cdot}aq.$—C_2AH_8—solution (Al_2O_3=0.681 g/l, CaO=0.324 g/l).

Alumina gel is able, after aging, to pass slowly to the gibbsite state, the representative curves distributing themselves, as already said, in form of a sheaf between the curve OP, representative of $Al_2O_3{\cdot}aq.$, and the curve OF of the perfectly crystallized gibbsite. (In the diagram, figure 12, three of these curves have been represented: OP corresponding to fresh precipitated alumina, and Op and Op′ corresponding to the same hydrated alumina after aging 11 days and 2 months, respectively.)

Finally, D'Ans and Eick observed, in regions V and III, for low-alumina concentrations, large hexagonal plates, tending to form mixed crystals with other hexagonal hydrates. The authors prepared them by reacting hydrated alumina with concentrated lime solutions.

The equilibrium curve JH for β-C_4AH_{13-14} has been drawn by the writers with rather little precision. It begins at point H, intersection with the line for C/A ratio=4/1, crosses the curve for C_3AH_6, and joins, very probably, the curve for α-C_4AH_{13} at point J.

It can be observed that the work by D'Ans and Eick confirms the suppositions and facts expressed or established first by Bessey, later by Wells, Clarke, and McMurdie. The establishment of a new metastable equilibrium curve (HJ) for β-C_4AH_{13-14} is, however, original with these authors.

Work of Peppler and Wells [43]

Peppler and Wells, in 1954, returned to the study of the system Al_2O_3–CaO–H_2O in a very complete way, and for a whole series of temperatures. Besides the study of the system at 21 and 90 °C, which was no more than a revision of the previous research by Wells, Clarke, and McMurdie, the following temperatures were investigated: 50, 120, 150, 200, and 250 °C. Only the temperature of 50 °C has been considered in the following. Its representation is given in figure 13.

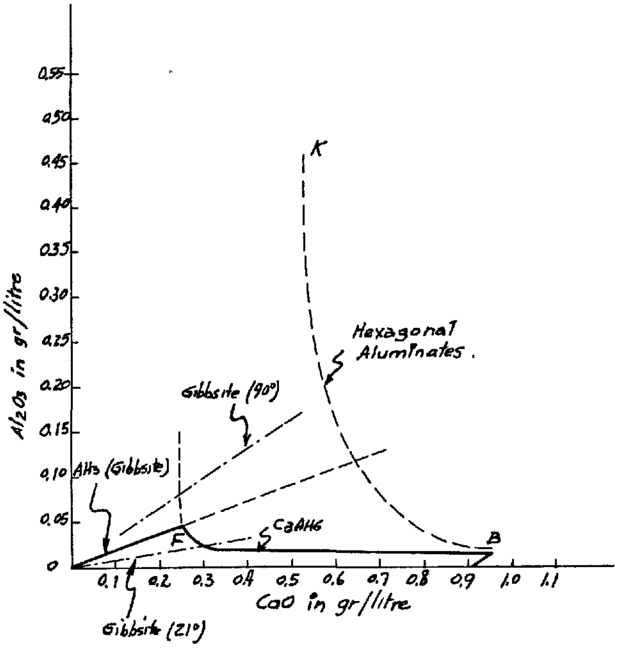

FIGURE 13. *The system* CaO—Al_2O_3—H_2O *at 50 °C.*
After Peppler and Wells, 1954 [43].

Using techniques analogous to those previously described, the authors tried to define the part played by the hexagonal phases in the system at 50 °C. The transformation of the hexagonal phases to the cubic aluminate is faster at 50 °C than at 21 °C. The authors felt, however, that this change was still too slow to permit them to define the exact position of the stable equilibrium curve for C_3AH_6 by starting from supersaturated solutions. This curve has been drawn, consequently, starting from undersaturated solutions; it was thus observed that, as at 21 °C, the cubic hydrate dissolves congruently in lime water, until the concentration corresponds to the invariant point C_3AH_6—$Ca(OH)_2$—solution.

The equilibrium curve for cubic C_3AH_6 at 50 °C presents the same aspect as the curves at 21 or 90 °C, and is situated between these. It is a member of a family of equilibrium curves, as was supposed by Wells, Clarke, and McMurdie.

Point B represents the invariant point $Ca(OH)_2$—C_3AH_6—solution (CaO=0.961 g/l, Al_2O_3=0.005 g/l).

Gibbsite (AH_3) tends towards its equilibrium curve much more slowly again than C_3AH_6.

It seems probable that alumina gel has a metastable existence at 50 °C, its equilibrium curve being situated above the stable curve of gibbsite (AH_3), crossing first the metastable prolongation of the curve for C_3AH_6 and then the metastable curve for the hexagonal aluminates. The solubility of $Al_2O_3{\cdot}aq.$ is a little higher at 50 °C than at 21 °C, gibbsite being the stable form of alumina in the system at 50 °C.

The invariant point C_3AH_6—AH_3—solution is at the intersection of the stable equilibrium curves for the two compounds. An attempt was made to verify its position by dissolving gibbsite and cubic aluminate in water and by analyzing, at regular intervals, the composition of the solution. This was found to be impossible.

The invariant point between the metastable hexagonal phases and the metastable prolongation of the stable curve for gibbsite is situated at: $Al_2O_3 = 0.130$ g/l, $CaO = 0.630$ g/l. This point corresponds fairly well to the point determined at 21 °C.

The solubility of $Ca(OH)_2$ is situated also, as was expected, in an intermediate position between those determined at 21 and 90 °C. The stable equilibrium curve for $Ca(OH)_2$ at 50 °C is, compared to the one determined at 21 °C, nearer the origin and longer.

Figure 14 shows the different positions for the essential curves of the diagram for the system Al_2O_3–CaO–H_2O at various temperatures between 5 and 90 °C. They were established by Buttler, whose work is detailed below, on the basis of data given by Wells, Clarke, and McMurdie [59], Peppler and Wells [43], and Bessey [4] as well as his own results.

All these diagrams are representative of the system Al_2O_3–CaO–H_2O at ambient temperatures or above. The range of temperature between 20 and 0 °C has been quite recently explored, first by Carlson [15] at 1 °C and later by Buttler [11] at 5 °C.

Work of Carlson [15]

The diagram proposed by Carlson, at temperature of 1 °C, is shown on figure 15. The author made the following remarks: The position of the solubility curve for gibbsite (OF) is only approximate. The position of B, solubility of $Ca(OH)_2$, has been fixed from various data found in the literature. The curve RB cannot cross the abscissa axis at point B; thus there must exist, in the vicinity of this last point, an invariant point for an Al_2O_3 concentration of about 0.001 g/l. Between R and this hypothetical invariant point are two curves, the lowest being representative of the stable equilibrium of C_4AH_{13}, the higher being the metastable equilibrium curve for C_2AH_8.

The curve QDR is essentially an "average" curve, experimentally drawn from data obtained by precipitation (supersaturation) and by dissolution (undersaturation).

Curve ED is the metastable equilibrium curve for CAH_{10} and appears for the first time in a diagram representative of the system Al_2O_3–CaO–H_2O. Its position is rather uncertain, because of the dispersion of the experimental results; nothing is known of its prolongation on the left.

This being established, it may be considered that, at 1 °C, the stable phases in the system are AH_3 (gibbsite), C_4AH_{13}, and $Ca(OH)_2$. The position of F, invariant point AH_3—C_4AH_{13}—solution, is ill defined. On the other hand, invariant point B for C_4AH_{13}—$Ca(OH)_2$—solution has the following coordinates; $Al_2O_3 = 0.001$ g/l, $CaO = 1.30$ g/l, thus corresponding fairly well with the solubility value of $Ca(OH)_2$ as given in the literature for this temperature.

The metastable equilibrium curve for C_2AH_8 is QDRB and, on the section RB, practically coincident with the stable equilibrium curve for C_4AH_{13}.

Point D is the metastable invariant point C_2AH_8—CAH_{10}—solution

The metastable solutions whose compositions lie at the right of QD precipitate C_2AH_8; as soon as their initial composition reaches QD, CAH_{10} is formed simultaneously, and the concentration moves towards D.

The solutions of highest lime content precipitate C_2AH_8 and C_4AH_{13} at the same time; as long as C_2AH_8 can precipitate, C_4AH_{13} controls the solution concentration, but as soon as the dical-

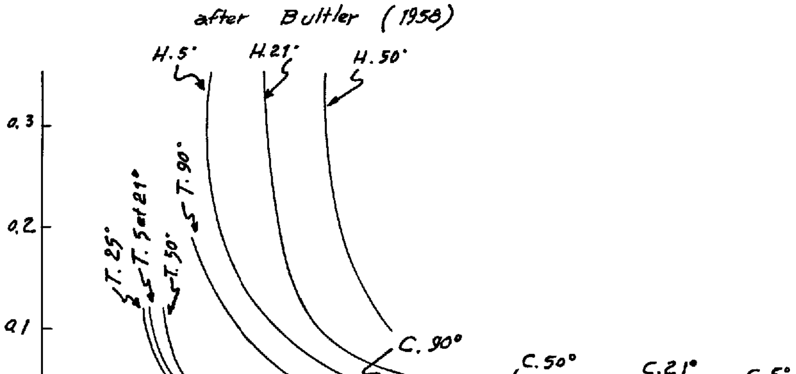

FIGURE 14. *The system* CaO—Al_2O_3—H_2O *at various temperatures.*

Equilibria curves for $Ca(OH)_2$ (curves C); C_3AH_6 (curves T); hexagonal aluminates (curves H).

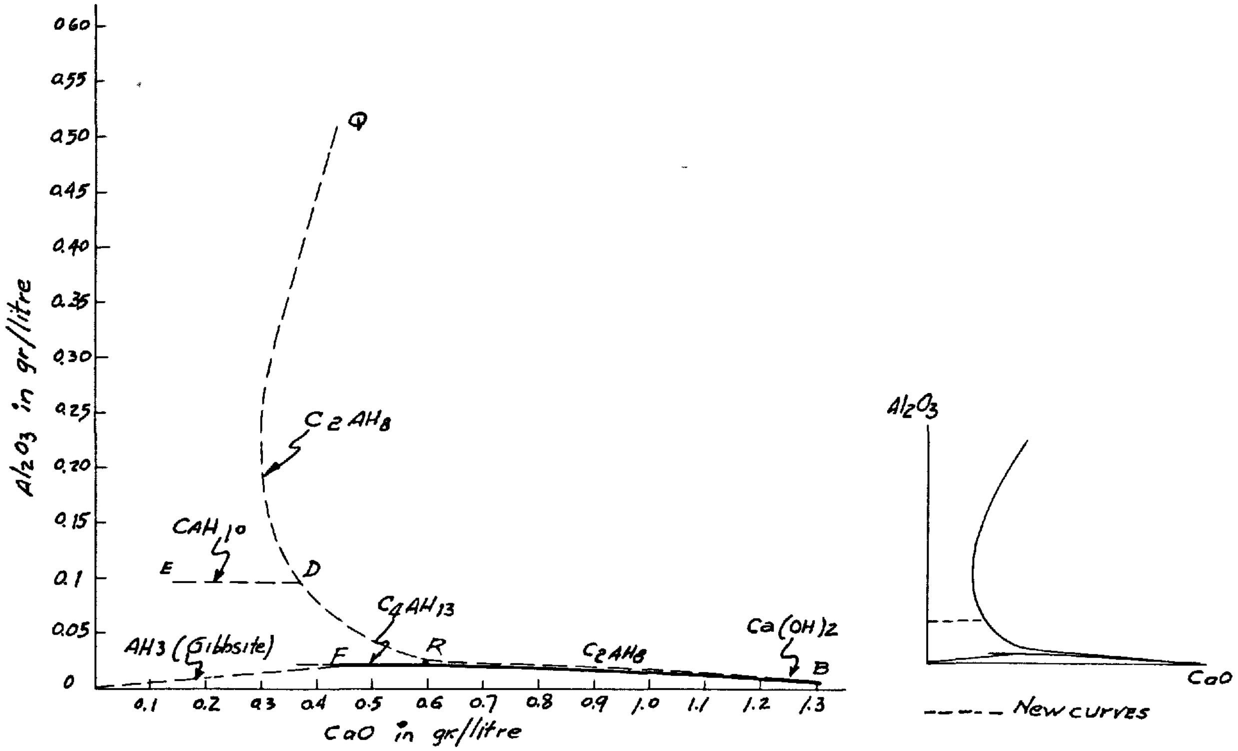

FIGURE 15. *The system* CaO—Al_2O_3—H_2O *at 1 °C.*

After Carlson, 1958 [15].

cium compound is wholly precipitated, the concentration goes from curve DR onto curve FR.

The area enclosed between the abscissa axis and OFRB is representative of stable solutions in the system at this temperature. Above OF, the solutions are metastable towards gibbsite, but the precipitation of this last compound, as already noted, is extremely slow. In region QDE, the solutions precipitate CAH_{10}.

It is interesting to compare this diagram at 1 °C with those traced by Wells and collaborators and by D'Ans and Eick: The diagram at 1 °C is first characterized by the drawing of a metastable equilibrium curve for CAH_{10} which had not yet appeared in previous diagrams. The curve QDRB presents no novel characteristic in comparison with the diagrams at 21 and 90 °C; it always presents a confused section between R and B. However, the diagram for the temperature of 21 °C does not present a stable solubility curve which can be compared to FR. It must be noted that D'Ans and Eick had drawn a solubility curve for β-C_4AH_{13-14} in the immediate vicinity of FR. Another important characteristic of the system CaO–Al_2O_3–H_2O at 1 °C is the lack of a stable equilibrium curve for cubic C_3AH_6.

This remark had been made as far back as 1952, by Longuet [36], in his potentiometric study of calcium aluminate solutions. This writer observed in particular that the solutions of aluminates give a monovalent aluminate ion. This aluminate ion, whatever its origin, gives identical compounds, under analogous conditions. Also, the dissolution of C_3AH_6 in water, followed by evaporation at low temperature, permits the changing of the cubic to the hexagonal form.

Work of Buttler [11]

The diagram of the system CaO–Al_2O_3–H_2O at 5 °C, as established by Buttler, is shown in figure 16. As had been done by D'Ans and Eick [17], Buttler has divided the diagram into various zones of precipitation, limited by the stable and metastable equilibrium curves.

In *Region 1* the solutions precipitate C_4AH_{13}, C_2AH_8, or both compounds simultaneously. It may be verified that when the C/A ratio is higher than 5, C_4AH_{13} precipitates alone, the final concentration of CaO being then 0.53 g/l minimum, while for a C/A ratio between 3 and 5, both hexagonal hydrated compounds, the di- and tetracalcium aluminates, crystallize. In any case, the equilibrium is always rapidly attained.

In *Region 2,* the precipitated solid is most often constituted by two phases, and the equilibrium is difficult to reach; CAH_{10}, C_2AH_8, C_4AH_{13} and Al_2O_3·aq. are formed. In most cases, these four compounds are formed simultaneously, but some of them disappear on aging. The compositions at equilibrium are situated along DQ. For a given total composition (solution + precipitate),

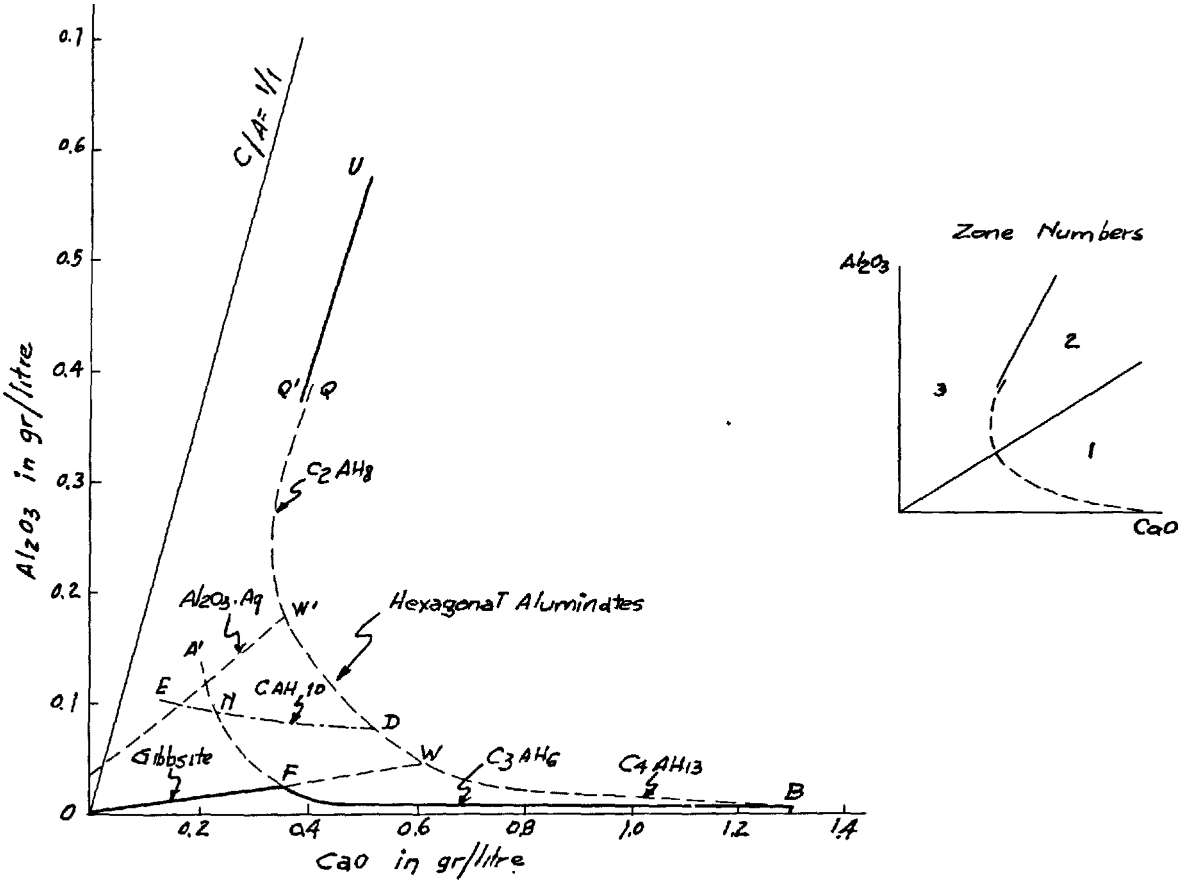

FIGURE 16. *The system* $CaO—Al_2O_3—H_2O$ *at 5 °C.*

After Buttler, 1958 [1].

that of the solution varies with time, running along this curve. It seems that, after a sufficient period of time, the solution composition may go above DQ, the C/A ratio in the solid lessening.

In agreement with the preceding facts, products obtained after a short enough delay have a high content of C_2AH_8 and at the same time contain C_4AH_{13}, while, on the contrary, products obtained after longer delay are frequently rich in CAH_{10} and Al_2O_3·aq.

The product formed essentially in *Region 3* is generally CAH_{10}, often mixed with Al_2O_3·aq., and the solutions at equilibrium possess compositions principally situated to the left of QD and on or above curve ED. The solution concentrations lessen with time and reach a point at least very near ED.

Curve Q'U is in a zone where precipitation of Al_2O_3·aq. occurs; this continues until the solution compositions reach the line Q'U, near point Q. The slope of the line corresponds to a molecular ratio C/A equal to unity. Then CAH_{10} precipitates, the compositions of the solutions varying towards the lower part of the diagram, in the part of region 3 situated above ED. Beyond Q, Al_2O_3·aq. is formed simultaneously with CAH_{10}, alumina tending to predominate. At last, after sufficient time, the solution compositions are stabilized a little above ED, and the precipitates consist of CAH_{10} mixed with ill-crystallized gibbsite.

With total compositions (solution + precipitate) in the vicinity of Q U, traces of C_2AH_8 and C_4AH_{13}, mixed with Al_2O_3·aq. are sometimes observed, and the solution compositions are very near, or on, DQ.

When the lime and alumina concentrations are very low, Al_2O_3· aq. is formed, which is eventually accompanied by CAH_{10}, and the compositions of the solutions are below point E. Al_2O_3·aq. may appear as bayerite (AH).

As the metastable phases persist for long periods, the study of the diagram cannot give much information about the stable phases. However, after the study of the equilibria at higher temperatures, it seems logical to suppose that the stable compounds at 5 °C are always gibbsite and cubic tricalcium aluminate, C_3AH_6. The equilibrium curves of the two compounds are respectively OFW and BFA'; they differ only slightly from the ones drawn at 20, 21, or 25 °C by previous investigators. The portions OF and BF alone are representative of stable equilibria; their prolongation and the other curves in the diagram represent metastable equilibria.

The compounds C_2AH_8 and C_4AH_{13}, both metastable, have, it has been said, very similar crystalline structures, and so it is difficult to trace individual metastable equilibrium curves for these compounds. Curve BWDQ is common to them; on the side of the high CaO concentrations, it corresponds to a metastable equilibrium for C_4AH_{13}; the other end, for high alumina concentrations, corresponding to C_2AH_8.

The triple point C_2AH_8—C_4AH_{13}—solution (R on the other drawings) is very difficult to place with precision; the curve BWDQ appears effectively as a continuous one, and an important section (approximately DW) is common to both hexagonal aluminates. It seems probable that this point is in the vicinity of the point corresponding to the maximum CaO concentration for which the presence of C_2AH_8 is observed. It must be noted that the determination of this triple point is difficult, whatever the temperature.

If C_4AH_{13} and C_2AH_8 are the true metastable phases in the system at 5 °C, it is no less true that the first one has a region where it is relatively stable for CaO concentrations higher than 0.5 g/l; C_2AH_8 is much more transitory. Between certain concentrations, this compound may be more stable than C_4AH_{13}, but it remains always metastable towards CAH_{10}. The latter presents a metastable equilibrium curve ED; its evolution is very slow and for concentrations lower than 0.5 g/l, it is stable towards C_2AH_8 and C_4AH_{13}. For higher concentrations, it reacts with the solution to give C_4AH_{13} and, finally, the stable phases C_3AH_6 and AH_3.

A well-defined solubility curve for Al_2O_3·aq. cannot be drawn because of the tendency for this compound to crystallize very slowly and poorly. It may be assumed that a whole family of curves corresponding to alumina hydrates is situated above the curve for gibbsite (OFW).

It has been said previously that, at 21 °C, the metastable hexagonal aluminates C_2AH_8 and C_4AH_{13} change rapidly (in about 10 days according to Wells, Clarke, and McMurdie [59]) into the cubic aluminate, C_3AH_6. At 5 °C, it is impossible to pass directly from C_2AH_8 or C_4AH_{13} to C_3AH_6; it is necessary to pass through the intermediary of CAH_{10}, and the transformation is always excessively slow. After 470 days, the author was unable to observe the formation of C_3AH_6 except in 3 experiments among 50, and then in very small quantities.

The compound CAH_{10} is not represented in the diagrams established by Wells, Clarke, and McMurdie, or D'Ans and Eick. Buttler, however, was able to trace its metastable equilibrium curve at 5 °C; AH_3 being never correctly crystallized, a part of this curve (EN) is stable not only towards C_2AH_8 and C_4AH_{13}, but also towards C_3AH_6.

A virtually stable mixture of CAH_{10} and Al_2O_3·aq. can be obtained as long as the curves for the two compounds cross on the left of point N. But if the crystalline state of Al_2O_3·aq. is near that of gibbsite, CAH_{10} can dissolve with subsequent precipitation of C_3AH_6.

These two studies of the system CaO–Al_2O_3–H_2O at low temperatures, by Carlson and by Buttler, show, among other interesting data, the reality of a metastable solubility curve for the compound CAH_{10}. The work by Buttler, at 5 °C, confirms the results obtained by Carlson at 1 °C.

Work of Percival and Taylor [44]

The question may be asked if this curve for CAH_{10} can be traced at 21 °C, despite its absence from the diagrams by Bessey [4], Wells, Clarke, and McMurdie [59], D'Ans and Eick [17], and Peppler and Wells [43]. The work by Percival and Taylor, this same year 1958, gives an answer to the question.

The diagram at 21 °C, as it has been proposed by these investigators, is shown in figure 17. It must be noted that it differs from the diagram drawn by Wells, Clarke, and McMurdie [59], only by the tracing of the metastable equilibrium curve ED for CAH_{10} at such a temperature. It is situated much higher than the curves defined by Carlson [15] and Buttler [11], at temperatures of 1 and 5 °C. The authors made the following observations concerning CAH_{10} in the system CaO–Al_2O_3–H_2O at 21 °C: Treated with water or a lime solution whose concentration does not exceed 0.57 g/l, CAH_{10} persists as a principal phase. For concentrations between 0.53 and 0.57 g/l, small quantities of C_2AH_8 or C_4AH_{13}, or both simultaneously, are formed with CAH_{10}. For lime concentrations between 0.13 and 0.40 g/l, the dissolution of CAH_{10} is almost congruent. For concentrations lower than 0.13 g/l, small quantities of Al_2O_3·aq. are simultaneously precipitated.

Except in the case where CAH_{10} reacts with water, the approach to the curve ED is generally fast. Of the two limiting points of the curve: D is the triple point CAH_{10}—hexagonal aluminates—solution. E is the triple point CAH_{10}—Al_2O_3·aq.—solution.

When CAH_{10} is added to saturated lime solutions, the solution composition moves towards the equilibrium curve BWDQ for the hexagonal aluminates, in accord with the results observed by Wells, Clarke, and McMurdie. The precipitation gives first C_4AH_{19}, and after some time (30–40 days) the formation of C_2AH_8 may be observed, this compound disappearing after another period of time (ca. 190 days), leaving again C_4AH_{19} alone.

Point D was determined after examination of the solution obtained by treatment of CAH_{10} in such proportions that, at equilibrium, not only a mixture of C_2AH_8 and C_4AH_{19} was observed, but the persistence of CAH_{10} as well.

It was not possible to reveal the presence of CAH_{10} in the precipitates obtained from crystallization from supersaturated solutions, probably because the quantities are much too low. But

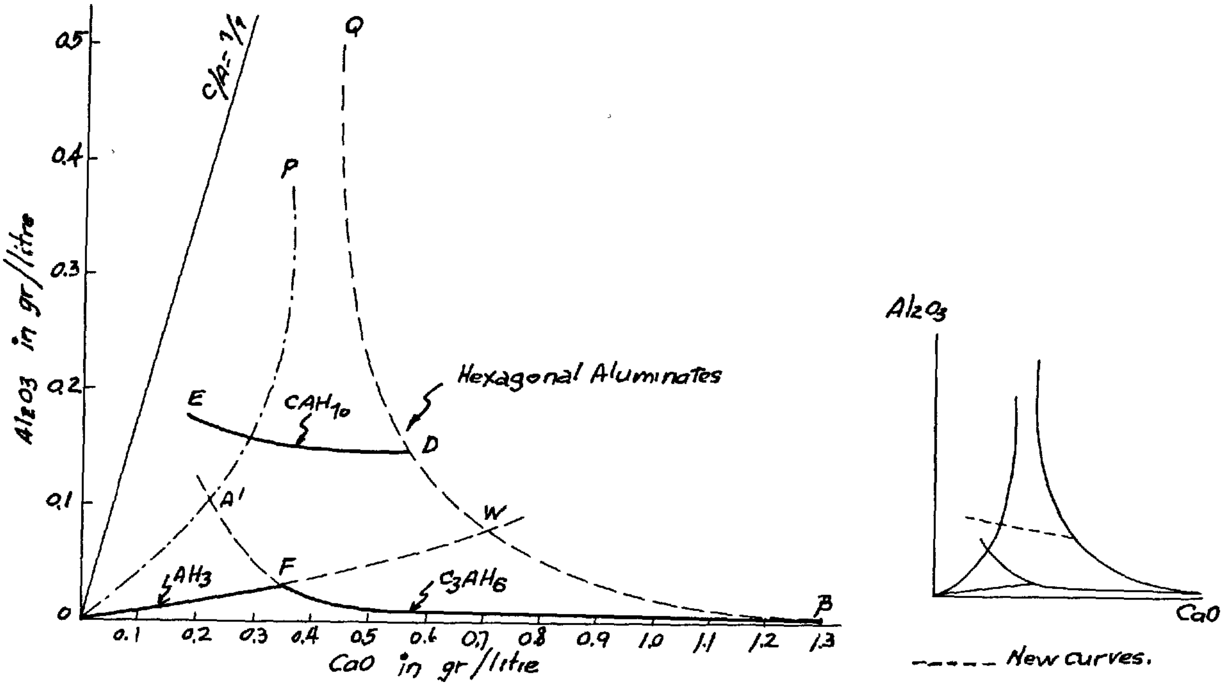

FIGURE 17. *The system* $CaO—Al_2O_3—H_2O$ *at 21 °C.*
After Percival and Taylor, 1958.

the authors think it significant that such a solution approaches curve ED, after a long enough period of time. It seems that by aging of the preparations, these compositions go towards the right side of the diagram, along the line ED. This movement is probably due to the fact that the crystallinity of the hydrated alumina initially formed becomes better with time, and that a certain quantity of CAH_{10} enters into solution.

In these experiments, the writers have not observed any formation of C_3AH_6. However, the observed modification in the solution compositions obtained when starting from CAH_{10} involves the formation of a compound of C/A ratio higher than 1, perhaps C_3AH_6.

Thus, the behavior of supersaturated solutions is somewhat similar to that observed at 5 °C, but at 21 °C the proportions of CAH_{10} formed are less than at the lower temperature. The most notable difference between the systems at 5 and 21 °C is the relative position occupied by the curves ED for CAH_{10} and BFA′ for C_3AH_6: At 5 °C, these two curves cross at a point N (see fig. 16) so that the section NA′ of the metastable prolongation of the curve for C_3AH_6 is metastable towards the section NE of the curve for CAH_{10}. Thus between N and E, CAH_{10} is metastable only towards gibbsite, and, as this crystallizes very slowly, ANE is a region of virtually stable existence for CAH_{10}. On the contrary, at 21 °C, the whole of the curve ED is situated above the curve BFA′ and, in this case, whatever be the lime concentration in the solution, CAH_{10} is always metastable towards C_3AH_6.

As a consequence, it is always possible to observe a transformation of CAH_{10} into cubic tricalcium aluminate, but this eventuality does not involve any knowledge of the speed of this transformation.

These works on equilibrium diagrams well define the regions of stability of the various calcium aluminates. But they do not solve all the problem concerning the respective existences of these compounds. Effectively, they present only a static solution of the problem. To resolve this completely, it would be necessary to consider the kinetic aspect of the transformations. Such a study would be probably very difficult to broach, considering the slowness of the reactions, on which the majority of the investigators agree. This slowness has sometimes forbidden the exact tracing of the equilibrium curves, as, e.g., that for gibbsite, for which, in many cases, it seems implied that it is only a theoretical curve.

The Hydration of Calcium Aluminates and High-Alumina Cements

The studies considered hereafter, made since Steinour's publication [53], concern the hydration of pure calcium aluminates and commercial cements.

These studies are by D'Ans and Eick (1953), Calvet and Longuet (1954), Lea (1956), Wells and Carlson (1956), Farran (1956), Goria and Cussino (1957), Carlson (1958), Buttler (1958), Schippa

(1958), Schneider (1959), and Buttler and Taylor (1959).

It is to be noted that in the following text, data relative to the hydration of C_2A have been systematically excluded, this compound being absent in high-alumina cements.

Work of D'Ans and Eick [17]

This work, published in 1953, is somewhat a continuation (see chapter "Equilibrium diagram") of the investigation by Wells, Clarke, and McMurdie [59]. As in the great majority of such studies the hydration of the aluminates was accomplished with a great excess of water. According to the authors C_2A gives a supersaturated solution, which precipitates very rapidly a mixture of hexagonal aluminates C_2AH_8 and C_4AH_{13} in which C_4AH_{13} is predominant. However, together with the precipitation of C_4AH_{13}, the dissolution of more C_2A occurs, so that the alumina content of the solution rises, and it is C_2AH_8 which finally precipitates. At the same time the dissolution of the anhydrous aluminate is retarded by formation of a superficial film of hydrated compound. As the hydration proceeds, after some days it can be observed that besides C_2AH_8 microcrystalline $Al_2O_3 \cdot aq.$ is also produced.

Monocalcium aluminate, CA, gives a supersaturated solution which is much more "stable" than that obtained from C_2A. The precipitation is slower to begin, and the C/A ratio in the crystallized solid has a value of about 1, this ratio being explained by D'Ans and Eick as the result of a simultaneous precipitation of C_2AH_8, C_3AH_{12}, and $Al_2O_3 \cdot aq$. The same retardation of hydration is observed, always due to the formation of a film of hydrated products at the surface of the anhydrous particles.

The investigators' conclusions are that the only aluminates of practical value as hydraulic binders are those whose supersaturated solutions are situated in the region II of their diagram (see fig. 12), the region of highest alumina content, and not in region IV. These compounds give metastable solutions, precipitating slowly, a fact which explains the lack of rapid setting.

D'Ans and Eick also studied the hydration of a commercial high-alumina cement in which the C/A ratio was about 1/1. This cement exhibited almost the same behavior as anhydrous CA, slight modifications appearing possibly because of the presence of secondary constituents: the dissolution of the cement was delayed because of the formation of a gel of silica on the surface of the particles and perhaps, too, because iron hydroxide was formed by hydration of C_4AF, as explained by Brocard [7].

The hydration of high-alumina cement with an excess of water leads, therefore, essentially to the formation of C_2AH_8 and $Al_2O_3 \cdot aq.$ (see Koyanagi [27]). D'Ans and Eick remark that neither α-C_4AH_{13} nor C_3AH_6 is formed at 20 °C. The transformation of the precipitates into cubic aluminate is possible, however, at temperatures as low as 30 °C, and the cement then loses a part of its mechanical resistance (see Seailles [52]).

The writers do not agree with Koyanagi, who thinks that the rapid setting of a high-alumina cement is due to the formation of C_3AH_6: they consider highly improbable the idea that such a phenomenon may be attributed to the formation of crystals with a very compact, almost spherical structure, especially when the formation of the said crystals is very slow.

Work of Calvet and Longuet [13]

In 1954, these investigators applied a microcalorimetric method to the study of the hydration of calcium aluminates, which would permit a survey of the thermokinetic aspects of the phenomena. They thus verified Le Chatelier's hypothesis, according to which a saturated solution of anhydrous product is formed first, before a less soluble hydrate may precipitate from the solution which is rapidly supersaturated towards this hydrated compound. They observed also that the crystallization of hydrated phases is complicated by hydrolysis phenomena, indicated by a higher evolution of heat than that observed in crystallization alone.

Moreover, the following observations were made by Calvet and Longuet: The anhydrous compound $C_{12}A_7$ (or C_5A_3) seems to have an important action in the control of the formation of the final hydrated phase. In dilute solutions, it seems that a strong hydrolysis is necessary to form the cubic hydrated aluminate.

Lea's Opinion [32]

Lea [32] examined a number of the various investigators' works, made between the years 1930–1950, and summarized his opinions in his book published in 1956: $C_{12}A_7$ (or C_5A_3) reacts very rapidly with an excess of water to give simultaneously hydrated aluminates and hydrated alumina. CA reacts less rapidly. CA_2 is practically inert.

Whatever the anhydrous compound, at relatively low temperatures under 15–20 °C it tends first to give CA·aq, but, as the temperature rises, it also forms $C_2A \cdot aq$. It seems probable that, in a general way, the tendency for an anhydrous aluminate to give CA·aq. is less marked when its C/A ratio is low. On the other hand, the transformation of hexagonal aluminates into cubic C_3AH_6 is accelerated by raising the temperature and, besides this factor, is more rapid when the C/A ratio in the anhydrous compound is high.

Work of Wells and Carlson [58]

An extensive study of the hydration of pure calcium aluminates and high-alumina cements was published in 1956 by Wells and Carlson.

Hydration of Pure Aluminates

The investigators studied the behavior during hydration of the three anhydrous compounds C_3A_5, CA, and C_5A_3. They observed that, in spite of their differences of composition, the three aluminates reacted in a very similar way with an excess of water. The resulting solutions reached, in every case, a C/A ratio of about 1/1. The maximum concentration was reached after times which varied with the starting compound. In the same way, the drop of concentration, due to the precipitation of solid phases, varied with the C/A ratio of the anhydrous compound. The drop was slower for CA than for the others.

Figure 18 gives the compositions of the solutions obtained with the three anhydrous compounds. At point a (CaO=0.5 g/l, Al_2O_3=0.6 g/l) the precipitation was, in a general way, very slow. The section ab on the curve is almost vertical, indicating a precipitation of alumina without variation of lime concentration. At point b, the *p*H of the solutions was 11.7–11.8, and the precipitated solids had C/A ratios a little less than 1/1. Under the microscope, the following phases could be distinguished: A hexagonal phase, the authors supposed to be C_2AH_n (and not C_3AH_n as was formerly thought); an amorphous phase apparently colloidal that the authors supposed to be Al_2O_3·aq.; in weak quantities, and accessorily, cubic crystals of C_3AH_6; and calcite probably formed by carbonation of the solid phases.

The hydration, with an excess of water, of the pure calcium aluminates would consequently be essentially characterized by the formation of C_2AH_8 and Al_2O_3·aq., as previously reported by D'Ans and Eick. Wells and Carlson think, as do Assarsson [2, 3], Forsen [21], and Hedin [25], that the dissolution of anhydrous aluminates in water proceeds first without hydrolysis. This occurs later with subsequent precipitation of Al_2O_3·aq., the quantities formed of this last compound varying with the composition of the anhydrous aluminate. The hydrated alumina being only partially soluble, a slight excess of lime is formed which tends to stop the hydrolysis. The immediate consequence is that the C/A molecular ratio of the aqueous aluminate solution, although situated in the vicinity of 1/1, is, in fact, a little higher than this value. In the experiments by Wells and Carlson, the C/A ratio in the precipitates was about 0.66, corresponding roughly to the formation of 2 moles of Al_2O_3·aq. to 1 mole of C_2A·aq.

A phenomenon which all investigators have noted is the marked persistence of solid phases in a metastable state. Besides the aluminates, whose transformations are very slow, alumina, which is one of the two true stable phases of the system $Al_2O_3-CaO-H_2O$, goes very slowly towards its final form, gibbsite. After a sufficient period of time, a microcrystalline alumina is formed which is an intermediary form between freshly precipitated gel and perfectly crystallized gibbsite. This very slow crystallization of alumina must, according to Wells and Carlson, exert a very important influence on the evolution of aluminates towards their final stable state.

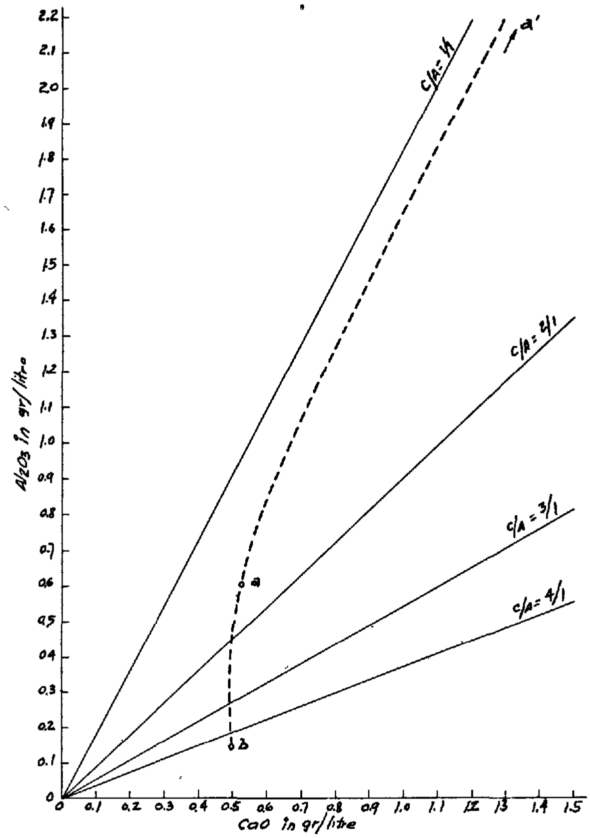

Figure 18. *Compositions of solutions formed by action of water on anhydrous aluminates.*

After Wells and Carlson [58].

In figure 19, the lined region contains the compositions of aluminates formed during setting and hardening of pure aluminates. This area covers, as may be seen, the highest part (corresponding to C_2AH_8) of the hexagonal-aluminate curve as defined by Wells, Clarke, and McMurdie. Wells and Carlson consider that in this zone the approach to final equilibrium proceeds by successive steps, for which the reaction velocities differ: first a metastable equilibrium is rapidly established, indicated by point b (hexagonal aluminates), and then those compounds are transformed, by a slower reaction, into compositions indicated by point F (AH_3—C_3AH_6—solution). It may be observed that the solubility curve for lime is situated far from this region, explaining the absence of this compound in high-alumina-cement hydration products.

It is a universally accepted opinion that the transformation of hydrated aluminates into cubic C_3AH_6 in concretes and mortars cured in damp atmosphere at temperatures above 35 °C is respon-

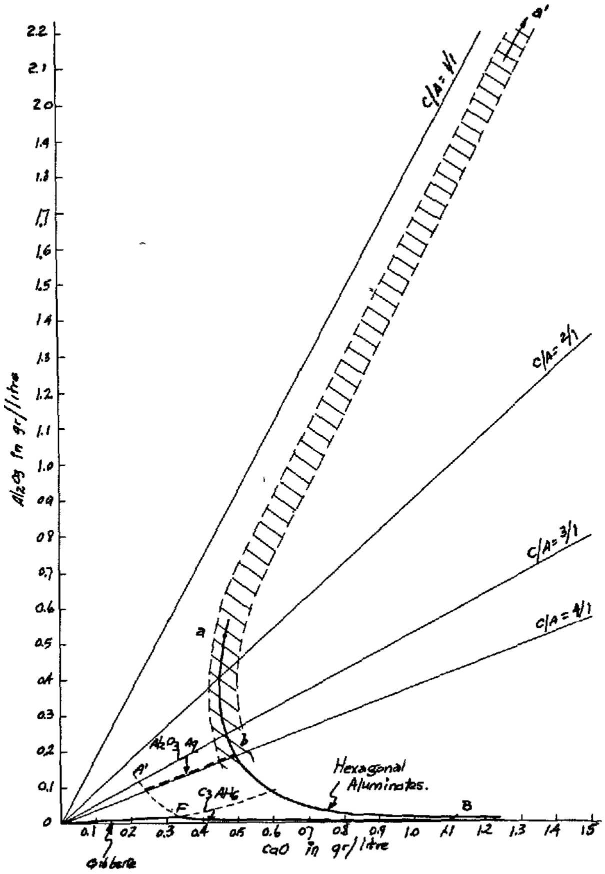

FIGURE 19. *Region in which the setting of high-alumina cements occurs, compared with the system* CaO—Al_2O_3—H_2O.

After Wells and Carlson [58].

sible for the observed loss of mechanical properties. Wells and Carlson agree, but observe that at 21 °C, at which temperature their experiments were conducted, this transformation is extremely slow.

Thus, in a general way, the evolution of the immediate hydration products of aluminates towards the two stable phases in the system Al_2O_3–CaO–H_2O, viz., the compounds C_3AH_6 and crystalline AH_3, is, at normal temperature, extremely slow.

Besides this low reaction speed, which is in favor of the high-alumina cements, another interesting factor must be considered, according to Wells and Carlson: Alumina formed during hydration, more or less in the form of a gel, has adhesive properties common to every kind of gel and acts in a certain sense as an "inorganic adhesive." Its contribution to the mechanical qualities of the hydraulic binder is not negligible.

Hydration of High-Alumina Cements

After their study on pure calcium aluminates, Wells and Carlson repeated their experiments with commercial aluminous cements, to make comparison. Their results were very similar to those obtained with isolated aluminates.

In a general manner, an aluminous binder treated with a large excess of water reacts rapidly to give, without consideration of its composition, a solution in which the C/A ratio is about 1/1, and the *p*H has a mean value of 11.25. Point a, of figure 19, is thus rapidly reached. Later, the solid phases precipitate, the separation of solid phases slackening with time. Point b, on figure 19, is thus slowly reached, and the *p*H at this point is about 11.75.

