PROCEEDINGS

OF THE [Second International]

SYMPOSIUM

ON THE

CHEMISTRY OF CEMENTS

STOCKHOLM 1938
(6th - 8th July)

Held under the auspices of

INGENIÖRSVETENSKAPSAKADEMIEN
(THE ROYAL SWEDISH INSTITUTE FOR ENGINEERING RESEARCH)

and

SVENSKA CEMENTFÖRENINGEN
(THE SWEDISH CEMENT ASSOCIATION)

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Discussion:

The System $CaO\text{-}Al_2O_3\text{-}H_2O$.

The System CaO-SiO_2-H_2O.

Discussion:

Discussion:

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[1] For the discussion on Professor SCHLÄPFER's paper see also the discussion on Dr. FORSÉN's paper and *vice versa*.

NOTES

The following abbreviated formulae are used in the text:

$C_3S = 3CaO \cdot SiO_2$
$C_2S = 2CaO \cdot SiO_2$
$C_3S_2 = 3CaO \cdot 2SiO_2$
$C_3A = 3CaO \cdot Al_2O_3$
$C_5A_3 = 5CaO \cdot 3Al_2O_3$
$CA = CaO \cdot Al_2O_3$
$C_3A_5 = 3CaO \cdot 5Al_2O_3$
$C_2AS = 2CaO \cdot Al_2O_3 \cdot SiO_2$
$C_2F = 2CaO \cdot Fe_2O_3$
$CF = CaO \cdot Fe_2O_3$
$C_4AF = 4CaO \cdot Al_2O_3 \cdot Fe_2O_3$

All temperatures are quoted in degrees Centigrade unless otherwise stated.

The literature references are given with abbreviations of the titles in accordance with the system indicated in Chemical Abstracts (U. S. A.), *25*, 6019.

REVIEW OF THE SYMPOSIUM

The Symposium on the Chemistry of Cements took place on the 6th, 7th, and 8th of July 1938 in Stockholm. Personal invitations to a number of research cement chemists and Swedish representatives had previously been sent out by Ingeniörsvetenskapsakademien (the Royal Swedish Institute for Engineering Research) and Svenska Cementföreningen (the Swedish Cement Association), the sponsors of the meeting. It had also been arranged with some prominent research scientists that they should prepare reports on separate fields of cement chemistry, which reports should serve as a basis for the Symposium.

Before the Symposium the foreign participants made a short excursion through Sweden beginning in Malmö the 5th of July and finishing the next day in Stockholm. The first day visits were made to the Limhamn Cement Works and Laboratories of the Skånska Cementaktiebolaget and to the factory of Dalby Siporex A. B. (light weight concrete). In the evening a dinner was given in Falsterbo by the Skånska Cementaktiebolaget where its President, Mr. E. WEHTJE, bade the foreign members heartily welcome to Sweden. The following day visits were made to power stations at Lilla Edet, Trollhättan and Vargön (low-heat cement was used for a part of the construction in Vargön) belonging to Kungl. Vattenfallsstyrelsen (the Royal Board of Waterfalls) and demonstrated by its Chief Engineer Mr. A. EKWALL, further to the pottery factories of A.B. Rörstrands Porslinsfabriker, Lidköpings-Porslinsfabrik in Lidköping and to the Hellekis Cement Plant of Skånska Cementaktiebolaget where the technical chief of the company Mr. N. DANIELSEN gave a luncheon.

The sessions of the Symposium were held at Grevturegatan 14 in the premises of the Royal Swedish Institute for Engineering Research. The papers to be discussed had been printed and distributed in advance as far as time had allowed. The remaining papers and the written contributions had been duplicated and were distributed at the meeting. The proceedings passed as follows[1].

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[1] The speakers used the English language with the exception of the German participants who talked in German. When desired translation was made from either language by the interpreter.

Wednesday, the 6th of July.

Forenoon Session.

The PRESIDENT, Professor A. F. ENSTRÖM, President of the Royal Swedish Institute for Engineering Research, opened the Symposium with a speech, in which he reminded his hearers of the importance of international co-operation in Science and Technics, and wished the meeting good success in exchanging knowledge and establishing friendships.

The VICE-PRESIDENT, Consul W. DE SHÂRENGRAD, President of the Swedish Cement Association, gave an address of welcome. The VICE-PRESIDENT reviewed the history of the Swedish Cement Industry and Research, referred to the Industry's wish to keep up good contact with the Science from the time of Professor A. E. TÖRNEBOHM until these days, and wished the participants a very hearty welcome.

Professor T. SVEDBERG, of the University of Upsala, gave a lecture on "The Study of Giant Molecules by Means of Ultracentrifugal Sedimentation, Diffusion, and Electrophoresis". (Pages 13—41 in this book.)

Professor J. A. HEDVALL, of the Technical University in Göteborg, gave a lecture on "Reactions between Substances in Solid State with Special Regard to Systems Containing Silica". (Pages 42—58 in this book.)

The PRESIDENT announced that during the following technical sessions the chair would be taken by Professor T. THORVALDSON, Professor W. EITEL, Dr. F. M. LEA, Professor P. SCHLÄPFER and Dr. R. H. BOGUE, successively, which gentlemen had kindly agreed to this arrangement and that Mr. S. GIERTZ-HEDSTRÖM would be the Secretary during the meeting.

Afternoon Session.

The CHAIRMAN, Professor T. THORVALDSON, of the University of Saskatchewan, opened the session and expressed on behalf of the participants in the meeting their appreciation of the initiative taken when the Symposium was organized. In calling upon Dr. R. H. BOGUE to speak the CHAIRMAN said that it was very appropriate that Dr. BOGUE, who during the last 15—20 years had done more than anyone else in cement chemistry and who represented here the National Bureau of Standards and the Portland Cement Association in U. S. A., both well known for their fundamental work on cement chemistry, was now to be the first speaker on the cement question and to do it on the most important theme, the constitution of Portland cement clinker.

Dr. R. H. BOGUE, of the Portland Cement Association Fellowship at the National Bureau of Standards, presented his paper on "Constitution of Portland Cement Clinker". (Pages 59—98 in this book.)

Dr. W. BÜSSEM, of the Kaiser-Wilhelm-Institut für Silikatforschung, presented his paper on "X-Rays and Cement Chemistry". (Pages 141—168 in this book.)

The CHAIRMAN said that he was sorry to have to announce that Dr. H. E. SCHWIETE, of the Universität Frankfurt/Main, who was to have presented a paper on "Thermochemistry of Portland Cement Compounds", was ill and not able to fulfil his obligation. The CHAIRMAN expressed the sympathy with Dr. SCHWIETE of everybody present and regretted that the meeting would not be able to discuss Dr. SCHWIETE's paper which should have presented much of interest, its author being well known for his work in this field.

The CHAIRMAN opened the *discussion* on Dr. BOGUE's and Dr. BÜSSEM's papers. Written contributions had been given in by Messrs. M. A. SWAYZE, T. W. PARKER, and B. TAVASCI. The following gentlemen took part in the discussion: Dr. M. A. SWAYZE, Dr. F. M. LEA (presenting Dr. T. W. PARKER's contribution), Professor W. EITEL (presenting Dr. B. TAVASCI's contribution), Dr. N. SUNDIUS, Mr. G. E. BESSEY, Dr. A. EIGER, Dr. E. BRANDENBERGER, Professor T. THORVALDSON, Dr. R. H. BOGUE, and Dr. W. BÜSSEM. (The final contributions to the discussion are reproduced on pages 99—140, and 169—177 in this book.) The discussion was continued in the Afternoon Session the next day.

The CHAIRMAN then called upon Dr. R. H. BOGUE, who did homage to the memory of the late Professor HENRY LE CHATELIER, the famous scientist and pioneer in cement chemistry. Dr. BOGUE suggested that an address of homage for HENRY LE CHATELIER should be sent to the Sorbonne, Paris. The SECRETARY read the address and the proposal by the CHAIRMAN to send this address was unanimously accepted by the meeting in a rising vote. (The speech by Dr. BOGUE and the address for HENRY LE CHATELIER are reproduced on pages 542—543 in this book.)

Thursday, the 7th of July.

Forenoon Session.

The CHAIRMAN, Professor W. EITEL, of the Kaiser-Wilhelm-Institut für Silikatforschung, opened the session. Reference was made to the International Subcommittee on Special Cements for Large Dams by Mr. B. HELLSTRÖM, Mr. A. EKWALL, Dr. F. M. LEA, Dr. R. H. BOGUE, and the Chairman. (An abstract of the speeches made on this occasion is given on pages 544—545 in this book.)

Mr. G. E. Bessey, of the Building Research Station, presented his paper on "The Calcium Aluminate and Silicate Hydrates". (Pages 178—215 in this book.)

Dr. F. M. Lea, of the Building Research Station, presented the paper by Mr. F. E. Jones (of the Building Research Station) on "The Calcium Aluminate Complex Salts". (Pages 231—245 in this book.)

Professor T. Thorvaldson, of the University of Saskatchewan, presented his paper on "Portland Cement and Hydrothermal Reactions". (Pages 246—267 in this book.)

The Chairman opened the *discussion* on Mr. Bessey's, Mr. Jones' and Professor Thorvaldson's papers. Written contributions had been given in by Messrs. B. Tavasci and A. Travers (two papers to be considered). The following gentlemen took part in the discussion: Professor T. Thorvaldson, Dr. G. Assarsson, Dr. E. Brandenberger, Mr. G. E. Bessey, and Dr. L. Forsén. (For the discussion see pages 216—230, and 268—269 in this book.)

Afternoon Session.

The Chairman, Dr. F. M. Lea, of the Building Research Station, opened the session.

Professor P. Schläpfer, of the Eidgenössische Technische Hochschule, presented his paper on "Effect of Water on Portland Cement". (Pages 270—284 in this book.)

Dr. L. Forsén, of the Skånska Cementaktiebolaget, presented his paper on "The Chemistry of Retarders and Accelerators". (Pages 298—363 in this book.)

The Chairman opened the *discussion* on Professor Schläpfer's and Dr. Forsén's papers. Written contributions had been given in by Messrs. C. Pontoppidan and G. E. Bessey. The following gentlemen took part in the discussion: Mr. C. Pontoppidan, Mr. G. E. Bessey, Dr. W. Büssem, Dr. R. H. Bogue, Dr. A. Eiger, Dr. G. Haegermann, Mr. D. C. Crichton, Dr. F. M. Lea, Professor P. Schläpfer, and Dr. L. Forsén. (For the discussion see pages 285—297, and 364—394 in this book.)

The Chairman said that as there was still time before the session had to be closed the discussion from yesterday might be continued, and he asked Professor T. Thorvaldson to take the chair for that purpose.

Professor T. Thorvaldson took the chair and re-opened the discussion on Dr. Bogue's and Dr. Büssem's papers. The following gentlemen took part in the discussion: Professor W. EITEL, Mr. R. G. FRANKLIN, Dr. F. M. LEA, Dr. L. FORSÉN, Dr. M. A. SWAYZE, and Dr. R. H. BOGUE. (For the discussion see pages 99—140, and 169—177 in this book.)

Friday, the 8th of July.

Forenoon Session.

The CHAIRMAN, Professor P. SCHLÄPFER, of the Eidgenössische Technische Hochschule in Zürich, opened the session.

Dr. N. SUNDIUS, of Sveriges Geologiska Undersökning (Geological Survey of Sweden), presented his paper on "The Mineral Content of Aluminous Cement". (Pages 395—421 in this book.)

Dr. G. ASSARSSON, of Sveriges Geologiska Undersökning (Geological Survey of Sweden), presented his paper on "Reactions of Aluminous Cement with Water". (Pages 441—458 in this book.)

The CHAIRMAN opened the *discussion* on Dr. SUNDIUS' and Dr. ASSARSSON's papers. A written contribution was given in by Mr. B. TAVASCI. The following gentlemen took part in the discussion: Professor W. EITEL (presenting the contribution by Professor B. TAVASCI), Dr. W. BÜSSEM, Dr. F. M. LEA, Dr. N. SUNDIUS, and Dr. G. ASSARSSON. (For the discussion see pages 422—440, and 459 in this book.)

As there was still time before the forenoon session had to be closed it was decided to continue with a part of the proceedings intended for the afternoon session, for which purpose Dr. R. H. BOGUE, of the Portland Cement Association Fellowship at the National Bureau of Standards, took over the chair.

Dr. F. M. LEA, of the Building Research Station, presented his paper on "The Chemistry of Pozzolanas". (Pages 460—490 in this book.)

Afternoon Session.

The CHAIRMAN, Dr. R. H. BOGUE, opened the session.

Mr. S. GIERTZ-HEDSTRÖM, of the Royal Swedish Institute for Engineering Research, presented his paper on "The Physical Structure of Hydrated Cements". (Pages 505—533 in this book.)

The CHAIRMAN opened the *discussion* on Dr. LEA's and Mr. GIERTZ-HEDSTRÖM's papers. No written contribution had been given in. The following gentlemen took part in the discussion: Mr. P. S. HÅKANSON, Dr. L. FORSÉN, Professor P. SCHLÄPFER, Mr. D. C. CRICHTON, Dr. W. BÜSSEM, Professor T. THORVALDSON, Dr. A. EIGER, Dr. D. G. R. BONNELL, Dr. F. M. LEA, and Mr. S. GIERTZ-HEDSTRÖM. (For the discussion see pages 491—504, and 534—541 in this book.)

The technical sessions now being finished, the CHAIRMAN called on the following gentlemen to speak:

Dr. M. A. SWAYZE, speaking of the two countries, Sweden and the "Country of Concrete", which the cement chemists had studied during the Symposium, wished to express the thanks of the participants in the meeting to the Royal Swedish Institute for Engineering Research and the Swedish Cement Association for their arranging the Symposium on the Chemistry of Cements. He also proposed a vote of thanks to Dr. L. FORSÉN and Mr. S. GIERTZ-HEDSTRÖM for the inspiration in getting the cement chemists together and the work done for its realization. Dr. SWAYZE hoped that a new meeting would be held in the not too distant future.

Professor W. EITEL underlined the value of meetings of this kind. He attached a very high value to the personal contacts made on these occasions and to the free exchange of experiences which had taken place. Professor EITEL expressed very heartily the thanks of the meeting to the PRESIDENT, Professor A. F. ENSTRÖM, and the VICE-PRESIDENT, Consul W. DE SHÀRENGRAD.

Dr. F. M. LEA endorsed the feelings expressed by Dr. SWAYZE and Professor EITEL and asked the CHAIRMAN to put to the meeting the following formal resolution:

> — "We, cement chemists gathered together from many lands, wish to express our very grateful appreciation of the kindness and hospitality which has been shown to us, and to offer our most sincere thanks to the Royal Swedish Institute for Engineering Research and the Swedish Cement Association for organizing this Symposium, which has been so fruitful for the advancement of the study of cements. The Symposium will remain a landmark in the history of cement chemistry and one which will always be associated with the names of the Royal Swedish Institute for Engineering Research and the Swedish Cement Association." —

The CHAIRMAN put the resolution to the meeting which accepted it by a rising vote. He then handed over the mallet to the PRESIDENT.

The PRESIDENT said that it was a great pleasure to him to see that the meeting had been a success. Several factors had contributed to that result. He expressed the thanks of the sponsors to the gentlemen who had prepared reports and to those who had taken part in the discussions and further to those gentlemen who had taken the chair during the sessions and conducted the discussions. The PRESIDENT hoped that when the participants next time gathered to a meeting of that kind they would bring fruits of new research in the endeavour of all present, the advancement of Science and Technics. Wishing the participants good luck the PRESIDENT declared the Symposium closed.

During the Symposium two official dinners were given. The Royal Swedish Institute for Engineering Research gave a dinner on the evening of Wednesday, the 6th of July, at Kungl. Djurgården, under the presidency of Professor A. F. ENSTRÖM. The Swedish Cement Association gave a dinner on the evening of Friday, the 8th of July, at Saltsjöbaden, under the presidency of Consul W. DE SHÀRENGRAD. The participants went from Stockholm to Saltsjöbaden by motor boats making a tour through the Stockholm archipelago.

The day after the Symposium, on Saturday the 9th of July, a sight-seeing tour in Stockholm was arranged by the Swedish Cement Association.

The lectures given at the Symposium and the papers presented are reproduced in the following. In sequence with each paper follows the appurtenant discussion. Prior to printing, the contributions to the discussions made at the meeting have been submitted for final alterations and have in some cases been completed with new contributions, it being open for the contributors to make alterations and for all invited to the meeting to prepare new contributions until 15th September. After that date the authors of the papers were given time for reply.

Stockholm 1st of October 1938.

STIG GIERTZ-HEDSTRÖM
SECRETARY OF THE SYMPOSIUM

LIST OF INVITED AND PARTICIPANTS[1]

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Bates, P. H., Dr., National Bureau of Standards, Washington D. C., U. S. A.
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Davis, R. E., Professor, 202 Engineering Materials Laboratory, University of California, Berkeley Calif., U. S. A.
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[1] The list includes all invited. Those marked with * have participated in the meeting and those marked with ** have sent contributions without having been present of the meeting.

Dunn, J. S., Dr., Casebourne & Co. Ltd., Billingham, c/o Durham, England.

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THE STUDY OF GIANT MOLECULES BY MEANS OF ULTRACENTRIFUGAL SEDIMENTATION, DIFFUSION AND ELECTROPHORESIS

BY

T. SVEDBERG
Phil. Dr., Professor
UNIVERSITY OF UPSALA, SWEDEN.

Mr. President, Gentlemen.

The invitation to speak before you about the work on high-molecular material or giant molecules done in my institute has embarrassed me a good deal. As a matter of fact I have no results whatever bearing directly on the chemistry of cements to report. Our investigations have so far been almost entirely confined to the study of high-molecular organic substances such as proteins and carbohydrates. A few inorganic colloids have been investigated but so far none containing silica. Under those circumstances it seemed to me that an account of the experimental technique which we have developed together with a few examples of measurements would best serve the purpose.

Introduction.

In recent years the study of molecular migration under the influence of different kinds of forces have furnished a number of data concerning the mass and shape of the molecules. Migration in a centrifugal field (sedimentation) is dependent on the *mass* and the *frictional constant,* the migration in an osmotic field (diffusion) depends on the *frictional constant,* and migration in an electric field (electrophoresis) on the *charge* and the *frictional constant.* By combining measurements of sedimentation and diffusion (either independent determinations or sedimentation equilibrium data) it is possible to eliminate the frictional constant and thus to arrive at values for molecular mass. An analogous elimination of the frictional constant from electrophoresis and diffusion measurements with the aim of obtaining the charge is not feasible at present. Electrophoresis data are, however, of high importance for the characterization of molecules of complicated structure. The frictional constant reflects to a certain degree the shape of the molecule. Unambiguous conclusions concerning the shape are not possible, though, without some additional data. Not only the shape of a molecule of a certain mass but also its volume influences the frictional constant and an abnormally high frictional constant may, therefore, be caused either by a high value of the specific surface or a high value of the specific volume (solvation). Even if we know that there is no solvation, definite conclusions concerning the shape of the molecule require studies of solutions with more or less orientated molecules.

In the following an account will be given of the experimental technique used in Upsala for the study of high-molecular compounds by means of ultracentrifugal sedimentation, diffusion, and electrophoresis.

Sedimentation.

In order to determine molecular sedimentation velocities centrifugal fields of high intensity have to be used so as to avoid undue blurring of the boundary due to diffusion (27) (FIG. 1). If the centrifuging is carried on long enough at a comparatively low speed an equilibrium between sedimentation and diffusion is finally reached (26) (FIG. 1, c).

Shape and Size of Sample.

In order to obtain convection-free sedimentation, which is essential in quantitative determinations, the sample of solution studied must be sectorial in shape and temperature changes must be kept low enough so as to prevent the formation of eddy-currents.

Principle of Cell.

To perform optical observations the sample has to be enclosed between plane-parallel windows transparent to various kinds of light and strong enough to withstand the enormous centrifugal forces (28).

Principle of Rotor.

The resolving power of the ultracentrifuge with regard to a mixture of different molecular species is proportional to the product of centrifugal field ($\omega^2 r$) and height of column of solution (h) (10), where ω is the angular velocity and r the distance from the centre of rotation to the centre of the column of solution. Rotors of equal form have the stress in any point proportional to $\omega^2 r^2$. Keeping the stress constant, the centrifugal field can therefore be doubled by doubling the angular velocity but decreasing the linear dimensions of the rotor by one half. The resolving power, however, is the same in both cases $(\omega^2 r\ h)$ and $[(2\ \omega)^2 r/2 \times h/2]$. At first sight it would seem, therefore, that a small rotor running at high speed and a large rotor running at low speed are just as good for ultracentrifugal analysis. In actual practice the large rotor is preferable. In the first place owing to construction difficulties with small rotors the resolving power $(\omega^2 r\ h)$ is somewhat higher for a large rotor than for a small one. Secondly, the accuracy in measuring the concentra-

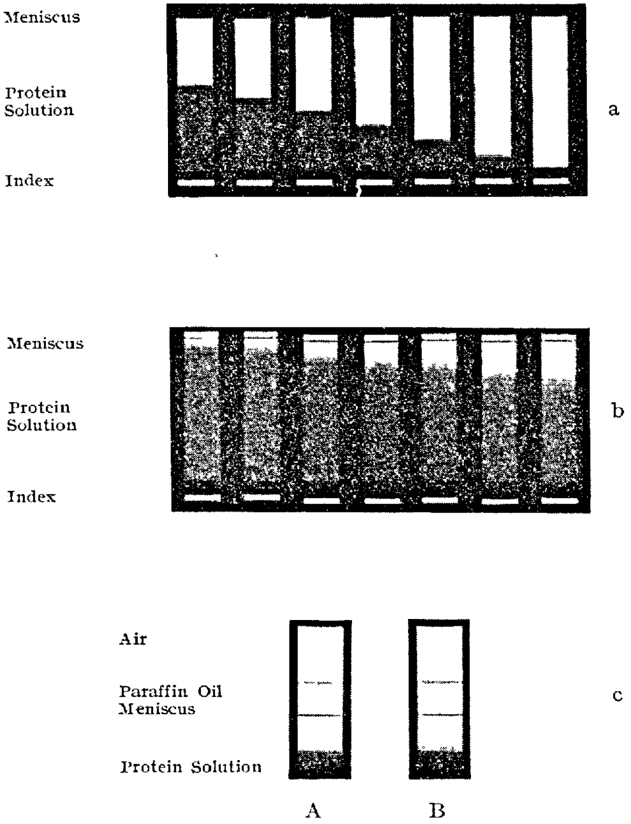

FIG. 1, a, b, c. Pictures obtained by Means of the Light Absorption Method showing the Sedimentation of Phycoerythrin (M = 290 000) in Centrifugal Fields of Different Intensity. (a) 260 000 times gravity, exposure interval 5 min.; (b) 23 500 times gravity, exposure interval 30 min.; (c) 2 300 times gravity. In the last case equilibrium between sedimentation and diffusion has been reached (A, 43 hours; B, 63 hours).

tion distribution—either by the absorption or the refractive index method—is less good in a low than in a high column of solution (4).

Cell Construction.

Experience in cell construction has shown that with the material available at present the cell has to be given a cylindrical outer surface with its axis at right angles to the windows (FIG. 2). This means round cell holes in the rotor.