In this case, the precipitated solid phases are the same as those observed during hydration of aluminates; namely, (1) a phase crystallizing in hexagonal plates, often assembled in spherolites, thought to be C_2AH_8, (2) an amorphous phase, apparently colloidal, or at least not highly crystalline, whose optical properties are those of gibbsite, (3) cubic C_3AH_6, in small quantities, and (4) calcite, always in very small quantities.

Thus, in the presence of an excess of water (and it is necessary to emphasize this point) the commercial high-alumina cements, like the various calcium aluminates, give after hydration a hexagonal phase which is essentially C_2AH_8, and (or almost) simultaneously, a colloidal precipitate of $Al_2O_3 \cdot aq$.

To observe what occurs when these cements are hydrated in presence of an amount of water corresponding to the quantity used in practice, Wells and Carlson performed experiments on neat cements (W/C=0.38) at various temperatures, but above the normal (24, 35, 50, and 80 °C).

The experiments were made on three samples of different commercial cements; the results in table 1 correspond to a hydration of 7 days.

TABLE 1. *Solid phases present in hydrated high-alumina cements, as determined by X-ray diffraction*

Based on work of Wells and Carlson [58]

Observed solid phase	Number of samples (among the 3 examined) showing the observed phase at hydration temperature of:			
	24 °C	35 °C	50 °C	80 °C
Cubic C_3AH_6	None	1 (traces)	2	3
$C_2A \cdot aq.$ (10.6 and 5.3 A) [a]	2 (traces)	3		
$CA \cdot aq.$ (14.6 and 7.3 A) [a]	3 (predominating phase).			
Phase "x" (unknown composition [b]).	2 (predominating phase).	2 (predominating phase).		
Phase "y" (12.5 and 6.85 A *but* very weak lines). [a]	[illegible]	3	3	
Phase "g" (4.85 A) [a] (probably gibbsite).		2 (small quantities).	3	3

[a] Characteristic lines in the X-ray pattern.

[b] Probably $CA \cdot CaCO_3 \cdot H_n$, Carlson [15] and Schippa [50].

The complete observations made by the authors are as follows:

(1) After 7 days, the hydration was still incomplete.

(2) The cements which, in the anhydrous state, presented the lines of gehlenite (C_2AS) presented

those same lines after 7 days hydration because of the well-known hydraulic inertness of this compound.

(3) At 24 °C, essentially CA·aq. was formed.

(4) At 35 °C, C_2A·aq. was formed essentially with two other phases, one of them, at least, being a hydrated calcium aluminate.

(5) At higher temperature C_3AH_6 was formed in quantities becoming larger with increased temperature, simultaneously with an ill-defined phase which was probably gibbsite.

(6) The various cements observed, in spite of their different compositions in the anhydrous state, all showed almost identical behavior, confirming the observations with pure aluminates in presence of an excess of water.

Work of Farran [19]

This author attempted as much as possible to make experiments in conditions analogous to those practiced in the preparation of high-alumina-cement concretes and mortars.

According to his results, the aggregates used may have a different influence on the composition of hydrated phases, at least in their immediate vicinity, according to whether they are active or inert. With inert aggregates, and around them, Farran observed the formation of an interfacial film presenting, at least at the beginning, the appearance of a gel, but which later precipitated a phase of hexagonal symmetry, that is to say CA·aq. Finely crystallized alumina was also formed. Under some conditions of experiment, assuming locally an excess of water, e.g., immersion in water of fissured prisms, C_2A·aq. was formed, as observed before by Lafuma [30] and by Wells and Carlson [58] who always obtained this compound in the presence of an excess of water.

Working with an active aggregate, e.g., calcite which may react with the cement paste, Farran observed that the interfacial film was constituted by a crystalline phase, of which the X-ray diagram showed essential lines at: 14.6, 7.7, 7.3, and 3.8 A. According to the author, the lines at 14.6 and 7.3 A are characteristic of CAH_n, while those at 7.7 and 3.8 A are characteristic of a solid solution of carboaluminate $C_3A{\cdot}CaCO_3{\cdot}H_n$ in C_4AH_{13}, a solid solution, whose existence was presumed by Assarsson [3] and Bessey [4].

Work of Goria and Cussino [23]

These two investigators think, as did Lafuma [31] that the formation of cubic aluminate during long periods of curing can be avoided by adding to high-alumina cement a certain proportion of pozzolan which fixes, in the form of a calcium silicate, the lime bound to alumina, this last compound being simultaneously liberated. Goria and Cussino think that under these conditions the formation of cubic C_3AH_6 is partially prevented. The loss of mechanical characteristics would be 10 percent less than that observed when no pozzolan is added to the aluminous binder.

Work of Carlson [15]

It has been previously mentioned that Carlson studied the system Al_2O_3–CaO–H_2O at 1 °C. According to this author, at this temperature, the solid phase which precipitates is CAH_{10}; however, he thinks it possible that C_2AH_8 is formed first but is almost immediately transformed into CAH_{10}. Carlson believes that at 24 °C as at 1 °C, CAH_{10} constitutes the main crystalline phase when the hydration is made with a normal amount of water and not in the presence of an excess. He supposes too that the carboaluminate has a great importance in the process of hydration, for it is impossible to avoid its formation. He thinks, however, that this compound does not form, at least at 1 °C, a solid solution with C_4AH_{13}, as was supposed by Farran [19].

Work of Buttler [11]

In his thesis, in 1958, this author studied the behavior, during hydration, of a high-alumina cement without iron, essentially constituted of CA and CA_2 in roughly equal parts. For comparison, he observed the hydration of CA and CA_2, considered separately. He found that:

(1) CA, at 5 °C, reacts vigorously with water and dissolves almost congruently, at the start of the reaction at least. The solutions thus obtained finally precipitate CAH_{10} and Al_2O_3·aq.

(2) CA_2 behaves differently. During the initial period of hydration no reaction can be observed, but later it starts and accelerates with time, while the CaO and Al_2O_3 contents of the solution rise. The solid finally precipitated is essentially Al_2O_3·aq.

(3) The industrial mixture of CA and CA_2 in reacting with water gave supersaturated solutions which precipitated CAH_{10} and Al_2O_3·aq. Formation of C_2AH_8 was scarcely observed.

Bayerite (AH) may sometimes be formed, instead of gibbsite (AH_3) but simultaneously with calcite. This observation confirms a general opinion, according to which bayerite is formed preferentially to gibbsite if small quantities of CO_2 ions are present.

Thus it may be seen that CA reacts with water more rapidly than CA_2. It is consequently sure that the rapid rising of the CaO and Al_2O_3 concentrations in the solutions obtained from this mixture of $CA+CA_2$ is essentially due to the CA content of the said mixture. The fall of the concentrations, later observed, is due to the CA_2 content of the mixture, but it is possible that the alkalies eventually present play a part in the process.

Buttler observed that the hydrate mainly formed at low temperatures is CAH_{10}. Its transformation into C_3AH_6 is not easy nor rapid, except if the temperature rises, and he was not able, in his experiments at 5 °C, to observe the transformation.

At 21 °C, Buttler also observed that the mixture $CA+CA_2$, and CA alone reacts very rapidly, but that the solution obtained with cement precipitates more rapidly than that obtained with CA alone.

The compound CA_2 reacts very slowly at this temperature also, and the supersaturated solution obtained lets precipitate a solid whose composition is very near the composition indicated by the hexagonal-aluminates curve, while with CA or $CA+CA_2$ the only hydration products seem to be CAH_{10} and $Al_2O_3\cdot aq$.

At 25 °C, on the contrary, the mixture $CA+CA_2$ leads to the formation of C_2AH_8, concurrently with CAH_{10} and $Al_2O_3\cdot aq$. This reaction has already been observed by Carlson [15].

Work of Schippa [50]

This author studied the hydration of aluminous cements gaged in the form of neat pastes ($W/C=0.4$) and cured in damp atmosphere at 15–20 °C. The X-ray examination of prisms showed him that the crystalline phases present were CAH_{10}, $C_3A\cdot CaCO_3\cdot H_{11}$ and, in some cases, C_3AH_6. Schippa supposes the "phase x" described by Wells and Carlson [58] to be the carboaluminate. He was unable to observe, with sufficient certainty, the presence of C_2AH_8.

Schippa thinks that the influence of carboaluminate formation on the hydration of pure aluminates or high-alumina cements is of first importance and that some uncertainties could disappear as a result of a study of the system Al_2O_3–CaO–CO_2–H_2O.

Work of Schneider [51]

This author's work was primarily intended to find a possible relation between physical property changes and structure modifications. He used for this purpose differential-thermal-analysis techniques. He believes that CAH_{10} is the only aluminate which is formed during hydration of high-alumina cements at ambient temperature. Raising the temperature leads to the formation of C_3AH_6 and AH_3, by way of a reaction that Schneider thinks to be of a hydrothermal sort: water coming from dehydration of a part of the CAH_{10} could react with the remainder of this compound, already partially dissociated. This author believes that the loss of mechanical strength of high-alumina-cement concretes is perhaps due to the tensions provoked by the loss of water when the prisms are heated, and not only to the nature of the aluminates formed at higher temperatures than the ambient.

Work of Buttler and Taylor [12]

Both authors came back to the study of hydration of CA and CA_2 in normal gaging conditions, which compounds, as was seen, had been the subjects of researches by Buttler in his thesis of 1958. It is now certain that separately CA reacts with water more rapidly than CA_2. However, in the case of a mixture of $CA+CA_2$, which is realized in the cement industry, the reaction of CA with water adds lime to the solution, and then the CA_2 reacts more rapidly.

The authors have recognized that the only hydration products present at 5°C are CAH_{10} and $Al_2O_3\cdot aq$. At this temperature, they have not observed the formation of C_3AH_6. With an excess of water, CA and CA_2 give solutions which precipitate only $Al_2O_3\cdot aq$.

During the past few years, the opinion seems to be unanimous concerning the hydration process for calcium aluminates and high-alumina cements. The action of temperature during the hydration seems to be highly important. It determines the nature of the hydrated aluminates obtained. It is interesting to note that hexagonal dicalcium aluminate, C_2AH_8, which had always been considered as the chief compound of the hydration products at ordinary temperature, is only very transitory, at least when the amount of hydration water corresponds to that used in the preparation of concretes and mortars. On the other hand, this compound is preferentially formed in the presence of a great excess of water.

Hexagonal Tricalcium Aluminate and Carboaluminate

The reality of the existence of hexahydrated tricalcium aluminate, C_3AH_6, of hydrated monocalcium aluminate CAH_{10}, and of both hexagonal hydrated di- and tetracalcium aluminates, C_2AH_8 and C_4AH_{13}, is well established. But a doubt always remains concerning the reality of a hexagonal hydrated tricalcium aluminate, C_3AH_{12}, as well as the existence of a tricalcium aluminate crystallizing as pseudo-hexagonal needles, $C_3AH_{18\text{-}21}$.

In the diagram by Wells, Clarke, and McMurdie [59], an equilibrium curve for hexagonal aluminates is drawn: along this curve, precipitates are in equilibrium with the solutions of aluminates whose compositions, at least at the beginning, are situated on the right of the curve, and show C/A ratios varying continuously from 2 to 4, C_2AH_8 and C_4AH_{13} being the extreme members of the series. Wells, Clarke, and McMurdie first attempted, as indicated in a preceding chapter, to replace the previous curve by two others representing respectively the equilibria for C_2AH_8 and C_4AH_{13}. The study by D'Ans and Eick has shown that these equilibrium curves are purely theoretical and that the compositions of the solids instead of corresponding, for example, to C_4AH_{13}, correspond in fact to compounds with less lime (see fig. 10 and 12).

The curve was considered, later, a unique curve whose higher part represents the metastable equilibrium for which C_2AH_8 is largely predominant, while the lower part corresponds to compositions in which C_4AH_{13} is more abundant. The middle part, however, remains vague. It seems to correspond to an overlapping of the two curves of di- and tetracalcium aluminates, which are practically the prolongation one of the other and must present a metastable invariant point C_2AH_8–C_4AH_{13}–solution which has never been determined with precision.

Other investigators trusted in the reality of a hexagonal compound C_3AH_n and like Wells, Clark, and McMurdie, gave preparation methods, optical characteristics, and dehydration curves. Among them were, before 1950, Assarsson [2], Lefol [33], and Travers and Sehnoutka [55]. In 1952, Koyanagi [28] obtained hexagonal plates whose composition corresponded to the formula $C_3AH_{10.5}$. The same year, Longuet [36], preparing C_3AH_6 by various methods, always obtained this compound mixed with more or less important quantities of C_3AH_{12}, recognized by X-ray examination.

D'Ans and Eick [17], in 1954, also noted the existence of C_3AH_{12} and acicular C_3AH_{18-21}, whose metastable equilibrium curves would be situated in the region between the two curves drawn for C_2AH_8 and C_4AH_{13}. However, they presumed that the existence of tricalcium aluminates with 12 or 18–21 moles of water, was much more transitory than that of C_2AH_8 or C_4AH_{13}. The compounds C_3AH_{12} and C_3AH_{18-21} could be transformed rapidly into di- and tetracalcium aluminates and alumina, their transformation velocity depending on the initial concentrations of the solution from which they precipitate.

In 1956, Brocard [10] asserted again that a hexagonal tricalcium aluminate really exists and that it may be obtained by hydration of C_3A. Around the same period, Govoroff [24] published a short study of the behavior on heating of three hexagonal aluminates. The differential thermal analysis and X-ray examinations show, according to this author, that by simple heating to 80 °C, a mixture of C_4AH_n, C_3AH_{12}, and C_2AH_7 is transformed into C_3AH_{12}, almost in a pure state, whose X-ray diagram presents one essential line at 7.65 A, while the diagram of the initial mixture presents three essential lines at 8.33, 7.65, and 10.6 A, in other words the lines of the three compounds. On the other hand, as soon as the results were published which led them to a publication of their conception of the equilibria diagram of the system Al_2O_3–CaO–H_2O, Wells, Clarke, and McMurdie [59] adopted a position opposed to the reality of a hexagonal tricalcium aluminate.

In the middle part of the curve, for which the C/A ratio in the precipitates at equilibrium is around 3, it may be thought that there occurs either a metastable equilibrium for a hexagonal hydrated tricalcium aluminate or an intercrystallization, in the solid phase, of C_2AH_8 and C_4AH_{13}. Those precipitates have been subjected to X-ray determination, and a diagram has been established.

Actually three theses are opposed, each one having its supporters:

(1) A hexagonal tricalcium aluminate C_3AH_n (n varying from 6 to 21) really exists, the established diagram corresponding to it.

(2) The C_3AH_n does not really exist but is an equimolecular mixture of C_2AH_8 and C_4AH_{13}, obtained by syncrystallization.

(3) The X-ray diagram assigned to C_3AH_n, pertains in fact to a carboaluminate $C_3A{\cdot}CaCO_3{\cdot}H_n$.

Hypothesis of a Hexagonal Hydrated Tricalcium Aluminated

The X-ray diagram of hexagonal tricalcium aluminate has been published by Thorvaldson, Grace, and Vigfusson [54], Bunn and Clark [6], and Brocard [7]. The essential lines are noted in table 2.

TABLE 2. $3CaO{\cdot}Al_2O_3{\cdot}12H_2O$ (*d* in A)

Thorvaldson and coll. (1929)	Bunn and Clark (1938)	Brocard (1948)
----	7.70	7.65
----	3.77	3.77
----	----	----
2.86	2.85	2.86
2.47	----	----
1.65	----	----
1.43	----	----

The diagrams established by Bunn and Clark and by Brocard are practically coincident. The one established by Thorvaldson, Grace, and Vigfusson has been realized only for $2\theta=30$–$90°$ where the aluminates offer no more than the weakest lines, the most intense lines being situated beyond the limits of these angles.

Hypothesis of a Syncrystallization of Di- and Tetracalcium Aluminates

For Wells, Clarke, and McMurdie [59], there would not be a definite compound, but a compound resulting from a syncrystallization of both hexagonal aluminates C_2AH_8 and C_4AH_{13}, in equimolecular proportions. Their arguments are based on the examination of X-ray diagrams for both compounds, whose essential lines are 10.6 A for C_2AH_8 and 8.2 A for C_4AH_{13}.

Wells, Clarke, and McMurdie observed that the precipitates for which the C/A ratio is between 2 and 4 always present strong lines at 10.6 and 8.2 A, the relative intensities depending on the proportions of both aluminates in the "mixture." As these hydrates have structures quite similar parallel to the *a* axis, they are able to syncrystallize in thin successive layers, in so inextricable a way that a refractive index may be observed which is the average value of the indices of both compounds considered separately.

In 1951, Steinour [53] in his general report on aluminates reviewed again the published results and was inclined to accept the hypothesis advanced by Wells, Clarke, and McMurdie, the proofs of the existence of hexagonal C_3AH_n appearing dubious.

In 1954, Peppler and Wells [43] wrote that the X-ray examinations made by Wells, Clarke, and McMurdie, led to the conclusion that there does not exist a hexagonal tricalcium aluminate. Again, Bogue [5] remarks that on the equilibrium curve for hexagonal aluminates, as defined by Wells, Clarke, and McMurdie, no steps can be observed for which the molecular C/A ratio in the solid phase is 2, 3, or 4.

Finally, in 1956, Lea [32] reported that the experiments by Brocard [7] had been repeated at the Building Research Station, and that the X-ray examination of the solids obtained failed to show other compounds besides the hydrated di- and tetracalcium aluminates.

Hypothesis of a Hydrated Carboaluminate

Facing these uncertain data, some authors preferred not to give an opinion. The question was thus unresolved until, in 1956, Schippa and Turriziani [49] observed that between 15 and 20 °C, in the system Al_2O_3–CaO–H_2O, there does not exist a hexagonal hydrated compound in which the C/A ratio is 3, whatever be the time allowed for equilibrium, or whatever the values of the C/A ratio in the initial solutions. The samples they prepared from supersaturated lime and alumina solutions, which, according to D'Ans and Eick [17] must contain hexagonal C_3AH_{12}, contained only C_2AH_8 and C_4AH_{13} as solid phases as demonstrated by the X-ray diagrams they obtained. Moreover, in the course of the hydration of C_3A with a saturated lime solution, the authors observed only C_4AH_{13} and $Ca(OH)_2$ (essential lines at respectively 8.41 and 4.92 A). The same results were obtained for preparations made from a fresh alumina gel and lime.

Schippa and Turriziani remark, on the other hand, that the spectra published by Bunn and Clark [6], and by Brocard [7] are practically identical with that of a carboaluminate formulated $3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}aq.$, whose diagram is given in table 3 (*d* in A).

TABLE 3. *X-ray diffraction pattern of carboaluminate and patterns formerly attributed to* C_3AH_{12} (d *in A*)

$C_3A{\cdot}CaCO_3{\cdot}H_n$	C_3AH_{12}	C_3AH_{12}
Schippa and Turriziani	Bunn and Clark	Brocard
7.74	7.70	7.65
3.79	3.77	3.77
2.89	2.85	2.86
2.55		
2.43		
2.366		
2.177		
2.118		
2.023		
1.955		

This carboaluminate, as well as the tricarboaluminate $C_3A{\cdot}3CaCO_3{\cdot}nH_2O$, had been already prepared by Jones [22], who reported the compound in a communication made in 1938, at the Stockholm Symposium. At the same time, Bessey [4] also made a private communication on the same subject.

It may be seen that the diagram obtained by Schippa and Turriziani shows an important line at 7.74 A, while the important lines given for C_3AH_{12} correspond generally, to lesser values (7.65 A, Brocard; 7.65 A, Govoroff; 7.70 A, Bunn and Clark.

Discussing the importance of this carboaluminate, Schippa, in another publication [50], insisted on the necessity of undertaking the study of the quaternary system Al_2O_3–CaO–CO_2–H_2O, and thus completing the study of the system Al_2O_3–CaO–H_2O.

Various investigators agreed with the conclusion of Schippa and Turriziani:

(1) Roberts [46], 1957, thinks that, the presence of CO_2 being unavoidable in the experiments and the carboaluminate being formed quite easily, it is probable that the compound first supposed to be C_3AH_{12} is nothing else than $C_3A{\cdot}CaCO_3{\cdot}H_n$.

(2) Carlson [15], 1958, having obtained in the course of his experiments hexagonal crystals whose composition was near enough C_3AH_{10}, hoped to verify that it was a hexagonal tricalcium aluminate, but, reading the work by Schippa and Turriziani published in the meanwhile, considered the question as settled.

(3) Buttler [11] on one hand, and Percival and Taylor [44] on the other, in their studies of the system Al_2O_3–CaO–H_2O at 5 and 21 °C, recognized the presence of $C_3A{\cdot}CaCO_3{\cdot}H_n$ in many preparations by the presence of the line at 7.6 A.

(4) On the other hand, Farran [19] in 1956, in his examination of the interfacial films between hardened high-alumina-cement pastes and aggregates on glass pans, attributed, as already mentioned, the presence of lines at 7.7 and 3.8 A to the existence of a solid solution of C_4AH_{13} and $C_3A{\cdot}CaCO_3{\cdot}H_n$. Farran determined also the refractive index of this carbonated compound as $n_\omega = 1.552$ and $n_\epsilon = 1.532$, those generally published as characteristic of C_3AH_{12} being $n_\omega = 1.550$ and $n_\epsilon = 1.530$.

In the actual state of our own results, the existence of C_3AH_{12} appears hypothetical. Working effectively, as far as possible, in absence of CO_2, we have been unable to prepare, as were Schippa and Turriziani [49], a compound of C/A ratio of 3. The X-ray diffraction spectrum of the product obtained shows the presence of lines indicating large interplanar spacings at 10.6 and 8.33 A which are those of C_2AH_7 and C_4AH_n. The X-ray pattern of the same product after submission to the action of CO_2 in moist atmosphere at about 20 °C indicates the disappearance of the line at 8.33 A and the appearance of a very strong line at 7.65 A, tending to prove that C_4AH_n has been transformed into monocarboaluminate with the C_2AH_8 remaining unaltered.

In any case, it must be noted that the authors who support the existence of C_3AH_{12}, do not mention the carbonate content of the compound studied. On the other hand, it is to be noted that according to a recent publication by Percival and Taylor [45] (see the following section) the line near 7.65 A could equally correspond to C_2AH_5, a partially dehydrated product of C_2AH_8.

Their comment cannot facilitate the resolution of this problem. In some cases, indeed, it is quite possible that the line at 7.65 A observed in the preparations may be a consequence of this partial dehydration, as seems to be the case, particularly, in our own experiments.

Dehydration of Aluminates

There is great variation in the number of molecules of water of crystallization attributed to the various hydrated aluminates as reported by different authors. It seems that, generally, at least a part of this water is bound in a rather loose manner and can be eliminated easily by raising the temperature only a few degrees, or by modifying the vapor pressure of the ambient atmosphere. It is normal that under these conditions disagreements between investigators should appear and that, in particular, the attribution of X-ray diagrams and of optical characteristics to definitely formulated hydrates should be difficult. A certain number of authors, whose works are summarized hereafter, have been preoccupied by these dehydration phenomena.

Hexagonal Tricalcium Aluminate

This compound, which is considered hypothetical by a number of investigators, has been the object of only a few publications during the last 10 yr.

Govoroff [24] thinks it is the stable compound up to 80 °C and that it represents, at this temperature, the product of the last stage of the dehydration of hexagonal aluminates. For samples heated between 20 and 80 °C, the essential line always observed in the X-ray pattern is situated, according to Govoroff, at 7.65 A.

The water content of hexagonal tricalcium aluminate is extremely variable, passing, according to the authors, through the values 2, 4, 6, 8, 9.5, 10.5, 12, or 14 (Assarsson [2]; Bessey [4]; Lefol [33]; Thorvaldson, Grace, and Vigfusson [54]).

Hexagonal Dicalcium Aluminate

The dehydration of hexagonal dicalcium aluminate has been studied by Roberts [46], Carlson [15], McMurdie [39], and Buttler [11] and has been recently reexamined by Percival and Taylor [45].

It seems that the water in the compound C_2AH_n presents a marked zeolitic character. McMurdie has shown that the loss of two moles of water takes place without important change in the crystal lattice, except perhaps a slight shortening of the c axis. In addition, Buttler noted that the dehydration curve for C_2AH_8 does not present steps, but only slight modifications of the slope of the curve at 50, 100, and 175 °C. On the other hand, it seems almost certain that C_2AH_8 exists in two polymorphic forms, α and β, whose essential lines are at 10.7 and 10.4 A (Roberts, Buttler).

Table 4 gives the characteristics defined by various workers, for various hydrates which were obtained by raising the temperature or by a change of the relative humidity of the atmosphere.

Table 4. *Characteristics of dicalcium aluminate hydrate as reported by several investigators*

Investigators	Mol. H_2O in the hydrate	*d* (A)	D	Refractive index
Salmoni [48], Carlson	11	10.8–10.9	------	------------
Roberts, Buttler	8 (α)	10.7	1.95	1.520–1.505
Percival and Taylor.	8 (β)	10.4	------	------------
Roberts, Percival, and Taylor	7.5	10.6	1.98	1.520–1.505
McMurdie	6	----------	------	------------
Roberts,	5	8.7	2.09	1.534–1.524
Percival, and, Taylor.	5 (little cryst.)	7.6	------	------------
Roberts, Percival, and Taylor	4	7.4–7.2	2.27	1.565–1.559

Until the content of water of crystallization is reduced below 5 H_2O, the transformation is reversible, but the hydrate with 4 H_2O cannot rehydrate, whatever may be the hygrometric conditions.

Hexagonal Tetracalcium Aluminate

The dehydration of this compound has also been studied by Roberts [46], who attributes to the product a water content of 13 molecules. It seems probable, however, that in the presence of the solution the compound may be formulated C_4AH_{19}, the passage to 13 H_2O being easily and reversibly made by drying.

The compound with 13 H_2O can exist in two polymorphic forms α and β (D'Ans and Eick [17], Roberts). This hydrate can easily lose two molecules of water, by a transformation which also is reversible. A more pronounced loss of water probably induces a breaking of the crystal lattice, which can be seen in the aspect of the X-ray diagram.

The dehydration curve of C_4AH_{13} has been studied by Buttler [11]; contrary to that for C_2AH_8, it presents distinct steps at 50 and 108 °C. Between 160 and 400°, the curve is a continuous one until a content of 3.5 moles of water is reached.

Table 5 summarizes the results obtained by various investigators.

From the crystallographic point of view, the loss of 2 molecules H_2O, from 13 to 11, is recognizable by a slight shortening of the *c* axis, but up to this point, the unit cell may regain its previous dimensions by rehydration (Dent [18]). Between 150 and 300° C, on the contrary, one can observe a partial dehydroxylation, and the reversibility is surely no longer possible.

Table 5. *Characteristics of tetracalcium aluminate hydrate as reported by several investigators*

Investigators	Mol. H_2O in the hydrate	*d* (A)	D	Refractive index
Roberts	19	10.6	1.79	1.500-1.485
Roberts	13 (α)	8.2	-------	------------
D'Ans and Eick	13 (β)	7.9	2.02	1.536-1.519
Roberts	11	7.4	2.08	1.539-1.524
Roberts	7	7.4	2.28	1.555-1.544
Buttler	3.5	?	-------	------------

Monocalcium Aluminate

The formula CAH_{10} was proposed by Assarsson [3] as early as 1936. Like the previously mentioned aluminates, this compound may easily lose its water of crystallization by heating or by modification of the hygrometric conditions. It is probable that the formula CAH_{10} is only an approximate one, and both Longuet [37] and Carlson [15] have described a CAH_7 hydrate. The loss of water does not modify the crystalline structure since the differences which can be observed in the respective positions of the lines in the X-ray diagram, do not exceed 0.02 A.

Buttler [11], who determined the dehydration curve of this hydrate, notes that it does not present steps, but around 100 °C, for a composition CAH_4, the X-ray diagram is modified and the essential line at 14.6 A has disappeared. At the same temperature, Longuet observed a hydrate $CAH_{2.5}$ giving no X-ray diagram and beyond 880 °C, Schneider [51] found CA, whose presence indicated that the dehydration was complete. These results are summarized in table 6.

Table 6. *Characteristics of monocalcium aluminate hydrate as reported by several investigators*

Investigators	Mol. H_2O in the hydrate	*d* (A)
Brocard Carlson Midgley [36] Longuet	10	14.3-14.6
Longuet Carlson	7	13.6
Buttler	4	------------
Longuet	2.5	------------

Cubic Tricalcium Aluminate

Schneider [51] studied the dehydration of C_3AH_6 by differential thermal analysis and observed two endothermic peaks at 340 and 550 °C, corresponding to successive dehydrations that he has not identified. Beyond 550 °C, he identified the formation of the two crystalline phases $C_{12}A_7$ and CaO.

Monocarboaluminate

Turriziani and Schippa [56] have studied the behavior of $C_3A \cdot CaCO_3 \cdot H_n$ at various temperatures. It is not possible to consider this behavior as a true dehydration but rather as an ignition loss, CO_2 being eliminated with H_2O. The authors, therefore, proceeded by comparison with $CaCO_3$. Water is entirely eliminated at 600 °C; at this temperature, the quantity of CO_2 eliminated is 23.2 percent of the theoretical quantity, against 0.03 percent for $CaCO_3$. The original X-ray diagram of the carboaluminate persists up to 500 °C, proving that the unit cell is not modified up to this point.

The studies made in recent years show that water in the hydrated calcium aluminates is loosely bound to the remaining molecule. The removal of water molecules, when it is important enough, is accompanied by a modification of the dimensions of the unit cell. Consequently, to be satisfactorily significant, the X-ray diagrams should be accompanied by a verification of the water content of the aluminate examined. This verification is especially important as the partially dehydrated compounds may present lines very near the lines of other aluminates (see the section on "Hexagonal Tricalcium Aluminate—Carboaluminate"). Moreover, dehydration, in some cases, makes the X-ray diagram disappear: this "amorphization" is comparable with the phenomena described by Mlle. Couillaud [16], in her thesis in 1945, for which no valid explanation has been given until now.

One is tempted to think that, at least in certain cases, identification with the help of X-ray techniques is not enough. Perhaps it would be desirable to try the value of infrared spectrography in this particular domain as Lehmann and Dutz [34] have started to do.

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Discussion

M. H. Roberts

With regard to M. Lhopitallier's review of the equilibria in the $CaO–Al_2O_3–H_2O$ system, it may be noted that a detailed study of this system at 25 °C has recently been made by Jones and Roberts [1]. Some of the results and conclusions given in this paper and a reinterpretation of results previously obtained by other workers have already been discussed by Jones [2] in another paper in this Symposium. In addition, however, Jones and Roberts discussed briefly the problem of carbonation of solid phases, and confirmed Lhopitallier's conclusion that confusion has arisen between $C_3A{\cdot}CaCO_3{\cdot}12H_2O$ and the alleged compound $C_3A{\cdot}12H_2O$. Carbonation, if it occurs to an appreciable extent, may have an important influence on any studies in the cement-water system, and the CO_2-containing aqueous systems therefore seem to warrant detailed investigation. In this connection, some limited tests have recently been done at the Building Research Station to examine the effect of the presence of carbonate on the equilibria in some CaO and Al_2O_3-containing aqueous systems at 25 °C. These involve shaking mixes of supersaturated monocalcium aluminate solution with lime to precipitate hydrated calcium aluminates, adding various amounts of $CaCO_3$, or Na_2CO_3, or each of these carbonates together with $CaSO_4{\cdot}2H_2O$, followed after further shaking by filtering, analyzing the filtrates, and examining the moist solid phases formed, by X-rays. Even with the relatively insoluble $CaCO_3$, it was found that complex carbonate compounds or solid solutions were usually formed, though after the shaking period (usually 7 days) a trace or a small amount of unreacted $CaCO_3$ was also present in most of the final solid phases.

With the supersaturated monocalcium aluminate solution without added lime, which precipitated mixtures of $C_2A{\cdot}8H_2O$ and hydrated alumina at 25 °C, in the presence of added $CaCO_3$ $\left(\text{initial } \frac{CaCO_3}{Al_2O_3}=0.66\right)$ no $C_2A{\cdot}8H_2O$ was formed. X-ray examination of the moist final solid phase showed only the presence of much $C_3A{\cdot}CaCO_3{\cdot}aq.$, some $A{\cdot}3H_2O$ and some unreacted $CaCO_3$. The final solution composition (0.193 g CaO per liter, 0.091 g Al_2O_3 per liter) was also markedly different from that observed in the absence of $CaCO_3$ (0.48 g CaO per liter, 0.24 g Al_2O_3 per liter). With additions of $CaCO_3$ $\left(\text{initial } \frac{CaCO_3}{Al_2O_3}=0.33 \text{ and } 0.66\right)$ to precipitated $C_2A{\cdot}8H_2O$ there was no marked change in solution composition but in addition to

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[1] F. E. Jones and M. H. Roberts, The system $CaO—Al_2O_3—H_2O$ at 25 °C in course of publication.

[2] F. E. Jones, Hydration of calcium aluminates and ferrites, this Symposium, paper III-3.

$C_2A{\cdot}8H_2O$ the final solid phase contained some $C_3A{\cdot}CaCO_3{\cdot}aq.$, a little unreacted $CaCO_3$, and with the larger addition of $CaCO_3$ some hydrated alumina as well. Additions of varying amounts of $CaCO_3\left(\text{initial }\frac{CaCO_3}{Al_2O_3}=0.33, 0.66, 1.0, \text{ and } 1.2\right)$ to precipitated $C_4A{\cdot}19H_2O$ resulted in an apparent increase in the lime concentration of the solution, while the Al_2O_3 concentration decreased. At the same time the $C_3A{\cdot}CaCO_3{\cdot}aq.$ compound and what appears to be a $C_3A{\cdot}CaCO_3{\cdot}aq.{-}C_4A{\cdot}aq.$ solid solution phase (longest basal spacing varying between 8.3 A and 8.1 A) were formed, and except with the smallest addition of $CaCO_3$ the initially formed $C_4A{\cdot}19H_2O$ disappeared.

On adding similar amounts of Na_2CO_3 to precipitated $C_4A{\cdot}19H_2O$ almost all of the Al_2O_3 was removed from solution, and either the solid solution phase or a mixture of this with $C_3A{\cdot}CaCO_3{\cdot}aq.$ was formed. The amount of $C_3A{\cdot}CaCO_3{\cdot}aq.$ in the final solid phase increased with increasing additions of Na_2CO_3 until with an initial $\frac{Na_2CO_3}{Al_2O_3}$ molar ratio of about 1 almost pure $C_3A{\cdot}CaCO_3{\cdot}aq.$ was obtained. Larger additions of $Na_2CO_3\left(\text{initial }\frac{Na_2CO_3}{Al_2O_3}=1.9 \text{ and } 2.8\right)$ were also tried to see whether the carbonate analog of high sulfate sulfoaluminate, $C_3A{\cdot}3CaCO_3{\cdot}aq.$, could be formed, but only mixtures of $C_3A{\cdot}CaCO_3{\cdot}aq.$ and $CaCO_3$ were obtained.

With additions of $CaSO_4{\cdot}2H_2O$ together with $CaCO_3\left(\text{initial }\frac{CaSO_4}{Al_2O_3}=0.9, \text{ and } \frac{CaCO_3}{Al_2O_3}=0.8\right)$ to precipitated $C_4A{\cdot}19H_2O$, instead of obtaining $C_3A{\cdot}CaSO_4{\cdot}aq.$ alone, the presence of $CaCO_3$ resulted in the formation of a mixture of $C_3A{\cdot}3CaSO_4{\cdot}aq.$, $C_3A{\cdot}CaSO_4{\cdot}aq.$, $C_3A{\cdot}CaCO_3{\cdot}aq.$, and a probable $C_3A{\cdot}CaCO_3{\cdot}aq.$—$C_4A{\cdot}aq.$ solid solution phase. A little unreacted $CaCO_3$ was also still present. With larger amounts of $CaSO_4{\cdot}2H_2O\left(\text{initial }\frac{CaSO_4}{Al_2O_3}=3\right)$ and with initial $\frac{CaCO_3}{Al_2O_3}$ ratios of 0.8 and 1.9, X-ray examination of the final solid phase showed only the presence of $C_3A{\cdot}3CaSO_4{\cdot}aq.$ and calcite. There was no indication of the formation of $C_3A{\cdot}3CaCO_3{\cdot}aq.$ or a possible $C_3A{\cdot}3CaCO_3{\cdot}aq.$—$C_3A{\cdot}3CaSO_4{\cdot}aq.$ solid solution phase, the X-ray pattern observed for the high sulfate sulfoaluminate in these mixes containing carbonate being identical to that of the pure compound. Similar results to the above were also obtained with additions of mixtures of $CaSO_4{\cdot}2H_2O$ and Na_2CO_3.

From the above results, it is clear that the presence of calcium carbonate or alkali carbonate, or even exposure to atmospheric CO_2, may have a marked effect on the solution equilibria in the $CaO{-}Al_2O_3{-}H_2O$ and related systems, and on the solid phases formed. Further work is required to establish the solution equilibria and solid phases formed in the presence of carbonate more precisely.

Paper VIII-S1. The Risk of Unsoundness Due to Periclase in High-Magnesia Blast-Furnace Slags*

N. Stutterheim

Synopsis

The production of slag as a waste product of blast-furnace operation is increasing, and interest in its utilization is growing. This is true also for high-magnesia slags.

It is evident from specifications for cement incorporating slag that there is a belief that magnesia unsoundness can occur with such slags, in a way analogous to the unsoundness which develops in portland cements with high magnesia content. However, the consensus of opinion among those who have experience with high-magnesia slags is that there are no grounds for this belief.

Experimental work done by the author has shown that cements made with granulated slags having from 13 to 21 percent of MgO yield sound concrete even after many years of moist storage. A study of the phase composition-liquidus temperature relationships was made, and it was found that those compositions in which periclase occurred either were near the periclase boundary, or their liquidus temperatures were high. Hence either they would not yield much periclase on cooling, or they would be unsuitable for blast-furnace operation because their effective viscosity, increased by periclase crystals in the slag, would be excessive. Work done by investigators on the optimum compositions for blast-furnace slags confirms this view.

It can therefore be concluded that the possibility of periclase formation in high-magnesia blast-furnace slags is remote, a conclusion which finds support also in the virtual absence of mention in the technical literature of periclase as a slag mineral.

Résumé

La production de laitier comme produit résiduel de l'opération des hauts-fourneaux augmente et avec elle s'accroît l'intérêt pour son utilisation. Ceci est vrai aussi pour les laitiers à forte teneur en magnésie.

Les stipulations pour le ciment incorporant le laitier indiquent clairement qu'il existe une croyance que l'inconstance de volume à cause de la magnésie peut se produire avec de tels laitiers, de façon analogue à l'inconstance qui se développe dans les ciments Portland à haute teneur en magnésie. Cependant, l'opinion est unanime parmi ceux qui ont fait des recherches avec les laitiers à forte teneur en magnésie que cette croyance n'est pas fondée.

Un travail de recherche effectué par l'auteur indique que les ciments faits de laitiers granulés contenant de 13 à 21% de MgO donnent un beton solide même après plusieurs années de conservation humide. Une étude des relations: composition de la phase—température liquidus fut faite et on trouva que les compositions dans lesquelles la périclase se produisait étaient soit celles proches de la limite de la périclase, soit celles dont les températures liquidus étaient hautes. De ce fait, ou elles ne produisaient pas beaucoup de périclase sur le refroidissement, ou elles ne convenaient pas à l'opération de haut-fourneau parce que leur viscosité effective, accrue par les cristaux de périclase dans le laitier, était excessive. Les travaux de recherche faits sur les conditions optimales pour les laitiers de haut fourneau confirment cette opinion.

Par conséquent on peut conclure que la possibilité de la formation de périclase dans les laitiers de haut fourneau à forte teneur en magnésie est peu probable, conclusion supportée aussi par le fait que dans la littérature technique il n'est virtuellement pas fait mention de la périclase en tant que minéral de laitier.

Zusammenfassung

Mehr und mehr Schlacke wird als Abfall in den Hochofenbetrieben hergestellt, daher ist man immer daran interessiert, wie man für eine solche Schlacke ein Awendungsgebiet finden kann. Das trifft auch für solche Schlacken zu, die viel Magnesia enthalten.

Wenn man sich die Normen durchliest, die die Zementindustrie für das Einverleiben der Schlacke in Zemente aufgestellt hat, bemerkt man sofort, daß die Industrie gegen einen hohen Magnesiagehalt ihre Bedenken hatte, welcher vermutlich von den schlechten Erfahrungen, die man mit magnesiareichen Portlandzementen gemacht hat, herrührt. Die Parteien, welche Schlacken, die magnesiareich waren, aufgearbeitet haben, weisen darauf hin, daß alle Furcht hier unbegründet ist.

Experimentalarbeiten des Vortragenden haben bewiesen, daß Zemente, die mit granulierten Schlacken mit 13–21% MgO-Gehalt hergestellt worden sind, einen guten Beton ergeben, der noch nach vielen Jahren Aufbewahrung in einer feuchten Umgebung zufriedenstellende Eigenschaften aufweist. Eine Untersuchung der Beziehungen zwischen Phasenzusammensetzung und Liquidustemperaturen zeigte, daß alle die Zusammensetzungen, in welchen Periklas auftritt, entweder sich in der Nahe der Periklasgrenze befinden, oder daß ihre Liquidustemperatur hoch ist. Das heißt, daß sie beim Abkühlen nicht viel Peri-

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the South African Council for Scientific and Industrial Research, Pretoria, South Africa.

klas hervorbringen, oder dass sie für das Arbeiten im Hochofen nicht benutzt werden können, da ihre Viskosität in der Gegenwart vieler Periklaskristalle in der Schlacke zu hoch liegen würde. Die Arbeiten, die über die beste Zusammensetzung der Hochofenschlacken veröffentlicht worden sind, bestätigen diese Ansicht.

Man kann daher schließen, daß eine Periklasbildung mit magnesiareichen Hochofenschlacken nicht zu befürchten ist, was auch dadurch bewiesen ist, daß Periklas fast nie in der Literatur als Schlackenmineral erwähnt worden ist.

Introduction

In his excellent review [1][1] of the state of knowledge concerning slag cements, as presented to the Third International Symposium on the Chemistry of Cements, Keil indicated that our knowledge of slag cements is not as far advanced as that of portland cements. Clinker is largely crystalline, so that its composition can be studied effectively by techniques such as those involving the microscope and X-ray and electron diffraction; on the other hand, the constitution of granulated slags as used for cement, being largely glassy, is more difficult to study. Moreover, portland cements have been known for a longer time and are applied in more ways than slag cements; also the tonnages employed far exceed those of the latter. It is not surprising, therefore, that more scientific endeavor has been devoted to the behavior of portland cement and more progress made in elucidating its constitution.

Blast-furnace slag is being produced in ever-increasing quantities, world production being roughly proportional to the output of steel. Having performed its metallurgical function, most slag has only nuisance value and is generally dumped. Because of the increasing value of industrial land required for dumping, the economic need for utilizing waste materials, and the ever-growing demand for mineral products, blast-furnace slag is being used increasingly for various purposes, particularly for cement manufacture.

Not all slags are considered suitable for the latter purpose. Several specifications for cements in which slag is incorporated place limitations on composition and, in particular, on the magnesia content of the slag. The limit for magnesia has been introduced to eliminate the risk of delayed unsoundness due to the presence of periclase in cement made from slag, using the experience with magnesia in portland cement as an analogy. For this reason, many cement technologists consider high-magnesia slags unsuitable for cement manufacture.

However, in many countries blast-furnace operators use magnesian limestone or dolomite as a blast-furnace flux, for technical or economic reasons. Interest in the possibility of utilizing the resultant high-magnesia slag for the manufacture of constructional cements has grown considerably in the last three decades.

General Methods of Using Slag for Cement Manufacture

There are two general ways in which a slag can be used for cement production:

1. As a raw material for the manufacture of portland cement clinker;
2. As a major ingredient of a slag cement for which the slag, in the rapidly chilled form, is finely ground and mixed with substances capable of releasing the latent hydraulicity of the slag.

High-magnesia slag cannot be employed in any quantity as a raw material for portland cement manufacture in view of the well-established risk of unsoundness with portland cements in which the magnesia content exceeds about 4 percent [2, 3]. This paper is concerned only with the second use of high-magnesia slag mentioned above.

Magnesia and Periclase in Cements

The only known form of free magnesia is periclase, an isotropic crystalline mineral whose hydration is associated with an increase in volume of the order of 110 percent of the original volume. The rate of hydration, unlike that of CaO, is slow; it depends on the temperature of periclase formation [4], on the periclase grain size [4, 5], and on external conditions; for instance, whereas CaO hydrates in the presence of both liquid and gaseous water, MgO appears to hydrate only in the presence of water in the liquid phase [4].

Free magnesia, i.e., periclase, is therefore responsible for magnesia unsoundness. If the magnesia is combined to form a compound, or if it is dissolved in a glass, it no longer expands on hydration. [3, 6]

High magnesia content per se in a slag, is therefore not an indication that the material is necessarily unsound, though it can be said, particularly in view of the large volume of the periclase primary phase field in the quaternary system $CaO–MgO–Al_2O_3–SiO_2$, that there is a strong prima facie case for caution.

A number of investigators who have studied the feasibility of using high-magnesia slags for cement manufacture, have expressed opinions on the question of soundness. In a study of the strengths of slag-portland cement mixtures including, inter alia, some high-magnesia slags (range 7.2 to 18.5 per-

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[1] Figures in brackets indicate the literature references at the end of this paper.

cent of MgO), Grün [7] observed that there was no evidence of unsoundness up to 2 yr, and concluded that the MgO in slag is bound differently from that in portland cement clinker. Nurse and Midgley [8] examined the minerals present in slags of a wide range of compositions, including high-magnesia slags, but found no periclase.

Stutterheim and Nurse [9] found no unsoundness in portland blast-furnace cement concretes made with high-magnesia slags (15 to 18 percent of MgO) even after 3 yr moist storage; autoclave expansions of the cements ranged from 0.05 to 0.22 percent.

Schumann [10] reviews the question of limitations placed by various countries on the permissible MgO content of slags intended for cement manufacture, and concludes that there is experimental evidence and a considerable weight of opinion in favor of allowing fairly high contents, much higher than were laid down in the United States of America. Appiano [11] presents a similar review of evidence and draws attention to the undue restrictiveness in this respect of the present specification for slags in Italy. Cirilli and Brisi [12] describe a particular case of a slag with an MgO content of 32 percent which proved completely sound.

Hence, although these authors do not present many systematic experimental data, there is a consensus of opinion among those with experience of this type of material that high-magnesia slags are sound.

In 1947 the author started an investigation initially in collaboration with R. W. Nurse of the Building Research Station, England, and continued later at the South African Council for Scientific and Industrial Research, Pretoria, on the question of soundness of high-magnesia blast-furnace slags. This investigation involved a study on the system gehlenite-spinel [13], as well as an investigation of the performance of high-magnesia slags from iron works in the northeast of England [9], followed by an exploration of the region of compositions of slags as produced at blast-furnaces operated with dolomite fluxes in South Africa [14]. In the latter work an attempt was made to allow for the presence also of oxides other than CaO,MgO, SiO_2, and Al_2O_3 by using slag as parent material and modifying its composition as desired by fusion with known amounts of the required oxides or carbonates. Some of the results of the primary-phase and liquidus-temperature determinations are presented in table 1, the compositions being recorded as though the specimens were four-component mixtures. For the sake of brevity only some of the results, listed in increasing order of MgO content, selected from a series of 109 quench determinations and representative of the range of MgO contents examined, are given.

TABLE 1.—*Primary phases and liquidus temperatures for synthetic slags of high-magnesia content*

Quench specimen No.	Composition (calculated four-component)				Primary phase	Liquidus temperature
	SiO_2	Al_2O_3	CaO	MgO		
	%	%	%	%		°C
89	35.0	5.0	44.0	16.0	C_2S	1,650
80	42.0	5.0	37.0	16.0	Melilite	1,415
104	33.0	9.5	41.5	16.0	Merwinite	1,480
85	28.0	14.6	41.4	16.0	Periclase	1,490
81	28.0	24.1	31.9	16.0	Spinel	1,560
94	39.1	5.0	37.4	18.5	Periclase	1,500
13	39.6	12.9	28.9	18.6	Spinel	1,375
12	35.2	11.5	33.4	19.9	Spinel	1,380
79	37.4	5.0	36.8	20.8	Monticellite	1,410
41	35.9	7.5	34.7	21.9	Periclase	1,565
5	39.1	10.4	28.6	21.9	Forsterite	1,390
3	37.2	12.6	28.3	21.9	Spinel	1,390
31	32.5	14.0	31.5	22.0	Spinel	1,400
53	28.0	21.1	26.5	24.4	Spinel	1,590
87	36.8	8.0	29.6	25.6	Periclase	1,450
97	34.4	12.6	26.7	26.3	Spinel	1,470
48	31.1	15.5	26.8	26.6	Spinel	1,505
61	28.0	18.8	26.0	27.2	Periclase	1,570
52	38.4	5.0	29.1	27.5	Periclase	1,650
45	39.6	7.2	25.3	27.9	Forsterite	1,500
46	35.9	10.0	25.2	28.9	Forsterite-Periclase	1,475
38	34.4	12.8	23.9	28.9	Spinel	1,480
22	31.1	13.9	25.8	29.2	Periclase	1,600
62	28.0	18.7	23.3	30.0	Periclase	1,610
54	30.6	18.8	20.0	30.6	Spinel	1,595
63	39.9	5.0	23.9	31.2	Periclase	1,650
39	40.0	6.8	21.7	31.5	Forsterite	1,600
19	34.4	10.9	23.0	31.7	Periclase	1,540
18	35.8	12.5	19.6	32.1	Forsterite	1,560
47	28.6	18.9	20.0	32.5	Periclase-Spinel	1,610
59	39.7	6.8	20.0	33.5	Forsterite	1,650
64	36.6	9.9	20.0	33.5	Forsterite	1,550
70	35.6	10.9	20.0	33.5	Periclase	1,540

Those specimens having periclase as primary phase mostly have compositions which lie near the periclase phase boundary. Where this is not the case the liquidus temperatures are relatively high, and slags having such compositions would therefore not properly perform their metallurgical functions in a blast furnace, since their effective viscosities at normal furnace-operating temperatures would be too high. Even with slags having compositions just inside the boundary of the periclase phase field, operation could be difficult because small variations in composition could lead to relatively large variations in effective viscosity, which would interfere with furnace control. For this reason the composition region bordering on the periclase phase field would be avoided by blast-furnace operators.

There is a possibility that an occasional tapping of slag has a composition within the primary phase field of periclase, though it could never be far in, for reasons already mentioned. On cooling under conditions of equilibrium, therefore, this mineral will make its appearance, with the result that the point representing the composition of the residual liquid will move away from the MgO apex along a line connecting that apex to the point representing the gross composition of the slag. Since the periclase boundary is near, the amount of periclase which would crystallize out would be small. The greatest likelihood for trespass into the periclase region is where liquidus temperatures are lowest, i.e., adjacent to the primary phase fields of merwinite, monticellite, and spinel. These are so situated that during crystallization the composition of the residual liquid moves away from the periclase field. Consequently, the amount of periclase that would crystallize out even from such an improbable slag would, at worst, be small.

It is interesting to examine the results of other investigators who have studied the quaternary system $CaO-SiO_2-Al_2O_3-MgO$ to determine optimum slag compositions for blast-furnace operation. In this respect the work of Osborne, De Vries, Gee, and Kraner [15] is particularly illuminating. They have the following to say about optimum blast-furnace slag compositions:

"For a blast-furnace to operate smoothly and with maximum efficiency, the slag should have the following characteristics:

"1. It should be a homogeneous liquid, that is, without notable variations in the properties of the liquid and without crystalline phases present.

"2. Its composition should be such that a wide latitude of variation in composition is possible without a troublesome slag developing. Under the best conditions of operation, raw materials vary sufficiently to cause significant variations in slag composition. The slag should tolerate such inevitable variations in composition without notable changes in its properties and performance.

"3. It should have a high potentiality for retaining sulfur.

"4. It should have a low viscosity at the temperatures prevailing in the furnace in order to melt down and move through and out of the furnace quickly and smoothly".

From these remarks it can be concluded that if the liquidus temperature of a slag is relatively high the slag will tend to be troublesome in the furnace, because its effective viscosity will increase markedly below this temperature. Moreover, in a region where the liquidus-temperature contours are steep, small changes in composition can lead to large variations in viscosity. It is therefore advisable to avoid operation near regions where this is the case, e.g., within the periclase and C_2S primary phase fields.

Hence, although there may be no concern on the part of blast-furnace operators about the nature of the particular primary phase which their slags would yield on cooling, there is much concern about the viscosity of the slag in the furnace. It is undoubtedly for this reason, that periclase is a rare, if not unknown, slag mineral.

It appears, therefore, that the composition-liquidus temperature relationships dictate the practical range of slag compositions and that, in a sense quite fortuitously, slags in the periclase primary phase region would have such variable properties and therefore such unpredictable performance characteristics that operators carefully avoid such compositions. Even if an occasional slag had a constitution falling within this region, which is possible though improbable, the amounts of periclase would at most be small, because the locus of points representing the composition of the residual liquid, after periclase starts crystallizing out, will move in the direction of the periclase boundary, which could never be far removed, because of the steep liquidus temperature contours of this primary phase region.

From the results of Osborn, De Vries, Gee, and Kraner it can also be deduced that if the composition of a slag falls just outside the periclase boundary, e.g., in the primary phase fields of merwinite, spinel, monticellite, or forsterite, the compositions of the liquid phase, as cooling occurs from the liquidus temperature, will follow paths which generally do not intersect the periclase boundary; for such slags no periclase can form.

The possibility of a slag falling within the primary phase field of C_2S is remote because, as in the case of the periclase primary field, here also the liquidus-temperature contours are very steep, and consequently such a slag would be troublesome in the furnace. However, there is a possibility that on occasion the composition of a slag might trespass into this field, although obviously only the low-temperature edge comes into consideration, i.e., the region below the 1,500 °C line. On cooling to below its liquidus temperature, the locus of points representing the composition of the residual liquid would move away from the point representing C_2S, until it reached the common boundary between the primary phase field of C_2S and merwinite; hence no periclase would form.

The various possibilities discussed in the previous paragraphs can be seen clearly from figure 1. This is part of the 10-percent Al_2O_3 plane of the quaternary system $CaO-MgO-Al_2O_3-SiO_2$ [15] with composition points representing various relevant minerals shown projected on it. The liquidus-temperature isothermals are shown, to indicate what composition fields come into consideration for slags free of crystalline phase while in the furnace. According to the authors quoted above, the components other than the four major oxides, normally found in blast-furnace slags to the extent of about 5 percent, tend to depress the liquidus temperature by about 100 °C below that corresponding to the relevant figure for pure quaternary mixtures. Since blast-furnace slags must be completely liquid at temperatures of the order of 1,400 °C or lower, the 1,500 °C liquidus-temperature contour in figure 1 is virtually a boundary in the sense that slags of compositions below it will be troublesome in the furnace. This contour has been drawn more boldly in the figure.

It is immediately apparent that very limited scope exists for operating blast furnaces with slags from which periclase could crystallize. Although only the 10-percent Al_2O_3 diagram is shown, examination of other sections through the composition tetrahedron lead to the same conclusion.

The considerations given above undoubtedly explain why the literature is virtually free of any reference to positive identification of periclase in blast-furnace slags. The author has found indirect evidence also, in that several hundred A.S.T.M. autoclave soundness tests have been carried out on cements in which high-magnesia slags were a major ingredient, without any expansion values in excess of 0.3 percent having been found. The slags concerned ranged in magnesia content from 13 to 20 percent.

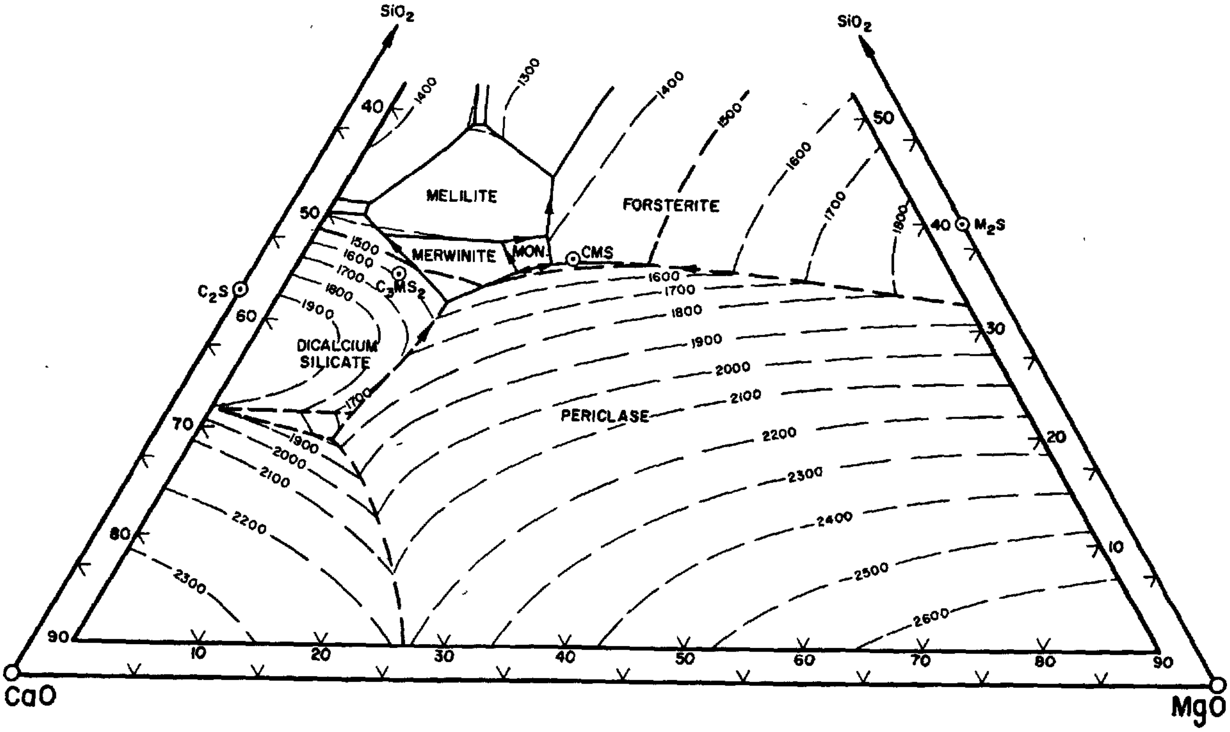

FIGURE 1. *Phase diagram for the quaternary system* CaO—Al_2O_3—SiO_2—MgO *at the 10-percent level.*
Temperature contours (°C) and other relevant data are superimposed.

Conclusion

It can be said that the possibility of periclase formation, and therefore of unsoundness due to this mineral in high-magnesia blast-furnace slags is remote.

Since, however, it cannot be said to be impossible, for reasons which must be clear from the discussion above, and since, furthermore, the use of a slag with several percent of magnesia could lead to disruption of a product made from it, care is required to insure that such material will never be used for cement manufacture. The granulation process, which is an essential one in the preparation of slag for cement manufacture, is, of course, aimed at insuring that the material is present in the glassy state. However, in practice this objective is never fully achieved, either because at the moment of granulation the slag is already below its liquidus temperature, or because the chilling process is not sufficiently rapid to prevent some crystallization.

There is, however, a very useful, practical, test in the form of the autoclave test, already referred to above, which allows one to distinguish between sound and unsound material. This test, which was specifically designed to establish whether periclase is present in portland cements, can be applied equally well to blast-furnace slags. By its adoption as a routine test procedure on all batches of granulates intended for cement manufacture, a relatively inexpensive means of insuring the use of sound material is provided.

In South Africa, portland blast-furnace slag cements have been used experimentally since 1948 in the laboratory, and since 1953 in pilot-stage field trials. Examination of the concrete made with this cement, under a wide variety of circumstances, has shown no evidence of unsoundness or poor durability. These experiments and trials have also proved that high-magnesia slags can have satisfactory cementitious properties, as already described elsewhere [16]. It is for these reasons that it became possible to produce cements having high-magnesia slag granulate as a major ingredient, on a commercial basis in South Africa. This is now a growing industry, which during the current year had a production of the order of 300,000 tons.

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Discussion

Levi S. Brown

Essentially this paper considers the effects of two pairs of extremes. One pair looks upon blast-furnace slag as either completely crystalline or all glass (water-granulated). The other pair considers the slag used as raw material in the manufacture of cement or as a finished material to be interground with cement clinker in preparation of slag cement.

As a raw component in the manufacture of cement, the crystalline or glassy state is of no moment nor is the chemical composition critical. The only requirement is that the chemical composition be known and that the proportion of the slag never be greater than that yielding maximum permissible chemical magnesia in the eventual portland cement. In view of these fixed limitations, the paper has no further concern with such use.

As an interground component of slag cement, however, the slag preserves its identity, and it is imperative to be properly advised as to occurrence of free magnesia in the slag. The paper devotes much attention to phase relations of systems appropriate to blast-furnace operation. It is shown that chemical magnesia may be high without occurrence or likelihood of occurrence of free magnesia. Such consideration assumes per se a complete crystallinity, whereby the magnesia content is largely tied up in minerals such as melilites, ferro-magnesians, or other magnesian silicates, which are stable and do not have the potentially damaging properties of periclase.

But, as noted in the paper, it is essential that granulated slag be used for slag cement manufacture, for the advantage of hydraulicity of the glassy state. Properties of the glass may be very different from those of the same composition completely crystalline. There may be no periclase perceivable as a unique phase. Yet the disorder of the glassy state implies that the magnesia is free and unbonded. May it not be regarded correctly as a distribution of periclase in units of molecular dimension?

This thought has rested with the writer since adoption in 1937 of the autoclave test for delayed unsoundness of portland cement. The notable reduction of autoclave expansion effected by quick cooling of clinker was well recognized. It was considered, by way of explanation, that magnesia as periclase was taken out of circulation by solution in the glass. But may not that be only a dispersion of molecular units? And may not a single molecule, unattached, have the same properties as a group of free molecules?

Introduction of these comments is made at this time to report an observation some time ago of an occurrence of slag disintegration that seemed to answer these questions. This was a blast-furnace slag with about 17 percent chemically determined magnesia. It had been effectively quenched, so that physically it was essentially a single phase, all glass, without perceivable periclase. The glass was minutely cracked. The fractures were lined with a uniform development of secondary brucite, indentified by unique optical properties of refractive index and birefringence. It was quite evident, further, that this secondary development was instrumental in the mechanics of disintegration of the slag.

It is indicated in this observation that a glassy slag high in magnesia may react and may function in a manner essentially similar to periclase. The paper suggests that the autoclave test, though specifically designed to establish whether periclase is present in portland cements, can be applied equally well to blast-furnace slags, to distinguish between sound and unsound material. Considering the above observation, the suggestion appears to be well taken, even though a comprehensive review of experience and experiment with blast-furnace slags and slag compositions shows performance to have been very generally good.

Closure

N. Stutterheim

Dr. Brown raises an interesting point, viz., whether the magnesia dissolved in a glass is not still capable of hydrating to form brucite and in the process to expand, so leading to unsoundness. He submits that the magnesia in a glass could well be present as unattached molecules and hence free to behave like crystalline periclase.

To clinch the point, he describes a case of a glass containing about 17 percent MgO which was microfractured, and secondary material in the cracks was identified as brucite.

If this were so then presumably all the oxides present in a glass would also behave as they would in the crystalline state. In particular, CaO in a glass would behave like free lime and in addition to brucite, hydrated lime should have been present in the microcracks and would have been a cocontributor to the observed unsoundness. Hence not only high-magnesia glasses but all high-lime glasses would be unsound. Is there any evidence for this?

The fractures in the high-magnesia slag particles, to which Dr. Brown refers, could perhaps have been due to stress-relief or to devitrification, in which cases brucite could still have developed subsequently. One would, however, expect other hydrates to be present too.

That magnesia present in a glassy slag could hydrate to form brucite is quite likely; but this does not necessarily mean that the reaction will be accompanied by unsoundness. Very finely divided periclase such as that formed when dolomite is burnt at temperatures below 900 °C exhibits no unsoundness upon hydration, even in the autoclave test [1]. The identification of periclase or of brucite must therefore not in itself be associated with unsoundness.

For magnesia unsoundness to occur, a prerequisite appears to be that the periclase is present in relatively large particles. The gross expansion in unsound paste, mortar or concrete is not equivalent to the volume increase associated with the $MgO \rightarrow Mg(OH)_2$ transformation, but is much greater, being due to opening up of cracks in a rigid material by the swelling particles. Hence a small number of large periclase particles will in general have a much more pronounced effect than an equal weight of smaller more numerous particles.

In South Africa more than a million tons of cement containing granulated high-magnesia slag as a constituent has been used under a wide range of conditions [2] and some of the concrete is now over 10 yr old. No evidence of periclase unsoundness has been observed in any of these applications, neither has any expansion beyond the acceptable limit been observed in the autoclave tests. In fact, as mentioned by Sandler during discussion at the Symposium sessions in Washington, any autoclave expansion in portland cement clinker, whether due to free lime or to free magnesia, is suppressed if slag (whether high-magnesia or not) is added as an admixture.

While therefore ready to agree with Dr. Brown that one cannot be dogmatic on this matter, the author submits that the evidence supports the view that high-magnesia blast-furnace slags do not lead to unsoundness in cements of which they form a constituent.

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Paper VIII–S2. Special Masonry Cement Having a High Slag Content*

S. Nagai

Synopsis

As the waste product of blast-furnace iron-making operation, water-granulated slag is being increasingly utilized in portland blast-furnace cement (in Japan about 1,500,000 to 2,000,000 tons per year in 1959 to 1960). This use of slag as an admixture to portland cement has gradually developed in the past 50 yr, but the use as slag-lime cement or masonry mortar cement is not well developed, owing to its slow and low hydration property. However, the special use of cement as masonry mortar for high concrete buildings and fireproof mortar plastering of wood buildings is a most urgent problem in Japan.

For this reason, the author during these years has studied high-slag-content lime cement for masonry mortar use, by the addition of accelerating agents for the latent hydraulic property of water-granulated slag. Admixtures of natural or industrial waste siliceous matter as pozzolanic materials, or fine granular fused matter such as fly ash, were used for the purpose of accelerating the development of strength and diminishing efflorescence, or decreasing the water-cement ratio, or increasing the plastering power of cement mortar.

From these many experimental results, the present author proposed the limiting values of various physical properties in the Japanese Industrial Standard Specification for masonry cement, which is expected to be enacted in the near future, by comparing them with those values in the Japanese Industrial Standard Specifications of portland cement (JIS R 5210), portland blast-furnace cement (JIS R 5211), and portland silica cement (JIS R 5211) which have been in force for many years.

Résumé

Le produit résiduel dans l'opération de la fabrication du fer dans les hauts fourneaux, le laitier granulé est utilisé de plus en plus dans le ciment portland au laitier de haut fourneau (au Japon 1,500,000 à 2,000,000 tonnes environ par an en 1959–1960). Cette utilisation du laitier en tant qu'addition au ciment portland s'est graduellement développée au cours des 50 dernières années, mais son utilisation comme ciment de laitier à la chaux ou ciment à maçonner n'est pas très développée, à cause de sa propriété d'hydratation lente et basse. Pourtant l'utilisation spéciale du ciment comme mortier de maçonnerie pour les constructions élevées en béton et le crépissage au mortier réfractaire des constructions en bois est l'un des problèmes les plus urgents au Japon.

Pour cette raison l'auteur au cours de ces dernières années a étudié le ciment de chaux à forte teneur en laitier pour l'usage du mortier de maçonnerie, en ajoutant des agents accélérateurs pour la propriété hydraulique latente du laitier granulé. Les additions de produits siliceux naturels ou de déchets industriels comme les matériaux pouzzolaniques, ou de fines matières granuleuses fondues telles que la cendre volante furent utilisées dans le but d'accélérer le développement de la résistance et de diminuer l'efflorescence ou de décroître le rapport eau-ciment ou d'accroître la puissance de crépissage du mortier de ciment.

A partir de nombreux résultats expérimentaux, l'auteur a proposé les valeurs limitatives des propriétés physiques variées dans les Normes de L'Industrie Japonaise pour le ciment à maçonner, lesquelles sont en cours d'être établies, de la même manière que les valeurs dans les Normes de L'Industrie Japonaise du ciment portland (JIS R 5210), le ciment portland au laitier de haut fourneau (JIS R 5211), et le ciment portland de silice (JIS R 5211), qui sont en usage depuis de nombreuses années.

Zusammenfassung

Als Abfallprodukt des Eisenhochofenprozesses wird wassergranulierte Schlacke mehr und mehr in Portlandhochofenzementen angewandt (in Japan hat man 1,500,000 bis 2,000,000 Tonnen im Jahr vom 1959 bis 1960 benutzt). Über einen Zeitraum von 50 Jahren hat man mehr und mehr gelernt, solche Schlacke dem Portlandzement zuzufügen, aber für Schlackenkalkzemente oder Maurerzementmörtel hat man nicht so gerne solche Schlacken beigegeben, weil sie so langsam hydratisieren. Nun ist gerade in Japan die Anwendung der Zemente als Mauermörtel für hohe Betonbauten und als feuerbeständige Mörtelbekleidung in Holzbauten von großer Wichtigkeit.

Aus diesen Gründen hat der Vortragende seit einigen Jahren Kalkzemente, die einen hohen Schlackengehalt haben, in ihrer Anwendung als Mörtel für Mauerwerk studiert; er hat Beschleuniger hinzugefügt, damit die latenten hydraulischen Eigenschaften der wassergranulierten Schlacken schneller zur Wirkung kommen. Beimischungen natürlicher oder künstlicher, kieselsäureenthaltenden Abfallprodukte, wie Pozzolane, oder eines feinkörnigen, geschmolzenen Materials, wie Flugasche, wurden benutzt, mit dem Gedanken, dadurch eine schnellere Entwicklung der Festigkeit, eine Herabsetzung der Ausblühungen, eine Verkleinerung des Wasser-Zementverhältnisses oder eine Erhöhung der Bewurfskraft der Zementmörtel hervorzubringen.

Auf der Grundlage seiner Versuchsergebnisse schlägt der Vortragende vor, Grenzwerte für die verschiedenen physikalischen Werte in die japanischen Industrienormen für Mauer-

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Faculty of Engineering, National University, Yokohama, Japan.

zemente einzuverleiben, und das soll schon ziemlich bald geschehen. Diese Normen werden mit den japanischen Normen für Portlandzemente (JIS R 5210), Portlandhochofenschlackenzemente (JIS R 5211) und Portlandquarzzement (JIS R 5211) in Einklang stehen. Diese anderen Normen werden schon seit vielen Jahren benutzt.

Introduction

Incombustible and fireproof buildings are now extremely important in Japan, owing to the existence of large numbers of wooden buildings. For this purpose, the walls and ceilings must be plastered, and also building brick, tile, concrete block, and artificial or natural stone must be cemented firmly by cement-sand mortar from so-called masonry cement. The ordinary cement mortar is made from common portland cement, various mixed portland cements such as portland blast-furnace cement, portland-pozzolan cement, portland fly-ash cement, etc., which are all covered by the Japanese Industrial Standard Specifications. But for the above-mentioned masonry-cement-mortar use, it is most important that the masonry cement must be cheaper than the cement for ordinary constructional or concrete use, and also must have many other useful properties, such as a somewhat slower set, strong cementing power, less expansivity, less shrinkage, less cracking tendency, less efflorescence, etc.

In Japan it is said that about 130 million square meters of wall and ceiling will be plastered with cement mortar in 1 yr, and about 800,000–900,000 tons of cement will be needed for this purpose. Again a nearly equal amount of masonry cement will also be used for mortar for common brick, tile, concrete block, natural or artificial stone, etc.

Principle of Study

The amount of cement for these two uses will be about 1.5–2 million tons, which is about 10–12 percent of all cement or about 25 percent of cement for all building (architectural) use. For these purposes, the present author has already for about 30–35 yr studied and reported [2] on various kinds of cement, as medium-strength cement, special mortaring cement, miscellaneous-use cement, various mixed or blended cements, as slag-lime or lime-slag blended, pozzolan-lime or lime-pozzolan cement, etc.

In these studies water-granulated blast-furnace slag was mainly used for the principal raw material for making the masonry cement. This point of view is derived from the following idea: In Japan about 9–10 million tons of pig iron is now manufactured in 1 yr, so that about one-half as much, or 4–5 million tons, of slag is obtained as by-product. But only about 10–15 percent of the slag is water granulated and used for portland blast-furnace cement, slag-lime brick, and artificial stone or block, etc., a nearly equal part is used for ballast as gravel for road or railroad, and the other large part of the slag has now no use and is thrown into the sea, for reclaiming work at the seaside, etc.

This water-granulated or quenched slag has a latent hydraulic property, but the setting and hardening properties are very slow and weak, without other effective additional substances for accelerating this latent hydraulic property. For this stimulation, acceleration, or promotion of latent hydraulicity of water-granulated slag, slaked lime is commonly added, but its accelerating power is not great and sometimes a siliceous admixture must be added, when excess slaked lime or free calcium hydroxide is left over. The author has studied the stronger special accelerating agents such as chemical reagents in water solution or mortaring dilute solutions, or in the state of very fine powder added to the cement samples, in both cases the quantity being very small (about 2–3 percent).

Cement Samples

In the present studies, water-granulated slag was obtained from different iron works, analyzed chemically, examined as to its suitability for use as the main raw material of the masonry cement (about 50–70 parts), and then powdered to a fineness of about 1.4 percent residue on the 4,900-mesh sieve (170 meshes/in. or 0.088 mm or 88 μ).

The second raw material, the lime-bearing component, as accelerating or hardening admixture to the slag powder above prepared, is slaked lime from a quicklime slaking plant, or from a carbide-acetylene plant. This slaked lime has proved to be suitable as the second component of the present masonry cement. It contains 69–72 percent of CaO, about 23–27 percent loss on ignition (inclusive of combined water, CO_2, etc.), a very small amount (less than 1 percent) of SiO_2, Al_2O_3, Fe_2O_3, MgO, etc., which are nearly negligibly small impurities in the preparation of the masonry cement. Its fineness is very high, it being the chemically hydrated product of slaking quicklime or of decomposing calcium carbide with water. As the third raw material or admixture,

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[2] J. Japan. Ceramic Assoc. **41**, p. 399 (1933), **49**, p. 674 and 745 (1941), **51**, p. 488 (1942), **62**, p. 403 (1954); J. Soc. Ind. Chem., Japan **38**, p. 431 and 1137 (1935), **39**, p. 304 (1936); Gypsum & Lime, No. **32**, p. 1553 (1958), No. **35**, p. 5 (1958), No. **37**, p. 18 (1958), No. **40**, p. 12, No. **41**, p. 19 (1959).

various siliceous materials of natural origin, or waste byproducts from various chemical or metallurgical industries were used. One kind of siliceous admixture was fly ash from fine-coal-firing boilers of hydroelectric power plants, and the others were the siliceous residual matter or byproduct containing a large content of silica (about 90–92 percent), obtained from acidic hot springs, or from a pressure steam sulfur refinery plant. These three kinds of siliceous raw materials were analyzed and powdered to about 1–3 percent residue on the 4,900-mesh sieve. These siliceous admixtures were used in the mixing proportion of about 10–30 parts in the masonry cement samples.

These three kinds of components, slag, lime-bearing, and siliceous admixture, as above mentioned, for the masonry cement manufacturing, were intimately mixed and ground to fine powder in the following ratios: slag: 50–70 parts; slaked lime: 10–30 parts; siliceous matter: 10–30 parts. Many series of masonry cement samples were prepared by the same procedure. One masonry cement sample was obtained from the market and included for comparison.

Testing Methods

These prepared samples of masonry cements were tested for their various physical properties and chemical compositions. The analyses for chemical composition, and the testing of setting time of neat cement paste and bending and compressive strengths of 1:2 cement-sand mortar in prismatic (4 x 4 x 16 cm) test pieces were carried out by the testing methods in the Japanese Industrial Standard Specifications for cement (JIS R 5201 and 5202). The mixing water for neat cement paste for the setting-time test and for 1:2 cement-sand mortar-strength tests (bending and compressive strengths) was replaced by various dilute solutions (about 1–3 percent) of NaOH, Na_2CO_3, Na_2SiO_3, Na_2SO_4, etc., and the effects of these salts on the setting time and strength were compared with those obtained with water. The solutions proved clearly to be very effective in quickening the slow setting time and in increasing greatly the low strengths of these masonry cements, especially at earlier curing ages (3–7 days).

These inorganic salts were added in general in dilute solution, instead of mixing water, but in several cases were tested by adding very fine powder of Na_2CO_3 or Na_2SO_4 to the cement samples and mixing with water. The dilute solutions (about 1–3 percent) of these inorganic chemical salts were used in amounts of about 60–65 parts to 100 parts of masonry cement for mixing (or a water cement ratio of 0.60–0.65). Thus the amount of these salts in this volume of solution was only about 0.5–1.5 percent of the weight of the cement, which is a very small proportion of the cement mortar and less than the amount of gypsum in portland cement and various mixed cements such as portland blast-furnance cement, portland-pozzolan cement, portland fly-ash cement, etc.

The hardening of these masonry cements is very slow, in the case of mixing with water, but it can be accelerated by mixing with dilute solutions of NaOH, Na_2SiO_3, Na_2SO_4, etc., and the hardened strengths are high, quite enough for masonry-mortar use, even at short curing ages (less than 3–7 days).

Experimental Results

Many series of special cement samples for masonry-mortar use were prepared by the methods described above, using mainly granulated blast-furnace slag as the principal component, and siliceous and calcareous admixtures were mixed in reasonable amounts to accelerate the latent hydraulic property of the granulated slag. For mixing these three components, granulated slag powder, siliceous admixture, and slaked lime with fresh water, the common testing method was first carried out. Then the dilute solution of inorganic salt (NaOH, Na_2SO_4, etc.) was used for mixing, resulting in remarkably superior strengths. Especially, cement dust from the electric dust catcher, containing Na_2O, K_2O, and CaO, as Na_2SO_4, K_2SO_4, and $CaSO_4$, with some amount of free lime, gave superior results in various physical and chemical tests. In the following sections, test results of various series of prepared cement samples are reported and compared with those of common tests using fresh water.

First Series of Experiments

Two kinds of granulated slag powder, one kind of slaked lime, and fly ash from a powdered-coal-firing electric-power plant, were analyzed and the results are tabulated in table 1.

Two kinds of masonry cement samples were prepared by mixing these three raw materials, finely ground in the various ratios shown in table 2, and the results of tests on their sieve fineness and chemical composition are shown also in table 2.

These cement samples were tested for their setting and hardening properties, by the Japanese Industrial Standard Specifications method for portland cement and various mixed portland cements. The bending and compressive strengths were tested by 1:2 cement-sand plastic mortar. These results were shown in table 3.

From these results, the special masonry cements prepared by the author by using a large amount of granulated slag with siliceous admixture and

TABLE 1. *Chemical compositions of raw materials*
(Percent)

	Loss on ignition	Insol. Res	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Sulfide sulfur
Slag (1)	0.72	0.80	34.31	16.54	1.43	37.35	5.54	0.03	1.08
Slag (2)	.43	.28	33.75	18.00	1.03	39.14	5.76	.12	1.05
Slaked lime (1)	23.85	.23	.17	.18	.15	73.29	1.46	------	------
Fly ash (1)	.34	3.53	60.73	22.15	8.63	3.63	1.04	------	------

slaked lime, specially accelerated by dilute alkaline water, hardened quickly with remarkably high strengths at 7 and 28 days in air and even higher strengths when cured in water. The dilute caustic soda (NaOH) solution was better than the carbonate (Na_2CO_3) solution, owing to the reaction of Na_2CO_3 with slaked lime ($Ca(OH)_2$) to give $CaCO_3$. The dilute NaOH solution gave strengths about 2–3 times greater than those with fresh water. This increase is due to the remarkably beneficial effect of dilute alkaline solutions in accelerating the latent hydraulic property of the slag powder, which will be clearly seen by comparing the results in table 3 with the values in the Japanese Industrial Standard Specifications of various cements shown in table 4.

TABLE 2. *Mixing ratio, fineness, and chemical compositions of masonry cement samples*
(Percent)

	Sample A-1	Sample A-2	Market Sample
Mixing ratio			
Slag (1) or (2)	Slag (2) 80	Slag (1) 60	------------
Slaked lime (1)	10	20	------------
Fly ash (1)	10	20	------------
Sieve fineness (residue)			
ASTM 50 meshes/in	0.2	0.2	0.1
70 meshes/in	.4	.5	.3
100 meshes/in	1.0	.9	.6
150 meshes/in	2.4	2.4	1.4
200 meshes/in	3.5	4.0	2.6
Chemical composition			
Loss on ignition	2.04	6.71	17.00
Insoluble residue	8.58	18.25	6.54
SiO_2	26.78	19.13	12.26
Al_2O_3	15.90	10.57	3.33
Fe_2O_3	.90	1.72	1.60
MnO	.66	1.13	------------
CaO	38.47	38.32	57.26
MgO	3.42	3.32	1.74
SO_3	.08	.31	.75

Second Series of Experiments

Next, another series of tests on the special kind of masonry cement, the method of manufacture of which was proposed by the author, were carried out. The testing method is similar to that in the above first-series experiments, and the results are tabulated in tables 5 and 6.

TABLE 3. *Setting time of neat cement and bending and compressive strengths of 1:2 cement-sand plastic mortar*

Cement sample	Mixing solution		Flow table value	Setting time test			Bending strength (kg/cm²)			Compressive strength (kg/cm²)		
	Kind	Amount		Amount of water	Initial	Final	7 days (in air)	28 days (in water)	28 days (in air)	7 days (in air)	28 days (in water)	28 days (in air)
		Percent	*Percent*	*Percent*	*hr-min*	*hr-min*						
A-1	Fresh water	60	200	34	5–01	11–23	9.2	20.6	13 9	25	64	61
	2.5% NaOH	63	204	34.2	1–13	2–34	33.6	39.5	14.8	55	139	139
	5% NaOH	63	203	34.6	1–12	2–55	21.8	50.5	40.3	138	176	183
	10% NaOH	65	193	35.5	0–56	1–56	30.1	60.2	57.4	260	310	315
	5% Na_2CO_3	64	163	----------	Quick setting		19.6	38.2	32.0	65	93	88
	10% Na_2CO_3	65	153	----------	(Not examined)		20.5	51.3	46.5	185	207	212
A-2	Fresh water	60	206	35	5–05	11–45	8.4	19 9	21.4	43	91	126
	5% NaOH	60	180	35.8	2–02	3–40	25.6	51.9	25.7	106	139	143
	10% NaOH	60	169	36.5	1–17	2–36	30.8	56.9	41.5	278	329	372
	5% Na_2CO_3	65	193	43	1–12	3–10	18.1	39.1	30.7	68	99	43
Market sample	Fresh water	60	177	36.5	2–17	3–43	21.7	38.5	43.9	117	158	173

TABLE 4. *Setting time of neat cement paste, and bending and compressive strengths of 1:2 cement-sand plastic mortar in the Japanese Industrial Standard Specifications*

Kind of cement	Mixing medium	Amount	Flow table	Setting time test			Bending strength (kg/cm²)			Compressive strength (kg/cm²)		
				Amount water	Initial	Final	7 days (in water)	28 days (in water)	28 days (in air)	7 days (in water)	28 days (in water)	28 days (in air)
		Percent	*Percent*	*Percent*	*hr-min*	*hr-min*						
Common portland cement	Fresh water	65	200	----------	>1–00	<10–00	>25	>36	--------	>90	>200	--------
Rapid-hardening portland cement	do	65	200	----------	>1–00	<10–00	>40	>60	--------	>180	>280	--------
Moderate-heat portland cement	do	65	200	----------	>1–00	<10–00	>20	>30	--------	>70	>150	--------
Portland blast-furnace cement	do	65	200	----------	>1–00	<10–00	>25	>36	--------	>90	>200	--------
Portland pozzolan cement	do	65	200	----------	>1–00	<10–00	>25	>36	--------	>90	>180	--------
Miscellaneous-use cement [a]	do	65	200	----------		<24–00	>10	>18	--------	>30	>80	--------
Slag-lime cement [a]	do	65	200	----------	--------	<24–00	>10	>18	--------	>30	>80	--------
Masonry cement (proposed by Nagai).[b]	do	65	200	----------	--------	<24–00	>12	>20	--------	>40	>100	--------

[a] Now out of use.
[b] Now not determined.

TABLE 5. *Chemical compositions of raw materials*

[Percent]

	Loss on ignition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Basicity [b]		Fineness Residue on 0.088mm (88μ) sieve
							(1)	(2)	
Slag (3)	0.76	32.01	15.29	0.35	43.83	5.80	2.08	1.30	0 (all pass)
Slag (4)	.80	33.35	13.23	.45	46.25	5.37	1.93	1.32	0 (all pass).
Slaked lime (2)	21.08	1.14	.48	.18	50.37	26.84	-----	-----	0 (all pass).
Fly ash (1)	.34	60.72	22.15	8.63	3.64	1.04	-----	-----	2
Silica residue [a]	11.36	83.76	1.12	.81	.28	.08	-----	-----	0 (all pass).

[a] Residue from high pressure sulfur refinery plant.

[b] Basicity of slag (1): $(CaO+MgO+Al_2O_3)/SiO_2$; (2): $(CaO+MgO+1/3Al_2O_3)/(SiO_2+2/3Al_2O_3)$.

These masonry cement samples were also tested as to their properties of setting time and strength by the same methods as in the first series in table 3, and tabulated in table 7.

Some points can be clearly seen from these results: (1) these masonry cements have short setting times and high early strengths not less than the strength of common portland cement and other various mixed portland cements shown in table 4 (Japanese Industrial Standard Specifications), (2) the accelerating action of dilute NaOH solution is much better than that of dilute Na_2CO_3 solution, the results being quite similar to those already shown in table 3, (3) very large amounts (75–80 percent) of granulated slag, accelerated

TABLE 6. *Mixing ratios and chemical compositions of masonry cement samples*

[Percent]

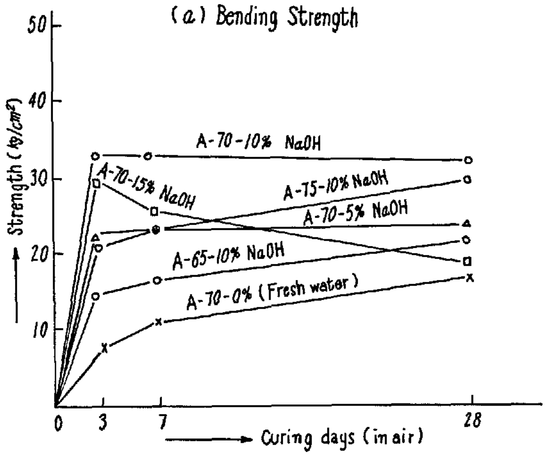
	A-series			B-series			C-series	D-series	Market sample [b]
	A-70	A-75	A-65	B-70	B-75	B-65	C-80	D-60	
Mixing ratios									
Slag (3) or (4)	(3) 70	(3) 75	(3) 65	(4) 70	(4) 75	(4) 65	(2) 80	(1) 60	Unknown
Slaked lime (1) or (2)	(2) 30	(2) 10	(2) 10	(2) 30	(2) 10	(2) 10	(1) 10	(1) 20	
Silica residue	----------	15	25	----------	15	25	10	20	
Chemical composition									
Insoluble residue	----------	----------	----------	----------	----------	----------	8.58	18.25	6.54
Loss on ignition	6.84	4.37	5.43	6.87	4.40	5.46	2.04	6.71	17.00
SiO_2	22.81	36.69	41.88	23.89	37.85	42.84	26.78	19.13	12.26
Al_2O_3	10.84	11.69	10.27	9.40	10.14	8.93	15.90	10.87	3.33
Fe_2O_3	.30	.40	.45	.37	.48	.51	.90	1.72	1.60
CaO	45.79	37.95	33.59	47.49	39.77	35.16	38.47	38.32	57.26
MgO [a]	12.11	7.04	6.47	11.91	6.72	6.19	5.42	3.32	1.74

[a] Large MgO content is due to slaked lime in table 5 (dolomitic slaked lime, so-called dolime).