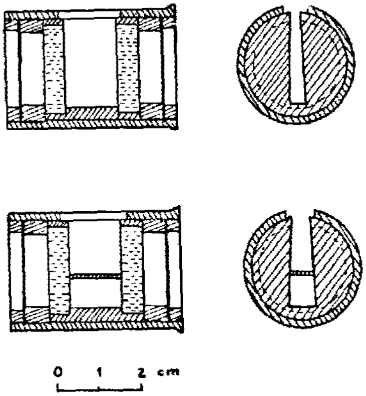

FIG. 2. Sections of Cells.
Upper Picture: Cell for optical determinations.
Lower Picture: Cell for separation under optical control.

Rotor Construction.

Both calculation and experience has given the result that the rotor should have oval shape with two thin vanes to screen off false light. The details of construction (FIG. 3) should aim at minimum stress which results in a bridge-like shape at the cell holes. Stress calculation further shows that the optimum value for the ratio between distance from centre of rotation to centre of cell, *r*, and cell hole diameter, *d*, is in the region 2.0 to 2.5 (4). Now for a given *r* the inhomogeneity of the centrifugal field increases with height of column of solution and therefore with *d*. This inhomogeneity tends to decrease the accuracy of measurement because of the general decrease of concentration with time of centrifuging (30) governed by the formula $c_2/c_1 = (x_1/x_2)^2$, where c_1 and c_2 are the concentrations in the uniform part of the solution when the boundary has reached the distances x_1 and x_2 from the centre of rotation. For this reason we have chosen the highest value of r/d compatible with optimum stress. The size of the rotor is limited by the danger of material defects in very large blanks.

Rotor Material.

As rotor material, steel has proved best. A comparatively soft chromium nickel steel of ultimate strength about 140 kg/mm^2 corresponding to a Brinell hardness of 400 should be chosen. Hard steel of higher tensile strength often cracks under the influence of centrifugal stresses. The use of some light metal alloy, *e. g.* duraluminium or electron metal, of a ratio between strength and density slightly higher than steel is not to be recommended because the stresses around the cell holes are to about 50 % due to the outward pull of the cell, the weight of which has already been reduced to the lowest possible amount. The highest resolving power is, therefore, at present reached with steel rotors.

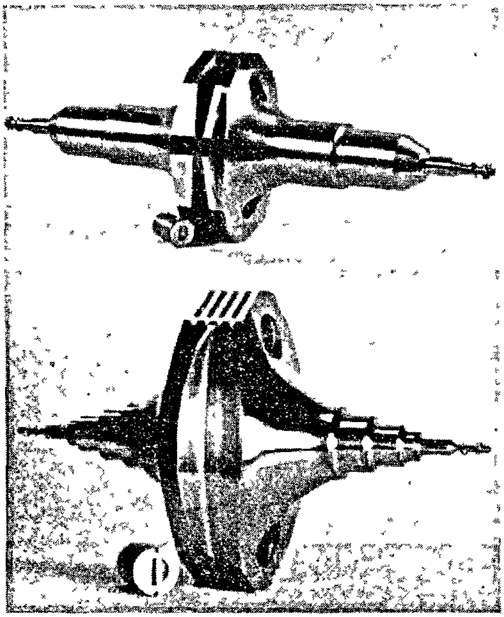

Fig. 3. Rotors and Cells.
Upper Picture: For centrifugal fields up to 710 000 times the force of gravity; largest diameter, 10.4 cm; mean active radius, 3.25 cm; height of column of solution, 0.8 cm.
Lower Picture: For centrifugal fields up to 300 000 times the force of gravity; largest diameter, 18 cm; mean active radius, 6.5 cm; height of column of solution, 1.8 cm.

Medium around Rotor.

To diminish friction the rotation has to take place in a medium of low viscosity. Vacuum is advisable only in such constructions where practically no heat from the bearings is transferred to the rotor. An atmosphere causing some friction but possessing a high heat conductivity is preferable. Under those circumstances the heat generated will be conducted away so quickly that satisfactory thermal conditions can be permanently maintained and convection currents avoided. For low-speed runs hydrogen of normal atmospheric pressure may be used, and for higher speeds hydrogen of about 20 mm pressure.

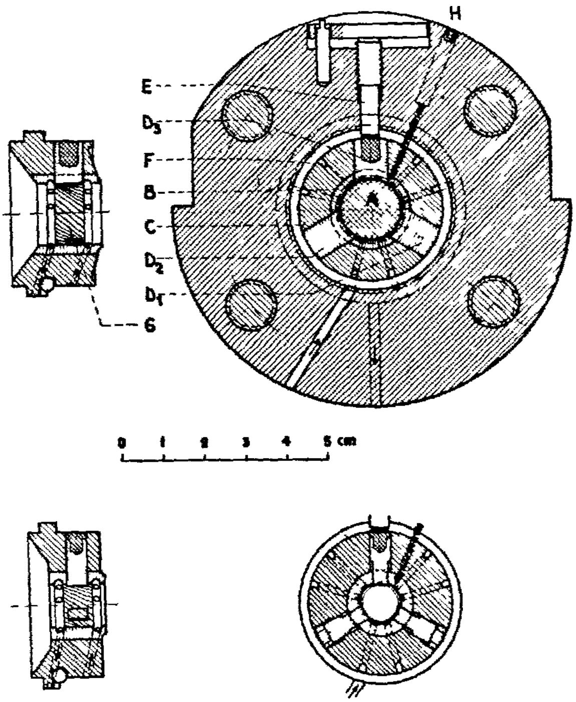

FIG. 4. Bearings with Damping Arrangement.

Bearings.

Up to speeds of about 20 000 r. p. m., or even somewhat higher, the rotor can be supported by ball-bearings. At high speed (20 000 to 160 000 r. p. m.) they become unreliable and have to be replaced by journal bearings or air-film bearings. In the Upsala constructions oil-lubricated white-metal was chosen.

Careful static and dynamic balance of the rotor is necessary but not sufficient for vibration-free rotation (28). Slight irregularities in the driving force or in the friction often tends to build up troublesome vibrations in spite of perfect balance. The rotor is carried in cylindrical journal bearings with its axis of rotation horizontal. A damping arrangement in the bearings takes care of the tendencies to vibration and ensures smooth running (Fig. 4). It is based on the following principle. The bearing surface is divided in six parts, three of which are fixed. The others form the end surfaces of loose pistons which are held against the journals by oil pressure. The play of the pistons is restricted by means of screws so that less clearance (diametrically about 0.02 mm) is left between the shaft and the pistons than between the shaft and the fixed parts of the bearings (diametrically about 0.12 mm). This reduces the friction considerably.

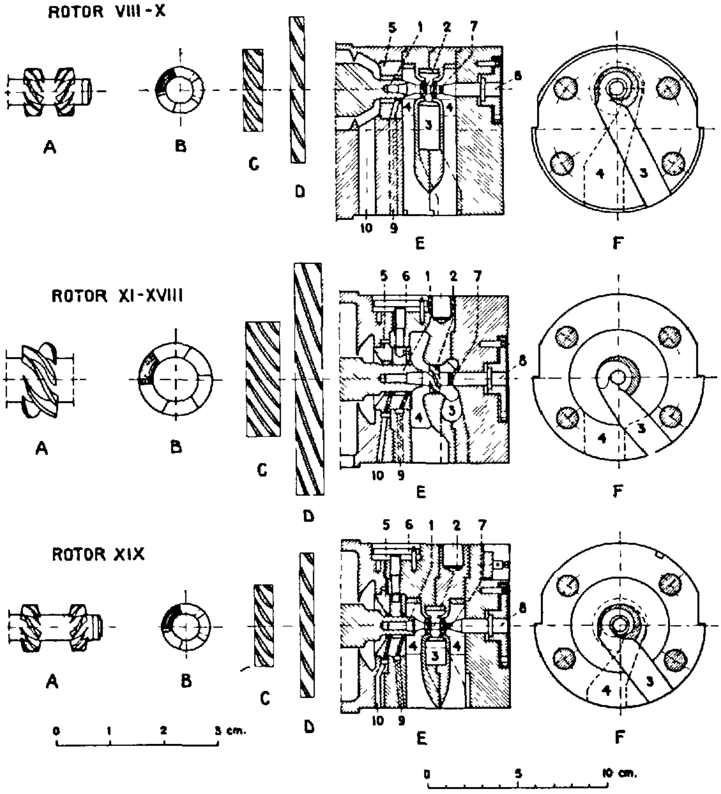

Fig. 5. Turbines and Turbine Chambers.

In the air-driven self-balancing ultracentrifuge developed by Beams and by Bauer the rotor is supported by an air-film bearing (1, 2). The air-turbine is sealed off from the vacuum chamber in which the rotor moves by surrounding the vertical shaft with an oiled gland-shaped bearing.

Drive.

Direct electric motor drive with the rotor self-balancing on a vertical shaft has proved very good for speeds up to 20 000 r. p. m. Beams has recently succeeded in spinning electrically a hanging duraluminium rotor supported by an air-film bearing up to 60 000 r. p. m. (3). For driving a heavy rotor at high speed, turbines appear to be the best means. Oil turbines have been chosen by us (FIG. 5). They are of axial flow reaction type with spiral inlet. No guide vanes are used. Twin turbines of a diameter slightly less than that of the journals have been found to give the best results. In order to shorten the time of stopping—especially in case of rotors with thin journals, where the friction is very low—a magnetic brake is used (energy consumption 50 watts).

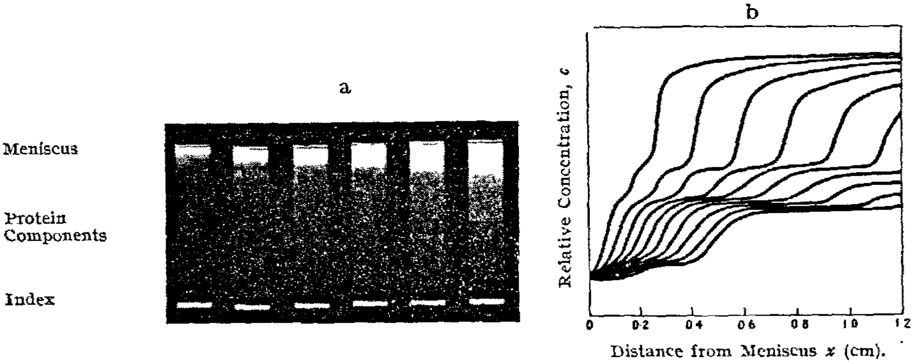

FIG. 6, a, b. Sedimentation Pictures (a) obtained by Means of the Light Absorption Method and Curves of Concentration Distribution (b) for Limulus Hemocyanin at P_H 6.8; Sedimentation Constants of Components 56.6, 34.6, 16.1, 5.9. Sedimentation constants are expressed in units of 10^{-13}; centrifugal force 120 000 times gravity; time between exposures 5 min.

Temperature.

For the calculation of sedimentation constants and molecular weights knowledge of the temperature in the rotating sample is necessary. In low-speed runs the temperature of the cell may with sufficient accuracy be taken as equal to the temperature in the thermostate bath surrounding the rotor chamber. In high-speed runs with the oil-turbine centrifuge, the steel casing surrounding the rotor may be thermostated by means of a stream of oil possessing the same temperature as the oil feeding the turbines. A thermocouple placed very close (0.15 mm) to the surface of the rotor near the cell hole registers the actual temperature of the cell.

Speed.

The angular velocity enters to the second power in the formulæ for sedimentation constant and molecular weight. The accurate determination of this quantity is therefore of great importance in ultracentrifugal technique. In the case of direct drive by an a. c. motor, a measurement of the frequency of the electric current suffices because with ball-bearings and the rotor running in hydrogen there is no noticeable slip. For the high-speed oil-turbine ultracentrifuge a stroboscopic tachometer was at first used. A more convenient magneto-electric method for speed measurement was worked out later on. Part of the shaft of the centrifuge rotor is magnetized and surrounded by a two-pole soft iron armature provided with coils. This device constitutes a magneto-electric generator which produces an a. c. current of the same frequency as the r. p. m. of the rotor. After amplifying this current is fed to a vibration frequency meter or to an oscillograph.

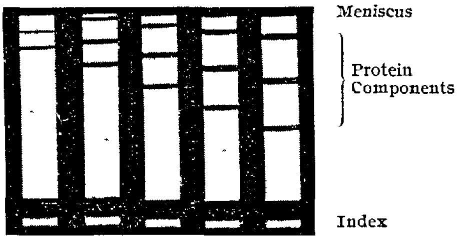

FIG. 7. Sedimentation Pictures for Limulus Hemocyanin obtained by Means of the TOEPLER Schlieren-Method at P_H 6.8 showing the Three Fastest Sedimenting Components of $s = 56.5$, 34.6, and 16.1. Centrifugal force 120 000 times gravity; time between exposures 5 min.

Measurements of Sedimentation Velocity.

The process of sedimentation is followed by optical means. Two different properties of the solute may be utilized for the determination of the concentration distribution in the rotating solution, *viz.* the light absorption and the refraction. In both cases the thickness of the layer of liquid studied necessitates long focus lenses in order to avoid parallactic errors.

Absorption Method.

When using the absorption method (27), photographic exposures of the sedimenting column are made from time to time by light of such a wavelength that the solute absorbes. These pictures are then registered by means of a microphotometer and give the relation between concentration c and distance x from centre of rotation. Each molecular species is brought out as a step on the c—x curve (FIG. 6).

Refraction Method.

The change in refractive index can be made use of in various ways. The simplest procedure is to apply the TOEPLER schlieren-method (35). The different molecular species present are then recorded on the plate like the lines of a mass-spectrum (Fig. 7). A more accurate procedure to obtain the real concentration distribution in the sample studied is to take pictures of a finely ruled scale through the sedimenting column of solution by light of a wave-length which is not absorbed (8, 9, 10). By measuring the displacement of the lines we get the concentration gradient *dc/dx* as a function of the distance from the centre of rotation. Each molecular species is therefore shown as a maximum on a curve (Fig. 8).

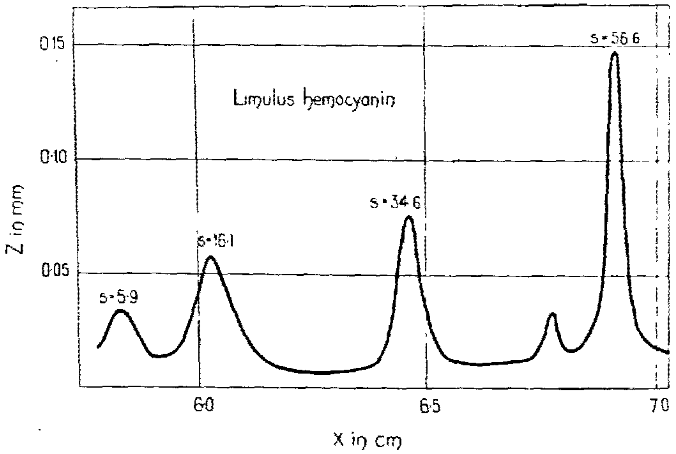

Fig. 8. Sedimentation Diagram for Limulus Hemocyanin obtained by Means of the Refractive Index Method at P_H 6.8 showing the Same Four Main Components as in Fig. 6 and also a Small Amount of a Fifth One. Centrifugal force 120 000 times gravity; time after reaching full speed 35 min.

By introducing a diagonal edge and a cylindrical lens in the optical path (15) it is possible to modify the schlieren-method so as to produce the sedimentation diagram by direct photography (Fig. 9).

Optically Controlled Separation.

In many cases (antibodies, enzymes, mixtures of proteins and carbohydrates) it would be of great value if a mechanical separation of part of the sample studied could be accomplished after a certain time of centrifuging and controlled by the optical observations. Analytical determination of sedimentation would then be possible. Experiments of this kind can now be performed using a cell with a membrane which divides it into two compartments (see p. 16) (36). Precipitation test on an antiserum centrifuged in this way is shown in Fig. 10.

Sedimentation Equilibrium Measurements.

In the case of sedimentation equilibrium measurements the shape of the cell is indifferent. A centrifugal force giving optimal concentration distribution has to be used. This force is for a given substance much lower than the force needed in sedimentation velocity determinations. The rotation has to be continued at constant temperature until test measurements have shown that equilibrium between sedimentation and diffusion is attained (this may take from a few hours up to several weeks with a 5 mm height of column of solution).

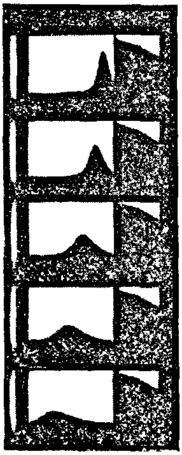

Fig. 9. Sedimentation Diagram of Lysozyme obtained by Means of Philpot's Modified Schlieren-Method. Centrifugal force 300 000 times gravity; time between exposures half an hour.

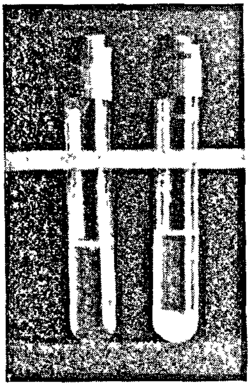

Fig. 10. Analytical Determination of Sedimentation (Horse Antibody Serum against Pneumococcus Type I Polysaccharide).

Construction of Oil-turbine Ultracentrifuge.

The high-speed oil-turbine ultracentrifuge equipment devised for sedimentation velocity measurements on substances of high molecular weight (in the case of proteins from 15 000 000 down to about 1 000) and for sedimentation equilibrium measurements on low-molecular substances is diagrammatically represented by Fig. 11. A detailed section of the centrifuge through the axis of rotation is shown in Fig. 12.

The rotor R is supported by horizontal bearings B_1 and B_2 and kept in rotation by the two small oil twin-turbines T_1 and T_2 one on each end of the shaft. Hydrogen is let in at the periphery and constantly pumped off so as to maintain a pressure of about 20 mm. Thermocouples Th_1 and Th_2 serve for temperature determinations of the bearings and the rotor. A beam of light from a mercury lamp L filtered through Lf_1, Lf_2, Lf_3 passes the cell C in the rotor on its way to the camera. The exposures are timed by means of the electromagnetic shutters S_1 and S_2. The stroboscope or the magnetic generator M enables the observer to measure the speed of the rotor. The pressure oil which feeds the turbines is produced by a special oil-compressor and cooled to a

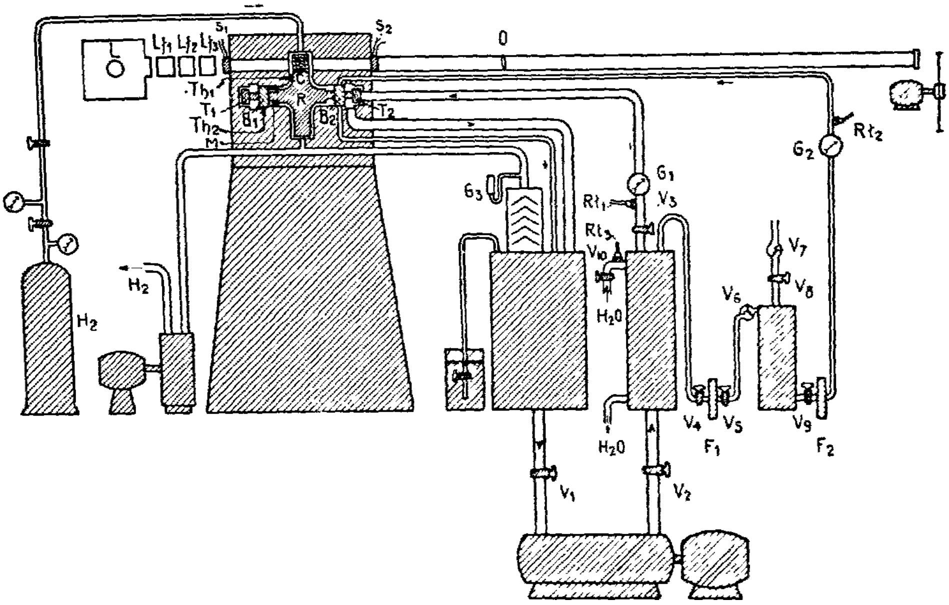

FIG. 11. Diagram of the High-Speed Oil-Turbine Ultracentrifuge Equipment.

suitable temperature before entering the turbine chambers. The lubricating oil for the bearings passes through an oil filter and is controlled by the valve V_9. By changing the speed of the motor which drives the compressor and by operating the valve V_3 the pressure of the oil entering the turbines may be regulated so as to make possible measurements at any desired speed between 20 000 and 140 000 (corresponding to centrifugal forces 30 000 to 700 000 times gravity). The resistance thermometers Rt_1, Rt_2, Rt_3 and the manometers G_1, G_2, G_3 enable the operator to control temperature and pressure in the various parts of the machinery.

FIG. 13 shows a picture of the oil-turbine ultracentrifuge with the upper part of the heavy steel casing lifted laying bare the rotor and the turbine chambers. The cell with its sector diaphragm is in vertical position upside down. Behind the centrifuge is the lamp house and the filters. The two halves of the thick steel casing are held together by bolts of chromium-nickel steel firmly anchored in a concrete foundation. The casing was designed to withstand centrifugal forces corresponding to a stress of 40 kg/mm^2 in the bolts which hold the two halves of the casing together. A calculation of the forces to be expected if the Rotor VII weighing about 9 kg had exploded at its highest test speed 78 500 r. p. m. gives 900 000 kg or about the same as the maximal force acting on the projectile of an 8 inch gun when firing. Taking into account the mass of the casing one gets an elastic deformation of 0.8 mm in the bolts corresponding to a stress of 48 kg/mm^2 which is on the safe side. The highest forces actually met with in a rotor explosion are 700 000 kg (Rotor XII of weight about 8 kg bursting at 84 000 r. p. m.). To reduce the amount of energy transmitted to the lower foundation the concrete pier itself is bolted to the lower foundation in such a way as to allow it to move a little round one side of the base surface, thereby straining the lower bolts elastically. The torque shock transmitted to the foundation is thus reduced to the magnitude 18 000 kgmetres. FIG. 14 gives a photograph of the whole installation showing the camera, the centrifuge on its foundation, the lamp-house, the oil container, the oil coolers and to the right the steps down to the machine pit.

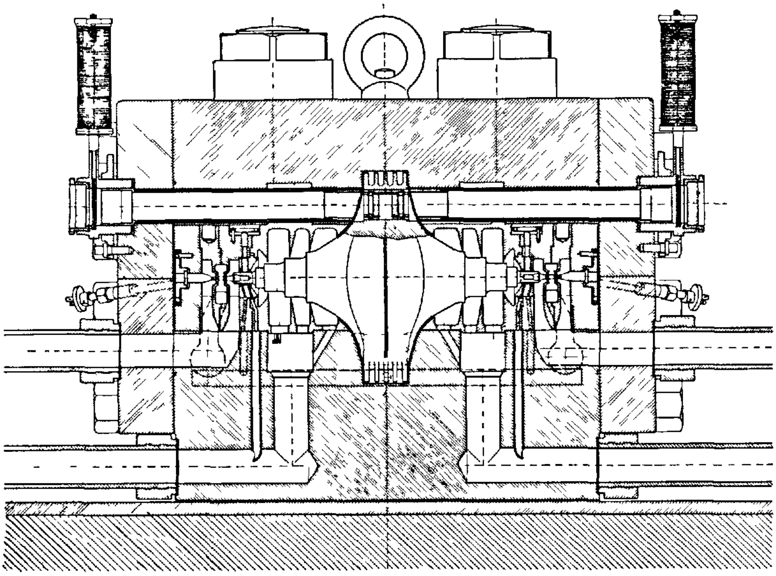

FIG. 12. Axial Section of the Oil-Turbine Ultracentrifuge.

Energy Considerations.