[b] This market sample of masonry cement was tested for fineness and strengths, as shown in tables 2 and 3.

TABLE 7. *Setting time of neat cement paste, and bending and compressive strengths of 1:2 cement-sand plastic mortar*

Cement sample	Mixing solution	Setting time test			Flow test		Bending strength (kg/cm^2)				Compressive strength (kg/cm^2)			
		Amount of solution	Initial	Final	Amount of solution	Flow	3 days (in air)	7 days (in air)	28 days (in water)	28 days (in air)	3 days (in air)	7 days (in air)	28 days (in water)	28 days (in air)
A-series:		*Percent*	*hr.-min.*	*hr.-min.*	*Percent*	*Percent*								
A-70	Fresh water	35.0	5-35	10-40	60	169	6.7	11.4	25.4	17.2	26	53	80	80
A-70	5% NaOH	34.9	2-12	5-05	60	169	23.0	23.5	30.9	24.3	46	56	81	89
A-70	10% NaOH	34.9	1-41	3-16	60	169	32.5	32.3	37.0	31.6	105	128	213	194
A-70	15% NaOH	34.7	1-12	2-50	60	169	30.1	24.9	40.3	18.3	89	102	163	159
A-75	10% NaOH	30.6	1-02	3-23	60	169	20.6	22.9	30.0	--------	61	91	126	--------
A-65	10% NaOH	34.3	1-45	4-25	60	169	14.3	17.6	21.8	--------	50	69	86	--------
B-series:														
B-70	Fresh water	35.5	3-55	8-35	60	169	6.9	11.0	19.9	13.5	42	86	130	133
B-70	5% Na_2CO_3	37.4	3-55	4-55	60	169	22.9	24.2	39.8	25.6	54	100	140	155
B-70	10% Na_2CO_3	43.3	1-30	2-30	60	169	26.8	30.7	53.6	30.9	111	148	211	323
B-75	10% Na_2CO_3	40.3	0-25	3-02	60	169	--------	6.4	7.0	--------	--------	18	21	--------
B-65	10% Na_2CO_3	40.3	0-40	3-37	60	169	--------	4.3	6.2	--------	--------	16	19	--------
C-series:														
C-80	Fresh water	34.0	5-01	11-23	60	200	--------	9.2	20.6	13.9	--------	25	64	61
C-80	2.5% NaOH	34.2	1-13	2-34	63	204	--------	33.6	39.3	34.8	--------	55	139	139
C-80	5% NaOH	34.1	1-12	2-35	63	203	--------	21.8	50.5	40.3	--------	138	176	183
C-80	10% NaOH	35.5	0-56	1-56	65	193	--------	30.1	60.2	57.4	--------	260	310	315
C-80	5% Na_2CO_3	--------	--------	--------	64	163	--------	19.6	38.2	32.0	--------	65	93	88
C-80	10% Na_2CO_3	--------	--------	--------	65	155	--------	20.8	51.3	46.5	--------	185	207	212
D-series:														
D-60	Fresh water	35.0	5-05	11-45	60	206	--------	8.4	19.9	21.4	--------	43	91	125
D-60	5% NaOH	35.8	2-03	3-40	60	180	--------	25.6	51.9	25.7	--------	106	139	142
D-60	10% NaOH	36.5	1-27	2-36	60	169	--------	30.8	56.9	41.5	--------	278	329	372
D-60	5% Na_2CO_3	43.0	1-12	3-10	65	193	--------	18.1	39.1	30.7	--------	68	94	91



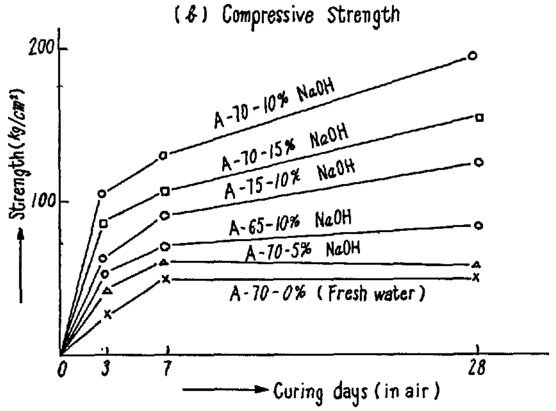


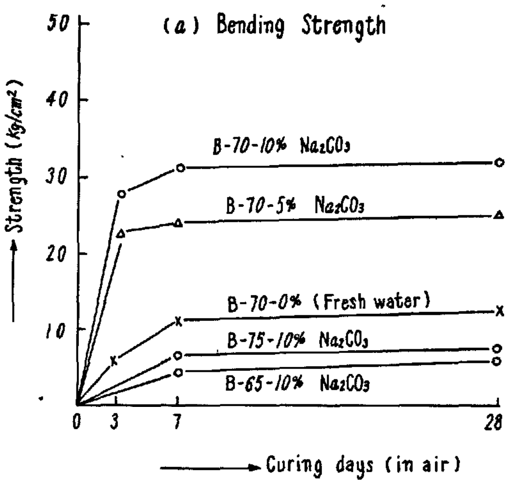
FIGURE 1. *Bending and compressive strengths of masonry cement mortars, series A.*

only by dilute NaOH solution, can be used with good results in respect to quick setting time and high early strength, (4) these early-setting and high-strength results obtained with acceleration by dilute NaOH solution are about 3–4 times greater than those obtained with fresh water, etc. The results of the strength tests are shown in figures 1–4. In all the figures, the curves of strengths obtained with fresh mixing water are all low; and in figure 2, the strengths obtained with dilute Na_2CO_3 solution are clearly lower than those obtained with fresh water.

Third Series of Experiments

Further tests were carried out in the same way on the special masonry cement, using a large amount of granulated slag mixed with slaked lime and siliceous admixture and mixing with dilute (1–5 percent) NaOH solution, the accelerating effect of which on the latent hydraulic property of granulated slag was clearly determined in the foregoing experiments (the first and second series).

In the third series of experiments, nine kinds of masonry cement samples were prepared by using slag, slaked lime, and siliceous admixture. The chemical compositions of these raw materials are tabulated in table 8. In this series, slaked limes (5) and (6) were obtained from a carbide acetylene-producing plant (by dry process), and natural pozzolanic materials were used instead of the siliceous residue from a pressure-steam sulfur refinery. One of the pozzolans is the famous high-silica (over 92 percent in the alkali-soluble state) material, nearly all soluble in dilute NaOH solution, obtained from the acidic hot spring, Beppu, in the Oita Prefecture.



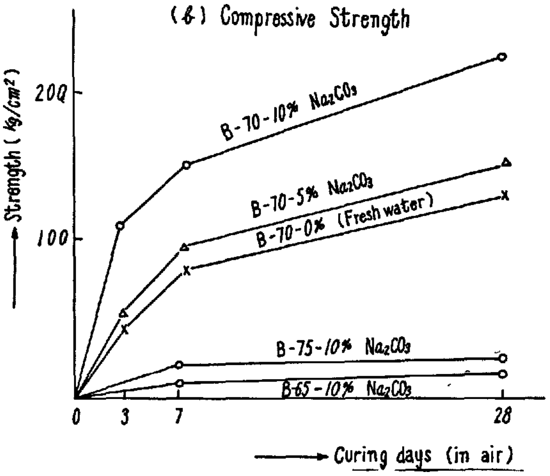


FIGURE 2. *Bending and compressive strengths of masonry cement mortars, series B.*

TABLE 8. *Chemical compositions of raw materials*

[Percent]

Kind of sample	Loss on ignition	Insoluble residue	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Sulfide sulfur
Slag (5)	0.45	0.24	32.19	18.28	0.77	41.26	6.23	0.97
Slag (6)	.71	.59	31.92	19.53	1.33	38.70	5.06	.96
Slag (7)	+.31[a]	.15	32.14	18.02	1.23	40.30	6.92	1.47
Slaked lime (5)	27.36	.92	1.51	1.14	1.14	69.02	.04	.50
Slaked lime (6)	23.47	.80	1.82	.80	.80	72.93	.54	.36
Fly ash (2)	3.78	-------	55.33	28.57	5.83	4.65	1.28	------
Natural pozzolan (1)	6.57	-------	58.37	20.76	7.39	2.57	2.97	------
Natural pozzolan (2)	3.94	-------	92.01	2.30	.49	.07	------	------

[a] Slag gained weight.

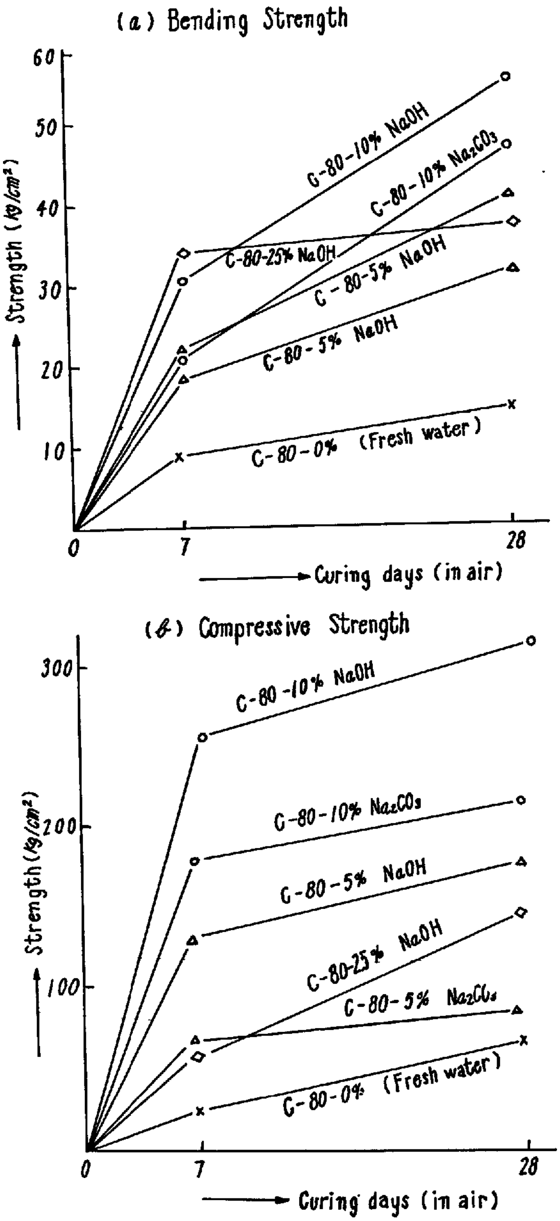


FIGURE 3. *Bending and compressive strengths of masonry cement mortars, series C.*

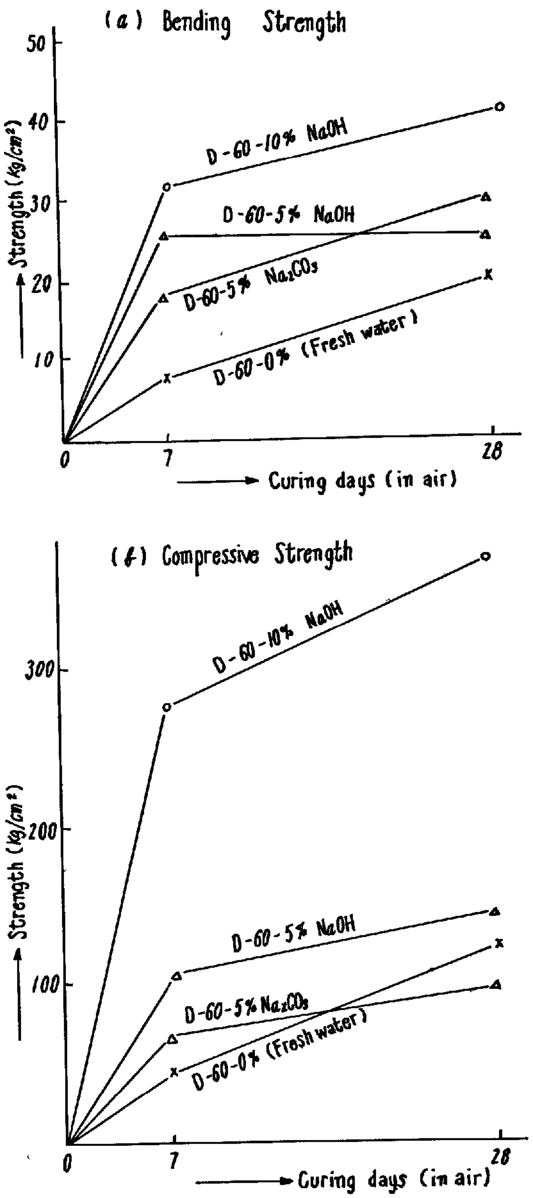


FIGURE 4. *Bending and compressive strengths of masonry cement mortars, series D.*

The mixing proportions for making the masonry cement samples, the finenesses, and the chemical compositions of the prepared cement samples are tabulated in table 9.

From the chemical compositions, it can be easily seen that these series of prepared cement samples contain large amounts of insoluble residue and, on the contrary, small amounts of SiO_2 and CaO, owing to the large mixing ratio (30 percent) of natural or artificial siliceous pozzolanic matter.

Next, these prepared cement samples were examined or tested in the same way as in the first and second series of experiments, with the comparable good results tabulated in table 10. In the present case, the accelerating alkaline solution was limited to dilute NaOH (1, 3, or 5 percent) solution, and the water-cement ratio (w/c), or in this case, the water solution-cement ratio, was limited to 0.60, so that the amount of alkali (Na_2O) was only about 0.37, 1.2, or 1.8 percent. The accelerating action of this alkaline solution on the setting time and the strengths is weak with the 1-percent solution and is adequate with the 3-percent solution. This amount of alkali is the important point for the masonry cement mortar in respect to various properties of soundness, expansion or contraction, surface hardness, efflorescence, etc. Some of these points were preliminarily examined in the present experiments, e.g., the soundness on setting and hardening of the

TABLE 9. *Mixing ratio of raw materials, fineness, and chemical compositions of masonry cement samples*

[Percent]

Designation of cement sample	Mixing ratio			Fineness (88-μ sieve residue)	Chemical composition (%)						
	Slag (No.)	Admixture (No.)	Slaked lime (No.)		Loss on ignition	Insol. res.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
A	(5):50	(1):30—Silica residue	(1):20	3.2	6.19	27.29	18.06	8.80	0.51	34.64	3.31
B	(5):50	(2):30—Fly ash	(1):20	2.8	6.51	22.48	18.59	10.86	1.04	35.40	3.55
C	(6):50	(2):30—Pozzolan	(5):20	3.2	7.53	24.62	15.52	13.24	.93	33.74	3.67
D	(7):50	(1):30—Fly ash	(5):20	3.2	4.54	26 23	16.78	10.74	1.94	34.51	2.97
E	(7):50	(3):30—Pozzolan	(5):20	3.8	7.40	23.91	19.88	9.93	1.56	34.07	3.03
F	(6):60	(2):30—Fly ash	(5):10	2.8	2.89	24.05	20.70	18.63	1 84	31.26	4.07
G	(6):60	(2):30—Pozzolan	(5):10	2.8	4.85	21.24	22.16	12.79	2.51	30.72	4.48
H	(7):60	(1):30—Fly ash	(5):10	2.6	1.97	25.46	24.12	11.24	2.45	31.14	3.48
I	(7):60	(3):30—Pozzolan	(6):10	3.6	3.65	20.54	27.10	9.74	1.50	32.28	3.68

TABLE 10. *Setting time of neat cement paste, and bending and compressive strengths of 1:2 cement-sand plastic mortar*

Cement sample		Mixing solution	Setting time tests			Flow test		Bending strength (kg/cm²)			Compressive strength (kg/cm²)		
			Amount	Initial	Final	Amount	Flow	7 days (in air)	28 days (in water)	28 day (in air)	7 days (in air)	28 days (in water)	28 days (in air)
			Percent	*hr-min*	*hr-min*	*Percent*	*Percent*						
A	a	Fresh water	39.2	5-51	12-02	60	185	12.3	32.2	29.9	23	88	97
	b	1% NaOH	40.0	3-53	7-17	60	181	24.3	40.4	39.5	60	121	112
	c	3% NaOH	40.2	1-52	4-03	60	169	24.1	42.1	38.6	60	85	88
B	a	Fresh water	38.0	4-55	13-17	60	208	8.6	27.8	24.7	10	78	84
	b	1% NaOH	39.0	3-51	7-16	60	202	22.0	46.3	34.7	85	170	146
	c	3% NaOH	39.5	2-27	4-24	60	201	22.3	49.3	28.0	72	99	98
C	a	Fresh water	33.8	10-28	19-53	60	183	9.9	26.1	16.8	20	71	66
	b	1% NaOH	34.0	5-18	9-53	60	176	25.4	43.8	34.6	75	128	122
	c	3% NaOH	34.0	1-53	3-48	60	176	37.8	42.6	33.3	57	82	80
D	a	Fresh water	32.0	5-04	11-32	60	230	10.7	22.6	20.3	19	56	64
	b	1% NaOH	34.0	4-19	6-07	60	224	17.2	39.1	31.8	71	126	120
	c	3% NaOH	34.0	1-37	3-00	60	222	31.9	45.4	37.1	70	102	96
	d	5% NaOH	34.2	1-17	2-06	60	215	28.0	60.5	47.1	119	170	166
E	a	Fresh water	40.0	4-38	8-46	60	165	15.1	43.8	34.1	64	89	67
	b	1% NaOH	40.0	3-22	6-23	60	160	17.6	42.2	35.9	89	156	168
	c	3% NaOH	42.5	1-36	3-00	60	159	18.9	49.8	40.8	67	104	102
	d	5% NaOH	42.5	1-10	2-10	60	154	31.8	58.7	44.3	131	183	179
F	a	Fresh water	32.5	11-48	22-14	60	231	8.9	21.7	21.5	14	53	51
	b	1% NaOH	33.3	8-18	12-15	60	230	22.5	40.8	35.6	60	120	105
	c	3% NaOH	33.7	4-45	5-42	60	230	24.1	48.5	38.1	66	101	90
G	a	Fresh water	32.0	8-17	20-09	60	222	12.6	29.4	23.7	30	85	65
	b	1% NaOH	32.5	6-00	10-06	60	206	26.2	37.7	25.2	47	122	120
	c	3% NaOH	32.5	1-51	4-18	60	205	25.4	35.7	32.2	64	90	87
H	a	Fresh water	30.0	5-28	8-33	60	230	12.4	14.1	20.0	49	72	64
	b	1% NaOH	31.5	4-47	5-51	60	228	12.0	38.2	25.8	69	122	120
	c	3% NaOH	31.5	2-17	3-22	60	225	24.6	44.6	30.8	76	126	125
	d	5% NaOH	31.7	2-12	3-05	60	222	39.9	64.6	37.5	143	198	193
I	a	Fresh water	40.0	4-27	8-57	60	172	19.6	32.5	26.9	60	90	90
	b	1% NaOH	41.0	3-37	6-43	60	170	21.4	30.6	28.6	75	121	120
	c	3% NaOH	42.0	1-58	4-11	60	168	24.7	37.4	31.0	66	122	122
	d	5% NaOH	42.0	1-28	2-55	60	165	35.0	46.4	38.0	135	183	187

neat cement paste, by the pat test on boiling for 3 hr or curing in water for 28 days, proved to be fully as satisfactory as that of common portland cement. The other tests will be reported in the next series of experiments.

Fourth Series of Experiments

Further tests were carried out in the same way, by using fly ash, slaked lime, or calcined gypsum as the mixing materials added to the principal slag component of the masonry cements. Another kind of masonry cement sample was prepared by mixing finely powdered dolomite with portland cement in various proportions. The chemical composition and finenesses of these raw materials were determined and tabulated in table 11.

In the present series, calcined gypsum was used instead of pozzolanic admixtures such as siliceous matter or fly ash, and another kind of masonry cement samples, prepared by mixing intimately portland cement with fine dolomite powder, was tested and compared with other masonry cement samples. These cement samples are tabulated in table 12, with their mixing ratios, finenesses, and chemical compositions.

Then, as shown in table 13, the special accelerating agent, dilute Na_2SO_4 solution, was used with or without dilute NaOH solution, and good results were obtained. Both initial and final setting times of neat cement paste were considerably accelerated by mixed 1.5-percent NaOH and 1.5-percent Na_2SO_4 solution or 3 percent NaOH solution alone, but 3-, 5-, or 10-percent Na_2SO_4 solution alone did not accelerate the setting time. But the 1:2 cement-sand mortar was quickly hardened, and both bending and compressive strengths were good with either NaOH (3 percent) or Na_2SO_4 solution. This action by dilute Na_2SO_4 solution causing slower setting, but very quick hardening, of mortar is very convenient for plastering of masonry cement mortar on concrete, wire, or wood lath for walls or ceilings, etc.

Another kind of masonry cement obtained from portland cement and finely powdered dolomite (in proportions of 70:30 or 50:50) has slower setting and weaker mortar strength with increasing proportion of dolomite.

TABLE 11. *Fineness and chemical compositions of raw materials*

[Percent]

Kind of sample	Fineness (residue on 88μ-sieve)	Chemical composition							
		Loss on ignition	Insoluble residue	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
Slag (8)	2.0	1.83	0.34	32.24	16.35	0.97	38.51	6.97	1.25
Fly ash (1)	2.0	.34	----	60.72	22.15	8.63	3.64	1.04	----
Slaked lime (6)	All pass	23.47	.80	.82	.80	.80	72.94	.54	.36
Portland cement (1)	3.6	1.78	.33	22.60	4.57	2.97	64.98	1.26	1.33
Dolomite powder (1)	5.4	46.78	.48	.03	.47	.47	34.57	18.04	----
Calcined gypsum (1)	All pass	----	2.93	2.93	.29	.50	39.62	.19	56.65

TABLE 12. *Mixing ratio, fineness, and chemical compositions of masonry cement samples*

[Percent]

Designation of sample	Mixing Ratios			Fineness (88μ-sieve residue)	Chemical compositions							
	Slag	Fly ash or calcined gypsum	Slaked lime		Loss on ignition	Insoluble residue	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
S_1	(8) 60	Fly Ash (1) 20	(6) 20	3.2	4.05	18.09	19.59	10.44	0.87	38.45	4.72	----
S_2	(8) 60	Fly Ash (1) 30	(6) 10	3.2	2.01	25.53	24.03	11.20	1.50	31.14	3 20	----
G_1	(8) 85	Calcined Gypsum (1) 10.	(5) 5	2.0	2.73	0.53	27.54	13.94	0.87	40.34	6.00	5.72
G_2	(8) 87	Calcined Gypsum (1) 8.	(5) 5	2.2	2.70	.50	27.50	13.90	.85	40.40	5.95	4.13
G_3	(8) 94	Calcined Gypsum (1) 0.	(5) 6	2.0	2.76	.45	27.52	13.93	.80	40.70	6.22	----
P_{100}	Portland cement (1) 100.	----	Dolomite powder (1) 0.	3.8	1.78	.33	22.60	4.57	2.97	64.98	1.26	1.33
P_{70}	Portland cement (1) 70.	----	Dolomite powder (1) 30.	4.0	15.28	.37	15.82	3.27	2.15	55.85	6.29	.93
P_{50}	Portland cement (1) 50.	----	Dolomite powder (1) 50.	4.5	24.23	.40	11.32	2.40	1.60	49.77	9.65	.66

TABLE 13. *Setting time and bending and compressive strengths of 1:2 cement-sand plastic mortar*

Designation of sample	Mixing solution	Setting time test			Flow test		Bending strength (kg/cm ^{2})			Compressive strength (kg/cm ^{2})		
		Amount	Initial	Final	Amount	Flow	7 days (in air)	28 days (in water)	28 days (in air)	7 days (in air)	28 days (in water)	28 days (in air)
		Percent	*hr-min*	*hr-min*	*Percent*	*Percent*						
S_1	Fresh water	32.0	7-31	17-23	60	224	4.1	7.0	10.0	4	11	12
	1.5% NaOH+1.5% Na_2SO_4.	32.5	1-00	2-10	60	205	16.6	36.1	36.0	66	130	131
	3% NaOH	32.5	1-49	4-01	60	210	17.9	40.3	39.0	68	115	110
	3% Na_2SO_4	32.5	3-35	5-38	60	190	26.6	40.0	38.5	71	104	102
S_2	Fresh water	30.0	8-59	16-27	60	262	----	6.4	8.5	----	6	6
	1.5% NaOH+1.5% Na_2SO_4.	30.8	3-55	5-26	60	260	28.0	37.5	36.1	85	134	123
	3% NaOH	31.0	2-05	4-18	60	260	27.0	41.5	39.1	77	120	108
	3% Na_2SO_4	31.2	9-27	11-55	60	260	33.5	40.2	41.2	79	104	103
	5% Na_2SO_4	32.0	9-07	12-13	60	254	25.9	47.6	44.0	124	169	161
	10% Na_2SO_4	33.0	9-14	11-48	60	250	29.6	70.8	61.0	138	216	211
G_1	Fresh water	30.0	10-20	15-50	60	240	40.1	62.5	57.4	135	229	221
G_2	3% Na_2SO_4	30.5	8-15	14-00	60	238	28.0	58.6	56.8	80	170	163
G_3	10% Na_2SO_4	33.0	8-05	10-45	60	205	28.7	93.1	82.1	287	390	375
P_{100}	Fresh water	28.0	2-02	3-03	60	250	47.1	69.5	70.8	226	397	415
P_{70}	Fresh water	25.8	2-12	3-14	60	240	37.6	55.3	47.7	151	228	187
P_{50}	Fresh water	24.5	2-28	3-44	60	240	24.3	34.9	38.3	82	124	116

The surface hardness of hardened mortar was tested by the degree of penetration of a modified Vicat tester. The results are tabulated in table 14, by comparison of the penetration depths on the hardened test pieces, cured for 28 days in air or in water, and it is observed that the surface hardness of masonry cement mortar is nearly uniform in the case of 28 days of water curing, but a little softer in the case of 28 days of air curing.

Next, the efflorescence was examined first by qualitative observation of white stain or white fibrous salt deposit. This efflorescence was wiped off and the specimen cured further to observe any further formation of the white efflorescence. The test pieces mixed with Na_2SO_4 solution were a little more stained by the white efflorescence. This test was carried out on 4- x 4- x 16-cm prismatic test pieces, cured 7 days in air and then dipped vertically half way (about 8 cm) in water. This efflorescence test was further used in the following series of experiments.

TABLE 14. *Surface-hardness testing of masonry cement mortar*

Kind of sample	Mixing solution	Penetration depth mm	
		28 days (in water)	28 days (in air)
S_1	Fresh water	0.1	0.2
	1.5% NaOH+1.5% Na_2SO_4	.1	.5
	3% NaOH	.1	.2
	3% Na_2SO_4	.1	.5
S_2	Fresh water	.1	.2
	1.5% NaOH+1.5% Na_2SO_4	.1	.5
	3% NaOH	.1	.2
	3% Na_2SO_4	.1	.5
	5% Na_2SO_4	.1	.5
	10% Na_2SO_4	.1	.5
G_1	Fresh water	.1	2.0
G_2	3% Na_2SO_4	.1	.5
G_3	10% Na_2SO_4	.1	.5
P_{100}	Fresh water	.1	.1
P_{70}	Fresh water	.1	.1
P_{50}	Fresh water	.1	.1

Fifth Series of Experiments

In this series of experiments, the purpose was to determine whether special cement samples produced by mixing granulated slag, slaked lime, and electric treater dust from a cement manufacturing plant are suitable for use for masonry cement mortar. The object of using cement dust from an electric dust-catching treater for mixing in the special masonry cement is, (1) to replace the dilute Na_2SO_4 solution, for accelerating the latent hydraulic property of slag in the foregoing experiments, by the Na_2SO_4 and K_2SO_4 contained in the cement dust (about 3–5 percent of Na_2SO_4 and 2–4 percent of K_2SO_4), (2) to make use of the weak hydraulic property of cement dust, (3) to use the free lime contained in the cement dust (about 5–15 percent), instead of the slaked lime used in the foregoing experiments, and (4) to use the free silica and alumina from the calcined clay part of the cement raw mixture (about 5–10 percent SiO_2 and 2–4 percent Al_2O_3 in the soluble state), instead of the pozzolanic admixture used in the foregoing experiments.

These raw materials for making the special series of masonry cement samples were analyzed, and the results are tabulated in table 15. The samples of electric-treater cement dust were collected from various cement plants using dry or wet processes, and observed to be quite different in content of alkali (Na_2O and K_2O) and CaO (especially free CaO) with differences in raw materials, burning process, dust-catching plant, etc.

The cement samples were prepared by using these raw materials in the proportions shown in table 16 and tested for fineness and chemical composition.

Next, these cement samples were tested in the same way, as to their setting times of neat cement paste and the bending and compressive strengths of 1:2 cement-sand plastic mortar, by the method in the Japanese Industrial Standard Specification (JIS R 5201). The data are given in table 17.

From these results the following points were observed, (1) Na_2SO_4 powder can be added to the cement and mixed with water, instead of the dilute Na_2SO_4 solution in the foregoing experiments, and nearly equal results obtained, so that it can be assumed that the electric-treater cement dust containing both Na_2SO_4 and K_2SO_4 will be

TABLE 15. *Chemical compositions of slag, slaked lime, and cement dust*

[Percent]

Kind of sample	Loss on ignition	Insol. residue	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Fineness (88-μ-sieve residue)
Slag (8)	1.83	0.34	32.24	16.35	0.97	38.51	6.97	0.07			2.0
Slag (9)	.51	.13	31.73	18 30	.76	38.47	8.30	.12			1.2
Slag (10)	+.15[a]	.25	31.24	17.09	.61	38.61	7.76	.08			1.8
Slag (11)		.22	31.78	10.03	.73	38.20	6.97	.07			.6
Fly ash (1)	.34		60.73	22.15	8.63	3.64	1.04				2.0
Fly ash (3)	5.23		53.87	27.31	6.52	2.75	1.28				2.9
Slaked lime (6)	23.47	.80	.82	.80	.80	72 93	.54				(All pass)
Slaked lime (7)	26.97	1.13	.83	.96	.12	68.30	.25				do
Slaked lime (8)	28.06	3.37	3.37	1.43	.67	66.17	.15				6.8
Slaked lime (9)	26.90	.69	1.23	.51	.51	67.34	.55				(All pass)
Cement Dust (1)	16.41		14.35	4.37	1.53	35.41	1.03	13.16	4.48	3.60	8.8
Cement Dust (2)	13.42		18.77	5.36	1.65	52.37	1.21	3.91	2.00	2.38	2.0
Cement Dust (3)	9.38		24 02	6.83	2.78	45.59	1.60	5.05	2.07	2.28	2.3
Cement Dust (4)	27.36		15.85	3.41	2.75	40.46	1.63	2.77	2.05	1.89	2.5

[a] Gain in weight.

TABLE 16. *Mixing ratio, fineness, and chemical composition of cement samples*

[Percent]

Series designation	Mixing ratio			Fineness (88-μ-sieve residue)	Chemical composition									
	Slag	Fly ash or dust	Slaked lime		Loss on ignition	Insol. residue	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
A	(8) 60	Fly ash (1) 30	(6) 10	3.3	2.01	25.55	24.03	11.20	1.50	31.14	3.20	------	------	------
B	(10) 60	Fly ash (1) 20	(7) 20	3.0	5.74	18.15	18.15	12 84	.70	38.88	5 02	------	------	------
C-1	(9) 50	Dust (2) 50	--------	2.2	6.99	4.70	21.32	11.86	1.57	45.56	4.47	1.19	1.05	0.65
C-2	(8) 50	Dust (1) 50	--------	4.9	9.36	3.61	19.47	11.39	1.27	36.91	3 88	6.80	4.47	2.33
C-3	(8) 60	Dust (1) 40	--------	3.7	7.65	2.81	22.46	13.14	1.19	37.27	4 59	5.25	3 43	1.09
C-4	(8) 50	Dust (1) 30	(8) 20	5.6	11.51	2.21	18.61	11.01	1.09	43.06	3.78	4.02	2.62	1.36
C-5	(8) 60	Dust (1) 20	(8) 20	4.5	10.07	1.51	21.93	12.48	1.03	43 31	4.38	2.70	1.76	.92
D-1	(11) 50	Fly ash (3) 30	(9) 20	2.2	5.53	--------	34.57	16.45	3.22	33.74	3.93	1.10	------	------
D-2	(11) 60	Fly ash (3) 30	(9) 10	2.7	2.81	--------	37.95	11.27	3.76	37.46	3.87	1.42	------	------

TABLE 17. *Setting time, and bending and compressive strengths of 1:2 cement-sand plastic mortar*

Series of samples	Salt	Mixing medium	Setting time			Flow test		Bending strength (kg/cm²)			Compressive strength (kg/cm²)		
			Amount	Initial	Final	Amount	Flow	7 days (in air)	28 days (in water)	28 days (in air)	7 days (in air)	28 days (in water)	28 days (in air)
			Percent	*hr-min*	*hr-min*	*Percent*	*Percent*						
A	2% Na_2SiF_6	Fresh water	35.0	4-05	7-15	65	185	8.8	24.4	12.7	8	74	95
	3% $Na_2O{\cdot}3SiO_2$	Solution	39.5	2-13	6-10	65	154	11.7	34.6	15.7	68	123	94
	2% Na_2SO_4	Fresh water	35.0	8-15	11-35	64	199	24.5	45.4	17.4	113	157	160
	2% $Na_2SO_4{\cdot}10H_2O$	do	32.5	9-25	11-45	63	206	15.4	49.6	22.3	75	145	126
	3% Na_2SO_4	Solution	36.0	7-50	10-45	65	182	20.0	44.6	24.7	95	148	186
C-1		Fresh water	35.5	2-12	8-24	60	189	39.3	60.3	54.2	210	365	295
C-2		do	36.0	2-50	6-30	60	177	22.1	40.3	44.3	21	222	253
C-3		do	36.5	2-40	7-10	60	152	12.8	21.6	33.3	56	118	164
C-4		do	35.0	2-30	6-55	60	155	54.6	57.8	33.9	144	165	167
C-5		do	35.5	2-10	6-30	60	173	54.5	59.4	25.9	145	204	147

suitable for use as an admixture to masonry cement, (2) dilute water-glass solution (or $Na_2O{\cdot}3SiO_2$ solution) accelerates nearly as well as the dilute Na_2SO_4 solution (2–4 percent) used in the foregoing experiments, (3) the special cements prepared by mixing granulated slag (50–60 parts) with electric-treater cement dust (50–40 parts), or cement dust (30–20 parts) with about 20 parts of slaked lime, have moderate setting time of neat cement paste and remarkably quick and high strength of cement-sand plastic mortar. Thus, special masonry cement of good quality can easily and at very low cost be obtained by intimately mixing granulated slag with electric-treater cement dust with or without addition of slaked lime (as waste product from carbide acetylene-producing plant, better from the dry process than from the wet process). The addition and the amount of slaked lime depends on the amount of free lime contained in the cement dust, and, when the content of free lime is over about 15 percent and the total lime is over about 50 percent, the addition of slaked lime is not always necessary.

These mixed cements, composed of slag and cement dust, have remarkably good properties, as determined in the experiments, (1) moderate setting time, (2) superior rapid and high strength. Other points, (a) water-retention power, (b) effloresence, (c) expansion or contraction, etc., will be further considered.

The test for efflorescence on mortar surface was carried out by the same method adopted in the foregoing series of experiments. Prismatic test pieces, 4 x 4 x 16 cm, for testing of bending and compressive strengths were also used for this efflorescence test, after 7 days curing in air, by dipping vertically halfway (about 8 cm) in water, and observing the degree of white stain and white flower-type salt efflorescence on the hardened mortar surface of the test piece in air. By these experiments, the following points were observed, (1) the test pieces of slag-cement dust cement mortar did not produce any efflorescence even after dipping in water for many weeks, (2) the addition of a large amount of cement dust (about 40–50 parts) as the important component of the masonry cement is very effective, which effect is perhaps because of the proper content of alkali sulfates (Na_2SO_4 and K_2SO_4) in the cement dust, (3) the efflorescence was not produced on the pieces which were wiped clean of efflorescence with a wet towel and then again dipped in water for many weeks.

Next, the water-retention power was tested by the method prescribed in the Japanese Industrial Standard Specifications for hydrated lime, gypsum, and dolomite plasters (JIS A 6902, 6903, and 6904), and the results shown in table 18 were obtained.

From these results, the following points are to be observed: (1) slag-lime (with 30 percent of fly ash) cements (D-1 and D-2) have high water-retention power, higher when made with dilute

Table 18. *Water retention power and plasticity of neat cement paste*

Designation of sample	Mixing solution		Water retention power (percent)			Plasticity Coefficient	
	Kind	Amount	After 2 min	After 4 min	After 6 min	10 °C	15 °C
		percent					
C-5	Fresh water	29.8	87.4	80.2	80.2	10.20	12.75
D-1	3% NaOH	29.3	87.3	86.6	86.5	9.96	12.45
D-1	3% Na_2SO_4	28.7	92.0	91.3	91.2	10.16	12.70
D-2	3% NaOH	30.3	86.8	86.1	86.1	10.72	13.40
D-2	3% Na_2SO_4	30.2	89.5	88.2	88.2	10.12	12.65

Na_2SO_4 solution than when made with dilute NaOH solution, and (2) slag-lime (with 20 percent of cement-dust) cement (C–5) has a little lower water-retention power. The water-retention power is remarkably affected by the fineness, porosity, water-soluble parts, etc., of the slag and admixing materials (lime, fly ash, cement electric-treater dust, etc.); among them the cement dust contains a fairly large amount of water-soluble alkali salts, and these salts have a large effect on the water-retention power. Next, the plasticity or viscosity of neat cement paste mixed with water (C–5), or with 3-percent NaOH or Na_2SO_4 solution (D–1 and D–2), shown in table 18, was tested and determined to be considerably greater than the limit value (not less than 7.5 at 15 °C) in the Japanese Industrial Standard Specifications of gypsum, lime, and dolomite plasters (JIS A 6902, 6903, and 6904).

The expansion or contraction, or cracking, and the surface hardness of hardened test pieces were systematically tested by the methods specified in the Japanese Industrial Standard Specifications above cited, on 1:2 or 1:3 cement-sand mortar, and good results were obtained, superior to those defined in the standards cited above.

Conclusion

The special masonry cement for use with concrete block, artificial slag brick or stone, etc., and surface mortaring of concrete and wire or wood lath, especially in Japan for fireproofing of wooden buildings, is a most important material for all building. It is said that about 1.5–2 million tons of cement per year is now used for this purpose, and it is a most important point to make a proper mortaring and masonry cement of low price.

The author has studied various kinds of cementing materials for many years, especially the special cement used for plastering which must have several important features, e.g., (1) low price, (2) a suitable setting time, (3) adequate strength, (4) good consistency or high plasticity, (5) low expansion or contraction and less cracking, (6) high water-retentive power, (7) superior surface hardness.

In the present paper, test results are reported for many kinds of special cements for mortaring and plastering, especially of the special cement of high content of water-granulated blast-furnace slag, mixed with various kinds of siliceous material and slaked lime from a lime hydrating plant or carbide acetylene-producing plant, and small amounts of alkali or alkali salt in solution or powder form, which is a most important matter for the accelerating of the weak latent hydraulicity of water-granulated slag.

The following are some of the most important points obtained from the various series of experiments.

(a) The cement is considerably cheaper than the ordinary cements, e.g., portland cement, portland blast-furnace cement, portland-pozzolan cement, portland fly-ash cement, etc., owing to the low cost of all component materials, (1) water-granulated blast-furnace slag, (2) natural pozzolan or artificial byproduct siliceous matter, (3) fly ash from fine-powdered coal-firing electric plants, (4) cement dust from dust-catching electric treaters, (5) waste slaked lime from lime hydrating plants or byproduct lime waste from carbide acetylene plants, (6) with or without (in the case of using cement dust) small amounts of alkali or alkali salt in dilute solution in the mixing water, or alkali salt in powder form for preliminary addition to cement.

(b) The large content of water-granulated blast-furnace slag as the main component gives the cement a weak hardening property, owing to the weak latent hydraulicity of granulated slag, which must be accelerated by adding a proper amount of slaked lime, and the excess of slaked lime must then be hydrated to calcium hydrosilicate $x\mathrm{CaO}\cdot y\mathrm{SiO_2}\cdot z\mathrm{H_2O}$ by the active or soluble silica in the added pozzolanic siliceous matter of natural or artificial byproduct origin. The addition of fly ash is effective in increasing the plasticity, in decreasing the contraction or expansion, and in gradually developing over long periods the pozzolanic action characteristic of natural or artificial pozzolanic matter, etc.

(c) However, these special slag-lime cements are slow setting and low in strength, even with proper mixing of granulated blast-furnace slag, natural or artificial pozzolanic materials, and slaked lime. Thus, it is most important to accelerate the setting time and increase the strength by adding an affective accelerating agent. For this purpose, the addition of the proper small amount of alkali or alkali salt in dilute solution in place of the mixing water, or finely powdered alkali salt to the cement, is a most effective means of accelerating the setting and increasing the strength. The amount of alkali or alkali salt is very small, the amount necessary to accelerate the slow setting and weak strength of the special slag-lime cement being about 1–3 percent..

The cement dust from electric dust-catching plants, used for mixing (about 30–50 percent) with the cement as one of the main admixing components, is most effective for this purpose, owing to the following facts: (1) the content (about 2–5 percent) of both Na_2SO_4 and K_2SO_4 in the cement dust reacts as the accelerating agent above mentioned, (2) the content of free lime (about 10–18 percent) in the cement dust replaces slaked lime as one of the main components of the special slag-lime cement, (3) some calcium silicate, $m\mathrm{CaO}\cdot n\mathrm{SiO}_2$, of lower lime content contained in the dust, which was produced at the relatively lower temperature in the upper part of the cement rotary kiln, has a weak hardening property, which, even though very small, is effective in the cement, (4) the free silica and alumina, which were produced by calcining the clay part of the cement raw mixture in the upper part of the rotary kiln, react as siliceous admixtures replacing natural or artificial pozzolanic matter as above mentioned.

(d) The high-slag-content special slag-lime cement made by proper proportioning of water-granulated blast-furnace slag, slaked lime, natural or artificial siliceous pozzolanic matter, fly ash or cement dust, and a small amount of alkali or alkali salt, shows accelerated setting and increased strength and improvement in various properties needed for mortaring, plastering, and masonry uses, i.e., plasticity or consistency, water-retention power, decrease in expansion or contraction and cracking, decrease in efflorescence (especially by using cement dust), improved surface hardness, etc.

(e) For these purposes, the author for many years has studied many kinds of special slag-lime cement, especially for masonry, mortaring, and plastering uses, the provision of which is a most important problem in Japan for concrete, concrete block, wood or wire-lath building, etc. In Japan, there is now no marketable masonry cement, but some kinds of masonry cement are now being studied as to their marketable production, use for various purposes, and the official testing processes to be enacted in the near future as the Japanese Industrial Standard Specification.

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Paper VIII–S3. Blast-Furnace Cement in the USSR*

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Synopsis

The scientific basis for the use of slags in the manufacture of cement and practical means for improving the quality of blast-furnace cement are explained.

Nearly all kinds of slags derived from cast-iron, Bessemer, and Martin processing are used in the USSR in the manufacture of blast-furnace cements.

Broad studies of the composition, structure, and hydration process of blast-furnace slags have been made in the USSR. It is found that the activity of a blast-furnace slag depends on a number of factors such as its temperature when tapped from the furnace, its chemical composition, the method and rate of cooling, and the mineralogical composition resulting.

Blast-furnace cement is widely used in the USSR because of its various valuable properties such as high tensile strength, low water requirement, low heat of hydration, high corrosion resistance, low shrinkage, etc.

The relatively slow increase of strength of common blast-furnace cement in the early ages of hydration can be overcome by increasing the fineness. Superfine grinding makes it possible to manufacture a high-strength blast-furnace cement.

A method of manufacturing melted portland cements by the addition of lime and iron ore to molten slag in a specially designed converter has been worked out in the USSR.

Résumé

Cet exposé explique le principe scientifique pour l'utilisation des laitiers dans la production du ciment et les moyens pratiques d'améliorer la qualité du ciment de laitier de haut fourneau.

Presque toutes les sortes de laitiers de haut fourneau dérivés d'opérations de fonte sont utilisées à l'URSS dans la production des ciments de laitier de haut fourneau.

Des études étendues sur la composition, la structure et le procédé d'hydratation des laitiers de haut fourneau ont été faites en URSS. On a trouvé que l'activité du laitier du haut fourneau dépend d'un certain nombre de facteurs tels que la température de coulée de haut fourneau, la composition chimique, la méthode et la vitesse de refroidissement et la composition minéralogique qui en résulte.

Le ciment de laitier de haut fourneau est largement utilisé à l'URSS à cause de ses différentes propriétés valables, telles que la haute résistance à la traction, la faible exigence d'eau, la faible chaleur d'hydratation, la forte résistance à la corrosion, le faible retrait, etc.

L'accroissement relativement lent de la résistance du ciment de laitier de haut fourneau commun au début de l'hydratation peut être surmonté si on accroît la finesse. Un broyage extrêmement fin rend possible la fabrication d'un ciment de laitier de haut fourneau à haute résistance.

Une méthode a été développée à l'URSS qui permet la fabrication de ciments portland fondus au moyen d'une correction du laitier fondu dans un convertisseur spécialement construit.

Zusammenfassung

Die wissenschaftliche Grundlage der Verwendung von Schlacken in der Zementherstellung und das wirtschaftliche Verfahren für die Verbesserung der Qualität der Hochofenzemente werden beschrieben.

In der UdSSR werden beinahe alle Schlacken, die von Hochöfen, Bessemerbirnen, oder Martinöfen kommen, für die Anfertigung der Hochofenzemente verwendet.

Man hat in der UdSSR die Zusammensetzung, die Struktur und den Hydratationsprozeß der Hochofenschlacken gründlich studiert, und man hat herausgefunden, daß die Aktivität dieser Schlacken durch eine Anzahl Faktoren beeinflußt wird, wie zum Beispiel die Temperatur bei welcher der Hochofen angestochen wird, die chemische Zusammensetzung, die Kühlmethode und -geschwindigkeit, und die endgültige Mineralzusammensetzung.

Man benutzt die Hochofenzemente häufig in der UdSSR, da sie sehr wertvolle Eigenschafte, wie eine hohe Zugfestigkeit, einen geringen Bedarf an Anmachwasser, eine niedrige Hydratationswärme, eine hohe Korrosionsfestigkeit, ein kleines Schwindmaß usw. besitzen.

Die Festigkeitszunahme der gewöhnlichen Hochofenzemente vollzieht sich während der ersten Hydratationsstufen sehr langsam, aber dieser Nachteil kann durch ein Heraufsetzen der Feinheit beseitigt werden. Ein Ultrafeinmahlen bringt die Möglichkeit hervor, einen hochfestigen Hochofenzement herstellen zu können.

Man hat auch in der UdSSR ein Verfahren, in welchem geschmolzene Portlandzemente aus der geschmolzenen Schlacke in einer Spezialbirne hergestellt werden, ausgearbeitet. Man muß zu diesem Zwecke besondere Zuschläge in die Birne geben.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the Academy of Construction and Architecture, Moscow, USSR.

The use of blast-furnace slags for making various building materials has been known in the USSR for almost a century. In 1865, soon after the quenching of slag had been invented and its hydraulic properties revealed, the production of wall stones made from the mixture of lime and slag was started. In the cities of Dniepropetrovsk and Krivoy Rog the first large buildings were erected by use of blast-furnace-slag concrete in the last decade of the 19th century. Some time later, in 1913–1914, there was constructed in Dniepropetrovsk a works producing blast-furnace cement—the first one in Russia. At about that time the production of blast-furnace cement was started in Tula (Kosogorsk steel-works).

Despite the positive results of numerous tests and the accumulation of practical experience in using blast-furnace slag for construction, there passed some five years (1911–1916) between the issuing of technical specifications for this cement and its official introduction in concrete and reinforced-concrete constructions.

During the last 30 years the industry of cement and blast-furnace cement in the USSR showed a steep increase. Large plants for the production of blast-furnace cement were constructed in the Don Basin, Transcaucasus, central regions of the USSR in the Urals, and in West Siberia. The blast-furnace-cement production comprised as much as 35.3 percent of the total amount of the cement output during 1959.

In the USSR along with the construction of large up-to-date equipped plants for making blast-furnace-slag cement, deep theoretical investigations have been conducted. These were devoted to the study of the properties specific to metallurgical slags, to the means of their processing, and to the use of blast-furnace cement in the building industry. Blast-furnace cement has been used in the construction of dams at Dniepr, Kahovka, and other hydro-power stations as well as for many other very important construction projects.

Almost all kinds of slags derived from cast iron, Bessemer, and Martin processing are used to make blast-furnace cement in the USSR.

Nearly 95 percent of all the liquid blast-furnace slags used in the USSR undergo granulation. Granulated slags are used to make cement, mainly blast-furnace cement. They are also used as small additives (up to 15 percent) in making portland cement and as a raw component of clinker. Blast-furnace slags are widely used in the building industry for making grouts and concretes, and are processed for making of thermosit, slag wool, and some other building materials.

Various processing plants are employed to granulate slags. Depending on the moisture content in the granulated slag, these plants are classed as wet or semidry.

Although most of the granulated slag is made in wet granulated plants, its use is less economic as compared with slag from the semidry plants, since the transportation of the latter—especially in winter—and its processing are much less expensive. That is why new wet-granulation plants are not constructed any more, and the old ones are being converted to the semidry process wherever it is possible.

Central granulation plants which are mainly used in the USSR are very effective, and their production capacity amounts to as much as 200,000 to 800,000 tons a year.

They are located near blast-furnace departments and receive liquid slag from a number of furnaces in special slag-conveying buckets. Most of these central plants are destined for wet granulation and are of the granular basin type. There are only two or three steel works served by grout plants.

The drum method for semidry granulation of slags worked out in the USSR is widely used in this country [1].[1]

The principle of action of the drum plant is based on two successive stages of quenching of the liquid slag. During the first stage the melt is quenched with a small amount of water under high pressure, resulting in the foaming of the melt. The foaming depends on the temperature, chemical composition of the slag, and the amount of water supplied.

During the second stage, foamed but still hot and fluid slag is transported to the turning drum where it is quenched by mechanical breaking of its bulk into separate particles and ejecting them into the air. Fast movement of particles in the air helps their quenching and evaporation of the residual entrained moisture.

When using the semidry method of granulation, less decomposition of sulfides and less liberation of hydrogen sulfide take place.

The semidry granulated slag is of a more compact structure; its bulk density is some 1.5 times that of wet granulated slag of the same liquid melt.

The moisture content of wet-granulated slag amounts to 35 percent while that of semidry is up to 10 percent; the bulk density of these granulated slags is 400–1,000 and 600–1,300 kg/m^3 respectively.

According to the data obtained from the study conducted by "Niitsement" [21] the hydraulic properties of semidry and wet-granulated slags of the same chemical composition are practically equal. The chemical composition and hydraulic properties of slags processed by cement and construction industries of the USSR are of great variety. The slags derived from iron works of the south and those of the eastern regions of the USSR differ in both their chemical composition and hydraulicity.

Blast-furnace slags from the southern iron works have low alumina content (6 to 10 percent) and a comparatively high content of sulfide (up to 3 percent). On the other hand slags from the Uralo-Kuznetsk basin, using ores rich in alumina

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[1] Figures in brackets indicate the literature references at the end of this paper.

and low-sulfur coke, contain much alumina and little sulfide sulfur (up to 1 percent).

Research work conducted by Soviet scientists shows that, along with lime, alumina is one of the most important active components of granulated slag, which, other conditions being equal, insures high quality of the blast-furnace cement. That is why the evaluation, by its basicity, of any slag to be used for the production of cement has been abandoned in the USSR.

During the thirties it was recognized that the so-called acid granulated blast-furnace slags characterized by percent content of $\frac{CaO+MgO}{SiO_2+Al_2O_3}<1$ are also quite usable for making blast-furnace cement.

The correctness of this assertion was afterwards proved by the wide use of these slags in this country and in some others as well. In recent years, new formulas have been developed in which the content of alumina in slag is considered as a positive factor in the hydraulic properties of granulated blast furnace slag.

Blondiau [5] considers that in slags with sufficient hydraulicity the CaO/SiO_2 ratio should be of the order of 1.45 to 1.54, while the SiO_2/Al_2O_3 ratio should be 1.8 to 1.9.

But all these formulas apparently do not reflect the full relationship existing between the chemical composition of a slag and its hydraulicity.

Stutterheim [6] investigated a great number of slags with the aim of determining their chemical composition and strength at the ages of 28 and 91 days. He defined the hydraulicity of slags by the following series of formulas:

1. $\frac{CaO+MgO+Al_2O_3}{SiO_2}\geq 1$
2. $\frac{CaO+MgO+1/3Al_2O_3}{SiO_2+2/3Al_2O_3}\geq 1$
3. $\frac{CaO+CaS+1/2MgO+Al_2O_3}{SiO_2+MnO}>1.5$
4. $20+CaO+Al_2O_3+1/2MgO-2SiO>12$
5. $S=0.38G(M-0.72)+75$

where:

S=percentage strength of portland cement concrete at the age of 91 days,

G=content of the vitreous phase in granulate,

M=modulus defined by formula 1.

Stutterheim did not find any clearcut relationship between the features studied, indicating that the available formulas fail to reflect distinctly this relationship, which apparently, is considerably more complex.

Nevertheless some of the formulas make it possible to determine approximately the nature of slag.

P. P. Budnikov [7] in the USSR proposed a formula which characterizes the quality of slag by means of the quality factor Q:

$$Q=\frac{CaO+MgO+Al_2O_3}{SiO_2+MnO}>1.$$

One can mention the recent German specification which permits the use of acid slags containing appreciable amounts of alumina for the production of cement.

On the basis of the above, criteria of hydraulicity apparently lie in chemical composition, and the last formulas take into account even the content of manganese protoxide which is known to exercise negative influence on the hydraulicity of slag.

Investigation conducted in the "Niitsement" [8] showed that the low hydraulicity of slags obtained from the production of Martin cast iron, often coupled with an increased manganese content, is the consequence of their low basicity aggravated by the lack of alumina and of the comparatively cold operation of the blast furnace, rather than of the harmful effect exercised by their manganese content.

Slags formed during hot operation of the blast furnace and with an increased content of alumina, even slags with high content of manganese protoxide—e.g., slags of ferromanganese and specular cast irons—have a marked hydraulicity and may be considered suitable for making blast-furnace cement. This was proved by the studies conducted by a number of other investigators [9,10].

Studies conducted in the USSR and in some other countries [6,11] showed that manganese blast-furnace slags have sufficient hydraulicity.

The problems of the structure of the granulated blast-furnace slags are more or less broadly elucidated in special literature. It is proved that increased hydraulicity of quenched slags is the result of converting the structure into a vitreous one—with considerably greater storage of internal energy than is the case with slowly cooled crystallized slags.

A comparison of the heat of dissolving of granulated and slowly cooled slags of the same chemical composition proved what has been said before—i.e., granulated slags liberated more heat.

Microscopic study of basic granulated blast-furnace slags of high hydraulicity showed, however, that the amount of vitreous phase in these slags is comparatively limited, of the order of 15 to 45 percent. But acid granulated blast-furnace slags, vitrified during the granulation process to 80 percent and more, do not have hydraulicity comparable to basic slags. The hydraulicity of acid slags obtained from the charcoal cast-iron process is very low despite their complete vitrification.

In acid slags, along with the crystallization of the minerals of the melilite group, there often appears calcium silicate—$CaO \cdot SiO_2$—in the form of pseudowollastonite.

The crystallization of this mineral is specific for acid slags with relatively low alumina content. In the case of an increased content of alumina, predominance of the formation of anorthite—$CaO \cdot Al_2O_3 \cdot 2SiO_2$—is observed. The precipitation of calcium and manganese sulfides sometimes is also observed in acid granulated slags.

Studies conducted in our country [13] demonstrate that not all of the sulfide sulfur which is present in slags is combined in CaS. At first the sulfur combines with manganese and iron, and only after that does it combine with calcium. The calculation of the CaS content in blast-furnace slag should be made with due consideration of this fact.

Therefore the hydraulicity of slags is a function not only of high content of the vitreous phase but also of the chemical composition of this phase and of the crystalline formations.

Nowadays there is not any universally adopted theory on the hardening of slag cements. The roles of the mineralogical components and of the vitreous phase in this process are not yet completely clear.

It is supposed that under the influence of alkali hydroxide, colloidization of the surface layers of the vitreous grains takes place, since these grains are a less-stable phase due to the quenching of the granulation process; during this reaction, silica gel precipitates which partly reacts with lime and cements the grains of the slag into a solid monolithic body.

The process of hardening of blast-furnace slags is explained by some as a result of the formation of hydrated silicates and aluminates of calcium. This process is very slow but can be markedly accelerated under the influence of acid and sulfate stimulants.

Recently a theory of electrolytic activation of blast-furnace slags is attracting more and more attention. This theory is as follows. In melted blast-furnace slags a considerable part of the chemical compounds is in a state of dissociation. During the quenching there is no time for stable chemical compounds to form, and the melt has therefore a considerable amount of Ca, Mg, AlO_4 and SiO_4 ions. During hydration, water acts on these unstable dissociated groups; the slag glass is destroyed, and the ions are again able to be mobile in aqueous media. Under the influence of activators, neutralization of oppositely charged ions and crystallization of newly formed hydrated products take place.

Soviet scientists [13, 16, 19] investigated the problems of studying the features of sulfate and acid stimulation of slags; they studied new formations appearing in hydrating slag and slag binders.

The treatment of slags of different composition with water, gypsum water, lime water, and with the mixture of the last two show that the greatest effect is obtained when using lime—pure or with an addition of material having a common ion with lime (leaches, $CaCl_2$). The action of the last, without lime, is considerably weaker, and it is found that hydroxyl ion gives rise to more intensive hydration of slags than Ca ion ($CaCl_2$). It is possible that exchange reaction between leach and slag takes place in the first case, that is to say, that some lime is formed.

Gypsum also stimulates the hydration of slags through adsorption, forming poorly soluble complex salts with aluminates, etc.

Sulfates however, need a kind of a "mediator"—lime—and without it have no importance of their own.

It is found that if portland cement is used for an activator of a slag, then a small addition of it brings a sharp change in the qualities of the binder, with approximation to the more active component, i.e., to cement.

The investigation of new formations appearing during the interaction of the slag and the water shows that these new formations contain the same chemical constituents as the starting slag but in other proportions [19, 20, 21]. The nuclei of the new formations consist of the smallest particles of slag but not of its components. It is found as well that the basicity of the new formations is higher than that of the starting slag, that alumina characteristics develop, which indicate the active role of aluminates and, finally, that the new formation combines water vigorously.

In order to determine the hydraulic properties of the separate minerals of a slag, the "Niitsement" has conducted some studies [16]. These studies show that without activating agents neither mineral gehlenite nor gehlenite glass harden whether they are subjected to ordinary temperature, common steam curing, or high-pressure steam curing. These studies show that when gehlenite glass is mixed with lime water, hexagonal plates of calcium hydroaluminate appear; when some gypsum is added to this mixture, there occurs formation of needles of calcium hydrosulfoaluminate. Mineral akermanite hardens without adding activators only under high-pressure curing; akermanite glass hardens at ordinary temperature, but more intensively under steam curing—common and high-pressure as well. Crystalline anorthite and anorthite glass have no hydraulic properties.

High-alumina blast-furnace slags used in making alumina cement are characterized by different properties. For example, crystallized slags have higher strength when hardening than vitrified ones. Generally it can be stated that the minerals which, in their crystalline state, have obvious hydraulicity and are liable to independent hardening—e.g., calcium aluminates and silicates—lose this property in their vitreous state.

So, one can see that the hydraulicity of a blast-furnace slag obtained when processing either common cast iron or that destined for steel making depends on a combination of a great number of factors. These include: the temperature of the slag tapped off the blast furnace, its chemical composition, the character and the speed of granulation, and the resulting mineralogical composition of the slag.

The formulas derived from the chemical composition of a slag coupled with crystallo-optical data can give but an approximate indication of its hydraulicity. The degree of suitability of a particular quenched blast-furnace slag for cement manufacture should be determined mainly on the basis of study of test specimens of blast-furnace cement, the clinker of which is mixed with various portions of the slag, and which is ground to the specific surface common for this plant. There are some other practical methods to determine the hydraulicity of granulated slag, e.g., laboratory tests of specially combined mixtures of clinker, slag, and quartz sand [3], and measurement of the amount of gypsum absorbed when the slag powder is boiled in a lime-gypsum solution.

The last method has practical meaning as well for determination of the optimum content of gypsum when making blast-furnace slag cements of the highest strength. Besides these methods, there are some others.

In common practice of cement manufacture, clinker, dried granulated slag, and gypsum are ground together to the fineness (specific surface) desired.

Until recently it was supposed that the lowered output of compartment tube mills when grinding blast-furnace cement was a function of lower grindability of the slag. However, recent study by the "Niitsement" showed that basic wet-granulated blast-furnace slags, yielded when processing cast and steel-making iron, are ground relatively faster than clinker and are present in cement mainly in its finest fraction. The reduction of the mill output should be explained as a function of the low specific volume of slag which limits the possibility of filling up the mill sufficiently.

When using acid blast-furnace slags of wet—and especially semidry—granulation, other results are obtained. During ordinary grinding of clinker with these slags, they do not concentrate in the finest fraction of the cement powder, despite their considerable glass content.

High fineness of grinding—an increased specific surface—is especially necessary to display the potential physico-chemical activity of a slag; and it is natural that the less active the slag, the finer it should be ground.

This requirement should be taken into consideration when qualifying granulated blast-furnace slag as an active hydraulic component of blast-furnace cement.

Long experience in the production and application of blast-furnace cement has revealed a number of very important construction properties.

Wide scientific and experimental investigations devoted to the study and improvement of the properties of blast-furnace slag cement are being conducted in the USSR.

Blast-furnace cement is a complex binding agent. Its properties depend on a great number of factors the combination of which makes a complicated system of interaction.

The brilliant feature of blast-furnace slag cement is the comparatively high value of its tensile strength which results in a low ratio of compressive strength to tensile strength.

As distinct from pozzolanic cements, blast-furnace cement does not require increased water consumption when used for grouts and concrete mixtures. Though there is rather delayed attainment of strength during the first period after mixing, this cement is distinguished by intense attainment of strength at later ages.

It can be said, generally, that the strength of portland cement between 1 and 7 days may approximately double, while that of blast-furnace cement may triple, under normal conditions of temperature and moisture.

The slower hardening of blast-furnace cement causes less heat liberation during the hydration, which is very important for the use of this cement in mass concrete.

Low water permeability and the higher corrosion resistance of blast-furnace cement in mineralized water make possible its use in hydraulic structures. Besides this, blast-furnace cement undergoes less contraction and has higher frost resistance in comparison with pozzolanic portland cements. But its most important property in comparison with pozzolanic cement is its relative stability in air, and this property provides normal hardening of concrete and reinforced concrete in land structures. Of course it does not exclude the necessity of carefully curing the concrete to protect it from drying and from low temperature during its first period of hardening.

Steam curing used in manufacture of concrete and reinforced-concrete articles is especially favorable for blast-furnace cement.

These are all reasons to consider blast-furnace slag cement a more universal binding agent than pozzolanic cement, and therefore it can be used for submarine, underground, and land structures and, practically, its most valuable properties can be used for the first two types of constructions mentioned.

The "Niitsement" has conducted studies of the properties of blast-furnace cement for using it in hydraulic structures [23].

The study of contraction and the combining of water during the hydration of blast-furnace cement reveals that the addition of slag lowers the contraction and that during the first day this lowering is proportional to slag content in the cement.

In the case of equal ratio of the slag and clinker, more contraction to the age of 30 days is observed in blast-furnace slag cement containing basic slags. The contraction of the blast-furnace slag cement with acid slags depends mainly on the chemical-mineralogical composition and the specific surface of the clinker component.

The amount of water combined by cements during the hydration depends mainly on the activity of their clinker component. To the age of 3 months, blast-furnace cements of various compositions combine some 10 to 12 percent of water relative to the weight of cement. In the case of blast-furnace cements with acid slags this amount of water binds mainly their clinker component, which, when different cements are ground to equal specific surface, is subjected to finer grinding in blast-furnace cements than in portland cement and therefore hydrates quicker. Quicker hydration of blast-furnace cement is a result of the fact that the particles of the slag move apart the grains of clinker and facilitate the access of water.

The heat liberation of blast-furnace slag cement appreciably depends on the exothermic effect taking place during the hydration process of the clinker component since acid slags in the course of 3 days hydrate only as much as 5 to 6 percent. It is quite natural, that with increase of clinker content in a blast-furnace cement its heat liberation increases as well.

The presence of a slag in cement lowers its heat liberation disproportionately to the amount of the slag added.

Acid or basic slag added to a portland cement in an amount of 50 to 70 percent decreases the heat of its hydration to the age of 3 days up to 30 to 58 percent.

The study of the phenomenon of contraction of blast-furnace cement has revealed that basic slags decrease the contraction of cement due to good adhesion of particles of the slag with hydrated grains of clinker, greater compactness of the cement paste, and less loss of water.

The reason for the contraction of blast-furnace cements in air hardening lies mainly in the removal of uncombined water; in the case of blast-furnace cements with small addition of slag—less than 50 percent—the contraction to some extent depends on the mineralogical composition of the clinker as well. Contraction strains in the case of a grout of blast-furnace cement with normal sand, of 1:3 ratio, at the age of 4 months of air hardening amount to 0.6 to 0.76 millimeters per meter with either 50 percent of acid or 70 percent of basic blast-furnace slag in the cement; contraction of pozzolanic cement taken for comparison amounted to 1.15 millimeters per meter.

Investigation of the resistance of blast-furnace cements containing acid or basic slags to the effect of leaching by distilled water shows that the addition of acid or basic slags to cements increases their durability to the effect of soft water, and this increase is characterized by decrease of the absolute amount of lime leached out of blast-furnace cement and by decreased loss of strength as compared with portland cement and pozzolanic portland cement.

Solid grains of a slag which hydrate rather slowly make a kind of additional rigid structure, and this, after the leaching of some part of the lime from the clinker constituent of the cement, suffers no change.

Blast-furnace cements have sufficient frost resistance which can be increased by adding some surface-active agents, decreasing the water-cement ratio, and by preliminary hardening for approximately 3 months before the frost exposure starts. Securing of these last conditions is especially important for blast-furnace cement made with acid slags which, containing more "weakly combined" water, are therefore less frost resistant than blast-furnace cements made with basic slags.

As to the water resistance of blast-furnace cement, the type and the degree of dispersion (specific surface) of the slag used are of essential importance.

Low water permeability of concretes made with blast-furnace cement can be attained by empirical determination of the necessary fineness of grind of the components of the cement.

Since fine grinding has a beneficial effect on the most important building properties of blast-furnace cement, its manufacture for hydraulic structures through separate grinding of slag and clinker should be considered rational. Wet grinding of slag, which considerably facilitates the making of fine fractions, also gives good results.

Nevertheless the retarded rate of strength attainment during the first period of hardening led to the endeavor to accelerate the rate of hardening of blast-furnace cement. Conditions for making high-grade blast-furnace cement on the basis of common granulated blast-furnace slags, of cast and steel-making iron, were studied in the "Niitsement" [24]. The results obtained show that for blast-furnace slag, and for portland cement as well, the chemical-mineralogical composition of the starting clinker has considerable importance. In this case, particularly, higher content of the clinker minerals most active at the earlier ages, C_3S and C_3A, is required.

Increase of the specific surface of blast-furnace cement, resulting in considerable activation of slag and clinker, is an effective means of accelerating the hardening.

Increase of the specific surface of the blast-furnace cement to 1.5 to 2.0 times (up to 4,000 to 4,500 cm^2/g, Blaine) helps to increase its strength to that of the starting portland cement with specific surface of 2,500 to 3,000 cm^2/g.

Investigation of the properties of blast-furnace cement made by fine and superfine grinding in the "Niitsement" [25] shows that it is possible to make blast-furnace-slag cement of high strength by means of finest grinding—even on the basis of weakly active granulated slags. The chemical composition of a slag has an essential influence on the activity of a superfine blast-furnace cement, but only during its early ages of hardening.

The strength of superfine blast-furnace cement at 28 days is 100 to 200 percent more than that of the same cement of usual fineness. However, sharp attainment of strength resulting from the superfine grinding of blast-furnace cement, is displayed at early ages of hardening.

Superfine grinding of blast-furnace cements made from weakly active acid and low basic slags is especially effective.

Superfine grinding makes possible wide use of weakly active slags in the cement industry.

One of the main methods of finer grinding of blast-furnace cement should be the separate grinding of slag and clinker which permits one to regulate and to pre-establish the most effective specific surface of every component.

This method should be especially necessary for blast-furnace cements made with acid slags inasmuch as acid blast-furnace slags, to reveal their potential hydraulicity, need finer grinding than basic slags.

Studies conducted in the "Niitsement" and in the "Yuzhgiprotsement" [26] show that high-early-strength blast-furnace cement with compressive strength at ages of 1 and 3 days like that of high-early-strength portland cement can be made with 30 to 40 percent of granulated blast-furnace slag, using active clinker and fine cement of common or separate grinding to approximately 4,500 to 5,000 cm^2/g, Blaine.

The production of high-early-strength blast-furnace cement is organized now on a commercial scale.

Introduction of 30 to 40 percent of basic blast-furnace slags into magnesia portland cement, having up to 10 percent of MgO, and made in our country in small quantity, is very effective.

Slag magnesia portland cement as well as blast-furnace cement is distinguished from portland cement by somewhat more retarded hardening and by lower strength.

Slag magnesia portland cement is used in our country for various types of construction.

The use of blast-furnace slags for the manufacture of melted cements is of great interest.

A method of slag processing to make melted cements was invented by V. V. Serov, a Soviet inventor, and this method is introduced in practice in the Soviet Union [27].

Up to the present there has been known only one secure method of making melted cement clinker by means of concentration of liquid slags outside of the blast-furnace. This method was offered by K. Wennerström, a Swedish engineer [28]. By this method, liquid slag is concentrated in an electric furnace lined with carbon and equipped with graphite electrodes. However, this method can be used on a commercial scale only when cheap power is available since its power consumption, according to the data of the inventor, amounts to 400 to 700 kwh per ton of clinker.

Besides this disadvantage, as a result of the contact between the carbon of the lining and the lime, an appreciable amount of calcium carbide forms. This, dissolving in the clinker, changes it for the worse.

From the very beginning, the experimental working out of Serov's converter was aimed at solving the most difficult task: to make melted portland cement clinker from liquid blast-furnace slags.

An important feature of the design of this converter is the absence of a refractory lining for which is substituted a layer of slag hardening on the surfaces of the steel caissons and cast-iron cooling plates which make up the walls and the dome of the converter. These caissons and plates are vigorously cooled by water (fig. 1). The converter is fired by mazut.

Air coming to the tuyeres of the converter is heated by the exit waste gas, for which purpose two hot-blast stoves serve. These resemble blast-furnace stoves. In order to reach the high temperature necessary, the air in the converter is, after this heating, supplied with additional oxygen.

The making of melted portland-cement clinker by concentrating liquid blast-furnace slag is as follows. As the temperature of the melt rises, lime (either limestone, or burned lime) is added to liquid slag poured from a slag bucket into the converter, approximately to the level of 1 meter above the material-and-fuel injecting pipe; to lower the temperature of melting of the product, iron oxide in the form of iron ore is added. The lime and the ore are ground to the size of 10 to 40 mm before being conveyed to the converter.

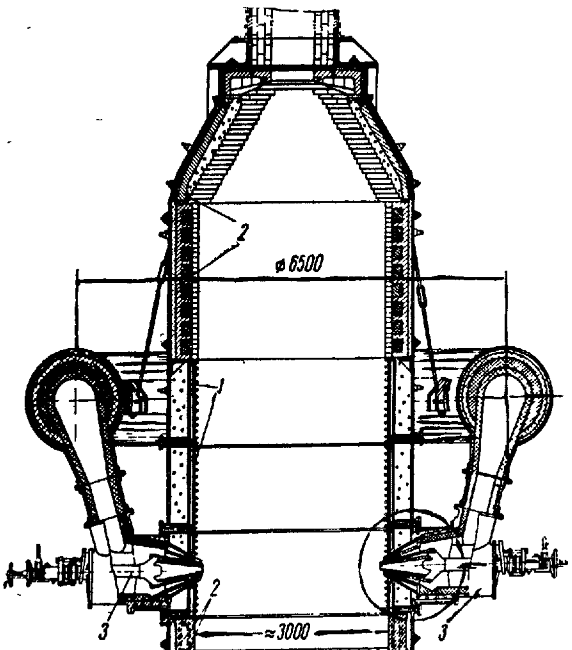

FIGURE 1. *Sectional drawing of the converter.*

1—steel caissons; 2—cast-iron cooling plates; 3—injection pipe for material and fuel.

The finished clinker melt is let out of the converter and subjected to granulation. With the aim of comparative investigation of the properties of the melt, it was either granulated or cooled in a layer.

Investigation of melted clinker reveals that granular clinkers are characterized by a very fine-granular and original structure of the minerals, which is not characteristic of the clinkers made by sintering. Alite has the form of very elongated prisms, which are sometimes almost acicular, with dimensions

$5 \times 25\mu$ to $5 \times 125\mu$.

There are groups of the finest grains of belite and the ferrous phase between the prisms (figs. 2 and 3).

The appearance of slowly cooled clinker, the specific feature of which was an extremely macrocrystalline mineral structure, was of a radically different nature.

The sizes of the crystals amounted to 400 to 500 μ. In some pieces of certain fusions the crystals of alite could be seen with the unaided eye.

Alite had the form of hexagonal plates with clearly shaped cleavage cracks and with a lot of defects in the form of air bubbles and ferrous inclusions.

The character of crystallization of belite also varied, depending on quenching.

In granulated clinkers belite either had the form of very fine rounded grains aggregating with one another and closely intergrown with ferrous phase or was in dendrite formations (fig. 4).

In slowly cooled clinkers we observed belite as shapeless formations and coarse rounded grains with highly perfect cleavages and granular surfaces.

High-grade melted portland-cement clinker was made with the following parameters of the process of melting:

FIGURE 3. *Microstructure of granulated clinker.* Reflected light. Magnification ×440.

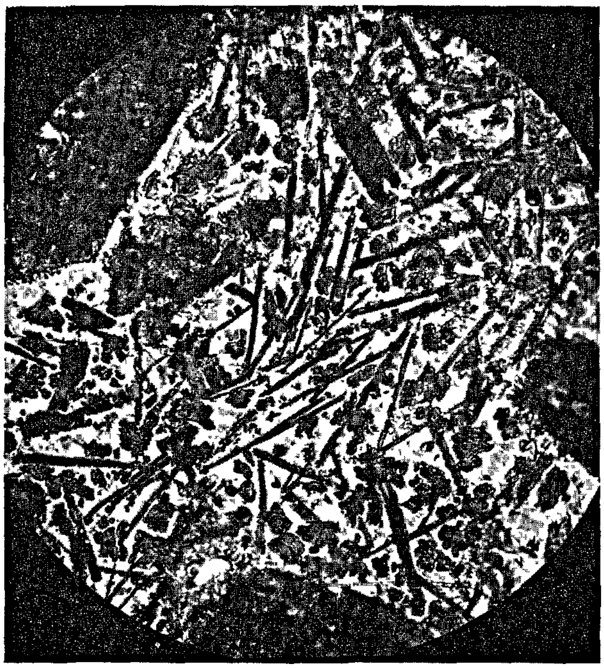

FIGURE 2. *Microstructure of granulated clinker.* Reflected light. Magnification ×440.

FIGURE 4. *Microstructure of belite in granulated clinker.* Reflected light. Magnification ×440.

CaO cement in blast-furnace slag charged to converter, percent	46–48
Temperature of the slag charged, °C	1, 300–1, 350
CaO content of the clinker melt discharged from converter, percent	60–63
Temperature of the clinker melt being discharged, °C	1, 900–2, 000
O_2 concentration in air, percent	26–28
Temperature of blowing, °C	700–800

The problem of using slags for the purposes of cement technology is being progressively solved by investigations. Great and important tasks are on the way to completion.

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Paper VIII–S4. High Chemical Resistance Pozzolanic Cements*

R. Turriziani and A. Rio

Synopsis

The influence of the reactive silica occurring in pozzolanic materials on the chemical resistance of pozzolanic cements from a general viewpoint and, particularly, towards selenitic water is pointed out by the authors.

The reactive silica seems to diminish the possibility of new formation of calcium aluminates and to fix preferably the hydrolysis lime of clinker. Furthermore, the gels of hydrated calcium silicate resulting from the reaction between silica and hydrolysis lime would have an efficacious protective action for the aluminates already present which are thus preserved from coming in contact with aggressive solutions.

Therefore, it is possible to graduate the chemical resistance of the pozzolanic cements to make them resistant even to the severe conditions of the Anstett test by modifying the reactive silica/reactive alumina ratio. This result is reached at a value of about 6.

Résumé

Les auteurs mettent en évidence l'influence que la silice réactive présente dans les matériaux pouzzolaniques manifeste sur la résistance chimique en général, en particulier aux eaux séléniteuses, des ciments confectionnés avec eux.

Il résulterait qu'une telle silice réactive diminue la possibilité de néo formation des aluminates de calcium, en fixant de préférence la chaux d'hydrolyse du clinker. Les gels de silicate de calcium hydraté produits par la réaction de la silice avec la chaux d'hydrolyse auraient en autre une action protectrice efficace sur les aluminates présentes en les préservant du contact des solutions aggressives.

Il est possible cependant de graduer, en modifiant le rapport entre la silice et l'alumine réactive présentes, la résistance chimique d'un ciment pouzzolanique jusqu'à le rendre résistant aux sévères conditions de l'essai Anstett. Ce résultat s'obtient avec une valeur du rapport d'environ 6.

Zusammenfassung

Die Verfasser heben den Einfluss der in puzzolanischen Stoffen anwesenden reaktiven Kieselsäure auf die Widerstandsfähigkeit gegen chemische Angriffe im allgemeinen hervor, und besonders gegen den Angriff der Sulfatwasser.

Reaktive Kieselsäure scheint die Möglichkeit der Neubildung von Kalziumaluminate zu vermindern, indem sie vorzüglich den Hydrolysekalk des Klinkers bindet. Die Gele des aus der Reaktion der Kieselsäure mit Kalk entstehenden hydratisierten Kalziumsilikates üben eine Schutzwirkung auf die anwesenden Aluminate aus, indem sie die letzte vor der Berührung mit aggressiven Lösungen bewahrt.

Es ist deshalb möglich, die chemische Widerstandsfähigkeit eines puzzolanischen Zementes so zu graduiren, indem das Verhältnis zwischen der anwesenden, aktiven Kieselsäure und Tonerde modifiziert ist, dass das Zement besteht sogar die strengen Bedingungen der Anstett- Probe. Dieses Ergebnis wird mit einem Werte von etwa 6 erreicht.

Introduction

In relation to the paper on the constitution and properties of pozzolanic cements by G. Malquori, we think it would be useful to make a more careful investigation of a certain characteristic aspect of the chemical resistance of the binders in question, that is the influence of reactive silica contained in pozzolanic materials on their usual chemical resistance from a general standpoint and particularly towards sulfate-bearing waters.

The present knowledge of the chemistry of hydraulic binders does not allow us to bring the differences found or supposed among the phases of hydrated pastes of portland or pozzolanic cements into relation with their different chemical resistance.

In this connection the investigators agree that, from a qualitative viewpoint, there are not sufficiently marked differences to account for the different behavior of the two binders in practice. Therefore, the undoubtedly better chemical resistance of pozzolanic cements would depend on a different phase distribution in the hydrated pastes.

To explain this difference, the indirect way seemed to be the more convenient, because of the availability of natural pozzolanic materials of very different compositions (some of them contain almost exclusively reactive silica).

We started, therefore, from the assumption that the different behavior of the two types of binders must be due to the different amount of hydrated calcium silicate gels in the pastes.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the University of Rome and Centro Studi della Società Cementisegni, Rome, Italy. (This paper was presented at the Symposium by A. R. Collins.)

It is not our purpose, at present, to investigate the possibility of a differentiation between structure and composition of the gels formed in both cases, although this side of the question would play an important role in the matter. At any rate we may foresee that the gels would effect a remarkable protective action on the phases more susceptible to attack, since by their nature they hinder the ion diffusion and exchange reactions between the hydrated products of the pastes and the contact solutions.

Experimental Investigation

The compositions of the materials used in our test are given in table 1. They are: a portland clinker with low iron modulus, a normal portland clinker, and two natural pozzolanic materials with different reactive-silica content. We indicated by P_1 a pozzolana with a high reactive-silica content and by P_2 a pozzolana whose content in reactive silica corresponds to that of the usual latial pozzolanas.

TABLE 1. *Composition of two clinkers and two pozzolanic materials*

	Chemical analysis			
	Normal portland clinker	Low-iron-modulus clinker	Pozzolana P_1	Pozzolana P_2
Ignition loss, %	1.60	0.60	4.80	5.63
SiO_2, %	21.00	21.45	88.25	44.92
Fe_2O_3, %	2.76	4.54	.32	9.70
Al_2O_3, %	6.34	3.96	1.80	17.58
CaO, %	66.50	66.20	1.68	11.02
MgO, %	1.00	1.20		
SO_3, %	.80	.63		
M.I.[a]	2.21	2.21		
M.S.[b]	2.30	2.52		
M.F.[c]	2.29	.87		
C_2S, %	51.58	64.00		
C_3S, %	21.32	13.00		
C_3A, %	12.13	3.00		
C_4AF, %	8.40	14.00		
Lime saturation, %	97.6	98.0		
Malquori residue, %	----------	----------	4.00	13.10

[a] Hydraulic modulus.
[b] Silica modulus.
[c] Iron modulus.

Progressive solubilization of SiO_2 and R_2O_3 according to Florentin, given as % total SiO_2 and R_2O_3

	Pozzolana P_1		Pozzolana P_2	
	SiO_2	R_2O_3	SiO_2	R_2O_3
Initial	5.84	32.04	6.67	44.71
After 3 days	8.87	32.52	11.02	45.99
After 7 days	30.48	41.26	19.44	54.20
After 28 days	52.96	62.62	29.02	66.37

Two series of cements were prepared with the two clinkers; that of the low-iron-modulus clinker is indicated by capital letters and that of the clinker with higher iron modulus by numbers. Each of them includes binary and ternary cements. The former were prepared by mixing clinker with one of the two pozzolanas, the latter by adding different amounts of both pozzolana P_1 and pozzolana P_2. The weight ratios of materials constituting each pozzolanic cement are shown in table 2.

TABLE 2. *Percentage of the materials composing the two series of cements*

Sample		Clinker	Pozzolana P_1	Pozzolana P_2
Series 1–10 normal portland clinker	Series A–L low-iron-modulus clinker			
1	A	100	----------	----------
2	B	65	----------	35
3	C	65	5	30
4	D	65	10	25
5	E	65	15	20
6	F	65	20	15
7	G	65	25	10
8	H	65	30	5
9	I	90	10	----------
10	L	80	20	----------

The whole pozzolanic addition was limited to a maximum of 35 percent, which value corresponds to the average pozzolana content of commercial pozzolanic cements. In this way two series of cements with different content in reactive silica and alumina were obtained.

The petrographic investigation shows that pozzolana P_1 is constituted by an amorphous or cryptocrystalline groundmass including a number of crystals at a different stage of alteration. The crystalline phases are feldspars and, less frequently, biotite, quartz, calcite, and zeolites; fragments of diatoms were also observed.

As may be inferred from the chemical constitution (low content of alumina, ferric oxide, calcium oxide, and carbon dioxide) and from the negligible residue after Malquori base-acid attack [1][1], the content in crystalline phases is very low. This is also confirmed by the X-ray pattern of this material which does not present a system of lines, but shows a band at 4.05 A (fig. 1), similar to the dried silica gels.

The infrared spectrum (fig. 2) was obtained with a double-beam Leitz apparatus. The sample was ground very fine, mixed with potassium bromide in a weight ratio of 1/10 and made up into tablets. The spectrum presents characteristic bands at 9.5–9.6μ, 10.6–10.8μ, and 12.5–12.6μ, respectively. The highest intensity is shown by the first band, which is very wide and irregularly defined. This band and the third one are characteristic of all types of silica, while the second band is probably due to SiOH groups. The position, form, and amplitude of the bands indicate that the material consists of silica gel. Similarly to silica gel, the material P_1 reacts quickly with calcium hydroxide forming a calcium silicate of the

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[1] Figures in brackets indicate the literature references at end of this paper.

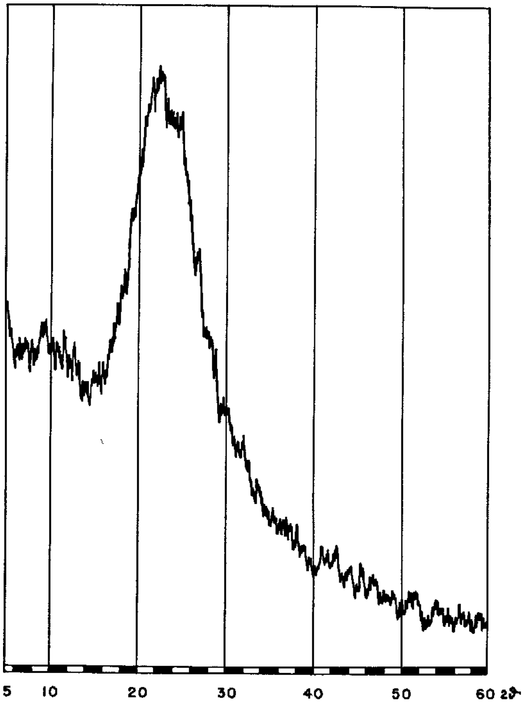

FIGURE 1. *X-ray diffraction pattern of pozzolana* P_1.

tobermoritic type. The reactive silica constitutes more than 90 percent of the total silica.

The silicate formation may be easily followed both by X-ray and by infrared methods. In the former case the phenomenon is revealed by the appearance of the reflection at 3.06 A, practically the only one of the whole spectrum, and by the disappearance of the band at 4.05 A.

In the latter case the presence of silicate is inferred by the position of the most intense band, which is displaced towards greater wavelengths and appears at about 10.2μ for the silicate with a ratio $CaO/SiO_2 > 0.8$ [2]. Launer [3] assumes that this band is characteristic of all silicates containing chains of SiO_2 tetrahedrons.

The pozzolana P_2 is a typical Roman pozzolana. Unlike the other type, this pozzolana fixes calcium hydroxide at a lower rate and in a smaller total amount, and, furthermore, it contains reactive alumina.

According to data in our possession, the maximum amount of lime that can be fixed by pozzolana P_2 is about 50–60 percent. In the case of materials almost saturated in lime, the quantities of silica and alumina rendered soluble by the Florentin acid attack amount to about 65–70 and 70–75 percent respectively, after a curing period of about 2 yr.