The energy problem of the ultracentrifuge may be specified as follows. The drive should provide for a sufficiently rapid speeding-up of the rotor and for maintenance of the rotation at constant speed. The length of the acceleration period is determined by the energy input, the moment of inertia (I) of the rotor, the desired ultimate speed and by the friction losses in the bearings and in the hydrogen surrounding the rotor. After the steady state has been reached the energy consumption in the centrifuge is limited to the friction losses.

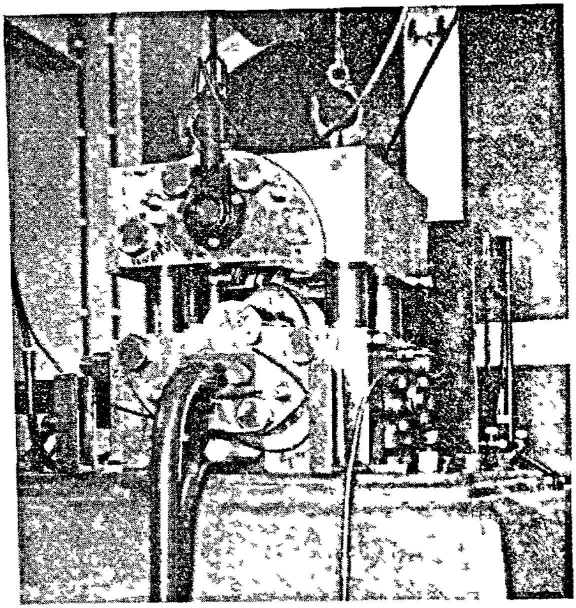

FIG. 13 Photograph of the Oil-Turbine Ultracentrifuge.

In our ultracentrifuge constructions we have aimed at the lowest expenditure of energy compatible with highest resolving power. The moment of inertia of the rotor is given by its size, shape and density, which factors are in their turn determined by the optimum conditions for sedimentation analysis. The friction losses can be reduced by chosing the hydrogen pressure low (10—15 mm) and by depressing the friction in the bearings. Vibrations cause by far the heaviest losses. The damping arrangement eliminates vibrations almost completely and the bearing friction can therefore be lowered effectively by chosing a small journal diameter (10 mm) and a short bearing surface (10 mm).

The overall efficiency of the oil-turbine ultracentrifuge is the product of the efficiency of the oil turbines, the oil pumps and the electromotor. If the values of velocity, Q, and pressure, P, of the oil stream necessary to keep the rotor going at constant speed is known for a number of different speeds, then the efficiency of the turbines may be calculated from acceleration experiments and the known moment of inertia of the rotor.

When the efficiency of the turbines is known, the actual frictional resistance may be calculated for the different speeds from the value of $P \times Q$ which is just necessary to maintain the rotor at a given speed. By varying the hydrogen pressure (p) but keeping the speed of the rotor constant, it is possible to compute the absolute bearing and gas frictional resistance separately. It was hereby found that the gas friction was proportional to $p^{3/2}$ for hydrogen pressure from about 10 mm and upwards. By comparing the energy consumed by the gas friction alone for different speeds of the centrifuge, it was observed that this was approximately proportional to the third power of the velocity. This indicates turbulent gas friction.

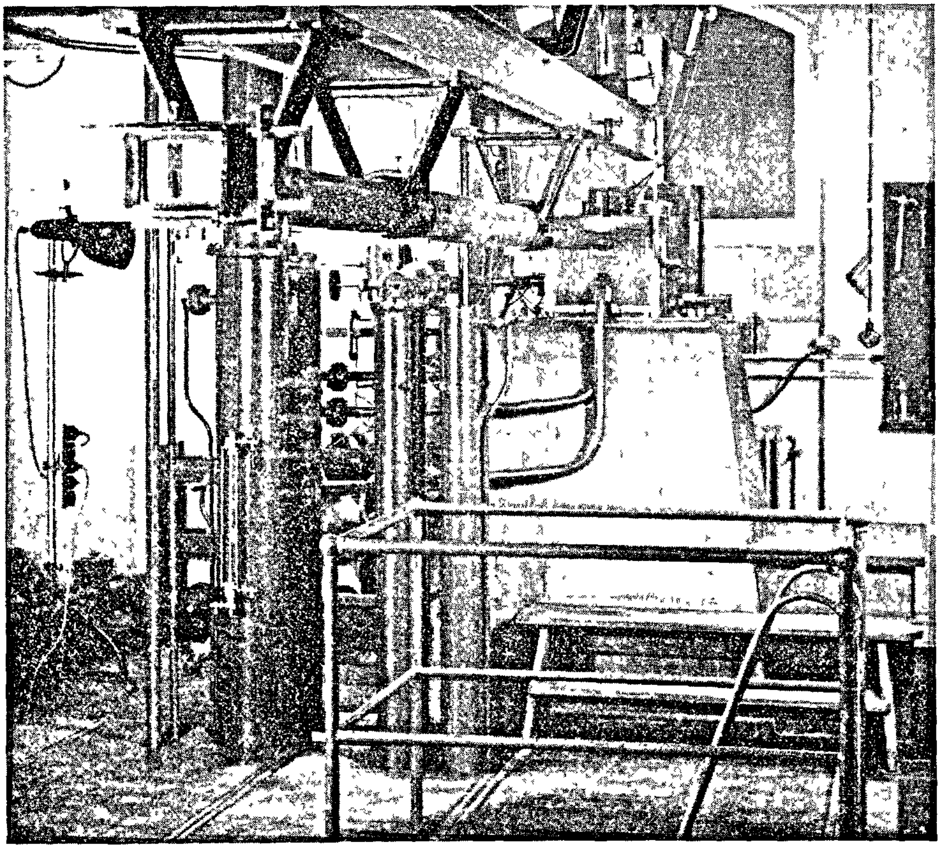

FIG. 14. Photograph of the Oil-Turbine Ultracentrifuge Installation.

By subtracting the gas friction from the total (absolute) frictional resistance, it was found that the bearing friction increased slightly more than ω^2.

The actual frictional resistance of Rotor III (9 kg) running at 60 000 r. p. m. in a hydrogen atmosphere of 20 mm Hg is only 301 watt. Of this the bearing friction accounts for 269 watt, whereas the gas friction amounts to only 32 watt. At 30 000 r. p. m. the corresponding values are: bearing friction 57 watt, gas friction 4.6 watt. These data were obtained with Rotor III after the diameter of the journals had been reduced from 18 mm to 10 mm with the latest bearing construction in which the journals rest only on the three pistons. By way of comparison it may be stated that for Rotor VII (with 18 mm journals) the power necessary to balance the frictional resistance in the bearings amounted to 1 490 watt at 55 000 r. p. m. and to 2 280 watt at 65 000 r. p. m. The gas friction consumed 30 watt, and 40 watt respectively (or approximately the same as was found in case of Rotor III).

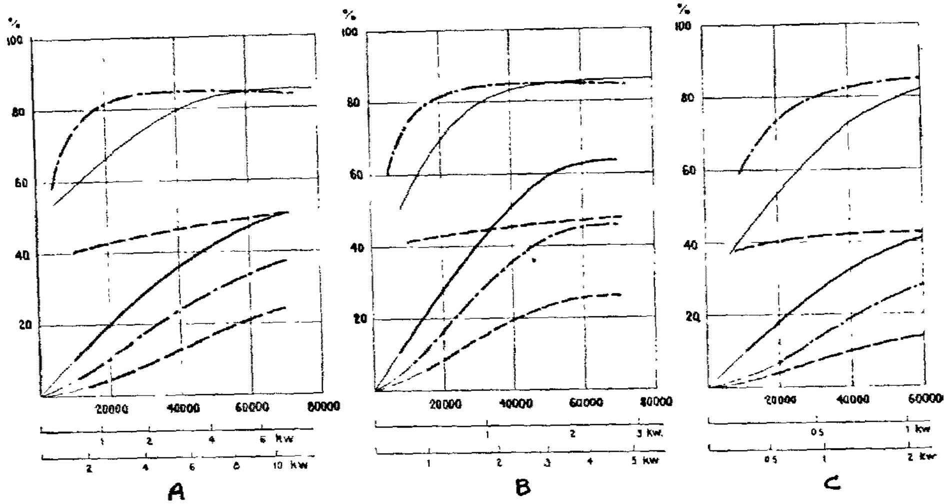

FIG. 15. Diagram showing for Different Rotors the Variation in the Total Efficiency and in the Efficiency of the Single Part of the Centrifuge System with the Speed of the Rotor.
A: Rotor VII (1933), 18 mm journals, single turbines.
B: Rotor XV (1936), 16 mm journals, single turbines.
C: Rotor III (1937), 10 mm journals, twin turbines.
The scales below the diagram give the power necessary to revolve the rotors at a given speed using the Imo-pump and the centrifugal pump, respectively.
———————— Efficiency of oil turbines;
———————— Efficiency of electric motor;
— - — - — - — - — Upper curve = efficiency of Imo-pump;
— - — - — - — - — Lower curve = total efficiency with Imo-pump;
- - - - - - - - - - - - Upper curve = efficiency of centrifugal pump;
- - - - - - - - - - - - Lower curve = total efficiency with centrifugal pump.

It has been found advisable to keep the hydrogen pressure at 10—20 mm Hg. For very low hydrogen pressures (below 5 mm) the friction increased strongly with decreasing hydrogen pressure. This behaviour is explained by unavoidable extremely small air leakage in the oil system (the vapour-pressure of the oil itself is around 0.01 mm Hg). By substituting air for hydrogen as the gas surrounding the rotor, it was found that the frictional losses were about 40 times higher with air than with hydrogen at the same pressure.

The efficiency of the pump may be calculated from the value for the system, motor + compressor, by inserting the efficiency of the motor. FIG. 15 shows how the efficiency of the motor, the pump, the turbines and the combined system varies with speed and with the power consumed by the electric motor.

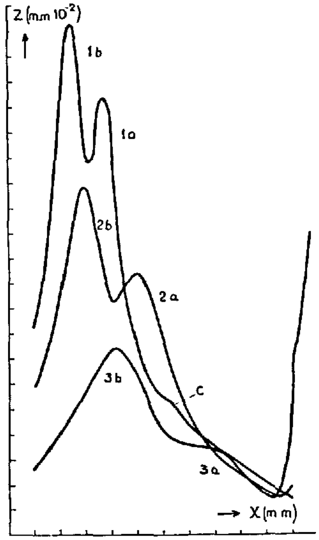

FIG. 16. Sedimentation Diagram of Starch treated with Acid.

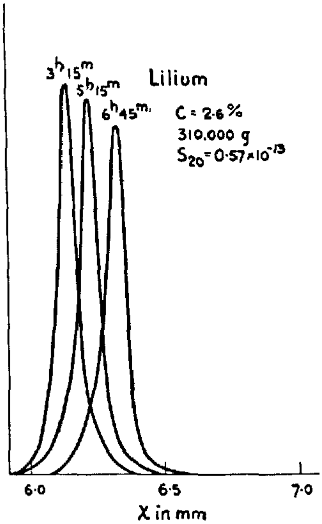

FIG. 17. Sedimentation Diagram of Carbohydrate in the Sap of Lilium Bulbs.

When chosing the size of the motor and compressor, it is necessary to know the energy required for accelerating the rotor to a given speed in a certain time. The compressor must be so powerful that this acceleration period is reasonably short.

When Rotor III ($I = 2.25 \times 10^5$ gram cm^2) is running at 60 000 r. p. m., its rotational energy amounts to 107 kg-cal. Assuming that the average efficiency of the system during the acceleration period (motor + centrifugal pump + turbines) is about 7 % (Imo-pump 14 %) and that a total time of half an hour is chosen for bringing the rotor up to full speed, an average power of 3.6 kW is used during this half hour in order to supply the rotor with rotational energy. For Rotor VII ($I = 1.80 \times 10^5$ gram cm^2) the rotational energy at 65 000 r. p. m. is 100 kg-cal. With an acceleration time of half an hour and an overall efficiency of 10 % (Imo-pump 20 %), an average of 2.4 kW (Imo-pump 1.2 kW) is used during 30 min. to supply the rotor with the necessary rotational energy.

From the known value of the frictional resistance of the bearings it is possible to calculate the primary energy required to revolve, for example, Rotor III electrically. The efficiency of a 1 000 cycle motor-generator is estimated at 25—30 per cent, whereas the efficiency of a single phase 1 000 cycle motor is estimated to be only 20 per cent, which means an overall efficiency of 5—6 per cent for the electrical system. The primary motor energy required to drive Rotor III electrically at 60 000 r. p. m. would therefore be 5—6 kW, or considerably more than with oil-turbine drive.

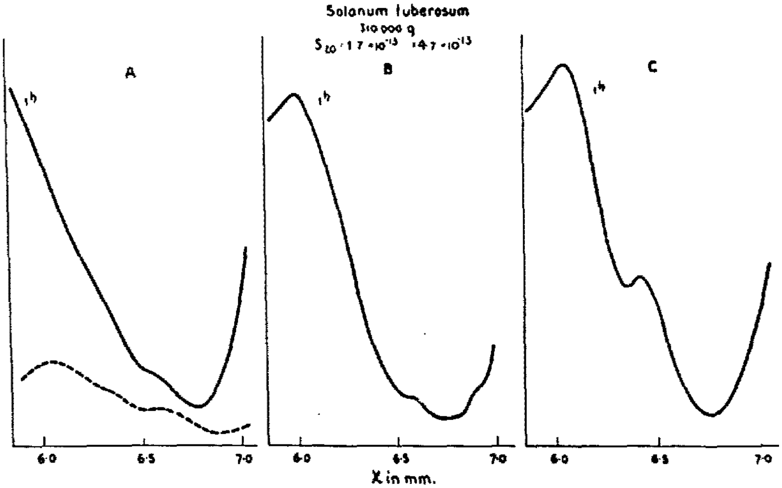

FIG. 18. Sedimentation Diagram of Carbohydrates in Potato.
A. From dormant tubers.
B. From tubers just beginning to sprout.
C. From tubers in the midst of sprouting.

A comparison between the oil-turbine and the air-turbine ultracentrifuge shows that, at the present time, the expenditure of energy is lower in the oil-turbine than in the air-turbine type. The efficiency of an air-compressor is about the same as that of a good oil pump (60—70 %), but the efficiency of the air-turbines is low (4 %) and therefore the overall efficiency is not more than about 2 %. The friction losses in the air-bearing are very low, but even so the total energy necessary for start and maintenance of speed amounts to about 7 hp.

From sedimentation velocity measurements the sedimentation constant is calculated by means of the formula

$$s = dx/dt \times 1/\omega^2 x \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots [1]$$

where dx/dt is the observed sedimentation velocity, ω the angular velocity, x the distance from the centre of rotation.

If the diffusion constant D is known the molecular weight is found by the expression (24, 27)

$$M = \frac{RT\,s}{D(1-V\varrho)} \quad \ldots\ldots\ldots\ldots\ldots\ldots [2]$$

where R is the gas constant, D the diffusion constant, V the partial specific value of the solute and ϱ the density of the solution.

Sedimentation equilibrium measurements are used for calculation of the molecular weight by means of the equation (24, 26)

$$M = \frac{2\,RT\,ln\,c_2/c_1}{(1-V\varrho)\omega^2(x_2^2-x_1^2)} \quad \ldots\ldots\ldots\ldots\ldots [3]$$

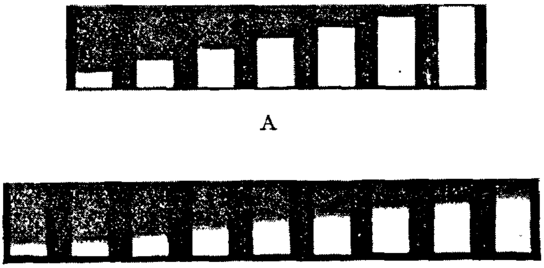

FIG. 19. Sedimentation Pictures of Polystyrene dissolved in Chlorophorm.
A. Interaction of the molecules.
B. Free sedimentation.

where c_1 and c_2 are the concentration at the distances x_1 and x_2 from the centre of rotation.

The utilization of the ultracentrifuge for the study of high-molecular compounds is only at its beginning. So far the main interest of application has been in the field of biology and medicine and the few examples of measurements given above have been taken from the study of proteins—those substances of paramount importance to all living beings (20, 21, 22, 23, 25). But there are also the vast fields of the carbohydrates (6, 7, 8, 13, 19), the hydrocarbons, the synthetic organic high-molecular compounds (12, 17, 18), and the various classes of inorganic colloids (14, 16). A number of important chemical industries are handling materials belonging to one or the other of these groups of substances. The cement industry would chiefly be interested in the study of silica-containing inorganic colloids by means of this new tool.

As an example of the study of a carbohydrate mixture, FIG. 16 shows the ultracentrifugal analysis of acid-treated starch revealing two maxima, one corresponding to amylose (molecular weight about 60 000) and the other to amylopectin (M ~ 200 000). Both substances are more or less polydisperse (7, 8). FIG. 17 gives the sedimentation diagram of a nearly monodisperse

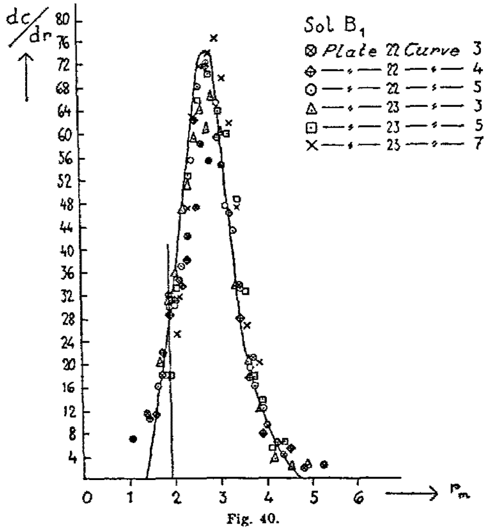

FIG. 20. Size-Distribution for a Gold Sol.

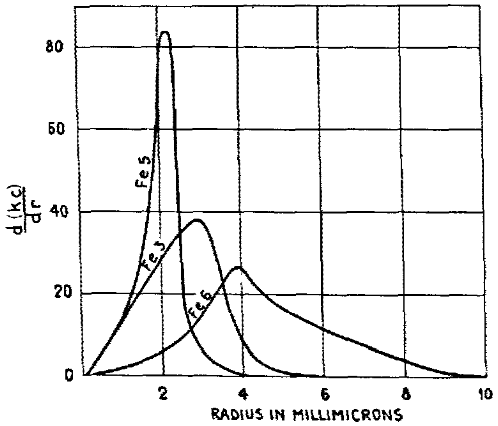

FIG. 21. Size-Distribution Curves for Ferric Oxide Sols.

carbohydrate found recently in the sap of Lilium bulbs (5) (M = 16 000). FIG. 18 shows the gradual production of two carbohydrate components in the potato tuber during sprouting (5).

As an example of an artificial organic polymerization product polystyrene may be mentioned (17, 18). FIG. 19 shows a photograph of the negative sedimentation in chlorophorm. Free movement was observed only in very dilute solutions.

Inorganic colloids constituted our first objects of ultracentrifugal study, but have been very much neglected in the following (16, 29, 30). FIG. 20 gives the size-distribution curve for a fine-grained gold colloid and FIG. 21 the size-distribution for a series of ferric oxide colloids (14).

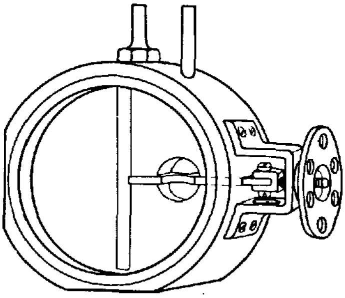

FIG. 22. Diffusion Cell.

Diffusion.

The diffusion constants required for the calculation of molecular weights from sedimentation velocity data were at first obtained by measuring the blurring of the boundary between solution and pure solvent in the ultracentrifuge cell (27). The conditions are not, however, suited for this kind of measurement and a higher degree of accuracy may be reached by studying the blurring of a boundary in a stationary cell (8, 11, 34).

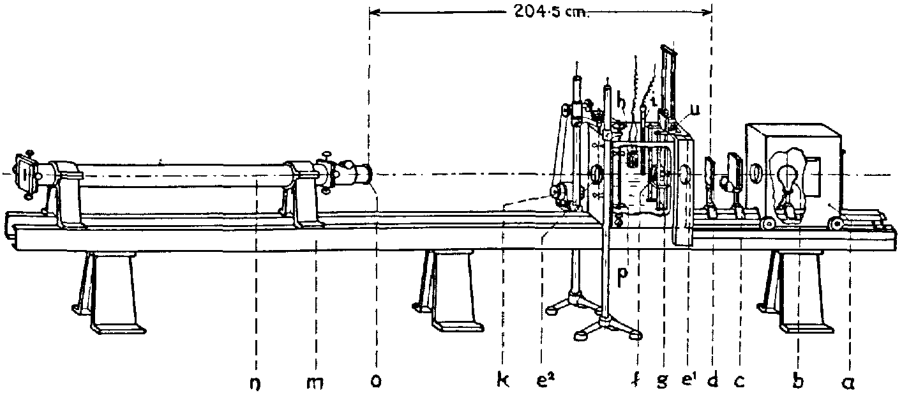

FIG. 23. Diagram of Equipment for Diffusion Measurements.

The light from a lamp, *b*, (FIG. 23) passes filters, *c*, and a transparent scale, *d*, on its way to the diffusion vessel, *f*, and the camera, *n*. A thermostate ensures constant temperature. For the earlier determinations a cylindrical diffusion tube was used requiring about 10 cc of solution. Recently a diffusion vessel with plane-parallel windows and requiring only about 1 cc of solution has been constructed (FIG. 22). By means of a movable slide the solvent can be placed in top of the solution. The change of concentration with time at the boundary between the two small, but from the point of view of diffusion, infinitely high columns of liquid is then followed optically. If the light absorption method is used the diffusion constant D is found from the following equations

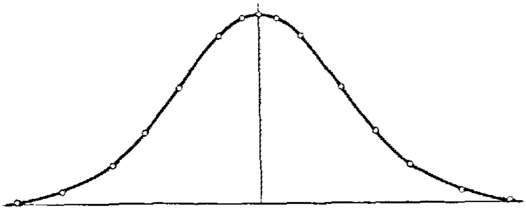

FIG. 24. Diffusion Curve for Purified Gliadin.

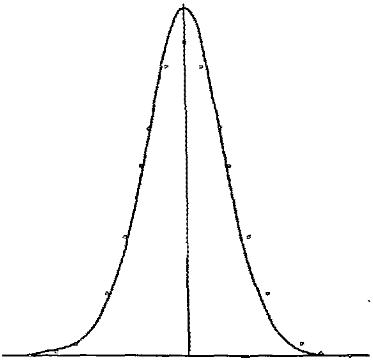

FIG. 25. Diffusion Curve for Crude Gliadin.

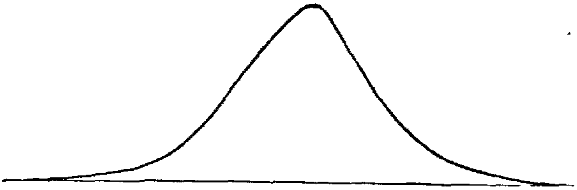

FIG. 26. Diffusion Curve for Metylated Cellulose.

$$D = z^2/4ty^2 \qquad (4a)$$

$$c_z = (c_0/2)\left[1 - (2/\sqrt{\pi})\int_0^y e^{-y^2}\,dy\right] \qquad (4b)$$

where z is the distance from the original boundary, t the time, c_0 the original concentration and c_z the concentration at the distance z.