Two types of test were used for controlling the chemical resistance of the pozzolanic cements having the compositions shown in table 2. They are as follows:

(1) Test for the long-time behavior of porous mortars cured under water and then immersed in aggressive magnesium sulfate heptahydrate solution.

(2) Resistance to Anstett test. This test consists in checking the expansion, after 90 days, of specimens prepared with hydrated cement pastes, ground, mixed with 50 percent by weight of gypsum, and cured in a humid atmosphere.

While the first method, in spite of the time required, is sufficiently indicative for the evaluation of the chemical resistance of the binder in operation, the Anstett test provides in this sense less reliable results, since the carrying out of the test omits a series of factors, such as mortar compactness and surface condition, which play an important role in the behavior of the manufactured product in contact with aggressive solutions.

Nevertheless, in spite of these omissions, the method was included in our program of work since, because of its particularly severe nature, it would have made it possible to ascertain, in the case of a negative result, the existence of the relationship between the content in reactive silica of pozzolana and the chemical resistance of pozzolanic cement.

The tests with aggressive solution of magnesium sulfate were carried out on 4 x 4 x 16-cm specimens, manufactured with monogranular quartz sand in

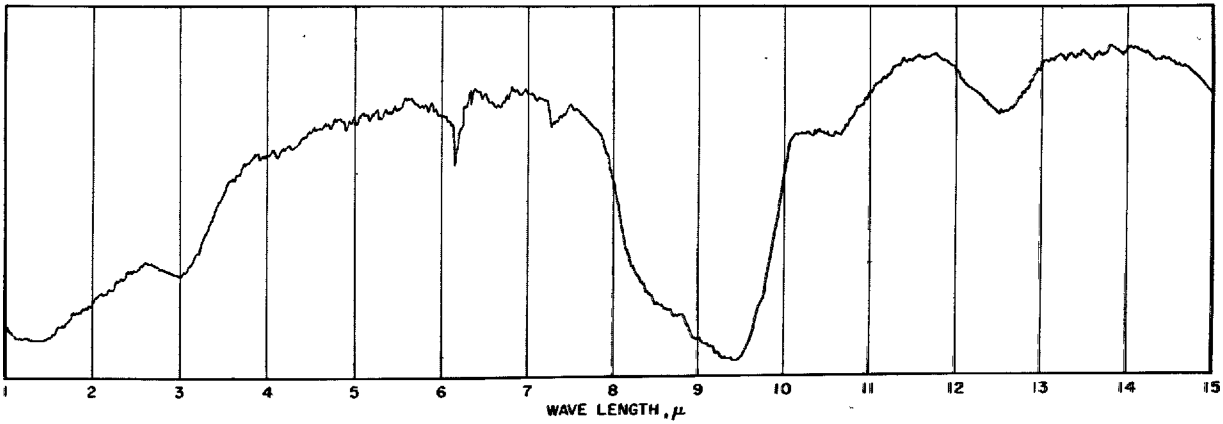

FIGURE 2. *Infrared absorption spectrum of pozzolana* P_1.

order to obtain a high percentage of voids, with a ratio of one part of binder to three parts of sand.

After curing for 28 days in water, they were half immersed in the aggressive solution. In this way two forms of contact were realized: in the lower part by direct imbibition and in the upper part by capillarity. The aggressive liquid consists of a 3 percent solution of $MgSO_4 \cdot 7H_2O$, renewed every week. The specimens remained under observation for 1 yr. The Anstett test was carried out as established by Blondiau [4].

For each paste tested by the Anstett method the diameter of the specimens was measured at 7, 30, and 90 days, and thus the expansion was determined. On the pastes stored for 90 days, besides expansion, the amount of silica and alumina soluble in the Florentin base-acid attack was determined, and the X-ray analysis was also carried out, to check the relationship between expansion and ettringite formation.

It would be considered that, in the case of portland cement pastes, silica and alumina soluble under the conditions of the Florentin attack correspond, in fact, to the content of the two oxides of the clinker. In the case of pozzolanic cements the situation is different: the amounts of soluble silica and alumina increase with the progress of the reaction between calcium hydroxide and pozzolanic material (see table 3).

TABLE 3. *Percentages of* SiO_2 *and* Al_2O_3 *soluble by the Florentin attack, and the* SiO_2/Al_2O_3 *ratio in solution*

(Cured for 3 months)

Sample	SiO_2	Al_2O_3	SiO_2/Al_2O_3
Series 1–10			
1	77.33	22.66	3.41
2	70.77	29.22	2.42
3	74.93	25.06	2.99
4	79.04	20.95	3.77
5	82.29	17.70	4.64
6	85.15	14.84	5.73
7	87.33	12.66	6.89
8	89.09	10.90	8.17
9	81.67	18.32	4.45
10	85.25	14.74	5.78
Series A–L			
A	84.11	15.88	5.29
B	74.50	25.50	2.92
C	78.61	21.38	3.67
D	82.65	17.34	4.76
E	85.79	14.20	6.04
F	87.95	12.04	7.30
G	90.15	9.84	9.16
H	91.98	8.01	11.48
I	87.24	12.75	6.84
L	89.74	10.25	8.75

Discussion of the Results

As was foreseen on the basis of the abovementioned reservation, the behavior of the two series of cement under study is different according to the method adopted for checking the chemical resistance.

While all pozzolanic cements show generally a good resistance by the method of storage in aggressive solution, confirming the results in practice, they behave differently under the Anstett test, according to their composition.

In particular, all the pozzolanic cements of the series indicated by letters proved resistant to the attack of the aggressive solution. Among the pozzolanic cements of the numbered series, specimen No. 9 showed its first cracks after 6 months, and appeared fissured after 1 yr (table 4). As was to be expected, the specimens manufactured with the two portland cements appeared attacked when the test was over. The specimens prepared with normal portland cements are entirely disintegrated, while those of low-iron-modulus cement show only some cracks. The etching of the latter was very slow, and the first cracks appeared after 90 days, when the specimens of normal portland cement were already split.

In figures 3 and 4 the expansion as percentage of the initial diameter of the specimens is plotted against time for the pastes of series A–L and for those of series 1–10, respectively.

TABLE 4. *Chemical resistance test of pozzolanic cement samples*

Behavior of specimens prepared with porous 1:3 mortar etched with an aggressive solution (3 percent $MgSO_4 \cdot 7H_2O$)—Specimen size 4 x 4 x 16 cm

Sample	Appearance of specimens at different curing times			
	1 month	3 months	6 months	1 yr
Series 1–10				
1	First cracks	Fissured	Disintegrated	Disintegrated.
2	Sound	Sound	Sound	Sound.
3	do	do	do	Do.
4	do	do	do	Do.
5	do	do	do	Do.
6	do	do	do	Do.
7	do	do	do	Do.
8	do	do	do	Do.
9	do	do	First cracks	Fissured.
10	do	do	Sound	Sound.
Series A–L				
A	Sound	First cracks	First cracks	Fissured.
B	do	Sound	Sound	Sound.
C	do	do	do	Do.
D	do	do	do	Do.
E	do	do	do	Do.
F	do	do	do	Do.
G	do	do	do	Do.
H	do	do	do	Do.
I	do	do	do	Do.
L	do	do	do	Do.

Table 3 shows the amounts of soluble silica and alumina for the two series of pastes after 90 days curing, given as percentages of the sum (sol. SiO_2+sol. Al_2O_3) related to the calcined sample, and the ratio of sol. SiO_2/sol. Al_2O_3.

The behavior of the two series of pozzolanic cements under the Anstett test is particularly indicative of the influence of the composition of pozzolanic materials.

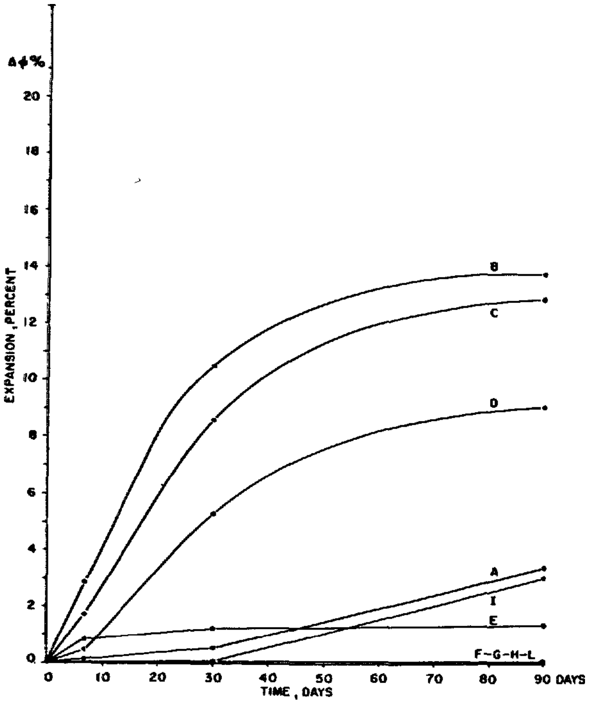

FIGURE 3. *Expansion of Anstett test specimens.*
Cements: Series A–L

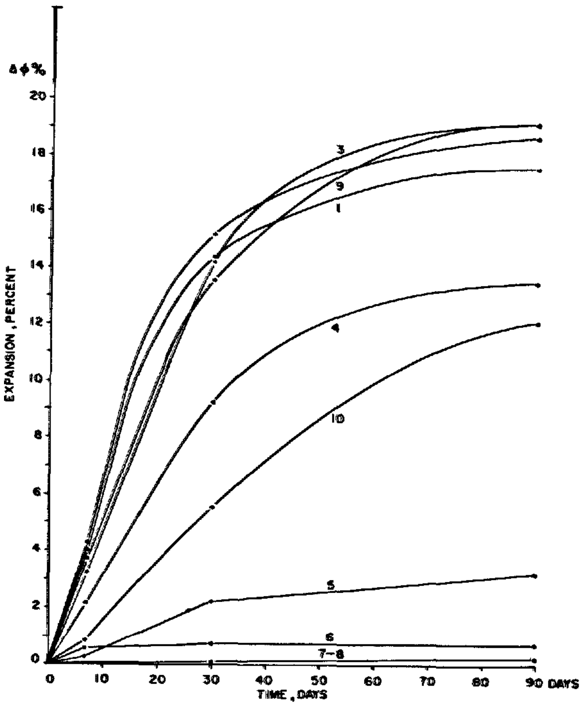

FIGURE 4. *Expansion of Anstett test specimens.*
Cements: Series 1-10

Already after 7 days, cements B, C, and D show a higher expansion than that of cement A without pozzolanic addition; after 90 days the percentage expansion of cements B and C is four times greater than that of cement A, while that of D is three times greater.

The different expansivity of cement A in comparison with cements B, C, and D and that of cements B and C versus cement D is due to the reactive alumina of pozzolanic material P_2. The lower expansivity of cement D is due to the smaller content of pozzolana P_2 rather than to the presence of pozzolana P_1. In fact the binary cement I containing 10 percent of pozzolana P_1, as cement D, shows a degree of expansion scarcely different from that of cement A without pozzolanic addition.

The low-iron-modulus clinker becomes resistant to the test when 20 percent of pozzolana is added, a result which agrees with the behavior of cements E, F, G, and H.

The results obtained with cements E, F, and I are indicative of the role played by the alumina of pozzolana P_2. Although for the first two cements the amount of reactive alumina supplied by pozzolana is still appreciable, as appears by comparing the values of soluble alumina with the silica/alumina ratio of the three cements (table 3), nevertheless resistance to the test is reached by cement E. On the other hand, for the cement F the reactivity to the sulfate is quite negligible.

As all the soluble alumina of cement I is due to the clinker, and the amount of clinker in cements E and F is only 65 percent against 90 percent for cement I, we can deduce that the alumina in the clinker and the reactive alumina in the pozzolana would not be equivalent as regards the sulfate susceptibility of a pozzolanic cement paste.

Such a conclusion is confirmed by the results obtained for the series 1–10 of the higher-iron-modulus cements. The decisive influence of the alumina in the clinker, compared with that of the reactive alumina in the pozzolana, is shown from the behavior of cements 1, 2, 3, and 9, which, at the different curing ages, present nearly identical expansions. The influence of the clinker composition becomes even more evident for cement 10 which appears highly expansive in contrast to the corresponding cement L in the series prepared with the low-iron-modulus clinker.

Cements 4 and 5, although containing 10 and 15 percent of pozzolana P_1 and 25 and 20 percent of pozzolana P_2 respectively, present a percentage expansion which is of the same order of that of cement 10 for the former, and about half as large for the latter. Cement 6, whose expansivity remains within the limits allowed by the test, demonstrates that the substitution of 15 parts of clinker by 15 parts of pozzolana P_2 is sufficient to allow the 20 parts of pozzolana P_1 to give the resulting cement a good resistance to the test.

The inequivalence of the influence of the reactive alumina in pozzolana and of the alumina in clinker on the sulfate susceptibility of pozzolanic cement pastes cannot be explained, at least at the present stage of knowledge, assuming that the reactive alumina of the pozzolana is combined in a form different from tetracalcium aluminate hydrate, which, together with the ettringite, constitutes, at the shortest curing times, the hydration product of tricalcium aluminate. As was related by Prof. Malquori, the reactive alumina of pozzolana P_2 combines with calcium hydroxide to form tetracalcium aluminate hydrate and the silicoaluminate of Strätling [5]; in the mortars of lime and pozzolana, and in those of pozzolanic cement [6], it was possible to ascertain only the presence of the tetracalcium aluminate hydrate and not that of the silicoaluminate.

The formation of the silicoaluminate is likely to occur in pastes water-cured for a long period, but even if we accept this assumption, which is not important for the aim of our discussion since by the Anstett method the test is carried out on pastes previously cured for only 15 days, it must be remembered that Malquori and Cirilli [7] stated also that the silicoaluminate decomposes in the presence of SO_4^{2-} ions and of $Ca(OH)_2$.

The following assumption appears the most acceptable, and it is furthermore, one of the most probable among those which explain the mechanism of the action of pozzolana P_1 in regard to the behavior of cements in the Anstett test. The reactive alumina and silica of pozzolana are thoroughly mixed in the glass phase, and therefore the product of the lime-alumina reaction will be embodied in the calcium silicate gels, the relative amount of which is much higher.

Recalling the particular geologic nature of pozzolana P_2 [9], there is no plausible reason to suppose a nonhomogeneous distribution of the composition of the glass, at least as regards the insoluble oxides such as silica and alumina. The difficulties met with in the microscopic analysis of the mortars are also evidence that the products of the lime-alumina reaction appear protected by the calcium silicate gels much more than in clinker, where dispersion between calcium silicates and aluminates is undoubtedly lower.

Such assumptions are in accordance with the different sulfate susceptibilities of clinkers of the same composition, but with a different content of glass phase, that is, with different content of crystalline calcium aluminate.

The X-ray examination of the pastes showed that the expansion is in direct relationship with the formation of ettringite. In the nonexpansive cement pastes the three main reflections of ettringite at 9.82, 5.71, and 3.86 A, respectively, are scarcely visible and, for some cements, unnoticeable, while in the pastes of expansive cements ettringite constitutes one of the predominant phases.

In the pastes of pozzolanic cement the very intense reflection of calcium hydroxide at $2\theta=18°$ has a very weak intensity, and in all the pastes with high content in pozzolana P_1 it is completely absent.

Conclusions

On the basis of the results hitherto related, the role of pozzolana P_1, rich in reactive silica, gains a particular importance. The influence of this pozzolana on the behavior of the two series of cements under testing shows two different aspects:

(1) It reduces the reactivity of pozzolanic material P_2 with calcium hydroxide.

(2) It reduces, and at certain ratios suppresses, the sulfate susceptibility of the cement.

The mechanism by which pozzolana P_1 affects the reactivity of pozzolana P_2 depends also on the reaction rate of both materials with calcium hydroxide. Pozzolana P_1 reacts at a higher rate than pozzolana P_2, and it is, therefore, possible to suppose that in a pozzolanic cement containing the two materials the hydrolysis lime is fixed principally by the silica of pozzolana P_1. Then the amount of the newly formed calcium aluminates derived from the alumina of pozzolana P_2 obviously will be lower than in a binary pozzolanic cement containing equal ratios of the same clinker and the same pozzolana.

This conclusion is confirmed by the fact that in the pozzolanic cement under examination, with an addition of 35 percent, the amount of soluble alumina obtained is not proportional to, but is lower than that corresponding to the quantity of the pozzolana P_2 present.

The influence of pozzolana P_1 on the susceptibility of the cement to sulfate attack may be included in what we have already said about the reasons for the inequivalence between the reactive alumina in the pozzolana and the alumina in the clinker.

It seems reasonable to suppose that calcium silicate hydrate gels, produced by the reaction of silica and pozzolana with hydrolysis calcium hydrate, exert an efficient protective action on the aluminates which is probably due to the very low diffusion rate of SO_4^{2-} ions through the gels.

However we cannot exclude the possibility that the stability of aluminates and ettringite in the absence of calcium hydroxide may be endangered by the presence of reactive silica. It is possible that both the above-mentioned assumptions are valid, since the one does not exclude the other, but each requires an experimental confirmation; therefore we are carrying out our investigation in this direction.

At the moment, we would point out particularly the decisive importance of the reactive silica content of the pozzolanic addition, and, in this connection, it is noteworthy that the chemical resistance of pozzolanic cement is closely connected with the relationship that may be established between reactive silica and alumina present in the same cements.

For this reason, such a relationship makes it possible to control the chemical resistance of a pozzolanic cement until it is able to withstand the severe conditions of the Anstett test, which although very far from reproducing the usual attack conditions, is nevertheless significant since it indicates an absolute intrinsic resistance of the binder itself.

From the reported data it would seem that the limited value of the above-mentioned ratio must be about 6 in order that the protective action of the silica become efficient under the conditions of the Anstett test.

Of course, in most cases, it is not necessary to reach such high values, which, however, could be requested for special uses.

It is therefore possible to prepare, by choosing suitable qualities of pozzolanic addition, highly resistant cements of this type. These cements, in this sense, can be compared to high-alumina and supersulfated cements. These particular types of pozzolanic cements have been used industrially in Italy for some years now, with results that may be considered wholly satisfactory.

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Paper VIII–S5. Refractory Barium-Aluminous Cement and Concrete*

Al. Braniski

Synopsis

Part I. Refractory cement. Eight refractory barium-aluminous cements with increasingly improved technological properties were prepared in the laboratory, and their physical, chemical, and mechanical properties were studied.

Certain theoretical and practical considerations concerning their mineralogical constitution are presented. Computation of their potential phase compositions is outlined, and the chemical reactions which take place during the hydration of these new cements are discussed.

The fire resistance of the barium-aluminous cements varies between 1,730 and 1,825 °C, their tensile strengths (at 7 days) vary between 30.4 and 36.9 and their compressive strengths (also at 7 days) between 380 and 445 kg/cm.^{2}

The effect of high temperatures (to 1,300 or 1,400 °C) on the dehydration and cold compressive strength of the hardened (hydrated) barium-aluminous cement was studied, and comparison is made with calcium-aluminous cement, strontium-aluminous cement, barium silicate cement, strontium silicate cement, and portland cement. The refractory barium-aluminous cement is recommended as a suitable cementing material for the production of basic highly refractory concrete.

Part II. Concrete, refractory and highly refractory. Nonrefractory, refractory, and highly refractory concretes were prepared in the laboratory by using white sintered bauxite or wastes of fire-clay, corundum, chrome-magnesite, and magnesite bricks with portland cement (with finely ground admixtures), conventional aluminous cement, white aluminous cement with monocalcium aluminate base, refractory aluminous cement with calcium dialuminate base, and two types of refractory barium-aluminous cement. Study was made of the dependence of refractoriness and resistance to thermal shock of the resulting concretes on the nature of the cement used.

Using the same aggregates and the two refractory barium-aluminous cements in different proportions, a number of refractory and highly refractory concretes were prepared and examined for their more important properties. These refractory and highly refractory concretes exhibit an extraordinary resistance to thermal shock, and the following refractoriness: fire-clay concretes, 1,670 to 1,690 and 1,730 to 1,745 °C, respectively; bauxite concretes 1,750 to 1,790 and 1,790 to 1,825 °C, respectively; corundum concretes 1,865 to 1,910 °C; chrome-magnesite concretes 1,880 to 1,960 °C; and magnesite concretes 1,920 to 1,980 °C.

Also studied were the effect of high temperatures on the dehydration and cold compressive strengths of concretes with refractory barium-aluminous cement, the relation of cold compressive strengths of concretes—uncalcined or calcined at 1,000 or 1,400 °C, respectively—to content of barium-aluminous cement, and the effect of cement content on Seger-cone collapse points of these concretes.

It is concluded that refractory and highly refractory concretes with refractory barium-aluminous cement are greatly superior to those with refractory aluminous cement with calcium dialuminate base, and thus to any refractory or highly refractory concrete made with any other known refractory cement.

Résumé

Première partie: Ciment réfractaire. L'auteur a obtenu au laboratoire huit ciments réfractaires alumineux de baryum aux caractéristiques technologiques graduellement améliorées. Il en étudie leur propriétés physiques, chimiques et mécaniques, fait quelques considérations théoriques et pratiques sur leur constitution minéralogique, sur le calcule de leur composition potentielle ou phasale, ainsi que sur les réactions chimiques qui ont lieu lors de l'hydratation de ces nouveaux ciments.

Les limites des résistances pyroscopiques des ciments réfractaires alumineux de baryum sont 1,730 et 1,825 °C, celles des résistances à la traction (après 7 jours) 30.4 et 36.9 et celles des résistances à la compression (après 7 jours) 380 et 445 kg/cm^2.

L'étude porte encore sur: l'effet des températures élevées (1,300 ou 1,400 °C) sur la déshydratation et les résistances à la compréssion à la température ordinaire du ciment réfractaire alumineux de baryum hydraté, en comparaison avec les ciments alumineux de calcium et de strontium et avec les ciments siliceux de baryum, de strontium et de calcium (ciment portland).

L'auteur recommande le ciment réfractaire alumineux de baryum comme le meilleur liant pour la production des bétons basiques super-réfractaires et réfractaires.

Deuxième partie: Béton réfractaire et super-réfractaire. L'auteur réalise au laboratoire des bétons nonréfractaires, réfractaires et super-réfractaires, en utilisant des agrégats réfractaires de bauxite frittée, de chamotte, de corindon, de chrome-magnésie et de magnésie avec du ciment portland (à ajouts très fins), du ciment fondu, du ciment blanc alumineux à base d'aluminate monocalcique, du ciment réfractaire alumineux à base de dialuminate

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de calcium, et deux sortes de ciments réfractaires alumineux de baryum. Il en étudie l'effet de la nature du ciment utilisé sur la réfractarité et la résistance aux variations brusques de température de ces bétons.

Utilisant les mêmes agrégats réfractaires et les deux sortes de ciments réfractaires alumineux de baryum en différents quantités, on a obtenu une série de bétons réfractaires et super-réfractaires et étudié leur propriétés spécifiques. Ces bétons réfractaires et super-réfractaires possèdent des résistances exceptionelles aux variations brusques de température et les résistances pyroscopiques suivants: bétons réfractaires à base d'argile 1,670 à 1,690 et 1,730 à 1,745 °C, de bauxite 1,750 à 1,790 et 1,790 à 1,825, de corindon 1,865 à 1,910, de chrome-magnésie 1,880 à 1,960 et de magnésie 1,920 à 1,980 °C.

L'étude porte aussi sur: l'effet des hautes températures sur la déshydratation et les résistances à la compression à la température ordinaire des bétons à ciment réfractaire alumineux de baryum, l'influence de la teneur en ciment réfractaire alumineux de baryum sur les résistances à la compression à la température ordinaire des bétons noncalcinés et calcinés à 1,000 ou 1,400 °C et l'effet de la teneur en ciment sur la résistance pyroscopique de ces nouveaux bétons réfractaires.

Pour conclure l'auteur montre que les bétons réfractaires et super-réfractaires à ciment réfractaire alumineux de baryum sont beaucoup supérieurs aux bétons à ciments réfractaire alumineux à base de dialuminate de calcium et par conséquent aux bétons réfractaires et super-réfractaires à n'importe quel ciment réfractaire connu.

Zusammenfassung

Teil I—Feuerfester Zement. Der Verfasser stellt im Laboratorium acht feuerfeste Barium-Tonerdezemente, mit stetig verbesserten technologischen Merkmalen her, und untersucht einige ihrer physikalischen, chemischen und mechanischen Eigenschaften.

Er macht ferner einige theoretische und praktische Betrachtungen über ihre mineralogische Konstitution, über die Berechnung ihrer potentiellen (phasalen) Zusammensetzung und über die chemischen Reaktionen, welche bei der Hydratation dieser neuen Zemente stattfinden.

Die Feuerfestigkeit der erhaltenen Barium-Tonerdezemente schwankt zwischen 1,730 und 1,825 °C, ihre Zugfestigkeiten (nach 7 Tagen) zwischen 30.4 und 36.9 und ihre Druckfestigkeiten (ebenfalls nach 7 Tagen) zwischen 380 und 445 kg/cm^2.

Der Verfasser untersucht schliesslich den Einfluss hoher Temperaturen (bis 1,300 bzw. 1,400 °C) auf die Entwässerung und die Kaltdruckfestigkeiten des erhärteten (hydratisierten) Barium-Tonerdezementes im Vergleich zum Kalzium-Tonerdezement, Strontium-Tonerdezement, silikatischem Bariumzement, silikatischem Strontiumzement und Portlandzement und empfiehlt den feuerfesten Barium-Tonerdezement als geeignetstes Bindemittel für die Herstellung basischer hochfeuerfester Betone.

Teil II—Feuerfester und hochfeuerfester Beton. Der Verfasser stellt im Laboratorium aus weissem Sinterbauzit bzw. Abfällen von Schamotte-, Korund-, Chrommagnesit- und Magnesitsteinen und Portlandzement (mit fein vermahlenen Zusatzstoffen), gewöhnlichem Tonerdezement, weissem Tonerdezement auf Monokalziumaluminat-Basis, feuerfestem Tonerdezement auf Kalziumdialuminat-Basis und zwei Arten feuerfestem Barium-Tonerdezement als Bindemittel nichtfeuerfeste, feuerfeste und hochfeuerfeste Betone her und untersucht die Abhängigkeit der Feuerfestigkeit und Temperaturwechselbeständigkeit der hergestellten Betone von der Art der als Bindemittel verwendeten Zemente.

Aus denselben Zuschlagstoffen und zwei feuerfesten Barium-Tonerdezementen in verschiedenen Verhältnissen stellt er eine Anzahl feuerfester und hochfeuerfester Betone her und untersucht ihre wichtigsten Eigenschaften. Diese hochwertigen feuerfesten und hochfeuerfesten Betone weisen eine aussergewöhnliche Temperaturwechselbeständigkeit und folgende Feuerfestigkeiten auf: Schamottebetone 1670–1690 bzw. 1,730–1,745 °C, Bauxitbetone 1,750–1,790 bzw. 1,790–1,825 ° C, Korundbetone 1,865–1,910 °C, Chrommagnesitbetone 1,880–1,960 und Magnesitbetone 1,920–1,980 °C.

Der Verfasser untersucht ferner den Einfluss hoher Temperaturen auf die Entwässerung und Kaltdruckfestigkeiten der Betone aus feuerfestem Barium-Tonerdezement, die Abhängigkeit der Kaltdruckfestigkeiten der ungebrannten und bei 1000 bzw. 1400 °C gebrannten Betone vom Barium-Tonerdezementgehalt und den Einfluss des Zementgehaltes auf den Segerkegel-Fallpunkt dieser Betone.

Er stellt schliesslich fest, dass der hochfeuerfeste Beton aus feuerfestem Barium-Tonerdezement dem hochfeuerfesten Beton aus feuerfestem Tonerdezement auf Kalziumdialuminat-Basis, und somit auch jedem feuerfesten oder hochfeuerfesten Beton aus anderem bekannten, feuerfesten Zement, weit überlegen ist.

Part I. Refractory Cement

Introduction

Conventional cements—portland cement and aluminous cement—are nonrefractory hydraulic cementing materials (they soften and even fuse below 1,580 °C). When a high-strength refractory concrete is desired, preference is given to *refractory* hydraulic binders, such as refractory aluminous cement with calcium dialuminate base or refractory barium-aluminous cement [1].[1]

Refractory aluminous cements with calcium dialuminate base [2] were studied in 1943 in the

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[1] Figures in brackets represent the literature references at the end of this paper.

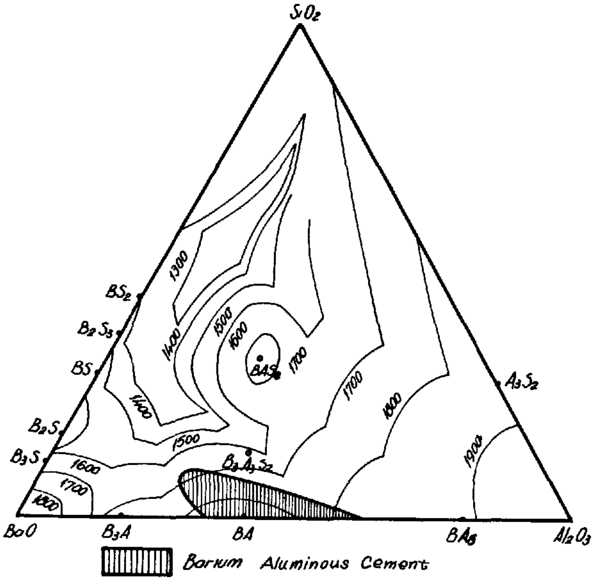

FIGURE 1. *Position of refractory barium-aluminous cement in the ternary system: barium oxide-alumina-silica, according to Toropov, Galachov, and Bondar-Braniski.*

United States of America and were produced industrially in England and France by 1950.

Barium-aluminous cements [1] are ordinary aluminous cements in which calcium oxide is replaced by barium oxide. The clinker is burned to sintering or fusion.

When these cements contain fluxing materials (iron oxide, silica, magnesia, soda, and potassa) in only very small quantities, they become *refractory* barium-aluminous cements with a fire resistance between 1,730 and 1,825 °C.

Figure 1 shows the location of refractory (without flux) barium-aluminous cement in the ternary system: barium oxide-alumina-silica [3] according to Toropov, Galachov, and Bondar-Braniski.

The diagram shows that the point of fusion, i.e., collapse of the Seger cone, of a refractory barium-aluminous cement is higher the closer its chemical composition approaches that of monobarium aluminate, BA.

Figure 2 presents a comparison of three binary systems: the system lime-alumina, according to Rankin and Wright [4], corrected by recent writers; the system strontium oxide-alumina according to Wartenberg and Reusch [5]; and the system barium oxide-alumina according to Toropov and Galachov [6].

The calcium, strontium, and barium aluminous cements show the alkaline earth monoaluminates as characteristic components.

Figure 2 shows that strontium monoaluminate, SrA, and barium monoaluminate, BA, have much higher fusion points than calcium monoaluminate, CA, or calcium dialuminate, CA_2.

Consequently, the strontium- and barium-aluminous cements must be considerably more fire-resistant than the corresponding calcium-aluminous cement, a fact which is proved experimentally every time a comparison is made.

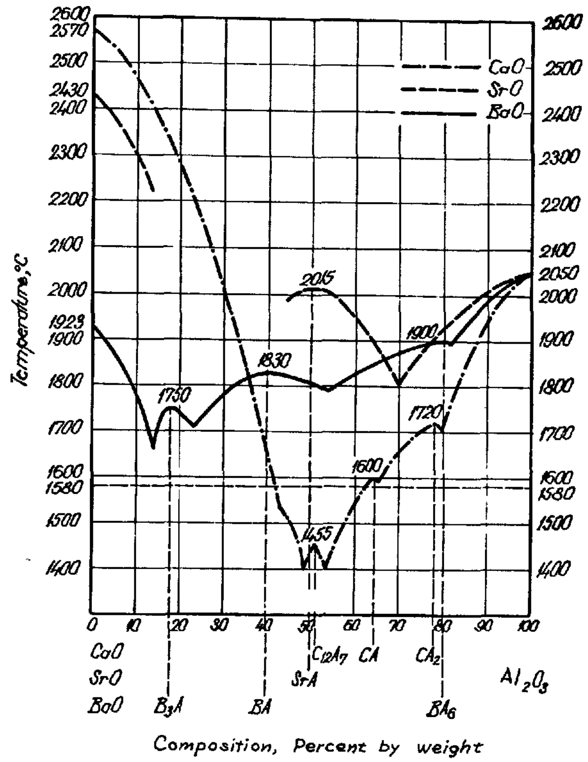

FIGURE 2. *Comparative diagram of the binary systems:* $CaO\text{-}Al_2O_3$, $SrO\text{-}Al_2O_3$, *and* $BaO\text{-}Al_2O_3$.

Experimental Procedure

Raw Materials for the Manufacture of a Refractory Barium-Aluminous Cement

Synthetic barium carbonate and barium sulfate, as well as alumina and fire clay, were used to produce refractory barium-aluminous cements. The chemical compositions of these raw materials are given in table 1.

TABLE 1. *Chemical compositions of raw materials used*

	Synthetic barium carbonate	Synthetic barium sulfate	Industrial alumina	Fire clay
	Percent	*Percent*	*Percent*	*Percent*
SiO_2			0.66	67.85
Al_2O_3			98.60	20.37
Fe_2O_3			.11	3.24
CaO			.46	.82
$BaCO_3$	98.10			
$BaSO_4$		99.82		
BaS	.81	.01		
MgO			.24	.43
Alkalies			.77	.57
Loss on ignition				6.72
Insoluble in HCl	.76			

Procedure in Synthesizing Refractory Barium-Aluminous Cement

The synthesis of barium-aluminous cement [1] is identical with that of conventional (calcium) aluminous cement, with the only difference that the burning temperature of the clinker is somewhat higher, thus causing a number of operational difficulties.

Cooling of cement clinker should not be rapid, as highest mechanical strengths are obtained with cements ground from slowly cooled clinker.

The finely ground materials were combined in specified proportions and homogenized in a dry state. Burning of the samples was carried out at temperatures between 1,580 and 1,630 °C, depending on the composition of the mix. Duration of burning amounted to 7 to 8 hr, of which 5 to 6 hr were spent in raising the temperature and 2 hr at maximum temperature.

The temperature was controlled by means of an optical pyrometer and Seger cones 26, 27, and 28.

Considerations on Refractory Barium-Aluminous Cements

Refractory barium-aluminous cements consist mainly of a large proportion of monobarium aluminate, $BaO \cdot Al_2O_3$, and a small proportion of dibarium silicate, $2BaO \cdot SiO_2$.

According to Wartenberg and Reusch, there exists only one barium aluminate, monobarium aluminate; according to Toropov, there are three, namely: tribarium aluminate, $3BaO \cdot Al_2O_3$, monobarium aluminate, $BaO \cdot Al_2O_3$, and barium hexaluminate, $BaO \cdot 6Al_2O_3$.

The binary system $BaO–Al_2O_3$ was studied in part by Wartenberg and Reusch [5], and in detail by Toropov and Galachov [6], and by Lagerqvist, Wallmark, and Westgren [7].

A comparison (fig. 2) of the diagrams of the system $BaO–Al_2O_3$, presented by Toropov and Galachov [6], of the system $SrO–Al_2O_3$ by Wartenberg and Reusch [5], and of the system $CaO–Al_2O_3$ by Rankin and Wright [4], shows that not very basic barium aluminates, of the type of barium monoaluminate and barium hexaluminate and their mixtures, in general have a much higher point of fusion, or higher fire resistance, than the respective calcium aluminates.

The regions around barium monoaluminate and calcium dialuminate correspond to refractory barium-aluminous cements and refractory calcium-aluminous cements.

We deduce further, that production of barium-aluminous cements with a base of barium aluminates of a higher alumina content than monobarium aluminate is of little significance, quite in contrast to calcium aluminous cement, for which the industrially produced aluminous cement with calcium dialuminate base results in increased fire resistance and represents a considerable advance.

Computation of the mineralogical (potential or phase) composition of a refractory barium-aluminous cement on the basis of its chemical analysis proceeds in accordance with Bogue's well-known method [8] for the portland cements, or according to Parker's special method [9] for conventional (calcium) aluminous cements, with the aid of simple mathematical formulae, derived on the basis of an assumed sequence of formation of the mineralogical components.

As refractory barium-aluminous cements, produced by sintering in an oxidizing atmosphere, contain very little Fe_2O_3 and hardly any FeO, one can ignore the possibility that clinkers of iron-containing aluminous cements will contain hexacalcium tetraluminate ferrosilicate, $6CaO \cdot 4Al_2O_3 \cdot FeO \cdot SiO_2$, and hexacalcium tetraluminate magnesium silicate, $6CaO \cdot 4Al_2O_3 \cdot MgO \cdot SiO_2$, two compounds discovered by Parker [9], and can assume the entire iron content to be in the Fe_2O_3 state.

Considering that alkali oxides Na_2O and K_2O become volatilized below 1,350 °C, one can assume the following sequence for the computation of the mineralogical components of refractory barium-aluminous cement:

1. tetracalcium aluminoferrite, $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$;
2. tetrabarium aluminoferrite, $4BaO \cdot Al_2O_2 \cdot Fe_2O_3$;
3. gehlenite, $2CaO \cdot Al_2O_3 \cdot SiO_2$;
4. dibarium silicate, $2BaO \cdot SiO_2$;
5. monocalcium aluminate, $CaO \cdot Al_2O_3$, and
6. monobarium aluminate, $BaO \cdot Al_2O_3$.

When there is an excess of Al_2O_3, an additional formation of a certain quantity of barium hexaluminate $BaO \cdot 6Al_2O_3$ may take place, according to Toropov [6] or of $3BaO \cdot 16Al_2O_3$, according to Lagerqvist [7]; additional formation of tribarium aluminate, $3BaO \cdot Al_2O_3$, may occur if there is excess BaO.

Barium dialuminate, $BaO \cdot 2Al_2O_3$ (corresponding to a calcium dialuminate $CaO \cdot 2Al_2O_3$) does not appear to exist. Its existence is confirmed by neither Toropov nor Lagerqvist.

Swayze [10] and other researchers have proved that tetracalcium aluminoferrite, known as brownmillerite, does not exist as a chemical compound, but only as a component of a series of solid solutions between the following chemical compounds: the hypothetical dicalcium aluminate, $2CaO \cdot Al_2O_3$, and dicalcium ferrite, $2CaO \cdot Fe_2O_3$, or between the given chemical compounds hexacalcium dialuminoferrite, $6CaO \cdot 2Al_2O_3 \cdot Fe_2O_3$, and hexacalcium aluminodiferrite, $6CaO \cdot Al_2O_3 \cdot 2Fe_2O_3$.

However, as the computation formulas for the mineralogical components of the cements are derived on the basis of tetracalcium aluminoferrite, it and tetrabarium aluminoferrite, $4BaO \cdot Al_2O_3 \cdot Fe_2O_3$, are treated as present.

In the following text we use: $S=SiO_2$; $A=Al_2O_3$; $F=Fe_2O_3$; $C=CaO$; and $B=BaO$. According to whether less or more than 4 molecules of CaO per molecule of Fe_2O_3 are present in the cement, two cases are distinguished in computing the mineral components (potential composition) of barium-aluminous cements from the chemical analysis.

In the first case, the lime is computed as tetracalcium aluminoferrite, C_4AF. From the remainder of the iron oxide one computes the content of tetrabarium aluminoferrite, B_4AF.

There follows a computation of dibarium silicate, B_2S, equivalent to all the silica, and computation of monobarium aluminate, BA, and additional tribarium aluminate, B_3A (if there is excess barium oxide), or additional barium hexaluminate, BA_6 (if there is excess alumina).

In the second case, the entire iron-oxide content is computed as tetracalcium aluminoferrite, C_4AF, and the excess lime as gehlenite, C_2AS, insofar as silica is available.

If there is residual free lime one computes the corresponding content of monocalcium aluminate, CA, without computing any dibarium silicate B_2S. Finally one computes the content of the main cement constituent, monobarium aluminate, BA, with, as the case may be, some additional tribarium aluminate, B_3A, or barium hexaluminate, BA_6.

When free lime is not sufficient for complete conversion of the silica to gehlenite, one computes, up to full silica utilization, the content of dibarium silicate, B_2S, and, subsequently, the content of monobarium aluminate, BA, with accompanying barium hexaluminate, BA_6, or tribarium aluminate, B_3A.

For computing the potential (phase) composition of barium-aluminous cement, the computation formulae, establishing the percentages of the various mineralogical components, are derived as for portland cement [8].

Synthesized Barium-Aluminous Cements and Their Properties

Using 5 parts of industrial alumina, 14.5 parts of synthetic barium carbonate, and 1.5 parts of refractory clay, or 5 parts industrial alumina, 17.5 parts industrial barium sulfate, and 1.5 parts by weight of refractory clay, of the compositions given in table 1, we produced two refractory barium-aluminous cements with identical technological properties (refractoriness 1,730 °C=SK 33), of which the first has the following chemical composition: 5.99 percent SiO_2, 29.60 percent Al_2O_3, 0.31 percent Fe_2O_3, 0.20 percent CaO, 63.53 percent BaO, 0.10 percent MgO, and 0.27 percent alkali oxides. (This cement is designated II in table 4.)

Computation of potential composition of refractory barium-aluminous cement II

(Molecular weights: SiO_2, 60.06; Al_2O_3, 101.92; Fe_2O_3, 159.68; CaO, 56.07; BaO, 153.36)

	Compute:	$5.99\ SiO_2+$	$29.60\ Al_2O_3+$	$0.31\ Fe_2O_3+$	$0.20\ CaO+63.53\ BaO$	to the following potential composition
0.20	CaO combines with		$0.09\ Al_2O_3+$	$0.14\ Fe_2O_3$	----------	giving 0.43 C_4AF
	Remainder		$29.51\ Al_2O_3$	$0.17\ Fe_2O_3$	----------	
0.17	Fe_2O_3 combines with		$0.11\ Al_2O_3$	----------	and 0.65 BaO	giving 0.93 B_4AF
	Remainder		$29.40\ Al_2O_3$	----------	62.88 BaO	
5.99	SiO_2 combines with	---------			30.59 BaO	giving 36.58 B_2S
	Remainder	---------		----------	32.29 BaO	
32.29	BaO combines with		$21.46\ Al_2O_3$		----------	giving 53.75 BA
	Remainder	---------	$7.94\ Al_2O_3$	----------	----------	
7.94	Al_2O_3 combines with		----------			4.00 BA giving 11.94 BA_6
	Remainder	---------	----------	----------	----------	49.75 BA giving 49.75 BA

Another refractory barium-aluminous cement was produced from one part industrial clay and two parts by weight synthetic barium carbonate. Its chemical composition is 0.68 percent SiO_2, 39.61 percent Al_2O_3, 0.24 percent Fe_2O_3, 0.37 percent CaO, 58.73 percent BaO, 0.15 percent MgO, and 0.22 percent alkali oxides.

Computation of potential composition of refractory barium-aluminous cement I

	Compute:	$0.68\ SiO_2+$	$39.61\ Al_2O_3+$	$0.24\ Fe_2O_3+$	$0.37\ CaO+$	$58.73\ BaO$	to the following potential composition
0.24	Fe_2O_3 combines with		$0.15\ Al_2O_3$	--------and	0.34 CaO		giving 0.73 C_4AF
	Remainder		$39.46\ Al_2O_3$	----------	0.03 CaO		
0.03	CaO combines with	$0.02\ SiO_2$	$0.03\ Al_2O_3$	----------	---------		giving 0.08 C_2AS
	Remainder	$0.66\ SiO_2$	$39.43\ Al_2O_3$	----------	---------		
0.66	SiO_2 combines with	---------				3.37 BaO	giving 4.03 B_2S
	Remainder	---------		----------	---------	55.36 BaO	
55.36	BaO combines with		$36.80\ Al_2O_3$			------------	giving 92.16 BA
	Remainder	---------	$2.63\ Al_2O_3$	----------	---------	------------	
2.63	Al_2O_3 combines with		----------				1.31 BA giving 3.94 BA_6
	Remainder	---------	----------	----------	---------	------------	90.85 BA giving 90.85 BA.

The setting time and soundness of this refractory barium-aluminous cement are normal, its refractoriness is 1810 °C, and its mechanical strengths at 7 and 28 days, respectively, in kg/cm² are : tensile strength—34.8 and 37.5 respectively, compressive strength—416 and 462 respectively.

As it was established that monobarium aluminate has excellent setting properties, has normal set, and hardens very rapidly in the first 24 hours, as is the case with ordinary calcium-aluminous cement, and, in addition, that silica acts as a fluxing agent, a series of five refractory barium-aluminous cements were prepared of pure raw materials with monobarium aluminate as base and with decreasing silica content. In this manner the refractoriness of these cements can be increased by 120 °C, as shown by table 2.

It was also established that the less silica contained in the cement, the faster the set.

In accordance with the viewpoint of Jules Bied [11], the discoverer of calcium-aluminous cement (ciment fondu), cement A was designed to consist of 2 moles of monobarium aluminate and 1 mole of dibarium silicate. Bied holds that the ordinary aluminous cement should have the following chemical composition:

$$2(CaO{\cdot}Al_2O_3)+2CaO{\cdot}SiO_2$$

Cements A, B, C, D, and E have a steadily decreasing silica content (from 7 to 1 percent), and this corresponds to an increase in monobarium aluminate content from 58 to 94 percent and a drop in dibarium silicate content from 42 to 6 percent. Dibarium silicate acts as a fluxing agent with respect to the highly refractory monobarium aluminate. This fact explains why a drop in dibarium silicate, i. e., in silica content, raises the fire resistance of a cement from 1,750 to 1,825 °C. It follows that fire resistance of barium-aluminous cement increases the more its chemical composition approaches that of monobarium aluminate (with as little silica, iron oxide, magnesium oxide, and alkalies as possible).

However, a low silica content of about 1 percent improves the sintering and reduces the fire resistance of cement by only 50 °C.

As monobarium aluminate and dibarium silicate form far below their fusion temperature, fire-resistant barium-aluminous cements of good quality can be produced by burning at temperatures of incomplete sintering, but above 1,450 °C, on condition that the raw materials used are very finely ground and thoroughly homogenized. It is recommended to cool the cement clinker slowly.

Refractory barium-aluminous cements A, B, C, D, and E, are water soluble. Their solubility in water increases (from cement A to cement E) with decreasing SiO_2, or $2BaO{\cdot}SiO_2$, content and increasing $BaO{\cdot}Al_2O_3$ content, which is natural, as the latter represents the soluble component of the cement.

Tensile and compressive strengths of these cements in kg/cm² at 7 days are given in table 3, their fire resistance in table 2.

Tables 2 and 3 show that the mechanical strengths of refractory barium-aluminous cements are higher the greater their content of monobarium aluminate. Refractory barium-aluminous cements require a much smaller quantity of water for hardening than calcium-aluminous cements.

Due to the high solubility of barium aluminates, the setting and hardening processes of refractory barium-aluminous cements are extremely complex. To investigate them is therefore much more difficult than with ordinary calcium-aluminous cements.

TABLE 2. *Chemical composition, mineralogical components, and refractoriness of some barium-aluminous cements*

Cement	A	B	C	D	E
SiO_2 *percent*	7.0	5.0	3.0	2.0	1.0
Al_2O_3 *percent*	23.2	28.0	32.8	35.2	37.6
BaO *percent*	69.8	67.0	64.2	62.8	61.4
Monobarium aluminate, $BaO{\cdot}Al_2O_3$ *percent*	58	70	82	88	94
Dibarium silicate, $2BaO{\cdot}SiO_2$ *percent*	42	30	18	12	6
Refractoriness °*C*	1,750	1,770	1,790	1,810	1,825

TABLE 3. *Tensile and compressive strengths of some barium-aluminous cements*

Cement	Tensile strength	Compressive strength
	kg/cm²	*kg/cm²*
A	30.4	380
B	29.6	386
C	33.7	401
D	35.4	432
E	36.9	445

The basic reactions of chemical hydration of refractory barium-aluminous cements consist primarily of the hydration reactions of monobarium aluminate and, secondarily, the hydration reactions of dibarium silicate.

Hydration of monobarium aluminate proceeds as follows:

$$BaO{\cdot}Al_2O_3+6H_2O=BaO{\cdot}Al_2O_3{\cdot}6H_2O$$

$$2(BaO{\cdot}Al_2O_3{\cdot}6H_2O) =2BaO{\cdot}Al_2O_3{\cdot}9H_2O+2Al(OH)_3$$

$$2BaO{\cdot}Al_2O_3{\cdot}9H_2O+BaO{\cdot}Al_2O_3 =3BaO{\cdot}Al_2O_3{\cdot}6H_2O+2Al(OH)_3.$$

There is early formation of a large quantity of aluminum hydroxygel or hydrated alumina, in the form of gibbsite ($2Al(OH)_3{=}Al_2O_3{\cdot}H_2O$), which produces an early hardening of cement, with attendant formation of dibarium and tribarium hydroaluminate.

The end products of the hydration process are, accordingly, gels of alumina trihydrate and tribarium aluminate hexahydrate.

Dibarium silicate hydrates much more slowly than monobarium aluminate, according to the reactions:

$$2BaO{\cdot}SiO_2+nH_2O=2BaO{\cdot}SiO_2{\cdot}nH_2O$$

$$2BaO{\cdot}SiO_2{\cdot}nH_2O=BaO{\cdot}SiO_2{\cdot}(n-1)H_2O+Ba(OH)_2$$

Hydrated monobarium silicate contributes during drying (gradual dehydration) to a slow hardening of the cement, as does barium hydroxide, which is readily changed to barium carbonate by contact with the carbon dioxide of the atmosphere.

Cement C was investigated under the microscope before and during hydration.

Thin sections of this cement clinker showed two different phases under the microscope. The first phase consists of isotropic, refractive particles with a glassy appearance. This phase constitutes 80 to 85 percent of the whole and consists of small crystals of white monobarium aluminate.

The second (secondary, 15–20 percent) phase consists of small birefringent dibarium silicate crystals with a higher refractive index.

Concerning the effect of water on this cement, it was established that soon after initial contact with water part of the cement grains dissolve to form an amorphous gel mass.

Ten to twelve hours after formation of the amorphous gel mass from the hydrated alumina there appears in several places under the microscope a series of very small white crystals of tribarium aluminate hexahydrate.

Dehydration of refractory barium-aluminous cement by heating to high temperatures is a very complicated process, which brings about a reduction in mechanical strength and a gradual decomposition of the hardened cement. It takes place at lower temperatures if the temperature increase is slow and the heating is prolonged; and the dehydration thus depends primarily on temperature and, secondarily, on the duration of heating.

Prolonged heating at a lower temperature can, consequently, result in greater impairment of strength in refractory concrete than a shorter heating at a higher temperature.

After 170 hr of heating at 400 to 420 °C, the hardened barium-aluminous cement loses about 92 percent of its original water. The remaining 8 percent is very strongly held and can be driven off only after a very long period of heating at temperatures above 800 °C.

Effect of Higher Temperatures on the Dehydration of Hardened (Hydrated) Refractory Barium-Aluminous Cement

Dehydration of hardened refractory barium-aluminous cement was studied by comparison with conventional (calcium) aluminous cement, strontium-aluminous cement, barium silicate cement, portland cement (calcium silicate cement), and strontium silicate cement, namely, by simultaneous heating of 100-g samples to different constant temperatures.

Heating to 105 °C was carried out in an electrically heated cabinet; further heating to 1,300 °C followed in an electric furnace with silicon carbide rods with automatic temperature control for maintenance of constant burning temperature.

The same specimens were subjected to heating at increasingly higher temperatures.

The water required for setting and hardening of the cements is taken as unity (100 percent) and the various weight losses in grams, obtained by successive weighings, are computed in percent.

The weight losses of hardened (hydrated) cements at increasingly higher, constant burning temperatures are expressed in percent in figure 3.

As can be seem, maximum water loss takes place for all cements below 105 °C, and, indeed, for all aluminous cements (calcium, strontium, barium) to a much greater degree than for silicate cements (portland, strontium, and barium cement). A very pronounced dehydration occurs at the time when "water of constitution" (chemically bound water) is withdrawn from the mineralogical cement components. This happens for calcium- and strontium-aluminous cements between 200 and 400 °C, for barium-aluminous cement between 200 and 500 °C and for silicate cements much later, namely, between 500 and 700 °C for portland cement, between 600 and 800 °C for strontium cement and between 700 and 900 °C for barium cement.

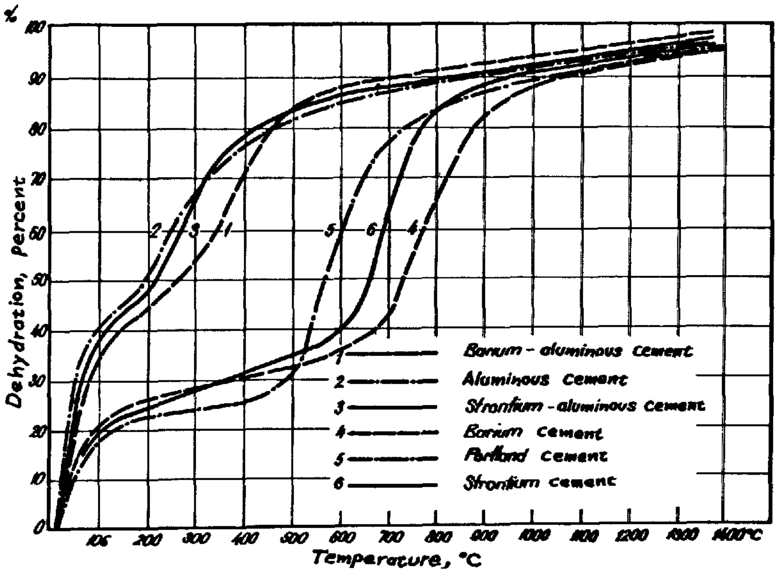

FIGURE 3. *Cement dehydration in percent at different burning temperatures.*

Cold Compressive Strength of Hardened Refractory Barium-Aluminous Cement as a Function of Heating to High Temperatures

Studies involved a comparison between conventional (calcium) aluminous cement, strontium-aluminous cement, barium silicate cement, strontium silicate cement, and portland cement. The 28-day compressive strengths of unheated specimens were taken as a basis of reference (100 percent).

Six-hour heating to constant temperatures proceeded simultaneously for all specimens, namely, to 105 °C in an electric heating cabinet, to temperatures between 300 and 1,300 °C in an electric furnace with silicon carbide rods, and to 1, 400 °C in a laboratory furnace heated with methane gas.

Figure 4 shows that the cold compressive strengths increase by heating to 105 °C, decrease as the temperature is raised, and increase again at 750 °C or 850 to 950 °C, respectively.

According to this, there takes place a partial destruction of the structure of hydrated cement through withdrawal of chemically combined water, followed (during sintering) by a "ceramic strengthening" of the dehydrated dissociation components, with accompanying gain in the corresponding cold compressive strengths of the cements in question.

When burned beyond 1350 °C the cold compressive strengths of all cements exceed their initial values.

The smallest decrease in cold compressive strength is exhibited by barium-aluminous cements, and the largest loss by strontium silicate cement. In general, aluminate cements (barium-, strontium-, and calcium-aluminous cement) show smaller maximum strength losses through heating to higher temperatures than do silicate cements (barium, strontium, and portland cement). Thus, in this respect also, aluminous cements (as binding materials for fire-resistant concrete) have an advantage over silicate cements.

Conclusion

1. Fire resistance (refractoriness) and mechanical strength of refractory barium-aluminous cement are higher the more its chemical composition approaches that of monobarium aluminate, i.e., the lower its content of silica, iron oxide, alkalies, etc., as impurities.

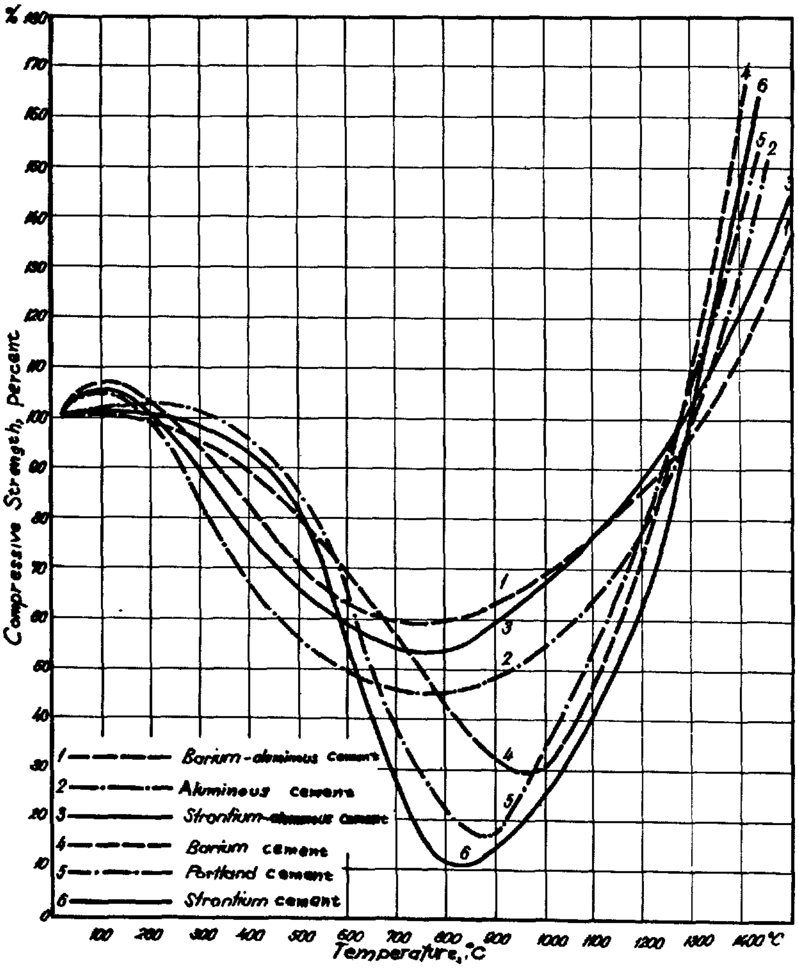

FIGURE 4. *Cold compressive strengths of cements following 6-hr heating to different temperatures.*

2. Refractory barium-aluminous cement fuses with much greater difficulty than the familiar refractory calcium-aluminous cement manufactured with calcium dialuminate base.

3. The setting and hardening properties of barium-aluminous cement are normal; its strengths are exceptionally high after a few hours. Thus barium-aluminous cement is a high-early-strength cement, similar to calcium- and strontium-aluminous cements.

4. In contrast to other cements, barium-aluminous cement is highly water soluble. Thus it is basically not a hydraulic, but an air-hardening cementing material.

5. Hardening of hydrated refractory barium-aluminous cement is produced, first, through the drying of hydrated alumina gel and, second, through the drying of the gels of the hydrated barium-aluminates and barium silicates or crystallization of tribarium-aluminate hexahydrate.

6. Of all known cements, refractory barium-aluminous cement shows the least loss of cold compressive strength through heating to high temperature.

7. On the basis of all the data presented here, refractory barium-aluminous cement is best suited for use in basic highly refractory concrete.

Part II. Concrete, Refractory and Highly Refractory

Introduction

By definition, a refractory concrete is a structural material consisting of a hydraulically hardening cement and suitable refractory aggregate whose Seger cone collapse lies above SK 26 (1,580 °C). A highly refractory concrete is characterized by SK over 36 (1,790 °C).

A highly refractory concrete is a structural material produced without burning, through a chemical bonding in the cold of highly refractory aggregates by means of a refractory cementing material. It differs from "nonburned highly refractory products," which are also denoted "chemically bonded highly refractory structural materials," in that it is a monolithic (jointless) highly refractory product produced *in situ*. Curt Platzmann took out the first patent for the manufacture of refractory concrete in 1922 in Germany. This concrete was resistant only up to 1,000 to 1,100 °C and consisted of coarsely granular fire clay (schamotte) and portland cement with addition of trass or some other finely ground siliceous admixture as binder. Portland cement without such an admixture was proven unsuitable, as the lime liberated during setting remains uncombined and reacts with the moisture of the air during cooling of the concrete to produce undesirable (destructive) unsoundness.

In 1949 in the USSR K. D. Nekrasov [12] brought to a conclusion the study and commercial production of the fire-resistant, but not truly refractory (fire-stable), concrete made with portland cement and ground admixtures.

P. Kestner [13] produced in 1926 the first—inappropriately called—"refractory" concrete made with calcium-aluminous cement (ciment fondu).

In 1934 Braniski [14] reported in a paper on "so-called refractory cements" that all previously known refractory cements, mortars and concretes were in reality not refractory, but only fire resistant to a limited extent, since they could not withstand temperatures above 1,580 °C.

The properties and method of manufacture of refractory aluminous cement concrete formed the subject of studies by Coss and Cent [15], Czernin [16], Hussey [17], Lepingle [18], Möser [19], Giles [20], Williams [21], Robson [22], Wygant and Bulkley [23] and other research workers. Lehmann and Mitusch [24] demonstrated recently that the behavior of refractory calcium-aluminous cement concrete at high temperatures should be interpreted on the basis of its chemical composition, and they derived a number of rules defining the composition of refractory aluminous fused-cement concrete adapted to the requirements of the times.

Figure 5 shows that even when basic highly refractory aggregates are used, highly refractory concrete can be obtained only when it contains *refractory* aluminous cement such as, for example, refractory (no iron oxide) barium-aluminous cement or refractory calcium-aluminous cement with calcium dialuminate base. The latter has been manufactured in France since 1950.

The purpose of the present work is to establish the relation of refractoriness and resistance to thermal shock of concrete (with identical aggregates, grading, degree of compaction, and consistency) to the nature of the cements used, and to examine the more important properties of refractory and highly refractory concrete made with refractory barium-aluminous cements.

Experimental Procedure

Raw Materials Used in the Preparation of the Nonrefractory, Refractory, and Highly Refractory Concretes That Were Studied

Six cements were used in the preparation of the concretes investigated: one portland cement, one conventional high-iron-oxide aluminous cement (ciment fondu), one white aluminous cement with monocalcium aluminate base, one refractory aluminous cement with calcium dialuminate base (of the type produced commercially), and two refractory barium-aluminous cements.

The chemical composition and refractoriness of these cements are given in table 4.

The properties and method of preparation of the two refractory barium-aluminous cements I and II are described in part I of this paper.

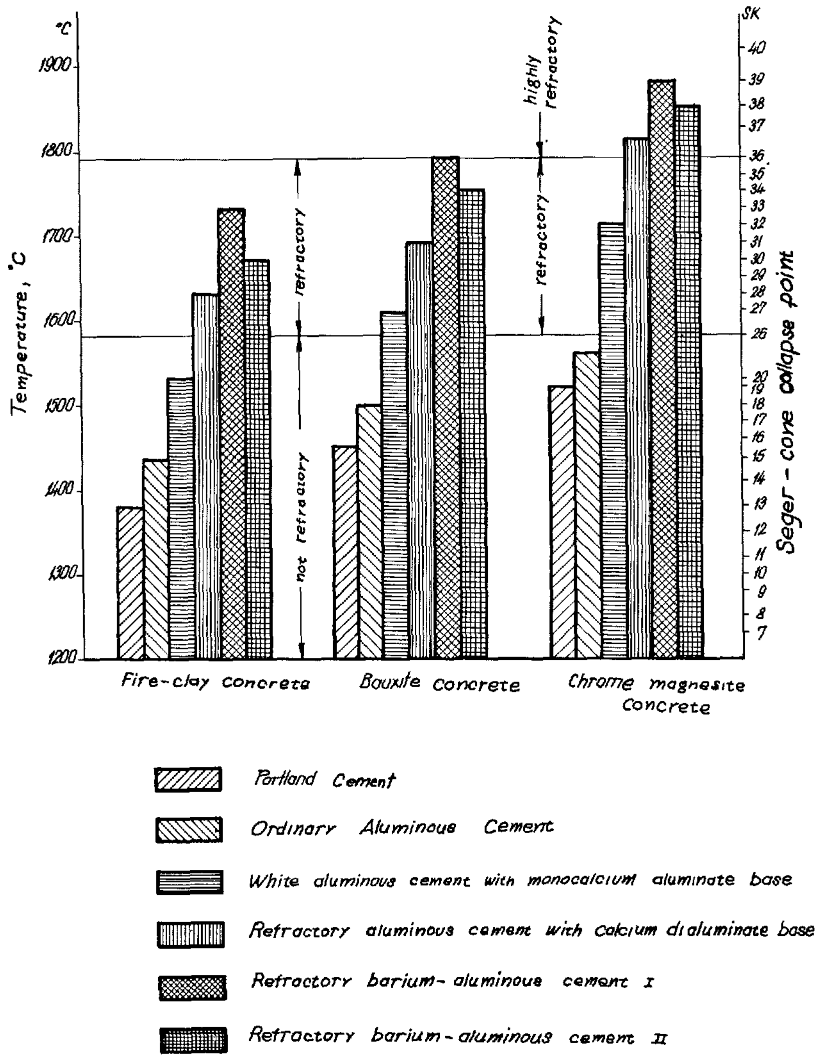

FIGURE 5. *Seger-cone collapse of fire-clay, bauxite, and chrome-magnesite concretes with different cements as binders.*

TABLE 4. *Chemical composition and refractoriness of the cements used*

[Percent]

	Portland cement	Conventional aluminous cement (ciment fondu)	White aluminous cement with monocalcium aluminate base	Refractory aluminous cement with calcium dialuminate base	Refractory barium-aluminous cement	
					I	II
SiO_2	21.43	4.23	0.45	0.34	0.68	5.99
Al_2O_3	5.71	37.18	61.81	72.73	39.61	29.60
Fe_2O_3	3.64	17.35	0.41	0.21	0.24	0.31
CaO	63.32	36.49	33.56	26.49	.37	.20
BaO	-----	-----	-----	-----	58.73	63.53
MgO	1.18	0.66	0.56	0.28	0.15	0.10
Alkalies	-----	-----	-----	-----	.22	.27
SO_3	1.69	-----	-----	-----	-----	-----
Insoluble	1.78	3.81	.25	.18	-----	-----
Loss on ignition	1.57	0.42	-----	-----	-----	-----
Total	100.32	100.14	100.04	100.23	100.00	100.00
Refractoriness						
°C	1,350	1,250	1,520	1,610	1,810	1,730
Sk	12	8	19	27	36/37	33

The following refractory aggregates were used: white sintered bauxite and wastes of fire clay (schamotte), corundum, chrome-magnesite, and magnesite brick. Their more important properties are given in table 5.

Table 6 presents the chemical composition of white sintered bauxite and firebrick wastes.

TABLE 5. *Properties of refractory aggregates used*

Technological properties	Aggregates				
	Fire-brick wastes	White sintered bauxite	Corundum brick wastes	Chrome-magnesite brick wastes	Magnesite brick wastes
Refractoriness *°C*	1,750	1,850	1,930	>2,000	>2,000
Collapse of Seger cone	34	38	40	>42	>42
Cold compressive strength *kg/cm²*	180	240	385	545	694
Apparent porosity *percent*	24	21	17	22	18
Weight per unit volume *g/cm³*	2.00	2.30	3.35	3.05	2.95
Resistance to thermal shock *cycles*	53	42	23	8	6

TABLE 6. *Chemical composition of firebrick wastes and white sintered bauxite*

[Percent]

Chemical composition	Firebrick wastes	White sintered bauxite
SiO_2	58.57	13.61
Al_2O_3	38.42	78.34
Fe_2O_3	2.35	5.85
CaO	.43	.96
MgO	Trace	.64
Alkalies	.47	.60
Total	100.24	100.00

Procedure for the Production of Concrete

In general the preparation of the concretes investigated here was the same as for conventional concrete.

The consistency of the concrete must be plastic, and the concrete should be as well compacted as possible. It is advisable not to wet in advance any porous aggregates, or to wet them only slightly, and to mix them in the dry or semidry condition.

The mechanical strengths of concretes depend—aside from cement content—on the quantity of mixing water and grading of the aggregates.

Too large a quantity of mixing water will produce porous concrete with reduced mechanical strenth. Too little water prevents complete hydration of the cement. An optimum quantity of mixing water should be used, which varies from case to case depending on the nature of the aggregates and the cement.

The particle size and, particularly, the maximum permissible diameter of the aggregate, varies with the thickness of a monolithic lining of refractory concrete. It should not exceed 1/5 of the thickness of the concrete. The grading should, in general, be as follows: 50 percent coarse size, 10 percent medium size, and 40 percent fine size (0–0.2mm).

The normal cement content is 10 to 20 percent of the total dry weight of the mix. The dry fine aggregate is mixed with the required quantity of cement and homogenized completely. Only then are the dry or semidry medium and coarse sizes added, followed by another mixing and homogenizing.

The required amount of water is added at the end and thoroughly mixed in. The plastic refractory concrete is then placed in the mold without delay and tamped.

One should take care that the setting and hardening of concrete during the first three days takes place in a wet atmosphere. To this end, it is cured under wet cloths, sacks, etc. Removal of refractory barium-aluminous cement from the mold can take place after 12 to 16 hr.

Following removal, however, the concrete should be kept wet for another two days.

The Resultant Concretes and Their Technical Properties

Using refractory barium-aluminous cement I in the proportions of 10, 15, and 20 percent and white sintered bauxite or wastes of fire clay, corundum, chrome-magnesite, or magnesite bricks in proportions of 90, 85, and 80 percent with given grading, various concrete cubes and prisms were prepared by tamping in metal and wood molds. The more important technical properties of these refractory and highly refractory concretes are given in table 7.

Table 7 shows that the cold compressive strength of concrete increases with increasing cement content and that it is higher after burning at 1,400 °C than prior to such burning. Furthermore one can see that the refractoriness of the concrete decreases with increasing cement content. The resistance of concrete to thermal shock is always higher than that of the corresponding refractory brick. The properties of refractory concrete depend first on the aggregates used and, second, on the cement serving as binder. They are particularly determined by the chemical reactions taking place at high temperatures between the aggregates and the cementing materials. By using suitable refractory aggregates one can prevent the formation of readily fusing ceramic compounds which reduce the refractoriness of the concrete.

Using barium-aluminous cement II in proportions of 10, 15, and 20 percent and wastes of fire brick or white sintered bauxite in the proportions of 90, 85, and 80 percent with identical grading, six types of refractory concrete were prepared whose properties are given in table 8.

To establish the effect of the cements used as binders on the properties of concrete we used 20 percent of portland cement, ordinary aluminous cement (ciment fondu), white aluminous cement

Table 7. *Properties of refractory and highly refractory concrete made with refractory barium-aluminous cement I*

Technological properties	Refractory and highly refractory concrete made with refractory barium-aluminous cement I														
	Fire-clay concretes			Bauxite concretes			Corundum concretes			Chrome-magnesite concretes			Magnesite concretes		
Cement content *Percent*	10	15	20	10	15	20	10	15	20	10	15	20	10	15	20
Refractoriness *°C*	1,745	1,740	1,730	1,825	1,810	1,790	1,910	1,880	1,865	1,960	1,930	1,880	1,980	1,950	1,920
Seger cone collapse	33/34	33/34	33	37	36/37	36	39/40	39	38/39	41	40/41	39	41/42	40/41	40
Cold compressive strength at 7 days:															
Before burning *kg/cm²*	118	124	151	159	171	206	175	189	208	184	200	230	198	205	240
After burning at 1,400 °C *kg/cm²*	223	232	279	203	208	234	186	200	214	290	330	345	253	272	324
Apparent porosity:															
Before burning *Percent*	24	24	23	21	20	20	18	18	19	22	21	21	19	19	18
After burning at:															
1,200 °C *do*	24	23	23	21	21	21	19	20	20	23	22	22	20	20	19
1,400 °C *do*	23	23	22	20	20	19	18	19	20	22	20	20	19	18	18
Shrinkage, burning temperature:															
1,200 °C *do*	0.3	0.5	0.6	0.4	0.5	0.6	0.5	0.6	0.7	0.7	0.8	0.9	0.6	0.7	0.8
1,400 °C *do*	0.5	0.6	0.8	0.5	0.7	0.8	0.6	0.7	0.8	0.8	0.9	1.1	0.8	0.8	0.9
Resistance to thermal shock *cycles*	67	79	86	54	64	70	25	33	35	11	13	13	8	9	10

with monocalcium aluminate base, refractory aluminous cement with calcium dialuminate base, refractory barium-aluminous cement I, or refractory barium-aluminous cement (II) to produce six each fire-clay (schamotte) concretes, bauxite concretes, and chrome-magnesite concretes under identical conditions.

The refractoriness and resistance to thermal shock of fire-clay concrete are given in table 9.

Similarly, the refractoriness and resistance to thermal shock of bauxite concretes prepared with different cements are given in table 10.

Table 11 shows the technical properties of chrome-magnesite concrete obtained with different cements as follows: refractoriness, cold compressive strength (at 7 days, before and after burning at 1400 °C), apparent porosity (before and after burning at 1200 and 1400 °C) and resistance to thermal shock.

Table 8. *Properties of refractory and highly refractory concrete made with refractory barium-aluminous cement II*

Technological properties	Refractory and highly refractory concrete made with refractory barium-aluminous cement II					
	Fire-clay concretes			Bauxite concretes		
Cement content *percent*	10	15	20	10	15	20
Refractoriness *°C*	1,690	1,690	1,670	1,790	1,770	1,750
Seger cone collapse	31	31	30	36	35	34
Cold compressive strength at 7 days:						
Before burning *kg/cm²*	120	128	155	161	174	203
After burning at 1,400 °C *kg/cm²*	283	317	435	283	348	337
Apparent porosity:						
Before burning *percent*	24	23	23	21	21	20
After burning at						
1,200 °C do	25	24	24	22	20	21
1,400 °C do	23	22	22	20	19	19
Shrinkage, burning temperature:						
1,200 °C do	0.4	0.5	0.6	0.4	0.5	0.6
1,400 °C do	0.6	0.7	0.8	0.6	0.8	0.8
Resistance to thermal shock *cycles*	61	69	76	53	63	62

Table 9. *Properties of fire-clay concretes made with different cements*

Technological properties	Fire-clay concrete with 20 percent					
	Portland cement	Conventional aluminous cement (ciment fondu)	White aluminous cement with monocalcium aluminate base	Refractory aluminous cement with calcium dialuminate base	Refractory barium-aluminous cement	
					I	II
Refractoriness *°C*	1,380	1,435	1,530	1,630	1,730	1,670
Seger cone collapse	13	15	20	28	33	33
Resistance to thermal shock *cycles*	65	72	79	88	88	83

Table 10. *Properties of bauxite concretes made with different cements*

Technological properties	Bauxite concrete with 20 percent					
	Portland cement	Conventional aluminous cement (ciment fondu)	White alumious cement with monocalcium aluminate base	Refractory aluminous cement with calcium dialuminate base	Refractory barium-aluminous cement	
					I	II
Refractoriness *°C*	1,450	1,500	1,610	1,690	1,790	1,750
Seger cone collapse	15/16	18	27	31	36	34
Resistance to thermal shock *cycles*	47	45	51	54	70	60

TABLE 11. *Properties of chrome-magnesite concretes made with different cements*

Technological properties	Chrome-magnesite concrete with 20%:					
	Portland cement	Conventional aluminous cement (ciment fondu)	White aluminous cement with monocalcium aluminate base	Refractory aluminous cement with calcium dialuminate base	Refractory barium-aluminous cement	
					I	II
Refractoriness *°C*	1, 520	1, 560	1, 710	1, 810	1, 880	1, 850
Seger cone collapse	19	20/26	32	36/37	39	38
Cold compressive strength at 7 days:						
Before burning *kg/cm²*	123	215	219	176	230	221
After burning at 1,400 °C *kg/cm²*	481	437	368	333	345	358
Apparent porosity:						
Before burning *percent*	23	23	22	22	21	21
After burning at:						
1,200 °C *do*	20	20	21	22	22	21
1,400 °C *do*	15	16	19	20	20	20
Shrinkage, burning temperature:						
1,200 °C *do*	1. 4	1. 2	0. 8	0. 9	0. 9	0. 9
1,400 °C *do*	---------	---------------	1. 2	1. 2	1. 1	1. 1
Resistance to thermal shock *cycles*	9	9	10	11	13	13

The effect of different cements on refractoriness (Seger-cone collapse point) of fire-clay, bauxite, and chrome-magnesite concretes is shown in figure 5 (cement content 20 percent; identical grading and degree of compaction; identical consistancy of concrete.)

Dehydration and Sintering of Refractory Concrete

In general the behavior of concretes shown in table 7 is the same under prolonged heating to 1,500 °C. Up to 105 °C, 40 and 50 percent of the mix water is driven off; up to 300 °C more than 50 percent, and at 900 °C more than 85 percent.

The initial development of the "ceramic bond" between particles of refractory aggregates was observed by means of a binocular (stereoscopic) magnifier.

The various refractory concretes were first exposed to burning temperatures of 800, 900, 1,000, 1,100, 1,200, 1,300, and 1,400 °C for six hours. In the case of chrome-magnesite concretes the "ceramic reaction" begins at about 900 °C, in fire-clay, bauxite, and magnesite concretes at about 1,000 °C, and in corundum concrete first at about 1,100 °C.

The progress of the pyrogenic chemical reactions between the dehydration products of cement and the fine particles of the aggregates can be easily detected in concretes burned at 1,200 °C. The finest particles of the refractory aggregate have almost entirely disappeared and in place of them are very fine voids. These fine voids (small pores) partially disappear at 1,300 °C and completely at 1,400 °C. At this temperature, the particles of aggregate are surrounded with liquid, which forms a glassy, strengthening mass upon cooling. This "ceramic mass" is the cause of "ceramic strengthening," i.e., of the high mechanical cold strengths of refractory concretes burned above 1,300 °C.

The Effect of High Temperature on the Dehydration of Refractory Concrete

The dehydration behavior of fire-clay, bauxite, chrome-magnesite, and magnesite concretes containing 20 percent refractory barium-aluminous cement I under the action of high temperatures up to 1,400 °C was tested on 250-g specimens.

Figure 6 shows that maximum water loss in concrete takes place below 105 °C. At 500 °C fire-clay concrete shows the maximum dehydration. It is followed by chrome-magnesite, bauxite, and magnesite concrete. The higher the apparent porosity of the refractory aggregate, the more readily does dehydration of refractory concrete take place at this temperature.

Effect of High Temperatures on the Cold Compressive Strength of Refractory Concrete

The effect of burning temperatures up to 1,400 °C on the compressive strength at room temperature of fire-clay, bauxite, chrome-magnesite, and magnesite concrete with 20 percent of barium-aluminous cement I was determined.

The compressive strengths of unburned specimens at 28 days were taken as a basis for comparison (100 percent). The cold compressive strength of concrete determined after six-hour heating to different temperatures between 100 and 1,400 °C is shown in figure 7, expressed in percent.

The cold compressive strengths of all concretes increase slightly up to 105 °C, decrease strongly thereafter to 300 °C, and less strongly up to 800–1,000 °C. Upon reaching a minimum, the cold compressive strengths begin to increase very sharply, and, for heating at 1,400 °C, they exceed the original compressive strengths. The diagram shows that due to the pyrogenic chemical reactions in the solid state between the dehydrated components of refractory barium-aluminous cement and the fine sizes of aggregates, a ceramic strengthening of the refractory aggregate particles begins to take place at about 750 °C for chrome-

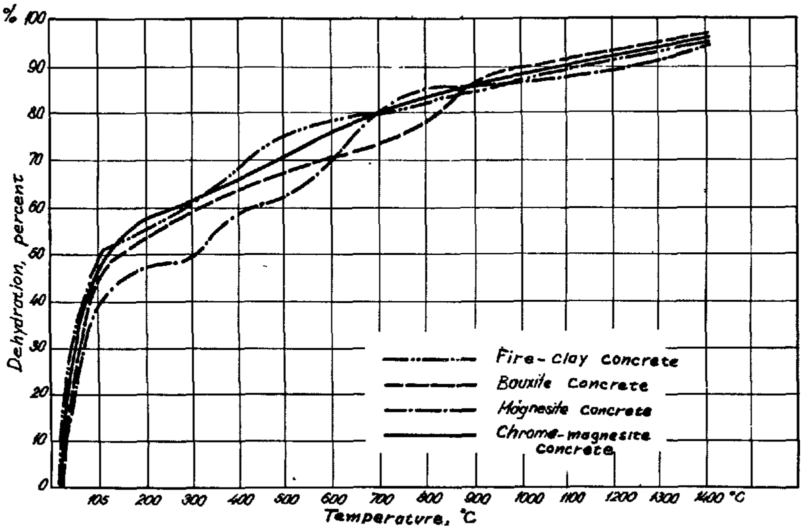

FIGURE 6. *Percent dehydration of fire-clay, bauxite, magnesite, and chrome-magnesite concrete with 20 percent refractory barium-aluminous cement I, for different burning temperatures.*

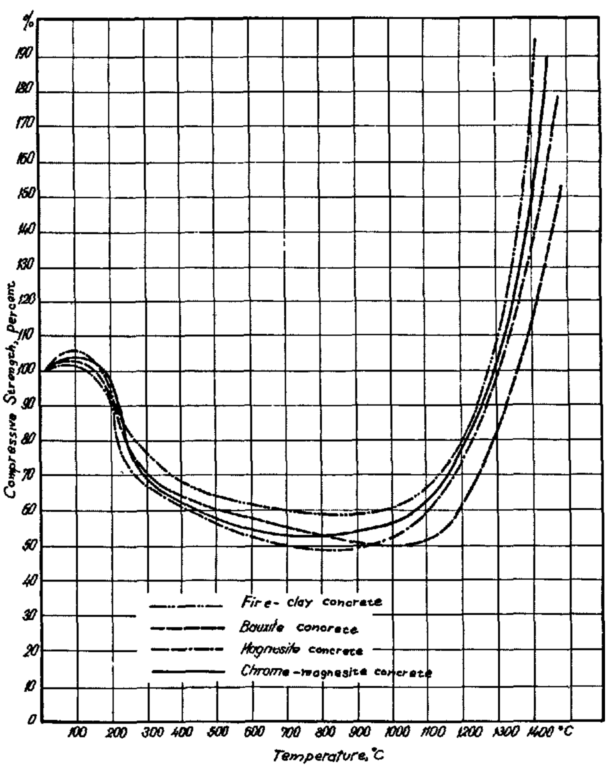

FIGURE 7. *Cold compressive strengths of fire-clay, bauxite, magnesite, and chrome-magnesite concrete with 20 percent refractory barium-aluminous cement I, following six-hour heating to different temperatures.*

magnesite concrete; at about 800 °C for magnesite concrete; at 900 °C for fire-clay concrete, and at 1,000 °C for bauxite concrete.

Following six-hour burning at 1,400 °C the cold compressive strengths exceed the original compressive strengths of unburned concretes.

Effect of Cement Content on the Cold Compressive Strengths of Refractory Concretes

The relation to cement content of the cold compressive strengths (at 7 days) of unburned concretes and those burned at 1,000° or 1,400 °C was studied on fire-clay, bauxite, corundum, chrome-magnesite, and magnesite concretes, with refractory barium-aluminous cement I. The results for the unburned concretes are reproduced in figure 8, those for concretes burned at 1,000 °C in figure 9, and those burned at 1,400 °C in figure 10.

Figure 8 shows that the compressive strengths of unburned refractory concretes depend to a certain extent on the average compressive strengths of their refractory aggregates. See table 5.

The compressive strengths of refractory concretes increase in general with increasing cement content.

Due to the inhomogeneity of refractory concretes, produced by the settlement of suspended cement particles [25], as well as by the more rapid settlement of the coarser aggregate particles with respect to the smaller, the gain in compressive strength is not uniform.

The effect of cement content on the cold compressive strengths of fire-clay, bauxite, corundum, chrome-magnesite, and magnesite concretes with barium-aluminous cement I at the so-called "critical point" (burning temperature giving lowest strengths=1,000 °C) is shown in figure 9. Compared to figure 8, the curves shown here are somewhat flatter. The effect of cement content on the increase in cold compressive strength of concretes is thus smaller at the "critical point."

The effect of cement content on the cold compressive strength of concretes after six-hour burning at 1,400 °C (burning temperature at which "ceramic strengthening" has been in effect for some time) is shown in figure 10. Compared to

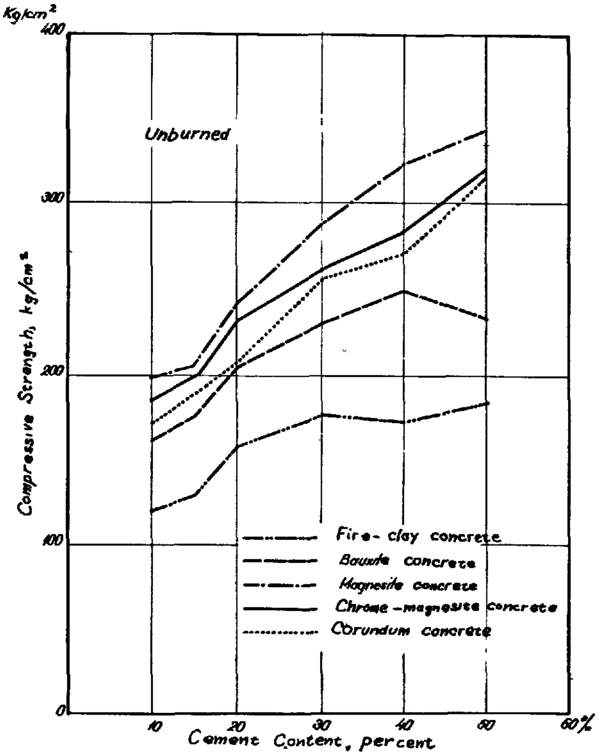

FIGURE 8. *Relation of compressive strengths to cement content for fire-clay, bauxite, corundum, chrome-magnesite, and magnesite concretes made with refractory barium-aluminous cement I, unburned, 7 days after setting.*

figure 9, the trend of the curve is considerably steeper. In this case the cold compressive strengths of concretes increase much more markedly with increasing cement content. The cement content thus has a relatively low effect on the cold compressive strength of concrete at the "critical point" and a much more marked effect on the cold compressive strength of unburned refractory concrete or that burned at 1,400 °C.

Relation of Collapse Point of Seger Cone to Cement Content of Refractory Concrete

The effect of cement content on the refractoriness of fireclay, bauxite, corundum, chrome-magnesite, and magnesite concretes with refractory barium-aluminous cement I is shown in figure 11 and table 12.

Table 12 and figure 11 show that in all cases refractoriness decreases with increasing cement content. The drop in refractoriness with increase in cement content from 10 to 30 percent is more marked than for an increase from 40 to 50 percent.

In spite of the greater drop in refractoriness of the magnesite- and chrome-magnesite concretes, the refractoriness of these concretes remains above that of the bauxite and fire-clay concretes.

An increase in cement content has a very pronounced effect on the drop in refractoriness of magnesite and chrome-magnesite concretes and a much smaller effect on the drop in refractoriness of corundum, bauxite, and fire-clay concretes.