In case of the refractive index method being used the equation

$$\frac{dn}{dz} = \frac{n_1 - n_0}{2\sqrt{\pi Dt}} e^{-z^2/4Dt} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

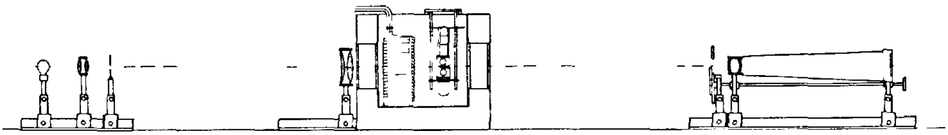

FIG 27 Diagram of Optical Arrangement for Electrophoresis Observation according to the TOEPLER Schlieren-Method

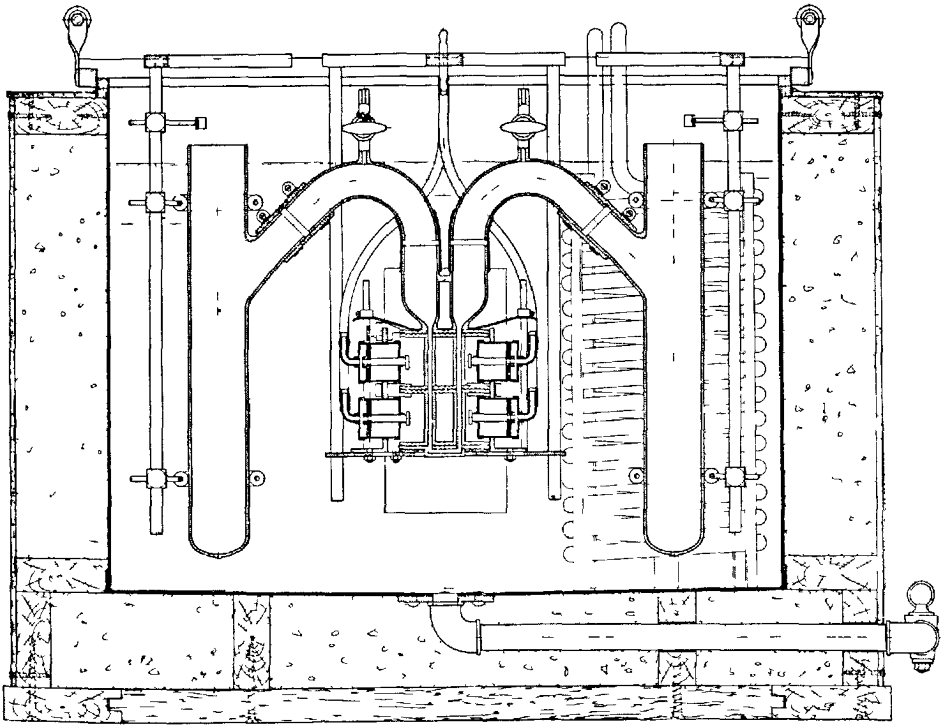

FIG 28. Scale Drawing of Improved Electrophoresis Apparatus (in Ice Thermostate).

or some formula derived from it serves for calculating the diffusion constant (11) Here n_1 is the refractive index of the solution, n_0 that of the solvent.

Diffusion diagrams of three different types of systems are shown in FIGS. 24, 25, 26. The first one represents a substance homogeneous with regard to molecular weight (purified gliadin); the measured and calculated values agree. The second one shows a substance inhomogeneous with regard to molecular weight (crude gliadin) while the third one demonstrates a case where there is interaction between the molecules (methylated cellulose); in the last instance the curve of concentration gradient is dissymmetrical.

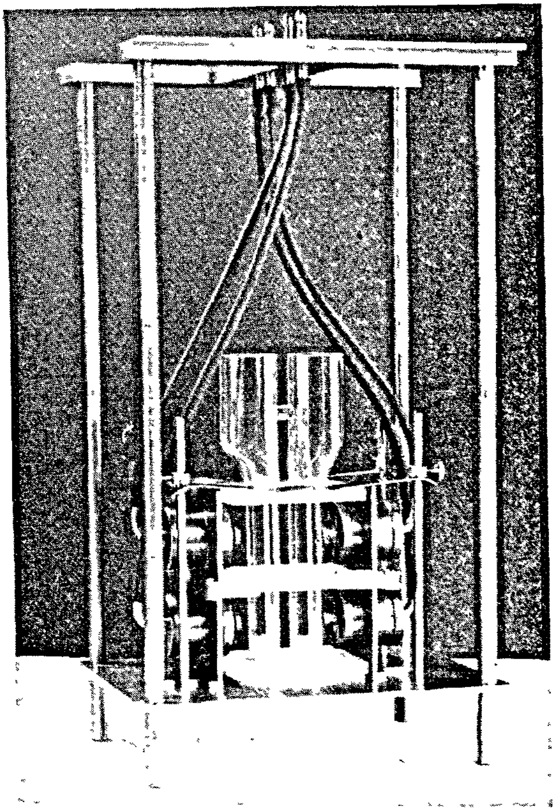

FIG. 29. Photograph of Cell for Improved Electrophoresis Apparatus.

Electrophoresis.

In a U-tube of good optical quality, preferably with plane-parallel front walls, the solution to be studied is placed underneath the solvent and an electric potential gradient created over reversible electrodes. From observations on the movement of the boundary by means of the light absorption method or one of the refraction methods the electrophoretic mobility is derived. A plot of such data as a function of P_H furnishes two important constants, *viz.* the isoelectric point and the mobility per P_H-unit in the isoelectric region.

The following general experimental arrangement was used by TISELIUS in his measurements (31, 32). Light from a mercury lamp passes the electrophoresis tube immersed in a water thermostate and then one or several suitable filters. By means of a long-focus lens an image of the moving boundary is thrown on a photographic plate. Later on LAMM's refractive index scale-method was applied and recently TISELIUS has developed an observation method based on the TOEPLER schlieren-principle which has given excellent results especially in the analysis of mixtures (33). (FIG. 27.)

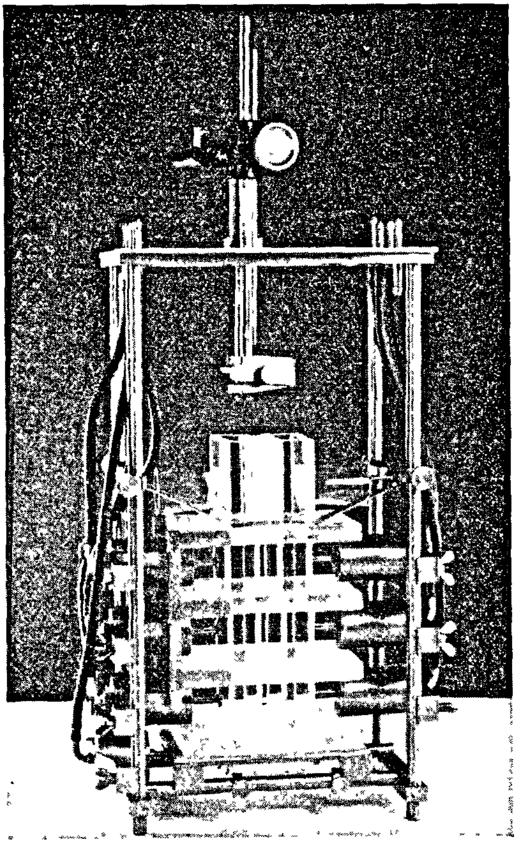

FIG. 30. Photograph of Cell containing 200 cc, built for Preparative Work, and the Screw Arrangement for pipetting out the Different Fractions.

Recently TISELIUS has constructed a very much improved electrophoresis tube (FIGS. 28, 29, 30) for the application of the schlieren-method, and for actual separation of the components of a mixture (33). The straight limbs of the tube are rectangular in section, thus offering a larger surface for the conducting-away of the heat. The front walls are plane-parallel so as to allow accurate optical observations to be carried out. The limbs are divided into two parts which on both ends are cemented to precision-ground glass plates. Corresponding plates are also cemented to adjacent top and bottom parts of the U-tube. This makes it possible to divide the column of solution after a suitable migration time. In order to minimize the danger of thermal convection currents and at the same time allow higher voltages to be applied, the electrophoresis is conducted at about 4° where water has its density maximum and where the change of density with temperature, therefore, is zero. A further feature of considerable importance for the analysis of mixtures

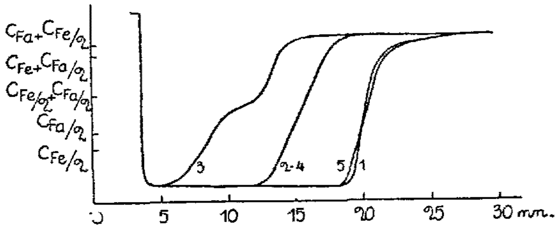

FIG. 31. Concentration Distribution Curves for the Electrophoretic Migration of Phycocyan and Phycoerythrin (Light Absorption Method).

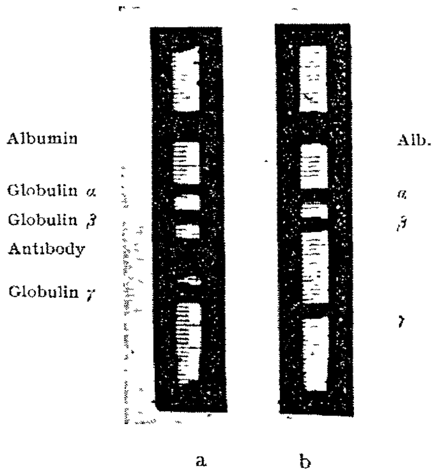

FIG. 32. Schlieren-Photographs of Serum:
a) Containing pneumococcus antibody;
b) After removal of the antibody.

consists in giving the whole column of liquid in which the electrophoretic migration takes place a constant motion so as to prevent the boundaries to move out from the straight limbs of the U-tube in long-timed experiments. To this end a glass cylinder is slowly lifted out of the liquid in one of the

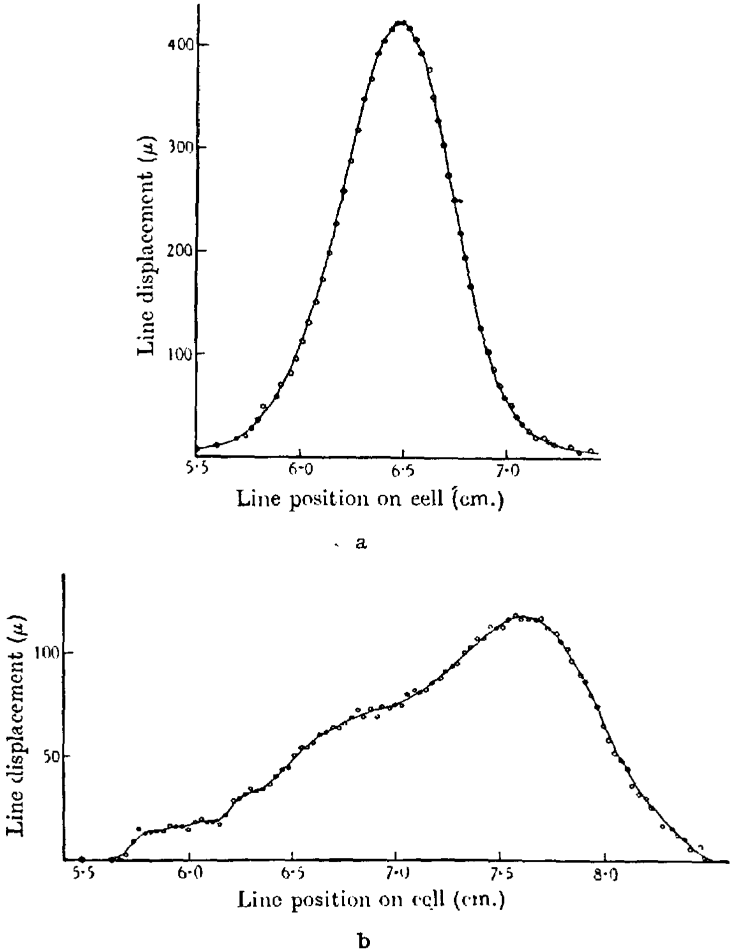

FIG. 33. Scale Photographs of a Migrating Boundary of:
a) Egg albumin;
b) Egg albumin split with papain.

electrod vessels by means of a clockwork. The apparatus is at present built in three different sizes for 2, 10 and 200 cc.

As examples of the different methods of observing electrophoretic migration FIGS. 31, 32, 33 show the curves of concentration distribution for a mixture of phycocyan and phycoerythrin (light absorption method), photographs of boundaries in serum (schlieren-method) and concentration gradient distribution for a single boundary of a homogeneous and an inhomogeneous protein (scale-method).

Although so far the field of research of the methods just outlined has been mainly in the domain of organic matter, there is a fair probability that this new technique might be used for helping to elucidate the complicated processes of cement chemistry. I take it that this is an idea cherished by our President Mr. ENSTRÖM and it has procured for me, a non-cement-chemist, the pleasure and the honour to speak before you and to take part in this Symposium on the Chemistry of Cements.

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REACTIONS BETWEEN SUBSTANCES IN SOLID STATE WITH SPECIAL REGARD TO SYSTEMS CONTAINING SILICA

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Introduction.

The production of synthetic cement has from the very first been something of a work of precision. Untiring research work has been done in attempting to change the function composition—properties from implicit to explicit. This work met with great difficulties, and it is only lately that a number of important problems concerning composition and treatment have been made clear to such an extent that the term "work of precision" has attained not only a quantitative but a deeper qualitative significance. With the expression "a deeper qualitative significance" I want to convey that it is founded on knowledge of particularities of both the course and the type of the chemical reactions during different periods of production, and, with special regard to cement, its use. The complete solution of these problems has not yet been finally reached, but it is now dimly visible. For this situation we have for the most part to thank those research institutions which are represented at this Symposium.

The laying of such solid foundations were absolutely necessary to make possible the meeting of increasing demands for adaptation. To-day it is no prophesy but only a plain statement of fact, when we say that the trend towards specialization, which for a long time has reigned in the production of optical glass, ceramics and fine glazings, now to a certain extent also has come to determine the line of development for the making of cheap glassware, furnace brick and Portland cement. In other words, this continuous development will increase the number of special products, and this will require a deeper knowledge of the quantitative and qualitative influences of new substances added in the process. This was adequately elucidated already by SEGER (1839—1893), at that time the leading personality in the field of silica chemistry.

But nowadays we go one step farther in our pretentions to master the effects of the quantitative and qualitative factors. We demand the substitution of systematic knowledge for those valuable experiences and rules which have been collected in thousands of empirical recipes, and which deal with reactivity and yield as influenced by the crystallographic build, form, provenance and preparation of the solids. We consider, then, that the surface activity is of extreme importance, because it is naturally the surface which is first attacked. We know that the character of this surface is highly dependent on such factors as those just mentioned, and also on a multitude of others. Therefore, modern crystal chemistry, and especially that branch of it which we call *topochemistry*, does possess a particular interest when dealing with those systems where the reactivity of matter in solid state plays a part. It was in metallography, metallurgy and the applied chemistry of oxides that the importance of such reactions was first realized. Owing to this fact the old Aristotelean rule that substances cannot react in the solid state certainly lost its dogmatic infallibility somewhat earlier than would otherwise have been the case.

Later I shall quote some characteristic instances of the importance of these reactions for our problems, and there is no longer any need for me to prove, neither that solids are able to react with other solids, nor that reactions of this kind considering their direct or indirect results are worthy of cognizance. I need only quote a passage from that excellent work by LEA and DESCH, *The Chemistry of Cement and Concrete:* "the burning of cement consists of a series of reactions taking place between finely divided solids, and it is only in the final stages of burning that a liquid is formed and becomes the medium through which reaction occurs" (31). This statement does of course also refer to that indirect effect brought about by such reactions on the starting temperatures and the completeness of later reactions and sinterings, when liquid phases also do appear.

I believe that the best way for me is to make this introductory lecture into an account, firstly of some theoretical aspects of the general mechanism of these reactions, and, secondly, of some practical experiences which are the results of experiments with a view to increase the reactivity of solids in different ways. Especially when dealing with highly resistant substances some remarkable and for practical purposes important effects have been obtained. These are of such recent date, at least in part, that they cannot, perhaps, be considered as generally known. I am not, however, going to mention earlier and now probably well-known results, which deal with normal reactions of oxides of the kind which interest us here, but shall limit myself to references to some of them, which in their time did influence progress. Although COBB

(4) himself like most of his contemporaries hesitated to explain the reactions which he got between silicon dioxide or aluminum oxide on one hand, and calcium sulphate or calcium carbonate on the other, as real reactions in the solid state—he speaks instead of "a quasi-vapourous film"—these experiments are certainly worth mentioning in this connection.

The first systematic investigations of reactions in non-metallic systems on the basis of an understood reactivity also in such solid substances were performed shortly afterwards (HEDVALL). They dealt both with the formation of a number of colouring substances used in ceramic work (8), and with reactions between oxides or carbonates of the alkaline earth metals and silicon dioxide, the latter in different modifications (9). The most important results of these researches were the discovery of an unexpectedly great reactivity even at rather low temperatures, and the proof that crystallographic differences clearly influenced the reactivity and yield also in such systems (9). DYCKERHOFF (5) extended these investigations and noted the important fact, that it is the orthosilicate which is most readily formed in calcium oxide—silicon dioxide mixtures. His investigations were conducted in close touch with the industrial working of Portland cement kilns. In later years his results have been confirmed and more details added, for instance by HILD and TRÖMEL (23), WEYER (38), CARLSON (3), NAGAI (32), and TAYLOR (35). Most of this work also deals with the reactivity of aluminum oxide (6), and the conditions of formation of various aluminates. Especially on problems pertaining to glass TURNER and his collaborators have done good work.

The velocity of such processes can be expressed by an equation of the type:

$$v = A \cdot e^{-\frac{q}{RT}};$$

where A is a constant depending on the texture of the material, but relatively independent of temperature; R is the gas constant; T is the absolute temperature; and q a quantity which can be called the energy of loosening the lattice for the phase in question. It really means the energy necessary to detach a particle from its neighbours in the crystal lattice, and to bring it to a state of reactivity.

It is evident that the transportation of matter is augmented when A is increasing, and especially when q is decreasing. In the following exposition we pay no attention to the self-evident increase with rising temperature. With regard to A it is used to express the influence of for instance change in particle size, conditions of contact, &c. This is also generally well-known. Instead we shall focus our attention on the influence of q, which in a way does measure the interior rigidity. It is evident that every possibility to decrease it must tend to increase reactivity. There do exist a number of such possibilities, which have a practical interest also.

Regarding the reaction film, this is generally in a crystallographically imperfect state. The particles have not yet found their true positions in the lattice of the resulting compound. Characteristic for this layer are low ϱ-values, and it shows relatively weak resistance to the transportation of matter. We speak in this connection of active states of change, which above all are important in catalysis and other processes where sorption is involved.

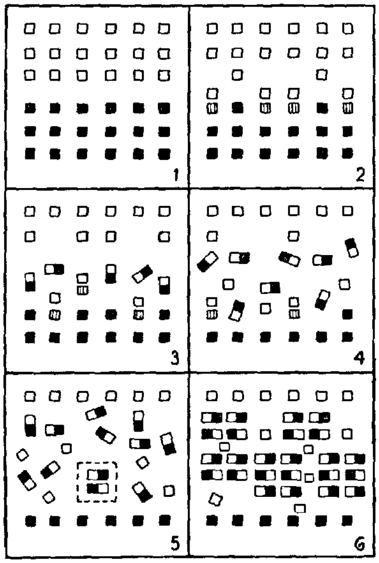

FIG. 1. The Progress of Reaction as pictured by JANDER.

The above figure from JANDER (26) gives a picture of the progress of the reaction between two solid substances. The white and the black squares denote the two components A and B. The shaded ones denote those zones where stoichiometrically faulty reaction product A_mB_n has formed. The combination of white and black squares denotes the stoichiometrically correct compound AB. Only in part five of the figure there are to be found crystallographically perfect lattices of it. The inclined position in fields 3 and 4 denotes the faulty lattices during the transition states.

Under isothermic conditions the layer of reaction product increases according to the formula

$$y^2 = 2k\Theta;$$

where k is a constant, the magnitude of which is determined by mobility and diffusion factors in the system, and Θ is the time of the reaction. This has been shown by TAMMANN (34), BRAUNE (1), and JANDER (27). JANDER (28) has also made some valuable determinations of the diffusability of the different components, and he has been able to show that, for instance in a system of lime and silica, the orthosilicate is first formed, whatever the original composition of the mixture may be. This, because calcium oxide has the greater velocity of diffusion. If the original mixture has been given proportions corresponding to the metasilicate, this latter is formed through a secondary reaction between the orthosilicate and the silicon dioxide, as is shown by the following figure from JANDER (28).

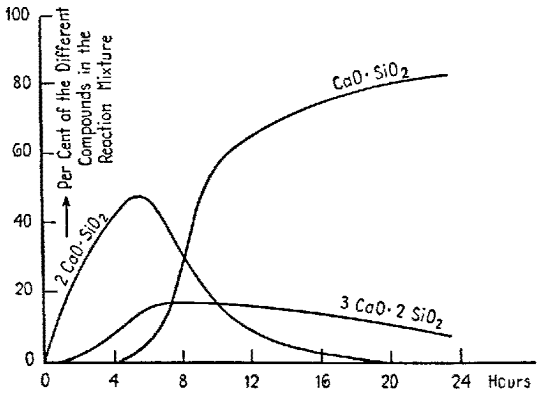

FIG. 2. The Sequence of Formation of the Different Compounds in the System $CaO + SiO_2$ according to JANDER.

We are not going to occupy ourselves in considering these matters any more, but will instead give our attention to such possibilities of lowering the inner cohesion of the components as are of interest because they facilitate the reactions. Accordingly the less the resistance to the diffusion through the undeveloped phase of the reaction film, the more importance must be given to the transportation of reactive particles from the interior of lattices of the reaction partners.

Every disturbance in the distribution of energy or particles in the normal lattice will therefore be of advantage. In the following are given some instances of such changes, which happen automatically or are brought about deliberately.

Exchange Reactions with Substances the Lattices of which pass from Ionic to Anhydride Type.

Calcium sulphate, $CaSO_4$, at ordinary temperature is composed of Ca^{2+}- and SO_4^{2-}-ions. At a temperature of about 1 000° a noticeable decomposition begins with the liberation of gaseous SO_2. This of course implies that already at a much lower temperature the lattice has partially changed to a lattice of anhydride type composed of CaO and SO_3. The extent of this change increases with rising temperature according to a potential function. Now, if there is present an oxide, *e. g.* BaO, to which the temporarily existing SO_3-molecules have a greater affinity than to the original oxide (CaO), then, at and above a certain temperature where a minimum concentration has been reached to make the resulting reaction measurable, there occurs an exchange according to the formula:

$$BaO + CaO \cdot SO_3 = BaSO_4 + CaO + Q;$$

where Q denotes the heat of reaction, and the salt formed at the reaction must have a greater thermic stability than the original one. The above-mentioned reaction occurs at about 370° and is almost complete in a few seconds. As may be seen from the following table (HEDVALL and HEUBERGER 17) this type of reaction has a general validity when these conditions are satisfied. No attention has here been given to the primary process between particles of ionic type, because this is as yet not known in detail. This treatment is the more reasonable as a certain mobility of larger reaction blocks (as shown in the formula) seems to be probable in those imperfect parts of the lattice, on the surface as well as in the interior, with which we are now dealing (37).

The most striking thing in this table is the fact that different salts react with one oxide within rather narrow temperature limits, determined by the type of oxide added. I shall pass over the explanation of this matter, which, roughly, can be explained by a mobility of entire anhydride complexes, and I beg to refer to the treatment of these things in my book "Reaktionsfähigkeit fester Stoffe", (Leipzig 1938) pp. 69, 70.

Silicates, spinels &c. in many cases do also react according to this principle (10). As an example may be cited the following reaction which can be used in the production of furnace lining brick:

$$MgO + FeO \cdot Cr_2O_3 = MgO \cdot Cr_2O_3 + FeO;$$

to which we shall return in another connection. In certain cases, double salts or solid solutions can be formed. Such reactions have also been carefully studied especially by KRAUSE (30), chiefly on account of their importance for coloured glazes in the ceramic industry. They were even some twenty years earlier the first instances of reactions between solid non-metallic substances to be observed (HEDVALL 1912—1915) (11).

Influence of Crystallographic Transitions.

Obviously, a crystal lattice that is undergoing a transition process from one modification to another, *e. g.* silica passing from α-Quartz to Crystobalite,

Table 1.

	Salts	Reaction Temperature with BaO	Reaction Product	Reaction Temperature with SrO	Reaction Product	Reaction Temperature with CaO	Reaction Product
Carbonates....	$SrCO_3$	395°	$BaCO_3 + SrO$	—	—	—	—
	$CaCO_3$	345°	$BaCO_3 + CaO$	465°	$SrCO_3 + CaO$	—	—
	$MgCO_3$	345°	$BaCO_3 + MgO$	455°	$SrCO_3 + MgO$	525°	$CaCO_3 + MgO$
Sulphates......	$SrSO_4$	370°	$BaSO_4 + SrO$	—	—	—	—
	$CaSO_4$	370°	$BaSO_4 + CaO$	450°	$SrSO_4 + CaO$	—	—
	$MgSO_4$	370°	$BaSO_4 + MgO$	440°	$SrSO_4 + MgO$	540°	$CaSO_4 + MgO$
	$ZnSO_4$	340°	$BaSO_4 + ZnO$	425°	$SrSO_4 + ZnO$	520°	$CaSO_4 + ZnO$
	$CuSO_4$	345°	$BaSO_4 + CuO$	420°	$SrSO_4 + CuO$	515°	$CaSO_4 + CuO$
Phosphates....	$Sr_3(PO_4)_2$	350°	$Ba_3(PO_4)_2 + SrO$	—	—	—	—
	$Ca_3(PO_4)_2$	340°	$Ba_3(PO_4)_2 + CaO$	450°	$Sr_3(PO_4)_2 + CaO$	—	—
	$Pb_3(PO_4)_2$	335°	$Ba_3(PO_4)_2 + PbO$	455°	$Sr_3(PO_4)_2 + PbO$	525°	$Ca_3(PO_4)_2 + PbO$
	$Co_3(PO_4)_2$	355°	$Ba_3(PO_4)_2 + CoO$	465°	$Sr_3(PO_4)_2 + CoO$	520°	$Ca_3(PO_4)_2 + CoO$
	$CrPO_4$	340°	$Ba_3(PO_4)_2 + Cr_2O_3$	465°	$Sr_3(PO_4)_2 + Cr_2O_3$	515°	$Ca_3(PO_4)_2 + Cr_2O_3$
Silicates[1]......	$CaSiO_3$ (Wollastonite)	355°	$BaSiO_3 + CaO$	455°	$SrSiO_3 + CaO$	—	—
	$MgSiO_3$ (Enstatite)	355°	$BaSiO_3 + MgO$	455°	$SrSiO_3 + MgO$	560°	$CaSiO_3 + MgO$
	$MnSiO_3$ (Rhodonite)	355°	$BaSiO_3 + MnO$	465°	$SrSiO_3 + MnO$	565°	$CaSiO_3 + MnO$
	Al_2SiO_5 (Sillimanite)	355°	$BaSiO_3 + Al_2O_3$	430°	$SrSiO_3 + Al_2O_3$	530°	$CaSiO_3 + Al_2O_3$

---

[1] In this group, there can perhaps be formed complex silicates in some cases at higher temperature. Attention is called to the fact that the formulae are only schematically shown, there are certainly also formed orthosilicates.

is in an irregular intermediate state, which is characterized by low values for the energy of loosening the lattice. It can *a priori* be assumed that in this interval it should possess an abnormally great reactivity, which of course must not be confused with the reactivities of the stable high or low temperature modifications, and this, in fact, is also the case.

The first effects of this kind were found when (HEDVALL and HEUBERGER 18) using heating curves for mixtures which could give exchange reactions of the above-mentioned kind. As may be seen from the following table in conjunction with TABLE 1, the reactions do not occur at their normal temperatures but at the transition points of the salts used.

Table 2.

	$AgNO_3$			Ag_2SO_4		
Oxide added	React. Temp. Normal	React. Temp. found	Transition Point	React. Temp. Normal	React. Temp. found	Transition Point
BaO	—	170°	—	c. 345°	342°	—
SrO	—	172°	160°	c. 420°	422°	411°
CaO	—	164°	—	c. 515°	422°	—

With this method it is of course impossible to show the relative maximum of reactivity during the transition. This is only possible in certain cases, and always requires that the duration of the experiment is carefully suited to the transition velocity. Such experiments, therefore, are best performed by making diagrams of the reaction yield. The above figure (HEDVALL and collaborators) shows the typical course of oxidation when treating sulphur with a solution of potassium permanganate (14). The maximum is well-defined when passing from the rhombic to the monocline modification. The

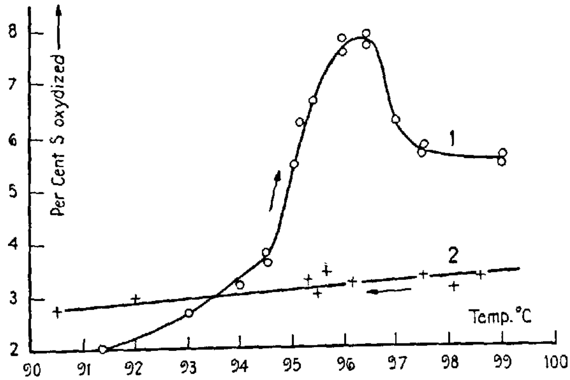

FIG. 3. The Influence of the Transition and its Velocity on the Oxidation Velocity of Sulphur with $KMnO_4 + H_2SO_4$.

much slower transition in the reverse direction with sinking temperatures shows, as expected, no effect in these experiments of sixty minutes duration.

At this occasion, our interest is centered on the results of the experiments with oxides of the kinds which are used in the applied chemistry of oxides. I would first mention the reactions between Quartz and ferric oxide when heating intimate mixtures of them. There is then formed a product resembling rose Quartz. It was shown through an X-ray investigation (HEDVALL and SJÖMAN 22) that the colouring resulted from ferric oxide diffusing into the silicon dioxide. As shown later, no silicate is formed, but only a kind of solid solution. Not even if we start with the hydrated silicate of tri-valent iron, Nontronite, and heat it in oxygen is an anhydrous silicate formed (STERZEL and LINDÉN 33). The most remarkable result of these experiments is that only when the silicon dioxide lattice is undergoing a crystallographic transition process does the ferric oxide enter it with any measurable velocity. As may be seen from the above figure, this happens in two stages, first at the β- α-transition at 575°, and then, after an interval, the reaction sets in again at about 900° when the formation of Crystobalite begins (22).

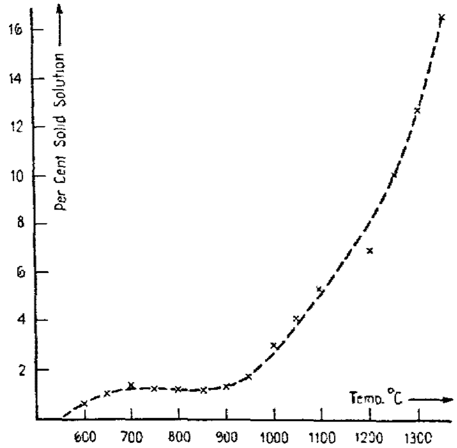

FIG. 4. The Influence of Crystallographic Transition on the Diffusion of Fe_2O_3 into SiO_2.

Exactly analogous results have lately been obtained by JAGITSCH (25) on the formation of calcium silicate. He found a very great increase of reaction velocity above 900°, and, in this case also, this was shown to depend upon a transition of the silica. As, however, amorphous silica had been used as starting material in these experiments, the transition consisted in the formation of Tridymite.

The effect of faulty lattices to increase reactivity is frequently so great that it surpasses by far the influence of the size of surface. A coarse powder of crystals with faulty lattices may therefore react much better than a fine powder of stable crystals. Naturally, this requires that experiments are not conducted at such high temperatures that the faulty lattices are rapidly changed into stable forms (13).

The Influence of the State of Substances during their Formation.

Very great effects are obtained in these reactions, if it is possible to arrange that both partners are in a state of transition of some kind. The following diagram (HEDVALL and SCHILLER 21) shows a comparison between the formation of silicate in mixtures of Quartz and nickelous oxide (NiO), on one hand, and Quartz and cobaltous cobaltite (Co_3O_4), on the other. The latter compound decomposes at the same time as Crystobalite begins to form at 900° and there is formed cobaltous oxide (CoO), which, *in statu nascendi*, has an imperfect lattice and therefore a high activity. Using the same time of heating, 30 minutes, the yield of silicate is nearly twenty per cent higher than in corresponding mixtures with nickelous oxide.

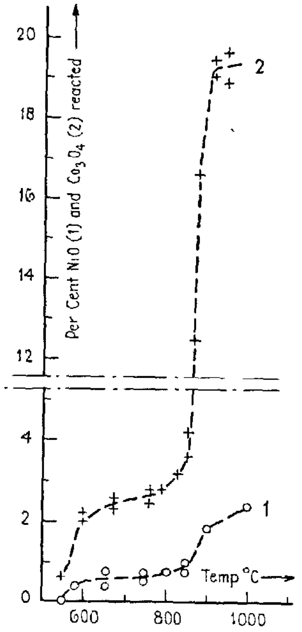

FIG. 5. Increase of Reactivity through Transition (NiO + + SiO_2) and through the Same with Loosening of the Lattice through Thermal Decomposition (Co_3O_4 + SiO_2).

The influence of the state of the lattice on the reactivity is also clearly shown by experiments made (HEDVALL and LEFFLER 19) with mixtures of cobalt oxides and aluminum oxide as shown in FIG. 6.

The ordinates represent the yield of reaction, and the abscissae the temperatures. The aluminum oxide used was made from aluminum hydroxide. When not heated to more than 800°, it is, in an imperfect and reactive state of transition, by and by changing to stable and less reactive γ-Al_2O_3 at 900° to 950°. Then comes a new period of transition from about 1 000°, where γ-Al_2O_3 changes to α-Al_2O_3. All these changes and also the above-mentioned thermal dissociation of cobaltous cobaltite, are reflected in the diagram.

From Curve 1 may be seen that the inner mobility during the formation of the γ-Al_2O_3-lattice between 900° and 950° strongly favours the reaction. At 1 000°, the transition velocity is so great that it has no noticeable influence on the yield during the time of heating used. If the heating time is shortened to five minutes (Curve 4), no irregularities at all are found, but, as could be expected, the curve is somewhat steeper than Curve 5, which was obtained using stable Corundum with a perfected lattice. As may be seen from the upper part of Curve 1, the formation of this lattice also gives an abnormal increase of the yield during the transition $\gamma\text{-}Al_2O_3 \rightarrow \alpha\text{-}Al_2O_3$. Curve 3, at last, shows, corresponding to our experiences of reactions with silica, the great increase in yield within the temperature interval where the following reaction takes place:

$$Co_3O_4 = 3CoO + \tfrac{1}{2}O_2.$$

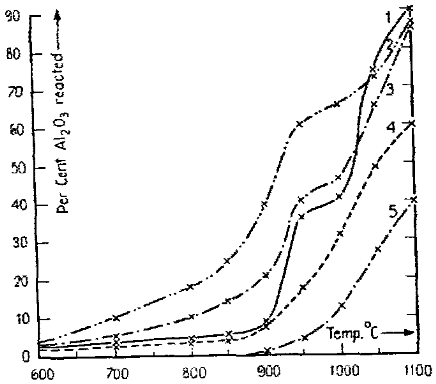

FIG. 6. The Influence of Topochemical Differences (ageing), Transitions and Thermal Decomposition on the Formation of Spinel from CoO or Co_3O_4 and Al_2O_3.

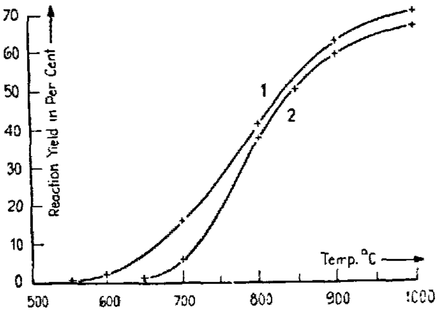

FIG. 7. Yields of Reaction between Ferrous Chromite and Magnesium Carbonate (Curve 1) or Magnesium Oxide (Curve 2).

The increased reactivity during the formation of a compound is also shown (HEDVALL and NY 20) in a work dealing with reactions between ferrous chromite and magnesium oxide or magnesium carbonate, according to the formulae

$$MgO + FeO \cdot Cr_2O_3 = MgO \cdot Cr_2O_3 + FeO$$
$$MgCO_3 + FeO \cdot Cr_2O_3 = MgO \cdot Cr_2O_3 + FeO + CO_2.$$

As may be seen from the figure, the reaction yield in the carbonate mixtures (Curve 1) reaches somewhat higher values and the reaction begins at a temperature about 100° lower than in the oxide mixtures. Approximately, this temperature corresponds to the temperature interval where a rapid decomposition of the carbonate sets in, *i. e.* where magnesium oxide begins to form in considerable quantities.

Closely related hereto are the results from some investigations (HEDVALL and HELIN 16) on dry sintering effects in powders free from liquid phase. It was then found that high compression strengths could be obtained, if such powders were heated above the re-crystallization temperature for the substance in question, and that these values reached a considerably higher level if the substance used had a faulty lattice. Yet another appreciable increase was obtained if during the heating the powder was exposed to a chemical change, *e. g.* oxidation or reduction, but still without any formation of liquid. The following figures show the results obtained with ferric oxide made from ferrous oxalate and possessing a perfect lattice, and the same oxide made from ferrous sulphate and with a highly imperfect lattice. The curves numbered 1 represent only heating without reaction, curves numbered 2 heating with reduction to Fe_3O_4, and curves numbered 3 heating with reduction as before and re-oxidation to ferric oxide. As may be seen from the various diagrams the values for the "sulphate oxide" with its faulty lattice are practically the double of those of the other one, in spite of its greater grain-size.

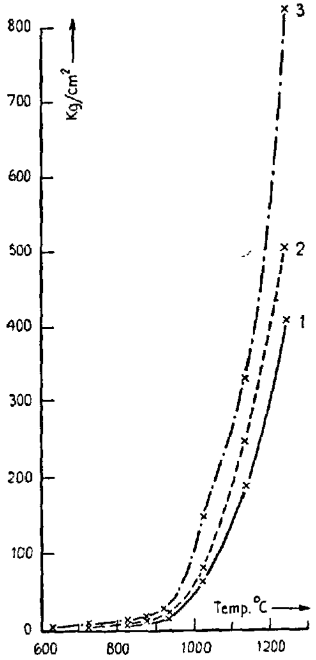

Fig. 8. Dry Sintering of Inactive Fe_2O_3 from Oxalate, Compression Strength.

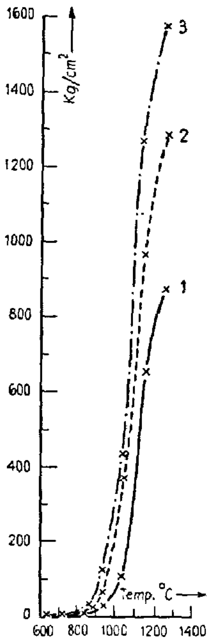

Fig. 9. Dry Sintering of Active Fe_2O_3 from Sulphate, Compression Strength.

The Influence of Crystallographically Different Surfaces.

I shall now mention something about the various reactivities of crystallographically different faces belonging to crystals with stable perfect lattices.

Such differences have been known for a long time, and have been shown in such processes as etching and dissolution experiments, and investigations on the growth of crystals. From the following figures, Nos. 10 and 11, may be seen that such differences can be shown in the technically important process known as thermal dissociation. HEDVALL and HEDIN (15) heated for instance crystals of Calcite, ground to different shapes, at various temperatures for a certain time, and for various periods at a certain temperature, and determined the dissociation velocity per surface unit. The results obtained with Calcite are shown in the following figures.

It is rather astonishing that the differences are so marked as is the case. Even the most careful grinding and polishing will give a surface where there exist not only the desired planes,

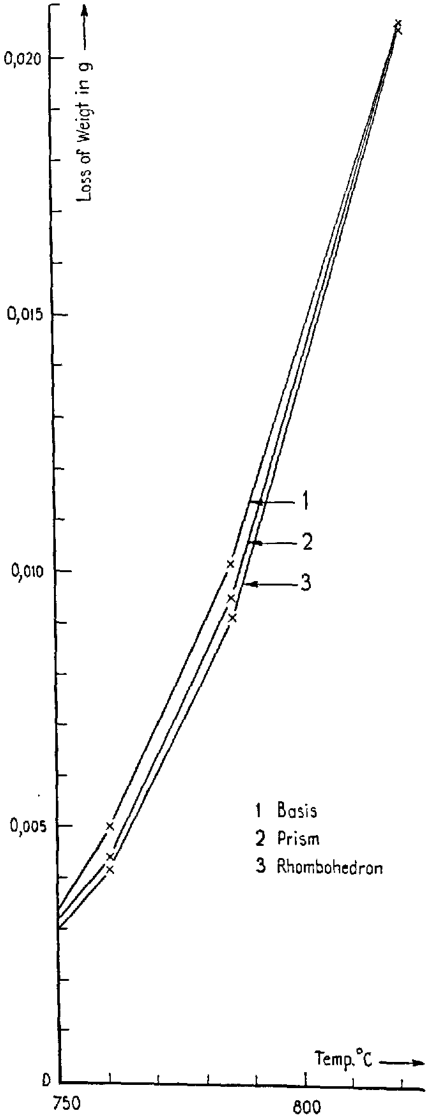

FIG. 10. The Influence of Different Crystal Faces on the Velocity of the Thermal Dissociation of $CaCO_3$ at Various Temperatures.

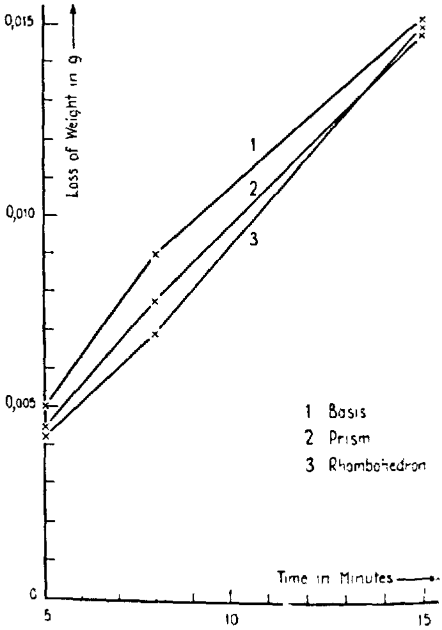

FIG. 11. The Influence of Different Crystal Faces on the Velocity of the Thermal Dissociation of $CaCO_3$ using Various Times for the Experiment.

but also others. An increase of time or temperature above certain optima will result in levelling up the differences through diffusion processes and through the influence of the solid phase (CaO) formed, just as could be expected. Effects of this or similar type have been found to play a part in several industrial processes, exemplified by the connection between the compounding of the glass mixture and the course of its homogenization in the furnace.

The Influence of Foreign Substances in the Lattice.

Even geometrically perfect lattices can be brought into such a condition that the inner diffusion, and, consequently, the diffusion during the reaction, is made easy. This is the case if foreign particles are built into the lattice, e. g. as solid solutions. The effect of such an interference with the normal lattice of course increases with increasing differences of volume or ionic structure between the normal and the foreign particles of the lattice. This fact is of a great practical interest, because generally in industrial processes neither the raw materials nor the finished products are chemically pure substances.

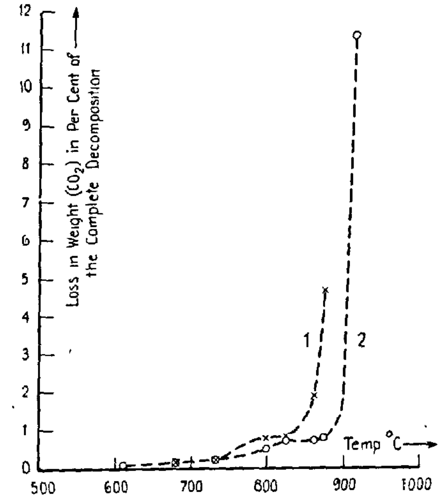

Fig. 12. The Influence of the Loosening of the Lattice through the Formation of a Solid Solution of Fe_2O_3 in SiO_2 on the Reaction between SiO_2 and $CaCO_3$.

This may be exemplified by quoting from an investigation by Hedvall and Hedin (15). It was shown that when calcium carbonate was allowed to react with pure Crystobalite, on the one hand, and with Crystobalite containing ferric oxide in solid solution, on the other, both with the same grain-size, then, the latter did react with the greater facility. As may be seen from Fig. 12, Curve 1, the intensive reaction sets in at a temperature about 50° lower than the one obtained when using pure Crystobalite. As those minerals used as raw materials for industrial purposes often contain impurities of similar kind, it is easy to perceive the practical importance of these matters, both on account of the possibility of lowering reaction temperatures and the formation of liquid phases.

Another case is taken straight from the chemistry of Portland cement. Büssem and Schwiete (2) have shown that tricalcium silicate in cement can contain up to 4 per cent tricalcium aluminate in solid solution. Investigations by Insley of the Bureau of Standards have shown (24) that the lattice of the tricalcium silicate is also changed in the process. Thorvaldson (36), as well as Forsén (7), has found out, that even when steam-cured pure tricalcium silicate possesses a considerable stability, an hydrate of tricalcium silicate being, in fact, formed. With the silicate found in cement, however, this is not the case, and Jander has shown that this has some connection with the loosening of the lattice through the inmixture of aluminate (29).

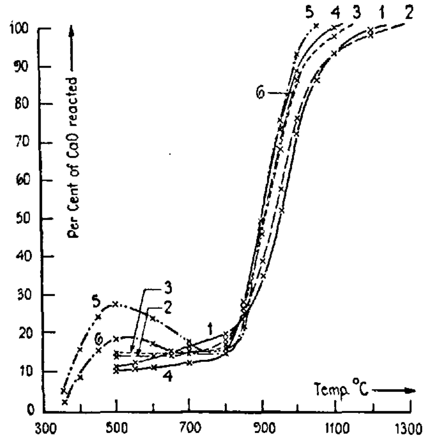

Fig. 13. The Influence of the Treatment of the Hydrated China Clay in the Reaction Yield with CaO.