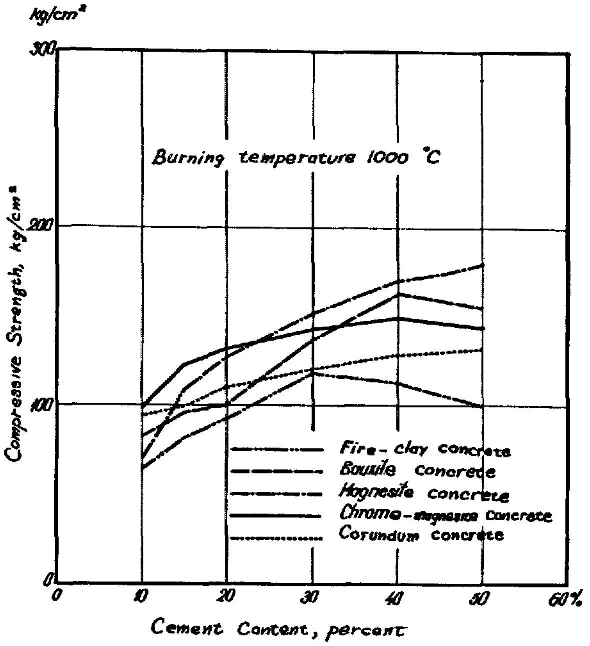

FIGURE 9. *Relation of cold compressive strengths to cement content for fire-clay, bauxite, corundum, chrome-magnesite, and magnesite concretes made with refractory barium-aluminous cement I and burned at 1,000 °C at 7 days after setting.*

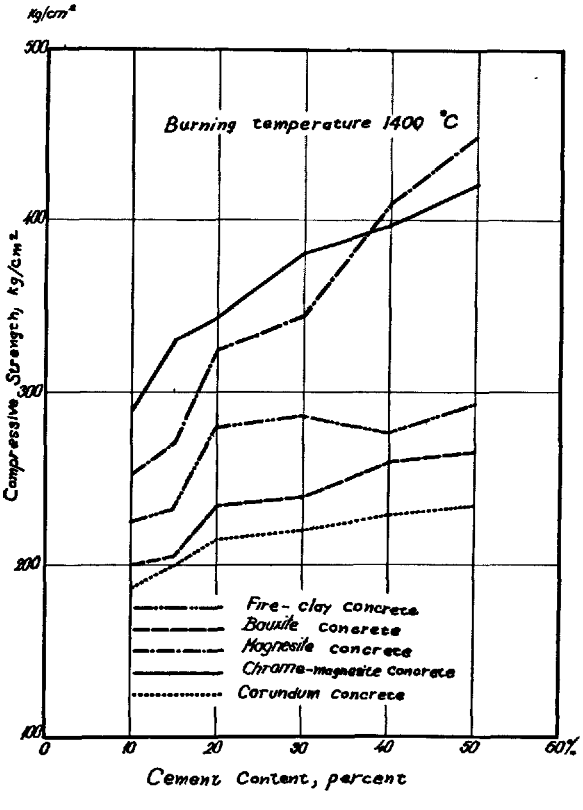

FIGURE 10. *Relation of cold compressive strengths to cement content for fire-clay, bauxite, corundum, chrome-magnesite, and magnesite concretes made with barium-aluminous cement I and burned at 1,400 °C at 7 days after setting.*

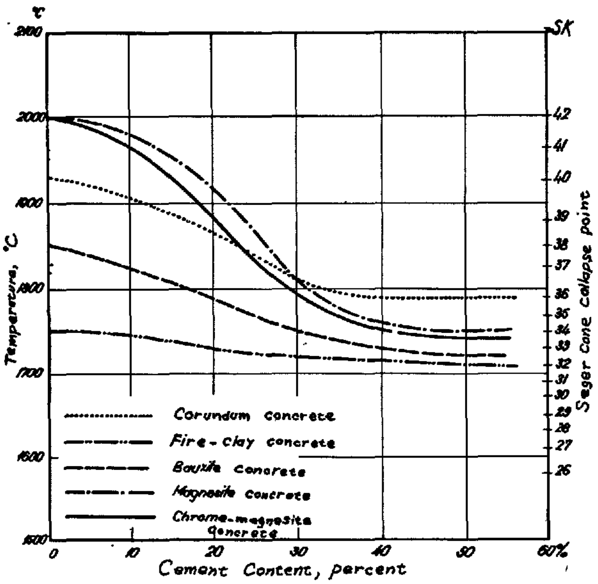

FIGURE 11. *Relation of refractoriness to cement content. in fire-clay, bauxite, corundum, chrome-magnesite, and magnesite concretes made with refractory barium-aluminous cement I.*

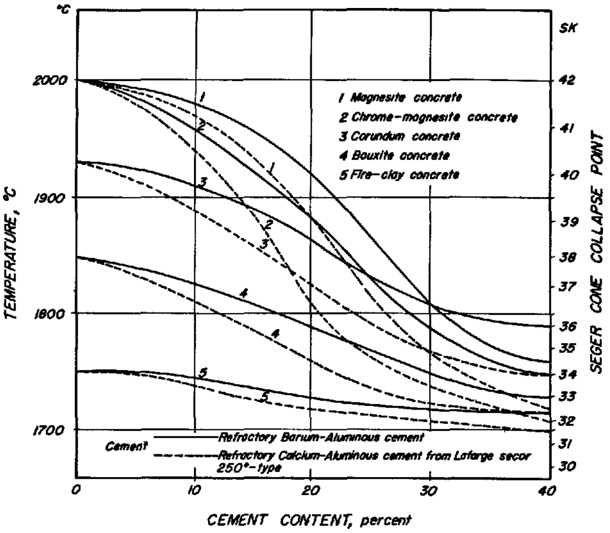

FIGURE 12. *Comparison of refractoriness of magnesite, chrome-magnesite, corundum, bauxite, and fire-clay concretes made with refractory barium-aluminous cement I and refractory calcium aluminous cement with calcium dialuminate base in relation to increasing cement content.*

TABLE 12. *Refractoriness of concretes made with different amounts of barium-aluminous cement I*

Cement content	Refractory concrete				
	Fire-clay concrete	Bauxite concrete	Corundum concrete	Chrome-magnesite concrete	Magnesite concrete
Percent	°*C*	°*C*	°*C*	°*C*	°*C*
0	1,750	1,850	1,930	2,000	2,000
10	1,745	1,825	1,910	1,960	1,980
20	1,730	1,790	1,865	1,880	1,920
30	1,720	1,750	1,810	1,790	1,810
40	1,715	1,730	1,790	1,750	1,760
50	1,710	1,720	1,790	1,740	1,750

Seger Cone Collapse Point of Highly Refractory and Refractory Concretes With Barium-Aluminous Cement I and Those With Refractory Calcium-Aluminous Cement With Calcium Dialuminate Base as Related to Increasing Cement Content

The superiority of refractory barium-aluminous cements I and II with respect to the outstanding, widely used refractory aluminous cement with calcium dialuminate base is revealed in figure 12 even more clearly than in figure 5.

The magnesite, chrome-magnesite, corundum, bauxite, and fire-clay concretes were mixed with indentical grading (50 percent coarse, 10 percent medium, and 40 percent fines below 0.2 mm) to identical plastic consistencies and were molded with an identical degree of compaction.

The porosity of highly refractory and refractory concretes with increasing cement content (10 to 40 percent) is 15 to 25 percent higher than the porosity of the aggregates used. It follows—and this has been proved experimentally—that the concretes have lower heat conductivity and higher resistance to thermal shock than the corresponding aggregates, or refractory structural materials, from which they are derived.

Figure 12 shows that with a usual cement content of 20 percent the refractoriness of basic highly refractory concretes (magnesite, chrome-magnesite, and corundum concretes) with refractory barium-aluminous cement is 35 to 70 percent higher than that of the corresponding concretes made with refractory aluminous cement with a calcium dialuminate base.

The difference in refractoriness under load is, however, considerably greater for these concretes and indicates the superiority of concrete with refractory barium-aluminous cement.

Thus it is very advantageous, particularly with basic higher refractory concretes, to replace the refractory *calcium-aluminous* cements by refractory *barium-aluminous* cements.

Conclusions

1. From refractory and highly refractory aggregates and portland cement (with finely ground admixtures) only low-grade nonrefractory concretes can be produced which cannot withstand service temperatures above 1,520 °C, when the usual cement content of 20 percent is used.
2. Silicate cements are not suitable for the manufacture of refractory and highly refractory concretes; only aluminate cements, such as refractory barium- and calcium-aluminous cements, should be used. In these the combined water is driven off easily and uniformly at high temperatures without causing destruction of the concrete structure.

3. Conventional aluminous cements with high iron oxide content combined with refractory and highly refractory aggregates produce good, nonrefractory concretes for service temperatures below 1,580 °C.

4. White calcium-aluminous cements with monocalcium aluminate base yield good, refractory concretes only when combined with suitable highly refractory aggregates.

5. Refractory calcium-aluminous cements (with calcium dialuminate base) and refractory barium-aluminous cements yield highly refractory concretes when combined with any basic or neutral refractory aggregates.

6. Highly refractory concretes can be produced only from highly refractory basic neutral aggregates and refractory barium-aluminous cements or refractory calcium-aluminous cements with calcium dialuminate base (with more than 70% Al_2O_3 and less than 1% $Fe_2O_3+SiO_2+MgO+$ alkalies). Of these highly refractory concretes, those containing refractory barium-aluminous cements exhibit the best properties.

7. The thermal shock resistance of concrete depends on the nature of the aggregates, the particle-size gradation, and the quantity of cement. This resistance is considerably higher than that of the corresponding refractory aggregates.

The highest resistance to thermal shock is shown by concretes with barium-aluminous cement. In decreasing order we have: concretes with refractory calcium-aluminous cement with calcium dialuminate base; white aluminous cement with monocalcium-aluminate base; and ordinary (conventional) aluminous cement (ciment fondu). The lowest resistance to thermal shock is shown by portland cement concrete.

Exceptionally high resistance to thermal shock is shown as a rule by fire-clay concretes. These are followed by bauxite, corundum and chrome-magnesite concretes. The lowest resistance to thermal shock is shown by magnesite concretes.

The progress of destruction caused by a severe thermal shock is quite different in the investigated concretes and in the corresponding refractory aggregates. Namely, we deal here with a fine-scale collapse of the concrete rather than with a breaking off of large sections as in refractory brick; this difference is due to the considerably greater inhomogeneity of the concrete.

8. The refractoriness of concrete drops, and its compressive strength increases with increasing cement content. After burning at temperatures of about 1,400 °C the cold compressive strengths of concrete exceed the compressive strengths of unburned concretes (at 7 days).

9. By using barium-aluminous cement as cementing material in combination with basic or neutral aggregates, one can produce refractory and highly refractory concretes, which are superior to those containing refractory calcium-aluminous cements, white aluminous cements, conventional aluminous cements (ciments fondus), or portland cements.

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Paper VIII–S6. Researches on the Hydration of Trass Cements*

U. Ludwig and H. E. Schwiete

Synopsis

The compositions of various Rhenish and Bavarian trasses were investigated chemically and mineralogically. It was found that considerable differences exist between the chemical as well as mineralogical constitutions of Rhenish and Bavarian trasses. The author explains the hydraulic activity of trass by its glassy matrix (groundmass). It was possible to establish that Bavarian trasses have a somewhat higher glass fraction than the Rhenish trasses. The higher hydraulicity of the Rhenish trasses is ascribed to the higher reactivity of the glassy phase of this trass.

The reaction of trass with lime was investigated by shaking trass with lime and water in excess, and also by studies on trass-lime pats, trass-lime suspensions, and trass-cement mortars. Besides this, the lime-combining capacities of the various mineral components of trass were studied. By means of heavy liquids it was also sought to separate the glass phase from the other mineral components, and to test the glass phase for reactivity with lime. On the basis of these tests it can be asserted that over 80 percent of the lime reaction in trass occurs through the glass phases.

With the help of microscopic, electron microscopic, X-ray, and thermal methods of investigation, it was sought to identify the new products formed in a trass-lime reaction. It was shown that the same hydrates form in the system trass-lime-gypsum-water as those familiar in the system portland cement-water. The following hydrates were observed:

$Ca(OH)_2$, $3CaO{\cdot}2SiO_2{\cdot}aq.$, $4CaO{\cdot}Al_2O_3{\cdot}13H_2O$,
$3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$(ettringite), $3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$.

Résumé

Des recherches chimiques et minéralogiques ont été faites sur la composition de différents trass Rhénans et Bavarois. On trouva que des différences considérables existent entre les constitutions chimiques aussi bien que minéralogiques des trass Rhénans et Bavarois. L'auteur explique l'activité hydraulique du trass par sa gangue vitreuse (milieu de base). Il fut possible d'établir que les trass Bavarois ont une fraction de verre quelque peu plus élevée que les trass Rhénans. L'activité hydraulique supérieure des trass Rhénans est attribuée à la réactivité plus élevée de la phase vitreuse de ce trass.

On examina tout particulièrement la réaction du trass avec la chaux. L'étude de la réaction du trass avec la chaux fut faite en agitant du trass avec de la chaux et de l'eau en excès, et on fit aussi des études sur des mottes de chaux et de trass, des suspensions de chaux et de trass, et des mortiers de ciment et de trass. En outre, les capacités des différents composés minéraux du trass à se combiner à la chaux furent étudiées. Au moyen de liquides lourds on chercha aussi à séparer la phase vitreuse des autres composants minéraux, et à éprouver la phase vitreuse quant à la réactivité avec la chaux. Sur la base de ces expériences on peut affirmer que plus de 80% de la réaction de la chaux dans le trass se produit dans les phases vitreuses.

A l'aide de méthodes de recherches microscopiques, electron microscopiques, de rayons X et thermiques, on chercha à identifier les nouveaux produits formés dans la réaction trass-chaux. On trouva que les hydrates qui se forment dans le système trass-chaux-gypse-eau sont les mêmes que ceux trouvés ordinairement dans le système ciment portland-eau. Ce qui signifie que les hydrates suivants ont été observés:

$Ca(OH)_2$, $3CaO{\cdot}2SiO_2{\cdot}aq.$, $4CaO{\cdot}Al_2O_3{\cdot}13H_2O$,
$3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$ (ettringite), $3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$.

Zusammenfassung

Verschiedene rheinische und bayrische Trasse wurden chemisch und mineralogisch auf ihre Zusammensetzung untersucht. Dabei ergab sich, daß zwischen dem chemischen und auch mineralogischen Aufbau der rheinischen und bayrischen Trasse wesentliche Unterschiede bestehen. Die Verfasser erklären die hydraulische Wirksamkeit der Trasse durch die glasige Grundmasse. Es konnte festgestellt werden, daß in den bayrischen Trassen ein etwas höherer Glasanteil enthalten ist als in den rheinischen Trassen. Die höhere Hydraulizität der rheinischen Trasse wird auf ein größeres Reaktionsvermögen der Glasphase dieses Trasses zurückgeführt.

Der Kalkbindung der Trasse wurde besondere Aufmerksamkeit gewidmet. Es wurde die Kalkbindung beim Schütteln von Traß mit Kalk und Wasser im überschuß, an Traßkalkkuchen, an Traßzement-Suspensionen und an Traßzement-Mörteln untersucht. Außerdem wurde zusätzlich das Kalkbindungsvermögen der verschiedenen am Aufbau der

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from Institut für Gesteinshüttenkunde, Rhein.-Westf. Technische Hochschule Aachen, Germany.

Trasse beteiligten Mineralien ermittelt. Zusätzlich wurde versucht, mit Hilfe schwerer Flüssigkeiten die Glasphase der Trasse von den übrigen Mineralkomponenten abzutrennen und diese auf ihr Kalkbindungsvermögen zu prüfen. Anhand dieser Versuche konnte nachgewiesen werden, daß über 80% der Kalkbindung der Trasse durch die Glasphasen erfolgt.

Mit Hilfe mikroskopischer, elektronenmikroskopischer, röntgenographischer und thermischer Untersuchungsmethoden wurde versucht, die bei dem Umsatz von Traß mit Kalk entstehenden Neubildungen zu identifizieren. Dabei zeigte es sich, daß im System Traß-Kalk-Gips-Wasser die gleichen Hydrate gebildet wurden, wie sie uns vom System Portlandzement-Wasser bekannt sind. Das heißt, es wurden folgende Hydrate beobachtet:

$Ca(OH)_2$, $3CaO{\cdot}2SiO_2{\cdot}aq.$, $4CaO{\cdot}Al_2O_3{\cdot}13H_2O$,
$3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$ (Ettringit), $3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$.

Introduction

Geologically, trass is a volcanic tuff; from the standpoint of building technology it is a hydraulic admixture which hardens hydraulically in combination with lime and water. Because of its ability to harden hydraulically, trass has been used in construction for centuries.

In Germany, trass deposits used industrially are found in the Eifel and in Nördlinger Ries. Other deposits occur in the Rhön and in Saxony.

The subject matter treated below is divided into three parts:

(a) the chemical and mineralogical composition of trass,

(b) the binding of lime by trass, and

(c) products formed during hydration of trass in the presence of lime.

Properties which trass imparts to mortar from the engineering standpoint will not be discussed in this paper, although numerous strength tests and measurements of workability and of water repellence in mortar were made.

Results of Investigations

The Chemical and Mineralogical Composition of Trass

Table 1 presents analytical results obtained in standard tests on Rhenish trass. In this analytical method the trass samples are boiled with 20 percent HCl for 1 hr with reflux condenser. The residue is then treated with 2-percent NaOH solution.

Table 2 presents results of standard analyses obtained with several kinds of Bavarian trass. These results differ from those for Rhenish trass in that Rhenish trass has an HCl-insoluble residue of 30–46 percent, while that for Bavarian trass is about 50–60 percent. On the other hand, Rhenish trass contains more alkalies and more water of hydration.

However, for explaining the action of trass, the chemical analyses and contents of individual oxides are not decisive, but instead the nature of the chemical binding of the oxides in trass glass and trass minerals. For this reason, up to about the middle thirties, attempts to explain the mineralogical structure of trass were based on combined chemical and microscopic methods. Of the many researchers, we mention the following: Hambloch [1], Hart [2], Lunge [3], Biehl and Wittekindt [4] and Tännhäuser [5].

Greatest care was taken in the present studies in determining the mineral composition of trass.

TABLE 1. *Chemical analyses of Rhenish trass*
(In accordance with DIN 1044)
[Percent]

Sample No.	1	2	3	4	5	6	7	8	9
Sample [a]	TaH	TuH	TiH	TaJ	TuJ	ObT	UnT	RöK	FrK
Loss on ignition	4.62	11.36	9.40	6.30	9.92	11.10	11.84	8.10	7.24
Insoluble	32.28	30.08	44.32	46.12	33.48	33.56	26.40	31.40	32.36
SiO_2	31.84	33.18	25.02	25.82	30.78	29.56	32.74	34.98	35.18
Fe_2O_3	4.12	3.48	3.87	3.87	3.87	4.38	4.27	2.94	3.13
Al_2O_3	15.18	14.00	9.63	10.75	12.41	13.54	14.05	14.10	13.39
CaO	2.52	3.34	3.09	2.10	3.33	3.30	2.71	2.29	1.80
MgO	1.22	.82	.76	1.04	1.10	1.00	1.05	.75	.65
SO_3 [b]	.04	Sp	Sp	Sp	Sp	Sp	Sp	.02	Sp
Mech. water	.92	4.02	2.20	1.16	4.88	4.11	4.05	2.71	1.46
Water of hydration	3.73	7.64	7.36	5.20	5.63	7.28	8.11	5.63	5.68
Total	91.82	96.26	97.09	96.00	95.21	96.44	93.06	94.68	93.75

[a] Trass samples dissolved in HCl.
[b] Sp=trace.

Table 2. *Chemical analyses of Bavarian trass*
(In accordance with DIN 1044)
[Percent]

Sample No.	12 [b]	13	14	15	16	17	18	19	20 [c]
Sample [a]	PC375	Tr_{01}	Tr_{02}	Tr_{03}	Tr_{04}	Tr_H	Tr_A	Tr_M	PC375
Water of hydration	------	5.54	3.24	3.44	3.67	3.10	4.37	7.00	------
Insoluble	0.17	51.57	54.62	58.09	53.60	59.36	52.73	53.15	0.22
SiO_2	20.92	23.50	25.43	22.10	23.44	19.21	23.62	19.84	19.80
Fe_2O_3	2.69	4.53	3.15	3.80	4.15	3.44	3.79	3.17	2.95
Al_2O_3	5.77	8.51	6.86	6.34	8.29	6.59	6.53	4.83	6.86
CaO	65.90	1.67	1.31	2.39	1.73	4.22	3.53	7.84	65.20
MgO	1.30	1.89	1.47	2.10	1.84	1.09	2.84	1.21	1.19
SO_3 [d]	2.71	.22	Sp	Sp	.33	Sp	Sp	Sp	3.31
Total	99.46	97.43	96.08	98.26	97.05	97.01	97.41	96.68	99.53
Na_2O [e]	.08	1.54	1.38	1.51	1.73	1.91	2.09	1.86	.07
K_2O [e]	.61	2.30	2.53	2.41	2.32	2.44	1.78	2.44	.65

[a] Trass samples dissolved in HCl.
[b] PC 375 No. 12: silicate mod.=2.47; alumina mod.=2.15; hydr. mod.=2.24.
[c] PC 375 No. 20: silicate mod.=2.02; alumina mod.=2.32; hydr. mod.=2.20.
[d] Sp=trace.
[e] Decomposed with hydrofluoric acid.

Samples were subjected to chemical analysis and examined optically and roentgenographically.

A comparison of the results of mineralogical investigations of trass obtained by Völzing [6] and Tannhäuser with those of the authors is presented in table 3. The important differences revealed in this comparison with earlier investigations consist in that recent tests showed greater quantities of quartz and leucite and small quantities of kaolinite and illite in the fine fractions of the prepared trass samples. In addition, the presence of cristobalite is also probable. On the other hand, accessory minerals such as apatite, titanite, hauynite, sodalite, and magnetite were not revealed in the new tests, which fact may be attributed to the rarity of their occurrence and to the different test methods used. Whereas, formerly, the samples were "grab" or random samples, our tests were carried out with average powdered samples. Accessory minerals obtained in our investigations, particularly illite, kaolinite, and chabazite, could not be detected earlier because of their great fineness which made identification with the light microscope impossible.

Table 3. *Mineral components of Rhenish trass*

Accdg. to Völzing (1907) and Tannhäuser (1911) Microscope			Authors' tests X-ray diffraction and microscope
	——	quartz	
	feldspar	←→ feldspar	
	hornblende	←→ hornblende	
	augite	←→ augite	
	apatite	—	
	titanite	—	
	biotite	←→ or muscovite	
	hauynite	chabazite	
	nosean	←→ analcite	
	sodalite	hematite	
	magnetite	cristobalite	
	—	lecuite	
	—	kaolinite	
	—	illite	
	glass (matrix)	←→ glass	

Table 4 presents a comparison of the chemical compositions of a Rhenish trass and a Bavarian trass and the compositions of the glass components separated from the two trass samples by means of heavy liquids.

Table 4. *Chemical and mineralogical composition of a Rhenish trass and Bavarian trass*

Chemical composition (%)					Mineralogical composition (%)		
	Rhenish trass		Bavarian trass			Rhenish trass	Bavarian trass
	Trass	Glass	Trass	Glass			
					Glass	55–60	62–67
Loss on ignition	11.10	7.83	7.41	5.15	Quartz	9	19
SiO_2	52.12	54.85	62.45	67.14	Feldspar	15	15
Fe_2O_3	5.81	4.55	4.41	1.95	Chabazite	3	------
Al_2O_3	------	18.14	------	15.34	Analcite	5	------
	18.29		16.47		Leucite	4	------
TiO_2	------	.76	------	0.64	Mica	2	------
CaO	4.94	4.40	3.39	2.76	Illite	------	------
MgO	1.20	1.92	.94	.93	Augite	<1	<1
SO_3 [a]	Sp	.34	Sp	1.06	Kaolinite	2	------
Na_2O	1.48	1.37	1.91	2.02	Hornblende	<1	------
K_2O	5.06	5.48	2.06	2.72			

[a] Sp=trace.

The results show that the analyses of trass glass and of the corresponding trass have a certain similarity. The glass in Bavarian trass is more acid and contains less alkalies, particularly less potassium.

The mineralogical compositions of Rhenish and Bavarian trass are quite different. As indicated by table 4, Bavarian trass contains neither zeolites nor leucite, but has a definitely higher quartz content.

Great significance was attributed to the magnitude of the content of water of hydration in the trass. This led to a renewed thorough investigation of the nature of the bonds by which water is held. It was established that only a small part of the chemically bound water is fixed in the crystalline components. The greater part of the water, which cannot be driven off at 110 °C, is fixed in the glassy phase of trass. Infrared spectroscopy studies established that even when trass glass was tempered at 200 °C adsorption water was still present along with chemically bound water. These results show that the importance of the water of hydration in trass with respect to the capacity for hydraulic hardening requires further verification.

The Binding of Lime by Trass

It is known that the trass component in trass cement reacts with the lime liberated during the hydration and hydrolysis. Consequently, trass-lime tests were given special attention in the present series. The degree of trass-lime reaction was studied on: (a) trass-lime suspensions, (b) trass-lime pats, (c) trass-cement suspensions, (d) trass-cement mortars. The test reactions extended over a period of 2 yrs. The free lime present as uncombined $Ca(OH)_2$ or, in mortars, partly as $CaCO_3$ was determined by the modified Franke method and gas volumetrically. The free lime going into solution in shaking tests was determined, together with the alkalies, by flame photometry. The investigated trass samples had a specific surface of 8,000–9,000 cm^2/g.

Figure 1 shows the lime binding of a Rhenish trass shaken up to 660 days in a lime suspension. Plotted as ordinates are: (a) CaO combined with trass, (b) free lime present in the solution and in the solids, (c) free alkalies present in the solution in mg/g trass. The abscissa shows the logarithm of time.

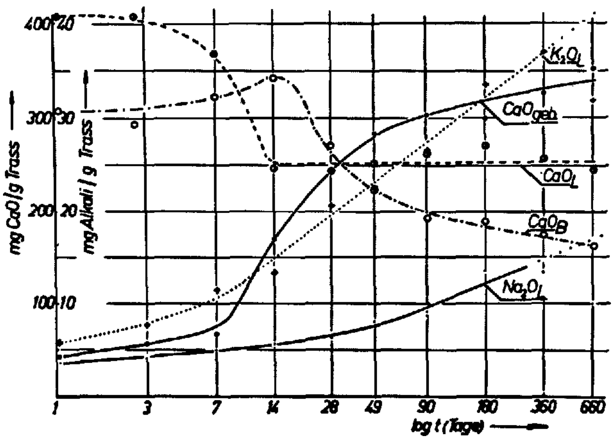

FIGURE 1. *Alkali separation and lime fixation of a Rhenish trass.*

CaO_{geb}=combined lime; CaO_B=free lime; other curves refer to amounts in solution; abscissa=time in days on log scale.

The diagram reveals an increasing solubility of alkalies. Strong lime supersaturation was first observed in the solution, which dropped to saturation concentration after 14 days. On the other hand, the free lime content in the solids at first increases, reaches a maximum after 14 days and drops thereafter, in accordance with the strong reaction of trass with lime. This gives a hyperbolically-shaped curve extending down to about 160 mg in the solids.

The S-shaped trend of the lime reaction curve can be explained by an initial lime adsorption which may be overlain by ion-exchange reactions (resulting from the zeolite content of trass), and a reaction beginning at 7 days (appearance of new formations) which after about 49 days passes into a period of lime saturation of the solids.

It should be mentioned at this point that alkali loss and lime fixation do not exhibit a proportional relation, i.e., that the extent of the lime reaction is to be explained not only through zeolitic reactions, but almost exclusively through chemical conversion reactions, which is confirmed by the observed new formations.

In an attempt to define the participation of the individual trass components in the lime reaction, several minerals, namely, quartz, feldspar, leucite, kaolinite, and analcite, and (in addition) obsidian were ground to ultrafineness, and their reactivity with lime was examined as for trass. The duration of the reaction was 28 days. Besides these, glassy phases of various specimens of Rhenish and Bavarian trass were separated from the crystalline phases by means of heavy liquids, and the ability of these glasses to react with lime was investigated. The results of these investigations are presented in table 5. An evaluation of the investigations shows that more than 80 percent of the lime reaction takes place through the glass phase. A study of Bavarian trass led to the same results.

TABLE 5. *The lime-binding capabilities of the principal trass minerals and their contributions to trass-lime binding*

Mineral component	Lime reaction	Free alkali		Average amount in Rhenish trass	Calculated lime reaction in Rhenish trass
		Na_2O	K_2O		
	mgCaO/g	*mg/g*	*mg/g*	*percent*	*mgCaO/g trass*
Quartz	43	1.5	0.4	13	5.6
Feldspar	117	1.1	.2	15	17.5
Leucite	90	1.3	1.8	6	5.4
Analcite	190	10.7	3.0	7	13.3
Kaolin	34	.3	2.1	2	.7
Glass phase (Rhenish)	364	18.0	24.0	55	200.0
Glass phase (Bavarian)	272	6.0	6.0	66	179.0
Obsidian glass	176	3.7	3.1		
Total				98	242.5

From the table the following can be deduced: The increasing fixation of lime in the series obsidian glass→trass glass (Bavarian)→trass glass (Rhenish), and the quantities of liberated alkalies increasing in the same order could be an indication that the reactivity of the glasses depends on the level of the alkali content, a view, however which needs the support of further studies.

In studies of trass-lime pats, the bound lime was determined after 360 days as 309 mg CaO or 408 mg $Ca(OH)_2$ per g trass. Table 6 presents the results obtained in these studies.

By shaking portland cement, trass cement, and "quartz cement" with an excess of water, the lime fixation of the Rhenish trass under study was established at the same level as in the earlier tests. In addition, the quartz flour used was found to show some reactivity with respect to lime. After a duration of the reaction of 1 yr, lime fixation by trass amounted to 329 mg CaO and that of quartz flour to 73 mg CaO per g trass or quartz, respectively.

TABLE 6. *Fixation of lime by Rhenish trass as a function of time* (W/B=1)

Duration of curing	Free $Ca(OH)_2$	Lime reaction with 1 g trass computed as	
		$Ca(OH)_2$	CaO
Days	*Percent*	*mg*	*mg*
0	50.3	0	0
3	48.7	32	24
7	45.1	104	79
14	39.1	224	170
28	36.4	278	211
92	33.9	328	248
180	33.7	332	252
360	29.9	408	309

The content of free lime found in studies of standard mortars made in accordance with DIN 1164, and the lime fixation calculated therefrom for the different Rhenish trass samples are presented in table 7.

After a 365-day duration of storage the average content of free lime in trass mortars amounts to about 26 mg, that in a portland-cement specimen to 63 mg, and in the comparable mortar specimen with 30 parts quartz flour to 38.2 mg free CaO per g mortar (ignited basis). The lime fixation by trass increases sharply as a function of time and amounts to 24 percent on the average after 1 yr water storage of mortar prisms. In comparison, quartz flour binds 7.9 percent CaO in the same interval.

Products Formed During Hydration of Trass in the Presence of Lime

Available for these investigations, besides the polarizing microscope were: an electron microscope, an X-ray diffraction apparatus, and the dynamic differential calorimeter, an advanced DTA method.

Figure 2 shows the X-ray diffraction charts of the Rhenish trass reacted with lime up to 660 days. It reveals a drop in free lime as a function of time, which is indicated by a decrease in intensity of diffraction lines at $\theta=9$ and 17°, respectively. These are the principal lines of $Ca(OH)_2$. The basic diffraction lines for the new hydration products lie in the range $\theta=5$–7°.

TABLE 7. *Lime liberation and lime fixation in standard mortars made according to DIN 1164*

No.	Cement	Free CaO in 1 g mortar				Lime binding by trass or quartz content							
		7d	28d	180d	365d	7d		28d		180d		365d	
		mg	*mg*	*mg*	*mg*	*mg* [a]	% [b]	*mg* [a]	% [b]	*mg* [a]	% [b]	*mg* [a]	% [b]
0	PC375	70.0	69.0	64.5	63.0								
1	30 percent Ta$_H$	45.1	39.7	33.2	27.9	3.9	5.2	8.6	11.4	12.0	16.0	16.2	21.6
2	30 percent Tu$_H$	44.0	35.9	29.0	22.6	5.0	6.7	12.4	16.5	16.2	21.6	21.5	28.6
3	30 percent Ti$_H$	45.3	41.8	34.2	28.6	3.7	4.7	6.5	8.7	11.0	14.6	15.5	20.6
4	30 percent Ta$_J$	43.9	40.2	34.1	27.6	5.1	6.8	10.4	13.8	11.1	14.8	16.5	22.0
5	30 percent Tu$_J$	43.8	37.0	33.0	23.9	5.2	6.9	11.3	15.0	12.2	16.2	20.2	26.9
6	30 percent Ob$_T$	44.3	38.4	32.8	26.5	4.7	6.3	9.9	13.2	12.4	16.5	17.6	23.4
7	30 percent Un$_T$	43.5	38.0	32.3	25.4	5.5	7.3	10.3	13.7	12.9	17.2	18.7	24.9
8	30 percent Rö$_K$	46.9	41.5	31.9	24.8	2.1	2.8	6.8	9.1	13.3	17.7	19.3	25.7
9	30 precent Fr$_K$	45.4	41.0	32.8	26.2	3.6	4.8	7.3	9.7	12.4	16.5	17.8	23.7
10	30 percent quartz	47.3	46.2	41.2	38.2	1.7	2.3	2.1	2.8	4.0	5.3	5.9	7.9

[a] On the basis of 1 g mortar.

[b] On the basis of the trass or quartz content of the mortar.

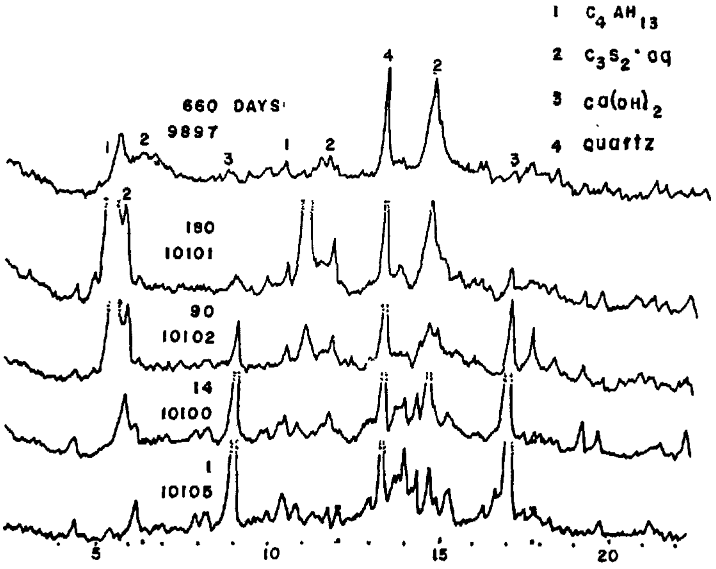

FIGURE 2. *X-ray diffraction patterns of Rhenish trass-lime mixtures shaken for periods up to 660 days.*

From bottom to top: 1 day, 14 days, 90 days, 180 days, 660 days. Abscissa scale, angle θ in degrees.

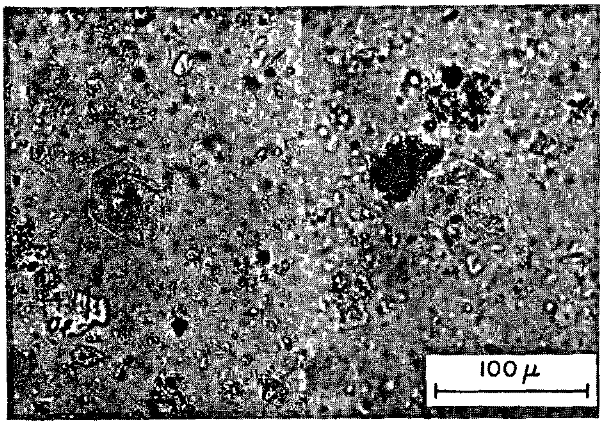

FIGURE 3. *Hydrated products of the reaction of trass with lime (photomicrograph).*

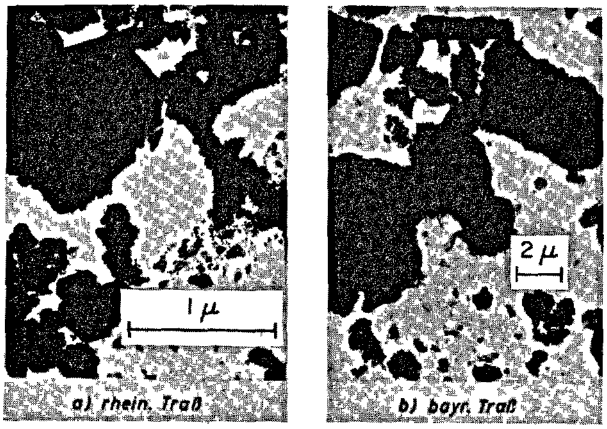

FIGURE 4. *Reaction products obtained by shaking (a) Rhenish trass, (b) Bavarian trass, with limewater (electron micrographs).*

The basic diffraction line of tricalcium disilicate hydrate makes its appearance after 14 days of the reaction, and another new product, C_4AH_{13}, is observed after 28 days, with its characteristic strong diffraction line at 5.3°. The calcium silicate hydrate phase is particularly characterized by a diffraction line at 14.5°.

No final explanation has yet been given for the displacement of the basic diffraction lines after a 660-day duration of the reaction. Specifically, it should be verified whether C_4AH_{13} changes by combining with silica into C_4ASH_{14}, first described by Flint and Wells [7] and later by Dörr [8], which has not as yet been synthesized in pure form.

Figure 3 shows a photomicrograph of hexagonal platelets of C_4AH_{13} formed in the trass-lime reaction.

Figure 4 presents the reaction products of (a) Rhenish trass and (b) Bavarian trass with lime.

In the reacted Rhenish trass are found, along with small hexagonal platelets consisting of C_4AH_{13}, some clearly transparent crystals with conchoidal fracture, which prove to be calcium silicate hydrate. In contrast to this, in the reaction of Bavarian trass with lime, one observes almost exclusively calcium silicate hydrate, which is particularly well revealed at the particle boundaries of the larger trass particles by its transparency and conchoidal fracture.

The observation that less aluminate hydrate forms in the reaction of Bavarian trass with lime than in that of Rhenish trass yields in this test a confirmation of the fact that in the system Rhenish trass-lime-gypsum-water one finds besides the already mentioned new products also ettringite and $3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$, which are present only in small degree in the Bavarian trass system.

The systems portland cement-water and trass cement-water yielded the same hydration products as were observed in the gypsum-containing system with Rhenish trass and lime. Marked differences in the X-ray charts are shown only by the contents of free lime While in hydrated trass cement $Ca(OH)_2$ was observed after prolonged shaking only to a small degree, the strong diffraction lines in portland cement indicate large quantities of free lime.

The individual hydrates observed in hydrated portland cement and trass cement were as follows:

$Ca(OH)_2$
$3CaO{\cdot}2SiO_2{\cdot}aq.$
$4CaO{\cdot}Al_2O_3{\cdot}13H_2O$
$3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$ (ettringite)
$3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$.

Thus our studies show that new products formed during the reaction of trass with lime in aqueous solutions are identical with those formed in the reaction of portland cement or trass cement with water.

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Paper VIII-S-7. High Strength Rapid-Hardening Concrete*

B. G. Skramtaev

Synopsis (By editor)

Methods by which concrete of high early strength is produced in the Soviet Union are briefly presented. These methods are: use of high early strength cement, additional grinding of the cement at the concrete plants, vibration to permit use of low water-cement ratio, use of calcium chloride admixture, conventional steam curing at steam temperatures up to 100 °C, steam curing at 100 °C with the concrete covered by rubber sheeting, high-pressure steam curing in autoclaves, and self-steaming in closed molds at 140–150 °C.

Résumé

Les méthodes selon lesquelles le béton de haute résistance initiale est produit en Union Soviétique sont présentées en bref. Ces méthodes sont les suivantes: l'utilisation de ciment à haute résistance initiale, le broyage supplémentaire du ciment dans les usines de béton, la vibration pour permettre l'usage d'un rapport eau-ciment peu élevé, l'utilisation d'addition de chlorure de calcium, la conservation normale à la vapeur à des températures de vapeur allant jusqu'à 100 °C, la conservation à la vapeur à 100 °C avec le béton sous revêtement de caoutchouc, la conservation à la vapeur sous haute pression dans des autoclaves, et l'autotraitement par vapeur dans des moules clos à 140–150 °C.

Zusammenfassung

Methoden mit deren Hilfe ein schnellerhärtender hochfestiger Beton in der Sowietunion hergestellt wird, werden kurz besprochen. Diese sind: Benutzung schnellerhärtender Zemente; nochmaliges Mahlen der Zemente in der Betonfabrik; Anwendung eines Rüttlers, sodass man mit einem niedrigen Wasser-Zementverhältnis arbeiten kann; Hinzumischung von Kalziumchlorid; ordinäre Dampfbehandlung bis 100 °C; Behandlung mit 100 °C Dampf, wobei der Beton mit Gummimatten bedeckt wird; Hochdruckdampfbehandlung im Autoklaven, und Selbstdampfentwicklung in verschlossenen Formen bei 140–150 °C.

Each country which produces precast and prestressed concrete has to have high strength rapid-hardening concrete, and therefore uses high-early-strength portland cement, steam curing, or heating of concrete. All three methods are used in the Soviet Union.

Generally we produce portland cement of five types according to its compressive strength after 28 days: 300–400–500–600–700 kg/cm^2. The last three types are used for making precast and prestressed concrete structures.

A part of this cement is high-early-strength portland cement. The demand of our technical specifications for this cement is: compressive strength at the age of 1 day (24 hr) no less than 200 kg/cm^2 (practically it reaches 250, sometimes more), at the age of 3 days no less than 300 kg/cm^2 (practically 350 kg/cm^2 and more).

For the production of high-early-strength portland cement we use a good clinker with the total content of C_3S and C_3A no less than 60 percent, a little higher addition of gypsum (up to 3.5 percent SO_3) and very fine grinding.

Sometimes to accelerate the hardening of cement and obtain fresh cement we use additional grinding of cement at the concrete plants, using the new mills, the so-called vibromills, and adding gypsum up to 6 percent SO_3.

An additional way of obtaining high-strength rapid-hardening concrete is the use of a dry concrete mixture with low water-cement ratio, less than 0.35, and vibration under load or vibropressure.

The next method of producing rapid-hardening concrete is the well-known admixture of calcium chloride, but we use it only for structures with reinforcement steel in diameter not less than 5 mm. The corrosion of steel is dangerous for thin wire.

The properties of rapid-hardening cement and concrete are active only under normal temperature conditions. Due to the severe climate of the larger part of the USSR we have to use very often the steam curing of concrete. In this case there is no necessity to have high-early-strength portland cement.

In the field of steam curing we have such a novelty as the high temperature of steam, up to 100 °C. Some years ago we were afraid of using steam with temperature higher than 70 °C. Now when we use pure wet steam and portland cement with the content of C_3A not higher than 8 percent, we have very good results with steam curing at the temperature up to 100 °C. Because of this we have shortened the period of steam curing down to 8 hr instead of 16 hr. After steam curing we obtain compressive strength not less than 70 percent of normal 28-day strength. This is good enough for the transportation and erection of precast concrete units.

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*Fourth International Symposium on the Chemistry of Cement, Washington, D.C., 1960. Contribution from the U.S.S.R. Academy of Construction and Architecture, Moscow, U.S.S.R.

When we produce the large wall and floor panels by roll machines we use the heating of concrete at the temperature 100 °C, but in this case the concrete is enclosed by a rubber sheet. After 3 hr of this treatment, we have a compressive strength of concrete not less than 200 kg/cm^2.

The most rapid hardening of concrete is under steam-pressure curing in autoclaves or new process-heating in closed molds, so-called self steaming. This process was developed by V. V. Mikhailov in 1937. Using a very dry concrete mixture with w/c=0.25, vibropressure, and heating at the temperature 140–150 °C, he obtained after 2 hr the compressive strength of concrete, 400 kg/cm^2, and after 28 days, 1,000 kg/cm^2.

This is indeed rapid-hardening and high-strength concrete. The process is used for making prestressed pipes.

Author Index

Combined author index for the two volumes of NBS Monograph 43

(Volume I, pages 1 to 575. Volume II, pages 577 to 1125.)

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