At last I am going to show a diagram corresponding to experiments with mixtures of CaO and dehydrated China Clay, an extensive work which has partly been carried out by means of subventions from the Skånska Cementaktiebolaget. The results will perhaps be of some interest for the chemistry of pozzolanas and for other reactions, *e. g.* the process of the production of Jungner cement. The Curve 1 shows the reaction yield—measured as combined CaO—when heating mixtures of CaO and China Clay, which has before been dehydrated at 600° during 60 min., for an hour at different temperatures. When compared with Curve 2, where the China Clay has been prepared at the same temperature during 300 min., it appears that the reactivity of the metakaoline has considerably decreased. At higher temperatures, *i. e.* the steep part of the curves, where transition processes and thermal mobility play the most important rôle, the differences of course are levelled up. In the same way as through a prolongation of the thermal treatment the reactivity of the metakaoline components decreases if it is prepared at higher temperatures even during shorter periods. This appears from the other curves at the reaction temperatures below about 900°. Finally, I will draw the attention to the small maxima at the low reaction temperatures which appear on Curves 5 and 6, corresponding to experiments with China Clay dehydrated at 1 000°. According to different treatment and preparates, the size of these maxima can change very much. We have occasionally noted up to 20 per cent, *e. g.* in mixtures of CaO and pure Sillimanite. Experiments which are not yet brought to an end will, I suppose, explain this observation, as well as the parts of the different factors which, more or less suddenly, increase the reactivity in the period 850°—900°.

The field of enquiry compassing the possibility of reactions between substances in the solid state was for an amazingly long time forgotten, not to say forbidden. With a few instances of results from actual research, however, I have tried to prove that the results attained, not only in several cases are able to explain old-established practical observations, but also open up new vistas of technical progress. The traditional and, in our time, once more lively contact maintained with the research workers in the fields of mineralogy and crystallography is obviously of the highest importance. It is equally obvious, that to acquire a more profound knowledge of the varied and in many ways peculiar characteristics of the surfaces is of great consequence, and for this reason: whether we want to protect or to attack a solid substance the surface must primarily be involved.

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CONSTITUTION OF PORTLAND CEMENT CLINKER[1]

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Abstract.

Modern developments in the technique of the identification and measurement of phases are shown to underlie recent advances in our understanding of the constitution of Portland cement clinker. Researches on glass in clinker have revealed its nature as a metastable phase and provided means for its approximation. Investigations have shown that commercial clinkers vary in glass content over a wide range and that the amount of this phase is profoundly affected by the rate with which the clinker is cooled through the higher temperatures. Equations have been developed by which the constitution of a clinker of known glass content may be calculated under given assumptions of the course of crystallization. The fate of the alkalies is still undetermined but their importance in affecting the clinker constitution is becoming recognized. A number of the effects on cement properties resulting from the presence of glass are discussed.

Elements of Progress.

Twenty years ago, on January 14, 1918, the Faraday Society sponsored a symposium, international in character, on "The Setting of Cements and Plasters" (50). Among the contributors to this symposium were such well-known names as LE CHATELIER of France, DESCH and DONNAN of England, and RANKIN and KLEIN of the United States. Although most of the discussion bore upon the processes of setting and hardening, the constitution was not neglected and the record may be taken as a true picture of the state of the science at that date.

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[1] Publication approved by the Director of the National Bureau of Standards of the U. S. Department of Commerce. Paper No. 38 of the Portland Cement Association Fellowship at the National Bureau of Standards.

Between 1918 and today there has been little further attempt to bring together the views of investigators on cement who are working in laboratories separated by the national frontiers. The present purpose, therefore, is to show the advances in our understanding of cement that have transpired during this score of years, to reveal the state of the science as of today, to discover the position of the science with relation to the problems and trends of the industry, and to foster the inspiration that comes from human contacts and makes for cooperation and good will both among individuals and among nations.

There cannot be said to have been any precise knowledge of the constitution of clinker prior to the microscopic examinations of LE CHATELIER (33) and of TÖRNEBOHM (51). These examinations were substantially in agreement with respect to the classification of phases, denoted by TÖRNEBOHM *alite, belite, celite, felite* and an *isotropic residue*, but the chemical nature of the phases has remained a matter of controversy up to recent years. Scores of papers have been written on the legend "What is Alite". Within the last decade it has been described as:

a lime-enriched dicalcium silicate (13),
a solid solution of lime-rich aluminate and silicate (31),
a solid solution of $3CaO \cdot SiO_2$ and $3CaO \cdot Al_2O_3$ (15),
a solid solution of $8CaO \cdot Al_2O_3 \cdot 2SiO_2$ and $2CaO \cdot SiO_2$ (29),
essentially $2CaO \cdot SiO_2$ (44).

Alite was considered to be $3CaO \cdot SiO_2$ by LE CHATELIER (34) in 1884 and this view has been confirmed by the investigations of RANKIN and WRIGHT (45) who demonstrated the existence of the compound, BATES and KLEIN (3) who showed its existence in clinker, HANSEN and BROWNMILLER (19) who identified its presence in clinker by X-ray means, GUTTMANN and GILLE (16) who separated the alite from clinker, and many others. But in 1931, conceding the evidence of the X-ray, GUTTMANN (17) closed the book with the proclamation "At last the fifty year old question 'What is Alite' is answered". A year later JÄNECKE (30) withdrew his entry, $8CaO \cdot Al_2O_3 \cdot 2SiO_2$, and a half century after the original announcement of LE CHATELIER, the alite of clinker is generally acknowledged to consist "essentially" of tricalcium silicate.

Modern progress is the result chiefly of advances in the technique of systematic study. Little could have been accomplished without the generalizations provided by an application of the phase rule within the various systems encountered in the complex of cement clinker. But the successful application requires tools for the positive identification of the phases that are produced by the heat treatments. The microscope was used by LE CHATELIER and TÖRNEBOHM but improvements and new developments in its use have opened up vastly greater possibilities in the resolution and identification of the clinker constituents. The X-ray was first applied to cement research in 1927 (24) but already it has become indispensable in the recognition of the cement compounds and in the still more basic understanding of the atomic rearrangements that occur in the cement kiln. To these should be added the fundamental information on phases gained by the study of heating curves (20) and heats of solution (35), the analytical insight made possible by the test for free lime (36), and other tools that are still in the process of development.

Twenty years ago clinker was conceded to be a mixture of compounds or solid solutions. The nature of the constituent phases was in dispute but some progressive investigators (50) were convinced that they included $3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$ and $3CaO \cdot Al_2O_3$. Nothing was known of the disposition of the iron, the magnesia or the alkalies. Glass was not recognized and the completeness of the reactions in the kiln was gauged chiefly by the soundness test (1) in one form or another. Control in manufacture was obtained through the use of empirical oxide ratios combined with the soundness test and other tests on the cement. The first paper had just been published (3) setting forth some of the hydraulic properties of the above cement compounds but little was known of the control of cement quality through a control of the constituent compounds.

The Identification of Phases.

The prime requirement in a study involving the differentiation of phases, which may include glass, solid solutions and minor compounds, is a means for their proper identification and measurement. The petrographic microscope in the past has not been altogether adequate for this task but new developments give promise that satisfactory methods will become available. In recent years the X-ray has become one of the most reliable tools for the identification of compounds and has been of prime value in advancing the knowledge of cement chemistry. The discovery of a metastable glassy phase, having an X-ray pattern similar to that of a crystalline compound, though unrelated chemically, has opened a field for research of a fundamental character. Such studies may not be justified by any prognosticated application to the improvement of the art (*i. e.* of cement manufacture) but it is the experience of industry that results obtained by such studies find use continuously, once uncovered, and make for large-stride advances in scientific technology.

It was first demonstrated by Tavasci (48) that polished sections of clinker, properly etched and viewed with reflected light are well suited for a study of the cement compounds. This subject has been materially advanced by Insley (26) and Ward (53). The specimen is generally impregnated with a resin (Bakelite No. Br. 0014 has been found suitable) and, after grinding, polished with a paste of rouge with water or alcohol on a rotating lap of coarse duck cloth. The best general etchant (etching solution) for clinker has been found to be a 1-per-cent solution of nitric acid in ethyl alcohol, the specimen being immersed about 5 seconds (26). For special purposes, however, different etchants are required.

The photomicrograph of PLATE I shows a polished section of clinker in which the major phases are easily distinguishable. The large crystals with hexagonal outlines are $3CaO \cdot SiO_2$. These often show zonal structure which suggests some degree of solid miscibility and sometimes also simple twinning. In thin sections of commercial clinker, interference figures of tricalcium silicate frequently depart considerably from perfect uniaxiality (26) while sections of crystals oblique to the optic axis often exhibit a change in extinction angle from interior to exterior of the crystal (5). Variations have been observed in the index of refraction of tricalcium silicate obtained from basic open-hearth slags. These have been attributed to solid solution (2). The X-ray diffraction pattern of the $3CaO \cdot SiO_2$ in clinker has also been observed to be slightly shifted from the position in the pure compound (26). Substantiating evidence of solid solution has not been obtained, however, in equilibrium studies on systems of pure components.

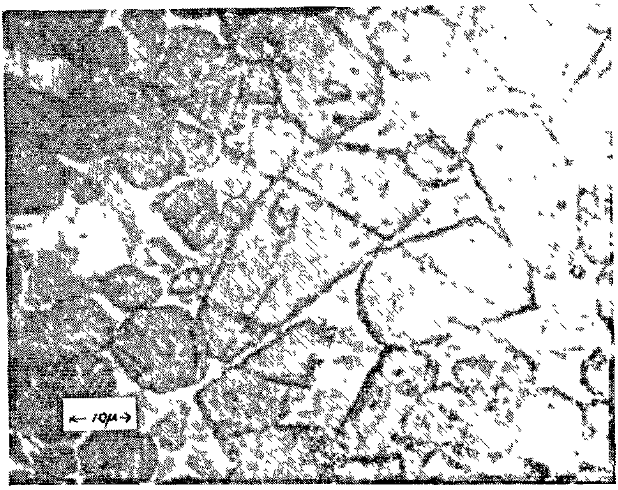

PLATE I. Photomicrograph of Polished Section of Clinker No. 3 *Q* showing $3CaO \cdot SiO_2$ (large clear crystals), $2CaO \cdot SiO_2$ (rounded striated grains), $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ (white interstitial material), and Glass (dark interstitial material, the form of which is determined by the crystallization of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$). Etched with distilled water for 5 seconds followed by 1 % HNO_3 *in alcohol for 2 seconds.* Magnification 1 000 ×. (WARD.)

The rounded heavily-striated grains are dicalcium silicate. SUNDIUS (47) believed these to be the α-form, characterized by two sets of fine polysynthetic twinning bands meeting at a steep angle. The β-form (obtained in synthetic preparations heated below the α—β inversion temperature, 1 420°), was characterized in his opinion by a single set of polysynthetic bands. INSLEY has pointed out, however, that the complex twinning found in clinkers that have been heated above 1 420° may be, in reality, only an indication that the crystal has at some time been in the α-state and offers as confirmation that the X-ray patterns of specimens heated above 1 450° and of similar specimens heated at 1 375° are identical. He differentiates three types of β-$2CaO \cdot SiO_2$.

> Type I, containing 2 or 3 sets of interpenetrating striations, each set being composed of parallel bands, obtained from compositions which have been heated above 1 420°.
>
> Type II, containing 1 set of polysynthetic bands, obtained from compositions which have been heated only to temperatures below the α—β inversion.
>
> Type III, containing no twinning bands, obtained only when moderately slow cooling below the α—β inversion temperature has been permitted before quenching.

The light material which occurs between the grains of the silicates has been identified as $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ or a solid solution of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ with $2CaO \cdot Fe_2O_3$ if the composition is such that an excess of Fe_2O_3 is present (26). A small amount of MgO also enters into solid solution with the $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. SCHWIETE and ZUR STRASSEN (46) limit this to 2 per cent but INSLEY and MCMURDIE (27) believe the solubility is not greater than 1 per cent. MCMURDIE (42) also finds that $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ may take up between 3 and 5 per cent of the calcium aluminates in solid solution. This phase occurs almost universally as prisms which are larger as the $Al_2O_3 : Fe_2O_3$ ratio is diminished and the cooling prolonged. It is scarcely affected by the etchant (1 per cent HNO_3 in alcohol), and has high reflectivity.

The dark irregular interstitial material, closely associated with $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, is considered to be glass (27). It is more readily etched by distilled water than the silicates and has a much lower reflectivity than the $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. WARD (53) has found that it is etched readily by a 1-per-cent solution of nitric acid in alcohol. It is usually isotropic but its composition and optical properties are probably dependent on the composition of the clinker and the heat-treatment to which it has been subjected.

Tricalcium aluminate has been observed in polished sections of a few commercial clinkers (53, 27) as large rectangular crystals, nearly or altogether isotropic, enclosing crystals of silicates. A photomicrograph of this material is shown in PLATE II. It is etched readily by water in 2 or 3 seconds and less readily by a 1-per-cent solution of nitric acid in alcohol. Through the development of a greatly improved technique in the making of thin sections, BROWN (6) had previously observed a phase, somewhat similar but generally of greater size, in laboratory clinkers having an $Al_2O_3:Fe_2O_3$ ratio above 1.38. Usually, however, the large crystals could not be seen in commercial clinkers but their presence was indicated by a mass birefringence of the $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$.

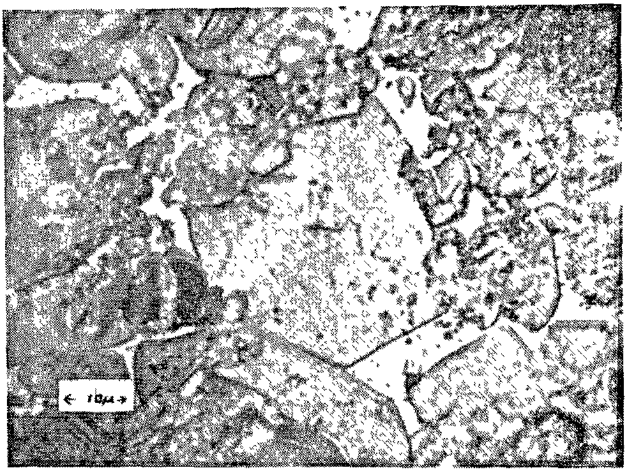

PLATE II. Photomicrograph of Polished Section of Clinker No. 6 *S* selected to show $3CaO \cdot Al_2O_3$, the Large Crystal at Center. Etched with distilled water for 5 seconds followed by 1 % HNO_3 in alcohol for 2 seconds. Magnification 1 000 ×. (WARD.)

There is also observed in the dark interstitial material of some clinkers a prismatic phase (27, 53) which may be readily distinguished from the amorphous glassy phase by its crystalline form and by its more rapid etching with distilled water. Examination in polished thin sections shows that these crystals have a low but distinct birefraction of about the order of $3CaO \cdot SiO_2$. A photomicrograph of this phase is shown in PLATE III.

In the course of a preliminary study to learn the nature of this material (27) a laboratory preparation was made consisting of CaO, Al_2O_3, SiO_2 and Fe_2O_3 in about the proportions in which they occur in Portland cement clinker. This was heated to 1 450° and cooled slowly. The clinker showed no prismatic dark interstitial material. The same mix was again clinkered with additions of alkali carbonates to give in the resulting mixtures 1.5 per cent Na_2O and 1.5 per cent K_2O respectively. The clinkers obtained showed prismatic crystals which appeared to be identical with those previously observed in the commercial clinkers. The optical properties of the prismatic phase agree with those of the compound $8CaO \cdot Na_2O \cdot 3Al_2O_3$ (7) with the exception of having higher indices of refraction which may be due to some Fe_2O_3 in solid solution (27).

INSLEY found that the ternary compound of CaO, Na_2O and Al_2O_3 forms a complete solid solution series with $3CaO \cdot Al_2O_3$ provided ample time is allowed for the action to take place (28). TAYLOR (49) has observed that, when quenches of compositions on the join $3CaO \cdot Al_2O_3$-$8CaO \cdot Na_2O \cdot 3Al_2O_3$ or within the triangle $3CaO \cdot Al_2O_3$-$8CaO \cdot Na_2O \cdot 3Al_2O_3$-$5CaO \cdot 3Al_2O_3$ are made along the liquidus, or when cooling from 1 500° to 1 425° has been rapid, there are found both $3CaO \cdot Al_2O_3$ and the alkali compound as independent phases. In charges which are cooled slowly and contain little or no glass, $3CaO \cdot Al_2O_3$ crystals are not observed, but instead a single solid solution phase in which the birefraction decreases as the calculated amount of $3CaO \cdot Al_2O_3$ increases.

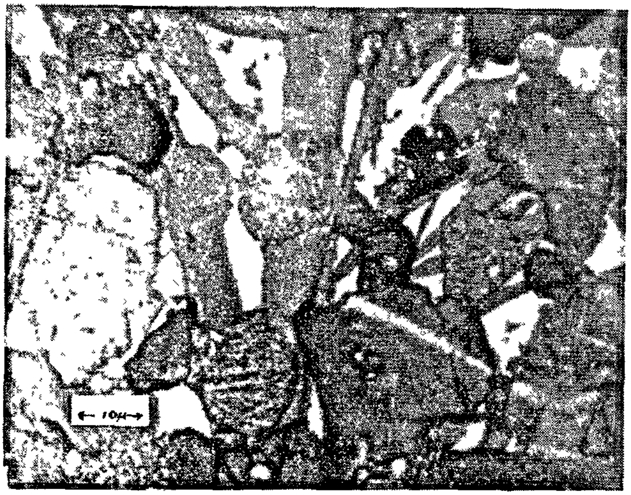

PLATE III. Photomicrograph of Polished Section of Clinker No. 2 *S* selected to show the Prismatic Dark Interstitial Phase. *Etched with distilled water for 5 seconds followed by 1 % HNO_3 in alcohol for 2 seconds.* Magnification 1 000 ×. (WARD.)

These observations suggest that the soda component of the prismatic dark interstitial material of clinker may contain or consist of a ternary compound of CaO, Na_2O and Al_2O_3 or a solid solution of that compound with $3CaO \cdot Al_2O_3$. It is probable also that a small amount of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ enters into the phase as evidenced by an increase in the refractive index of the alkali compound in the presence of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ (27). The common juxtaposition, however, of the prismatic phase with the light interstitial material indicates that the amount of solution of the $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ in the alkali compound is limited if, indeed, the prismatic phase is of this general composition, but further exploration of the field is required to establish the complete phase relationships involved.

The potash compound stable in the CaO-K_2O-Al_2O_3 system is $K_2O \cdot Al_2O_3$ (8). It is not yet clear what part this compound may play in the formation of the prismatic phase or if a different compound or solid solution is formed with some of the other constituents of Portland cement clinker.

The problem of the alkalies is discussed further below (see pp. 69—70).

Free CaO may occur in clinker either in aggregates or in single grains which often occur at the center of the $3CaO \cdot SiO_2$ crystals (27). The grains are etched easily by water and appear as slightly darkened round areas. A photomicrograph is shown in PLATE IV.

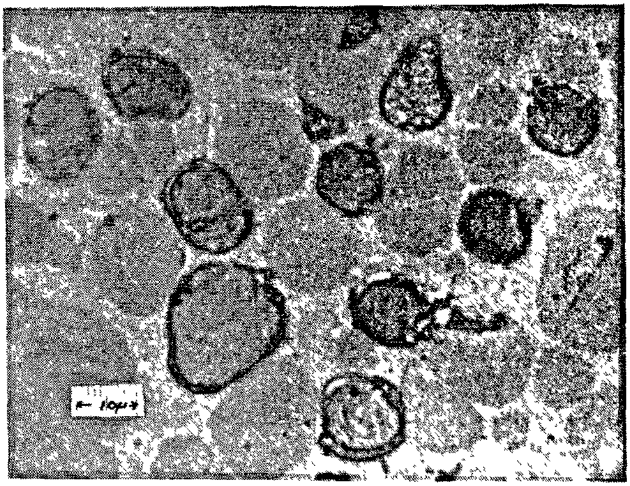

PLATE IV. Photomicrograph of Polished Section of Clinker No. 4 Q selected to show Grains of Free CaO. Etched with 1 : 3 water-alcohol for 60 seconds. Magnification 1 000 ×. (WARD.)

Periclase (free MgO) appears as irregular-shaped grains which are not readily etched with water and may be observed on unetched polished sections because of their high reflectivity (27). Especial care in polishing is necessary, however, because the grains are easily fragmented and the cracks filled with polishing medium. It is found mainly in the interstitial material but may occur as inclusions in the silicates. In PLATE V is shown a photomicrograph of Periclase in a commercial clinker that was reheated and cooled slowly. The same clinker reheated and cooled quickly is shown in PLATE VI. Magnesia is known to dissolve in the liquid (37) to the extent of 4 to 6 per cent depending on the $Al_2O_3:Fe_2O_3$ ratio. The smaller size of the grains in the quickly cooled (high glass) clinker is significant.

The contribution of the X-ray diffraction pattern in establishing the identity of the clinker compounds has been one of the outstanding achievements of the past decade. All of the major compounds have been prepared synthetically from pure materials, their X-ray patterns obtained and these compared with the patterns of commercial clinkers of various compositions. In this way a

PLATE V. Photomicrograph of Polished Section of Clinker No. 3 *S* selected to show Grains of Periclase as observed in slowly Cooled Clinkers. No etch. Magnification 1 000 ×. (WARD.)

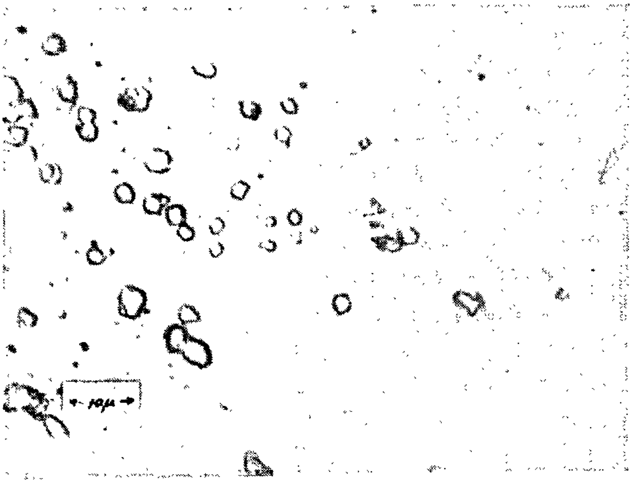

PLATE VI. Photomicrograph of Polished Section of Clinker No. 3 *Q* selected to show Grains of Periclase as observed in quickly Cooled Clinkers. No etch. Magnification 1 000 ×. (WARD.)

number of important questions of composition have been answered (9). Thus "alite" has been definitely identified as $3CaO \cdot SiO_2$, Periclase and free CaO have been observed, the course of reaction has been followed, solid solutions have been discovered and, more recently, the nature of the glassy phase has been studied (10). Even the means for the quantitative determination of the phases have been developed (25).

Still more generally useful in the plant and testing laboratory for learning the extent of the combinations in the kiln is the chemical test for free CaO (36). Many modifications in the original procedure have been proposed and the time required for the test has been shortened (43).

Equilibrium Crystallization.

The chemical nature of a Portland cement clinker is not defined by stating its oxide composition but by stating the proportions and character of the individual substances which may be present and which are referred to as "phases". Investigation of the conditions under which the various phases can exist in equilibrium with one another under any specified conditions of temperature and pressure is a necessary step in arriving at an understanding of the essential nature, that is, the chemical constitution, of clinker.

Recent work has indicated that, in the process of manufacturing Portland cement clinker, complete crystalline equilibrium is not necessarily attained and that the presence of glass as one of the phases must be taken into consideration when investigating the constitution of the clinker. Knowledge of phase equilibria is necessary, however, in determining the phenomena which will occur even when crystalline equilibrium is not attained. It is necessary, therefore, to continue the phase equilibria investigations with this in mind. It is of importance in arriving at a knowledge of the constitution of clinker that we obtain and analyze information on the course followed in the development of the cement compounds as they are normally found in commercial operations. But the first step in this undertaking is a study under the ideal conditions which obtain with only a selected number of the compounds and with heat-treatments such that equilibrium conditions are at all times maintained. Such studies have been completed for several of the systems of Portland cement and are still underway for other systems.

The Clinker Compounds. The publication by RANKIN and WRIGHT (45) of the system CaO-Al_2O_3-SiO_2 in 1915 marked the beginning of a period of extraordinary activity in research by the methods of high-temperature phase equilibria. In a compilation by HALL and INSLEY (18) of phase diagrams of interest to the silicate technologist, published up to 1933, 47 binary and 32 ternary systems are listed together with 32 sections of 3-component systems.

In the intervening five years, about 75 additional diagrams have appeared which are now being compiled for publication by the same authors.

RANKIN and WRIGHT showed that, in mixtures of CaO, Al_2O_3 and SiO_2 of the general composition of Portland cement clinker, there exist at complete equilibrium crystallization $3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$ and $3CaO \cdot Al_2O_3$.

The nature of the iron compound in clinker has been indicated by the identification, in the system $CaO\text{-}Al_2O_3\text{-}Fe_2O_3$, of the compound $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ (21), by numerous confirmations of its existence in more complex systems (32) and by the direct identification of its presence in commercial clinker (9).

The magnesia has been found to remain uncombined in the presence of CaO, SiO_2 and Al_2O_3 in the region of Portland cement (22) but a slight amount of solid solution may occur with $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ (46, 42) whereby that compound is changed in color from chocolate brown to black and the pleochroism is increased.

Study on the alkali compounds is still incomplete but in the systems containing only CaO, Al_2O_3, and the alkalies, the compounds $8CaO \cdot Na_2O \cdot 3Al_2O_3$ (7) and $K_2O \cdot Al_2O_3$ (8) appear to be the stable phases in the region near the CaO vertex. However, if cooling is not too rapid, the $8CaO \cdot Na_2O \cdot 3Al_2O_3$ may form a solid solution series with $3CaO \cdot Al_2O_3$ (28, 49) so that, in a mixture of the two, only one phase may be present.

Thus in a Portland cement mixture consisting of the components CaO, Al_2O_3, Fe_2O_3, SiO_2 and MgO, on complete equilibrium crystallization, we should expect to find $3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$, $3CaO \cdot Al_2O_3$, MgO and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ containing a small amount of MgO in solid solution.

The Alkali Components. It has been pointed out that a prismatic dark interstitial material is often observed in polished sections of clinker and that this phase appears to be associated with the alkalies inasmuch as it has not been observed, in laboratory clinkers, in the absence of soda and potash. Up to this writing the prismatic phase has not been definitely identified. Some evidence suggests that it may consist, so far as the soda component is concerned, of a ternary compound of CaO, Na_2O and Al_2O_3 or a solid solution of that compound with $3CaO \cdot Al_2O_3$ and containing also small amounts of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. On the other hand, some indications suggest that silica also may be involved, both in the soda and in the potash compounds which constitute the prismatic phase.

The potash compound $K_2O \cdot Al_2O_3$, stable in the system $CaO\text{-}Al_2O_3\text{-}K_2O$, has been studied with $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ and $2CaO \cdot Fe_2O_3$ (49). It has been found that $4CaO \cdot Al_2O_3 \cdot Fe_2O_3\text{-}K_2O \cdot Al_2O_3$ forms a binary system with no new compounds, having an eutectic at 81 % $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$—19 % $K_2O \cdot Al_2O_3$ and melting at 1 343° ± 5°. The melting temperatures rise sharply on the potash side of the eutectic. The $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ apparently takes up some $K_2O \cdot Al_2O_3$ in solid solution since there is a difference in pleochroism of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ upon the addition of $K_2O \cdot Al_2O_3$, but the failure to observe changes in indices of refraction indicates that the amount of such solution is probably small. The $K_2O \cdot Al_2O_3$ likewise takes up some $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ in solid solution as indicated by an increase in index of refraction from 1.603 to 1.625. The amount of this solution is also probably small, however, because the $K_2O \cdot Al_2O_3$ does not lose its isotropism.

An extension of this study to include the compounds $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, $2CaO \cdot Fe_2O_3$, $K_2O \cdot Al_2O_3$ has been made using mixtures of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ and $2CaO \cdot Fe_2O_3$, up to 50 per cent $2CaO \cdot Fe_2O_3$, with the addition of $K_2O \cdot Al_2O_3$ up to 25 per cent. Throughout this region the $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ and $2CaO \cdot Fe_2O_3$ form a continuous solid solution series and at any composition (within the range studied) the phase relations are those of a pseudo-binary system of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$-$2CaO \cdot Fe_2O_3$ solid solution plus $K_2O \cdot Al_2O_3$. The melting temperature of the lowest melting composition increases from 1 343° (in the system $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$-$K_2O \cdot Al_2O_3$) to 1 357° (in the mixture wherein the solid solution consists of equal parts of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ and $2CaO \cdot Fe_2O_3$). The composition of the lowest-melting composition contains slightly decreasing amounts of $K_2O \cdot Al_2O_3$ as the $2CaO \cdot Fe_2O_3$ content of the solid solution increases.

The dark prismatic material in laboratory clinkers containing CaO, Al_2O_3, Fe_2O_3, SiO_2 and K_2O, however, has optical characteristics different from those of $K_2O \cdot Al_2O_3$ so it appears probable that some reaction occurs in such mixtures between the potash and the silica producing the compound of potash observed as prismatic dark interstitial material. A knowledge of the nature of that phase awaits completion of studies now under way on the compounds $3CaO \cdot SiO_2$, $K_2O \cdot Al_2O_3$, Al_2O_3 and $2CaO \cdot SiO_2$, $K_2O \cdot Al_2O_3$, CaO.

Calculation of Compounds at Crystalline Equilibrium. With a knowledge of the phases formed at crystalline equilibrium from any given oxide composition, it is possible to calculate, within the systems explored, the potential compound composition of the product (4, 11). Such information is available for systems consisting of CaO, Al_2O_3, Fe_2O_3, SiO_2 and MgO in the region of Portland cement. It is recognized at the outset that such calculations cannot represent completely the true conditions of any commercial clinker both because of the presence in such clinker of components other than those listed, upon which adequate information is still lacking, and also because, in commercial clinker, a condition of complete crystalline equilibrium is rarely or never attained.

Through study of the compounds, individually and collectively, followed by the examination of laboratory and commercial cements of controlled or selected compositions, one finds, for example, that $3CaO \cdot SiO_2$ is the compound chiefly responsible for high early strength. If, then, one wishes to produce a high-early-strength cement, an obvious procedure is to use a mix that will give a high $3CaO \cdot SiO_2$ content. By the method of calculation described, the procedure for accomplishing this without impairment of other desirable properties is at once obvious. Such calculations have been found useful in the specification of cements for special purposes, such as high-early-strength cement, low-heat cement, modified cement and sulfate-resistant cement. Such computed values focus the attention of the chemist on the ultimate compounds which, through test, may be found to be desirable or undesirable and, with that information, point the way to a simple and direct solution of industrial problems. The method lacks precision but is less cumbersome than the equally unprecise method of oxide percentages and ratios, and possesses the advantage of fundamental soundness. As new information on the state of the minor constituents in clinker and the course of crystallization is revealed through research, such information, as a matter of course, is applied to a refinement of the procedure and new calculations must replace the old. Science does not stand still.

Arrested Crystallization.

In the manufacture of Portland cement, temperatures are employed which cause a part of the charge to liquefy and most of the reactions of clinker formation take place during the period while the liquid is present. The temperature of first liquid formation has been found (20) to be about 1 280° but commercial clinker is often burned at temperatures as high as 1 450° or higher. At these temperatures there may be from a quarter to a third of the total charge present in the liquid state. All of the alumina and ferric oxide, the alkalies and probably other minor constituents, part of the magnesia, a considerable amount of lime and some silica are then present in the liquid.

If the clinker cools very slowly, further reactions may take place between the liquid and the solid phases and, on final solidification, a condition obtain of crystalline equilibrium. Again, at a somewhat more rapid rate of cooling, the liquid may crystallize independently of further reaction with the solid phases; in this case the final compound composition of the clinker may be different from that of equilibrium crystallization. And, finally, with very rapid cooling, the liquid may solidify without crystallization and be present in the clinker as a glass. It is probable that, in commercial clinker, the cooling rate is rarely or never so slow that complete equilibrium crystallization obtains nor yet so rapid that all of the liquid solidifies as glass. It seems probable that some glass, but quite variable amounts, will be found in all commercial clinkers.

The splendid investigation by Lea and Parker (32) on the quaternary system $CaO\text{-}Al_2O_3\text{-}Fe_2O_3\text{-}SiO_2$ has provided the information by which the amount and composition of liquid formed with any mix of these components (within the portion of the system bounded by CaO-$2CaO \cdot SiO_2$-$5CaO \cdot 3Al_2O_3$-$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$) at any temperature may be computed. This information has greatly stimulated further research on the glassy phase since, for the first time, compositions representative of the liquid phase in clinkers of different compositions within this four-component system may be prepared for study. The finding (35) that 4 to 6 per cent of MgO dissolves in the liquid of the above system having $Al_2O_3 : Fe_2O_3$ ratios between 0.68 and 3.0, permits the inclusion of MgO as a fifth component in studies on the glassy phase.

Nature of the Glassy Phase. The appearance of the glassy phase in polished sections of clinker as an amorphous gray interstitial material has already been described. The nature of this material has been further investigated by BROWNMILLER (10). It was found that homogeneous glasses showing no evidence of orientation by optical or X-ray methods could be obtained only when very small charges (0.1 g or less), weighted with platinum, were instantaneously quenched by immersion in mercury. When somewhat larger charges were used and the quenching was rapid but not instantaneous, rearrangements were found to occur which, though not advanced to the condition represented by the formation of the equilibrium compounds, nevertheless gave a product which indicated periodicity. With yet slower cooling, the equilibrium compounds appeared.

The intermediate state, which we have designated the "metastable phase", was generally faintly birefracting, showed indices of refraction always uniformly higher than those of the true glasses of similar composition, and gave a strong X-ray diffraction pattern which, within the range studied, was independent of the composition. The startling observation was made that this pattern was nearly identical with the pattern of pure crystalline $3CaO \cdot Al_2O_3$. This suggested that $3CaO \cdot Al_2O_3$ might be present, though theoretically it should not exist in the charges examined even at crystalline equilibrium, and preparations were made containing no alumina whatsoever but the resulting metastable phase gave the same X-ray pattern, as shown in PLATE VII. Nor was the phase an unstable modification of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ as demonstrated by critical observations of refractive index and by direct studies with pure $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$.

An hypothesis has been proposed to account for the character of the phase premised on the assumption that oxygen polyhedra are formed, giving rise to the periodicity necessary for a strong X-ray pattern, but that the migration of the accessory atoms, necessary to the formation of crystalline compounds, has not occurred. It appears that in these melts the migration of atoms requires an appreciable period of time and, by the proper choice of temperature,

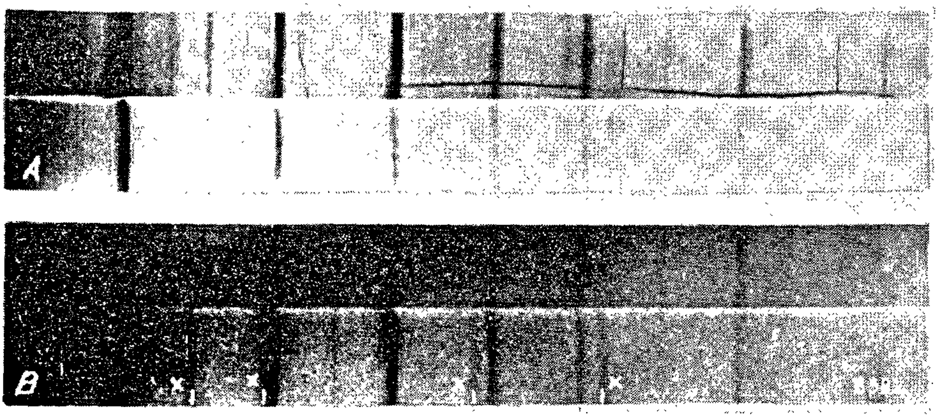

Plate VII. X-Ray Pattern of Crystalline $3CaO \cdot Al_2O_3$ and Quenched-Liquid Compositions.

(A) Upper—Pattern of crystalline $3CaO \cdot Al_2O_3$. Lower—Pattern of composition consisting of 53·9 % of CaO, 15·3 % of Al_2O_3, 6·8 % of SiO_2, 24·0 % of Fe_2O_3 quenched from 1 450°.

(B) Upper—Pattern of composition consisting of 53·9 % of CaO, 15·3 % of Al_2O_3, 6·8 % of SiO_2, 24·0 % of Fe_2O_3 quenched from 1450°. Lower—Pattern of composition consisting of 45·9 % of CaO, 7·0 % of SiO_2, 47·1 % of Fe_2O_3 quenched from 1 540°. x—Indicate platinum lines.

viscosity and time interval, an intermediate state of configuration may result wherein the arrangement is no longer entirely random nor the migration complete.

The metastable phase, therefore, may be considered as a mixture of isomorphous units whose chemical formula depends on the original composition of the liquid and the rate of cooling. It may be considered as a continuous structure consisting of oxygen polyhedra with the other atoms in random arrangement between the oxygen atoms. It cannot be considered as an example of the substitution type of solid solution, for in such solutions the structure is an intermediate one between the end members. The similarity of the X-ray diffraction pattern to that of $3CaO \cdot Al_2O_3$ may be accidental, since both $3CaO \cdot Al_2O_3$ and the metastable phase are built of units of approximately the same dimensions, or it may be that the relationship is more fundamental.

In Portland cement clinker, which is never cooled instantaneously, it seems that true glasses are not likely to be present, that is, in the sense that the undercooled solidified liquid shows no X-ray diffraction lines. However, a part of the interstitial material in clinker (the material which was liquid at the burning temperature) may remain essentially one phase having the composition of the liquid and this is the material which is referred to herein as "glass".

It should be pointed out that the above observations have indicated that the identification of $3CaO \cdot Al_2O_3$ by means of the X-ray pattern is not feasible.

Approximation of Glass Content. Although the microscopic examination of polished sections of clinker, as previously set forth, has revealed an amorphous interstitial phase, the lack of a confirming method for estimating the glass content has seriously curtailed research on that phase. Recognizing that heat is liberated when glass changes to the more stable crystalline state, a method has been reported by LERCH for the approximation of the glass content of clinker which is based on the latent heat of crystallization of the glass (35). Liquid compositions were prepared of $Al_2O_3 : Fe_2O_3$ ratios from 0.64 to 3.24 on the $3CaO \cdot SiO_2$-$2CaO \cdot SiO_2$ surface on the 1 400° isotherm. The latent heats of crystallization were determined by noting the differences in the heats of solution of these preparations following heat treatments such as to produce, on the one hand, complete crystallization and, on the other hand, complete undercooling and solidification wholly as glass. After correcting for the heat of inversion of β- to γ-$2CaO \cdot SiO_2$ (inversion occurred in the slowly cooled, completely crystalline charge) a curve was drawn, given in FIG. 1, representative of the latent heats of crystallization of liquid compositions throughout the range of Portland cements. Now if a specimen of clinker were tested for its heat of solution, and a duplicate specimen similarly tested following a heat-treatment designed to produce complete crystallization, then the difference between the two values, properly corrected, represents the latent heat of crystallization of the glass in the clinker. This value divided by the latent heat of crystallization of a pure glass of the same $Al_2O_3 : Fe_2O_3$ ratio (taken from the curve) gives the fractional part of glass in the clinker.

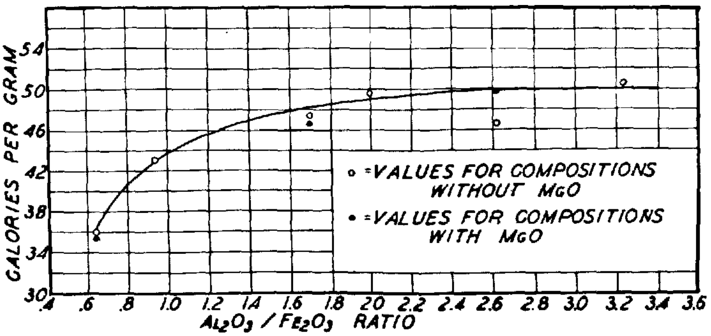

FIG. 1. Latent Heat of Crystallization of Liquid Compositions of varying Alumina: Ferric Oxide Ratios on the Tricalcium Silicate-Dicalcium Surface at 1 400°.

At present the method is regarded as only a rough approximation, since certain assumptions are made which are subject to modification. It is assumed, for example, that the glass in a cement clinker has the same $Al_2O_3 : Fe_2O_3$ ratio as the clinker itself, and that it is located on the 1 400° isotherm on the

$3CaO \cdot SiO_2$-$2CaO \cdot SiO_2$ surface. This cannot be true if the amount of glass is less than that expected at 1 400°. Another source of error is in the latent heats of crystallization, determined on liquid compositions which, by themselves, do not yield the same crystalline product as when present in clinker.

The chief difficulty in the way of securing an accurate method of estimating glass content is in the present lack of knowledge concerning the character of the course of crystallization in commercial clinker, whether normal or independent. An investigation intended to take into account the change in $Al_2O_3 : Fe_2O_3$ ratio of the liquid during crystallization is contemplated. When the method is modified to eliminate or reduce the error from this source, it may be possible to obtain a clue as to the character of the course of crystallization, through comparisons of calculated values with microscopic observations.

The results, however, are significant of definite changes induced in a clinker by the heat-treatment and probably are correctly interpreted as an expression of glass content. Although the order of reproducibility is such as to indicate a high precision, the uncertainties in interpretation suggest a conservative estimate of the absolute accuracy of the methods, perhaps in the order of $\pm$ 5 per cent.

Composition at Arrested Crystallization. As a part of a research on the effects of glass in clinker on the properties of the cement, a special study has been made of the glass content of 22 commercial clinkers obtained from plants in the United States selected to include a wide variation in composition and treatment. A portion of each clinker (49) was reheated to about 1 400° and cooled slowly (designated *S* samples) in order to obtain a minimum of glass; another portion was reheated and cooled quickly (designated *Q* samples) to obtain a maximum of glass; a third portion was taken from the plant clinker as received (designated *P* samples).

The glass content of each of the differently treated clinkers was approximated by the method given above (38). The results are tabulated in Table 1 and are shown graphically in Fig. 2, arranged in order of increasing glass content of the plant clinkers. Two points stand out clearly from these tests: 1. The glass content of the commercial clinkers as received varies over a wide range, from 2 to 21 per cent. 2. The glass content is definitely affected by the heat-treatment, that is, by the rate of cooling of the clinker. The glass in the quickly cooled clinkers varied between 8 and 22 per cent; that in the slowly cooled clinkers, between 0 and 3 per cent.

Forsén (14) pointed out five years ago that the time element in the recrystallizations, necessary in the systems of Portland cement in order to attain continuous equilibrium at the liquidus, is so great that it is unlikely that a state of equilibrium obtains in any commercial clinker. Thus, in the system CaO-Al_2O_3-SiO_2 the composition that has been known as "Jäneckite", $8CaO + Al_2O_3 +$

$+ 2SiO_2$, forms on slow cooling (23) $3CaO \cdot SiO_2 + 2CaO \cdot SiO_2 + 3CaO \cdot Al_2O_3$. The primary phase is $3CaO \cdot SiO_2$ which separates while the residual melt changes along a line from $3CaO \cdot SiO_2$ through $8CaO \cdot Al_2O_3 \cdot 2SiO_2$ until the field of $3CaO \cdot Al_2O_3$ is reached. Then $3CaO \cdot SiO_2$ and $3CaO \cdot Al_2O_3$ separate until, at 1 455°, point 16 (invariant point for $3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$ and $3CaO \cdot Al_2O_3$) is reached (45). On continued slow cooling, some $3CaO \cdot SiO_2$ is then dissolved and $2CaO \cdot SiO_2$ separates with $3CaO \cdot Al_2O_3$. But, if the cooling is rapid, this secondary transformation does not occur and the residual melt at point 16 may either solidify as a glass or it may crystallize without the resolution of the $3CaO \cdot SiO_2$. The probable product on rapid cooling is $3CaO \cdot SiO_2 +$ glass.

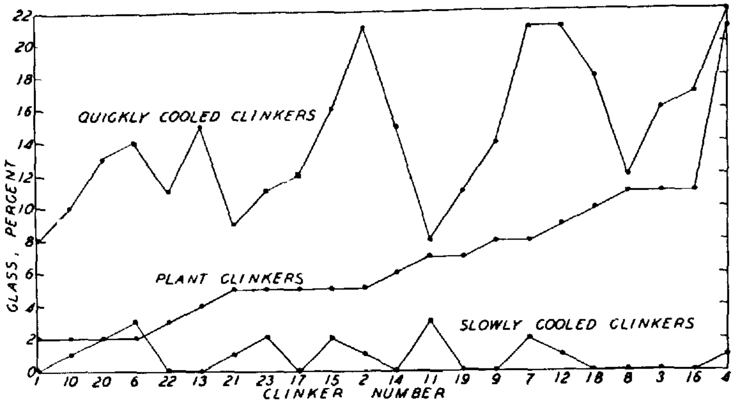

FIG. 2. The Approximated Glass Contents of Clinkers arranged in Order of Increasing Glass Content of the Plant Clinkers.

When ferric oxide is added, $3CaO \cdot SiO_2$, $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ and glass were believed to result and, with larger amounts of silica, $2CaO \cdot SiO_2$ also crystallized out. This reasoning led FORSÉN to the establishment of an upper lime limit (the weight ratio between CaO and the Al_2O_3 after allowing for $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$) which varied with the composition between 1 and 1.65, but usually was about 1.18.

LEA and PARKER (32) have calculated the compound compositions which may result from differences in the course followed by the liquid in solidification. They have calculated (TABLE 2) the theoretical composition of four clinkers under 8 conditions of hypothetical cooling, including the equilibrium crystallization; crystallization at the eutectic with liquid forming glass; and crystallization at the quintuple line, at 1 400° and at 1 450°, respectively, with liquid giving glass and with liquid crystallizing independently in each case. Other temperatures of reference could be selected for study from their data.

In these calculations there is postulated no partial solidification of the liquid as glass—it is assumed either to solidify completely as glass from the temperature or condition given or to crystallize completely but independently (except in the first case where equilibrium crystallization is assumed). Under these assumptions, even at complete independent crystallization, the percentages of the calculated compounds are seen to differ from those computed at equilibrium crystallization. A critical study of the basic data shows that, within the $Al_2O_3 : Fe_2O_3$ ratio range of 0.94 to 1.66, no change in composition results through the independent crystallization of the liquid but, with $Al_2O_3 : Fe_2O_3$ ratios below 0.94, the $3CaO \cdot SiO_2$ is decreased and $2CaO \cdot SiO_2$ increased (accompanied by the separation of free CaO) whereas, with ratios above 1.66, the reverse obtains. Furthermore, the $3CaO \cdot Al_2O_3$ is reduced at $Al_2O_3 : Fe_2O_3$ ratios above 1.66 and some Al_2O_3 separates out as $5CaO \cdot 3Al_2O_3$. These changes in composition for each per cent of liquid are shown graphically in FIG. 3, drawn from calculations of DAHL.

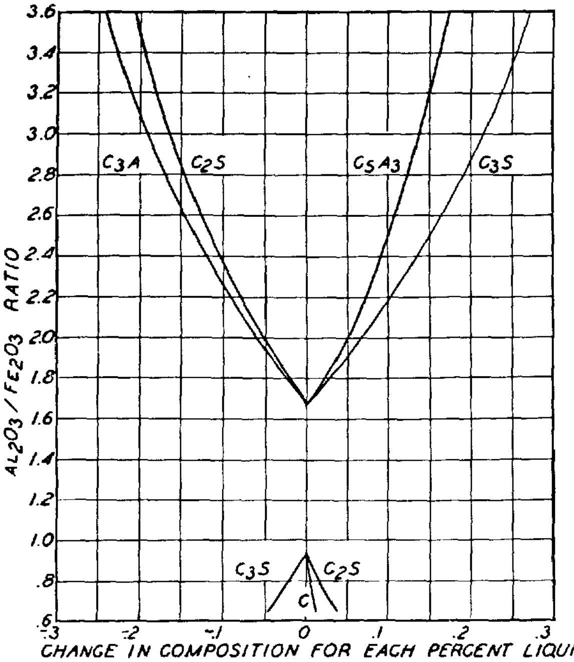

FIG. 3. Change in Composition of System through Complete Crystallization of Liquid independently from 1 400°.

On the assumption that all of the liquid solidifies as glass, the iron and alumina compounds are absent from the crystalline phases provided the crystallization occurs at some temperature above that of the point where the liquid composition leaves the $3CaO \cdot SiO_2$ boundary surface with

$3CaO \cdot Al_2O_3$ or $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. The same order of effect on the silicates is observed as in the condition of independent crystallization.

DAHL (12) has extended the computations of LEA and PARKER to include 7 types of composition wherein the course of crystallization differs from that of every other type in the 4-component system under consideration. These 7 types are shown in FIG. 4 where the points E_p, $(T_1)_p$ and $(T_2)_p$ are projections of the points E, T_1 and T_2 (cf. LEA and PARKER's Techn. Paper 16) from the $3CaO \cdot SiO_2$ point to the $2CaO \cdot SiO_2$-$3CaO \cdot Al_2O_3$-$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ plane.

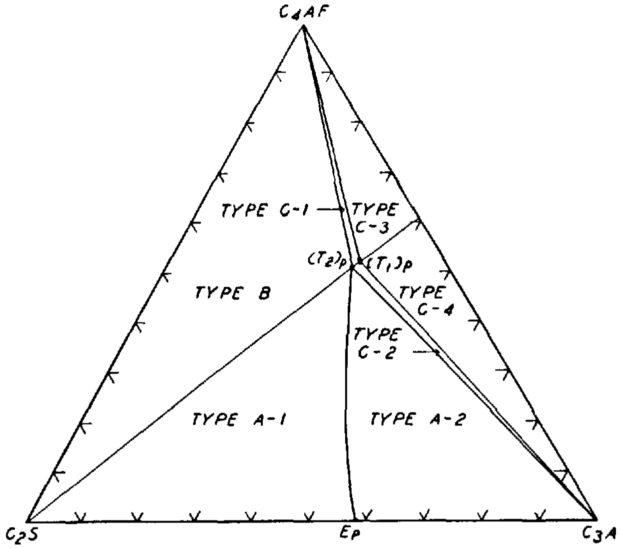

FIG. 4. Diagram showing Composition Types.

The course of crystallization followed by the 7 different types of cement is as follows:

Type *A-1*. At 1 450° and 1 400° the liquid is on the $3CaO \cdot SiO_2$-$2CaO \cdot SiO_2$ surface. It reaches the quintuple line T_2E at a temperature which depends on the composition (equations for the calculation of which are given in DAHL's paper), and solidifies at T_2 at 1 338°.

A-2. Liquid passes from CaO-$3CaO \cdot SiO_2$ surface to T_1D, thence to $3CaO \cdot SiO_2$-$3CaO \cdot Al_2O_3$ surface, thence to T_2E and solidifies at T_2.

B. Liquid passes from $3CaO \cdot SiO_2$-$2CaO \cdot SiO_2$ surface to T_2W, thence to T_2.

C-1. Liquid passes from CaO-$3CaO \cdot SiO_2$ surface to T_1X, thence to $3CaO \cdot SiO_2$-$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ surface, thence to T_1T_2 and solidifies at T_2.

C-2. Liquid passes from CaO-3CaO · Al_2O_3 surface to T_1D, thence to 3CaO · SiO_2-3CaO · Al_2O_3 surface, thence to T_1T_2 and solidifies at T_2.

C-3. Liquid passes from CaO-3CaO · SiO_2 surface to T_2X, thence to T_1, thence to T_1T_2 and solidifies at T_2.

C-4. Liquid passes from CaO-3CaO · SiO_2 surface to T_1D, thence to T_1, thence to T_1T_2 and solidifies at T_2.

The types *A-1*, *A-2*, *C-2* and *C-4* are included in LEA and PARKER's type (a) and the types *B*, *C-1*, and *C-3* in their type (b). Types *C-3* and *C-4* represent compositions of low 2CaO · SiO_2 content in which free CaO is present at equilibrium at 1 341°. Types *A-2*, *C-1*, and *C-2* include compositions which may contain free CaO at equilibrium at slightly higher temperatures, the temperature depending on the 2CaO · SiO_2 : 4CaO · Al_2O_3 · Fe_2O_3 ratio for types *A-2* and *C-2*, and on the 2CaO · SiO_2 : 3CaO · Al_2O_3 ratio for type *C-1*.

Equations have been set up by DAHL whereby the composition of the mixtures in the 4-component system may be calculated at each of the critical points referred to, under the following conditions of cooling: 1. For all types of composition, where all of the liquid in equilibrium at the temperature cited has solidified as glass; 2. For all types of composition, where all of the liquid has solidified by independent crystallization; 3. For type *A-1* and *B* compositions, where normal crystallization is assumed to have proceeded to an estimated glass content; and 4. For type *A-1* composition, where crystallization is assumed to have proceeded independently from 1 338°, 1 400°, and 1 450° to an estimated glass content.

The magnesia may be included on the assumption that liquids on surfaces or at invariant points in the quaternary system CaO-Al_2O_3-SiO_2-Fe_2O_3 may dissolve MgO up to a maximum of 6 per cent. It is thereby assumed that these liquids containing MgO, and containing the same proportions of the four components, may exist in equilibrium with the same solid phases as the original liquids, at a somewhat lower temperature. For example, in the quaternary system a liquid of the composition 54.8 % CaO, 22.7 % Al_2O_3, 6.0 % SiO_2, 16.5 % Fe_2O_3 is at an invariant point and, at 1 338° may exist in equilibrium with solid 3CaO · SiO_2, 2CaO · SiO_2, 3CaO · Al_2O_3 and 4CaO · Al_2O_3 · · Fe_2O_3. It is assumed that the liquid obtained by dissolving MgO in this liquid may exist in equilibrium with the same solid phases and that, when 6 per cent MgO is present, it may also exist in equilibrium with MgO. These postulations are not strictly sound but, in connection with studies of the properties of Portland cement, it is assumed as a working hypothesis that they are approximately correct.

The equations of Group 3, above, are reproduced in APPENDIX I, the assumption being that the liquid remains in equilibrium with the crystallizing phases until a temperature is reached at which all of the residual liquid solidifies as a glass. G represents the percentage of "quaternary glass". When magnesia is to be considered, the estimated percentage of glass, containing MgO, is not G but may be designated as P. Then, if M (designating MgO) is greater than $0.06P$, $G = 0.94P$ and free MgO $= M - 0.06P$. If M is less than $0.06P$, $G = P - M$ and free MgO $= O$.

A few calculations are shown in TABLE 3, obtained by the use of the above equations, which indicate probable changes in actual composition resulting from arrested crystallization. Eight commercial clinkers are represented (taken from the group listed in TABLE 1) each of which had been reheated to about 1 400° and cooled quickly with the purpose of producing relatively high glass content. Careful analyses were made, including free CaO, and the potential composition was calculated on the assumption of complete equilibrium crystallization. These data are set down opposite the designation "potential" in the table. The glass content was approximated by the heat of solution method described above, and the compositions were recalculated to include glass on the assumption that normal crystallization obtained to the estimated glass content. These values are set down under "calculated" in the table.

The same type of change is observed as in the calculations of LEA and PARKER but with the important difference that the glass recorded does not represent the total liquid content at 1 400° but rather the amount of glass as actually determined. Experimental confirmation of some of these changes in constitution due to the presence of glass is given below in this Paper.

Effect of Constitution on the Behavior of the Cement.

Shortly after RANKIN had defined the compounds of the $CaO\text{-}Al_2O_3\text{-}SiO_2$-system stable in the field of Portland cement, BATES (3) initiated the investigations at the National Bureau of Standards which have been continued up to the present time on the properties of the cement compounds and their effects in the cement. Chemists throughout the world have contributed a vast amount of literature on this subject but it is not the purpose of the author to review this progress in detail. A few examples will suffice to indicate important applications which have been made in the control of cement properties through a knowledge of clinker constitution.

A few years ago it was common practice to allow 21 days for the curing of a concrete highway but information on the relative hardening rates of $3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$, together with finer grinding, has pointed the way to the manufacture of cements that permit the opening of roads in from two to seven days.

The building of large dams has necessitated the use of cements having "low" heat generation on hydration in order to reduce the thermal contractions on cooling which might induce serious cracking. Such cements were made for Boulder Dam and cements of "moderate" heat generation are being used in many other structures. These cements are designed to restrict the amounts of $3CaO \cdot Al_2O_3$ and $3CaO \cdot SiO_2$ in the clinker since these are the high heat-producing constituents.

Concrete exposed to natural or factory waters high in sodium sulfate or magnesium sulfate may be corroded owing to the formation of calcium sulfoaluminate. A vastly improved resistance is attained by the use of cements designed to limit the amount of calcium sulfoaluminate that may be formed.

Through similar applications of information on the behavior of the compounds calculated to be present in clinker, cements have been improved in soundness, volume constancy and durability, the rate of set more satisfactorily controlled, flash set and false set largely eliminated, dusting avoided, warehouse caking overcome and grindability of the clinker improved.

Of particular interest at the moment, because the subject is still young, is the effect of the presence of glass, both directly and indirectly, on the properties of the cement. It already has been pointed out from theoretical reasoning that changes in the glass content are accompanied by changes in the amounts of crystalline constituents along certain directions. One of these changes involves Periclase (free MgO) since MgO dissolves in the liquid to the extent of about 4 to 6 per cent.

Glass Content and Delayed Unsoundness due to Periclase. Microscopical observations have been made (53) on the clinkers listed in Table I, one portion of each clinker being reheated and cooled quickly (*Q* sample), another portion similarly reheated and cooled slowly (*S* sample), and a third portion being the untreated plant clinker (*P* sample). Quite generally the amounts of Periclase observed in polished sections (as measured with a Wentworth micrometer) have been found to be less than the total MgO of the clinker. This confirms the belief that some of the magnesia dissolves in the liquid. Furthermore, the average grain-size of Periclase in the quickly cooled clinkers, high in glass, was notably smaller than in the slowly cooled clinker, low in glass (compare Plates V and VI).

Further confirmation of the solution of MgO in the liquid was obtained through the observation and examination of the residue obtained following the treatment of the clinker with nitric and hydrofluoric acids in the determination of heat of solution (38). The residue was identified by Lerch as Periclase. A systematic examination has revealed that, in the high-magnesia compositions, the slowly cooled clinkers showed consistently a higher residue than the corresponding quickly cooled clinkers. These data for the clinker given in TABLE 1, are shown in FIG. 5 where the Periclase remaining undissolved after a 10-minute treatment is plotted against the total MgO for both slowly and quickly cooled clinkers. It may be observed that, with compositions containing more than 2 per cent MgO, the Periclase residue increases with increasing total MgO much more rapidly in the slowly cooled than in the quickly cooled clinkers. This may be interpreted as indicating either that less Periclase is present in the quickly cooled clinkers (the MgO being dissolved in the glass) or that it is present in a finer state of subdivision permitting more rapid solution in the acid mixture. The evidence given indicates that both conditions actually obtain.

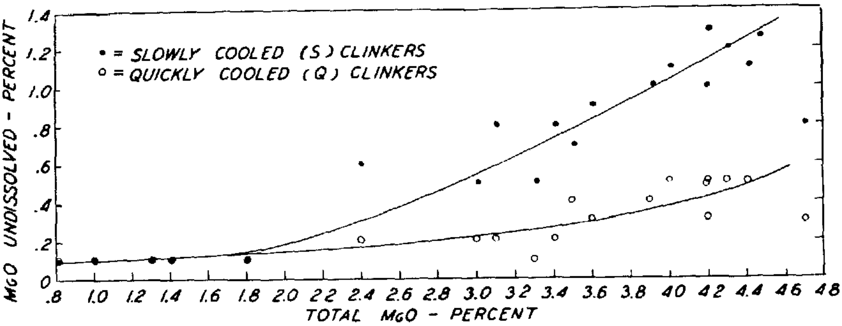

FIG. 5. Relation between Total MGO and the MGO remaining undissolved (420 g $2N\ HNO_3$ containing 5 ml 48 % HF) after 10 Minutes.

It has been known for some time (54) that magnesia may give rise to excessive expansions in test specimens of neat cement stored in water for several years. Furthermore, it has been believed by some observers that a delayed unsoundness, attributable to MgO or a combination of MgO and free CaO, has been responsible for certain expansions in concrete road slabs and other structures.

An examination of a large number of commercial cements has been made by LERCH and TAYLOR at the Fellowship Laboratory (37). Neat bars were prepared, 1×1×6 inches, with water to give normal consistency. After curing 1 day in the molds the bars were autoclaved for 72 hours at 177°. It was observed that the expansions were low when the MgO did not exceed 2.5 per cent and free CaO 0.5 per cent but that, with cements containing more than 2.5 per cent MgO (low free CaO), some expanded greatly and others but little. In other words, the MgO in one cement might cause serious expansion whereas the same amount of MgO in another cement might be without appreciable effect.

Clinkers were then prepared in a laboratory furnace and subjected to different heat-treatments designed to result, on the one hand, in high glass and, on the other hand, in low glass contents. When these clinkers were examined for autoclave expansion, it was observed that compositions containing 3 per cent MgO when slowly cooled (no glass) expanded seriously whereas the same compositions when cooled quickly (high glass) were scarcely affected.

This study was followed by the heat-treatment of the commercial clinkers referred to in Table I. Tests on the cements prepared from these clinkers (52) showed that, with MgO contents above 2.5 per cent, a quick cooling gave cements of very low autoclave expansion, whereas by slow cooling, the expansions increased with the MgO content. These data are shown graphically in Fig. 6. The conclusion appears that magnesia in the form of Periclase is responsible for a delayed unsoundness whereas the same amount of magnesia dissolved in glass (or, in part, reduced in grain-size) does not bring about that condition.

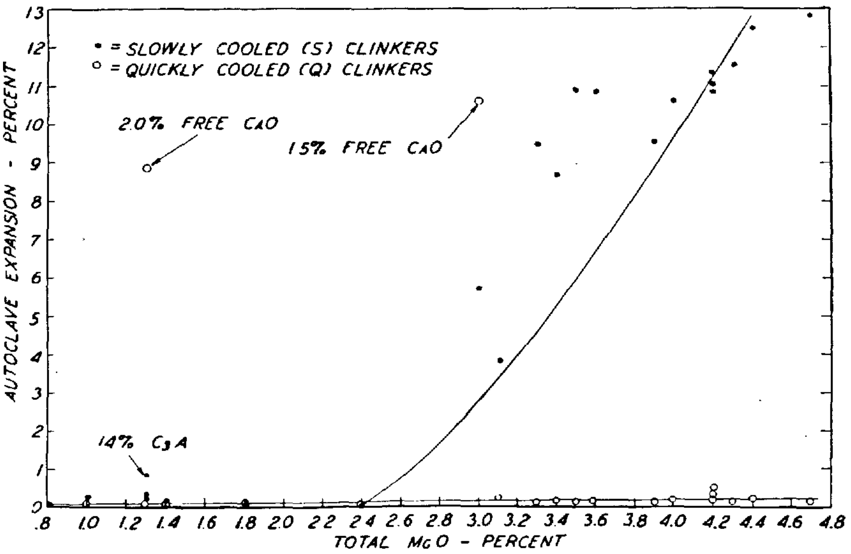

Fig. 6. Relation between MgO Content and Autoclave Expansion (5 Hrs at 215°).

A correlation between the autoclave expansion and the expansion of similar specimens in water and air over a long period has been made by Young (55). Parallel tests were made in the autoclave, in water and in air of 186 cements for periods ranging from 4 to 9 years. Of these cements, 18 showed autoclave expansions above 1 per cent and the water expansion of these 18 cements at 4 years was about 0.32 per cent as compared with a water expansion averaging about 0.20 per cent for the remaining 168 cements. At later ages the differences are more marked. In air storage (50 per cent relative humidity) there is a distinct tendency for the cements showing delayed unsoundness first to contract for 6 to 12 months and then expand until in many cases disintegration occurs.

Unsoundness due to free CaO. The effect of free CaO in producing unsoundness is well known (39) but additional information recently obtained by Lerch suggests a method by which the unsoundness due to free CaO and that due to MgO may be differentiated. Laboratory clinkers were prepared from commercial raw materials of such composition and heat-treatment that the free CaO was caused to vary with the $2CaO \cdot SiO_2$ or with the $3CaO \cdot SiO_2$ in several groups which differed in MgO content. The clinkers were uniformly quickly cooled. Bars of the neat cement paste, 6×1×1 in., mixed with water to give normal consistency, were cured in the molds 1 day and thereafter stored in water at 25°. Length measurements have been made on these bars through the 2-year period. An additional set of bars, similarly prepared, was autoclaved after 1 day in the molds, for 72 hours at 177°, and a third set steamed, after 1 day in the molds, for 5 hours at 100°.

A part of the data obtained is shown in Fig. 7 where the per cent expansion is plotted against the free CaO content for 6 groups which differ chiefly in their MgO content. There are shown, for each group, the expansion in water at 2 years; the expansion in steam, 5 hours at 100°; and the expansion in the autoclave, 72 hours at 177°.

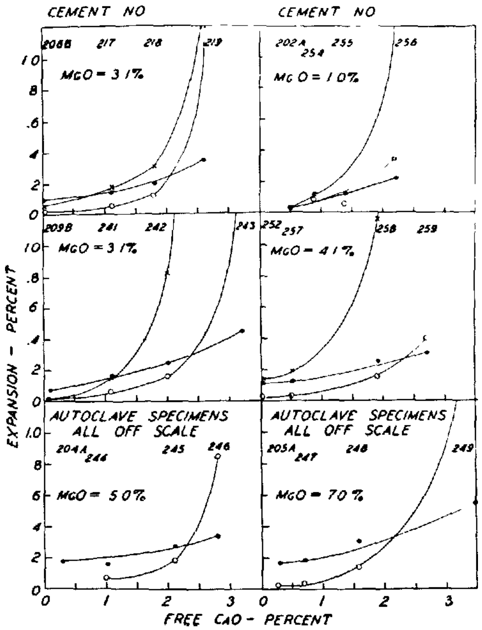

Fig. 7. Effect of Free CaO on Length Change of 1×1×6 in. Neat Bars in Water at 25° for 2 Yrs, in Steam at 100° for 5 Hrs, and in the Autoclave at 177° for 72 Hrs.

The expansions in water at 2 years are shown to have increased consistently in each group with increasing free CaO. The expansions in the autoclave increased with increasing free CaO, becoming very high in all specimens containing over 2 per cent of free CaO. In the high MgO groups, however, the autoclave expansions were high in all cases, regardless of the high free CaO content. In the steam at 100° the expansions also increased rapidly with increasing free CaO but in this case no effect due to the MgO was observed.

Thus, the expansions due to the free CaO and to the Periclase may be differentiated and the method may be useful in ascertaining the ultimate sources of expansive characteristics of a cement. Thus, two cements may both show high autoclave expansion (cf. Nos. 205A and 243) whereas one, in steam at 100°, may show low expansion (0.016 % for No. 205A) and the other high expansion (3.559 % for No. 243). This indicates that Periclase is responsible for the high value in the autoclave test in the former and free CaO largely or wholly responsible for the high value in the latter.

Unsoundness due to $3CaO \cdot Al_2O_3$. The influence of $3CaO \cdot Al_2O_3$ on the autoclave expansion is indicated by data obtained in the study of the effects of heat-treatment of commercial clinkers on properties of the cement. The cements selected for examination included all of the cements shown in TABLE I which contained less than 2 per cent of MgO. The autoclave expansions are plotted in FIG. 8 against the potential $3CaO \cdot Al_2O_3$ content. The upper curve represents these relationships for the slowly cooled clinkers. In this group the free CaO does not exceed 0.3 per cent and the glass does not exceed 3 per cent. Consequently the expansive effect due to Periclase and free CaO are reduced to negligible values and any other relationship may more readily be observed. Also, because of the low glass content, the actual $3CaO \cdot Al_2O_3$ (except as influenced by alkalies etc.) may be assumed to be closely indicated by the potential $3CaO \cdot Al_2O_3$. It may be observed that, at $3CaO \cdot Al_2O_3$ contents above 6 to 8 per cent, the autoclave expansion increases rapidly with increasing $3CaO \cdot Al_2O_3$.

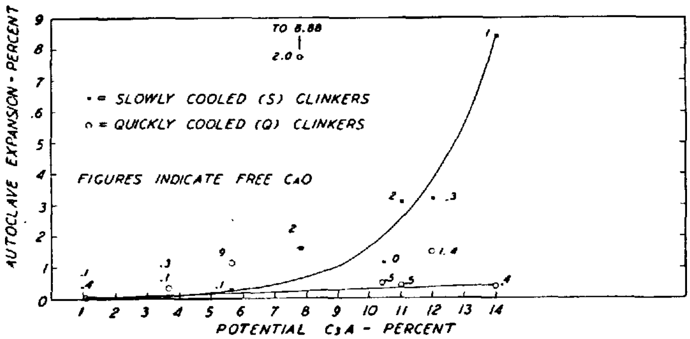

FIG. 8. Relation between Potential C_3A and Autoclave Expansion (5 Hrs at 215°) of slowly Cooled (*S*) Clinkers of less than 2 % MgO and Low Free CaO—and quickly Cooled (*Q*) Clinkers of the Same Composition.

The expansions of the quickly cooled cements of the same compositions are shown in the lower curve and, except where high free CaO materially raises the expansions, the values are consistently very low. This indicates, first, that crystalline $3CaO \cdot Al_2O_3$ is capable of giving rise to high expansions and, secondly, that when the components of the $3CaO \cdot Al_2O_3$ are caused to be present in the glass, the expansions due to their presence are very slight.

These experiments provide confirmation of the theoretical deduction that the Periclase and the $3CaO \cdot Al_2O_3$ are decreased in clinkers as the glass content is increased and they show some of the effects on the cements which are due directly to the Periclase and the $3CaO \cdot Al_2O_3$, but which may be attributed indirectly to the presence of glass.

Effect of Glass on Heat of Hydration. The effect, due to the formation of glass, on the heat of hydration was noted by Lerch by making the determination (40) at 3, 7, and 28 days on the commercial cements differently heat-treated as above described (41). The results on part of these cements are shown in Fig. 9 where the heats of hydration are plotted against the age of the slowly cooled and the quickly cooled cements. At 3 days there is observed to be generally very little difference in the heats of hydration. But, at later ages, the quickly cooled cements show consistently the higher values.

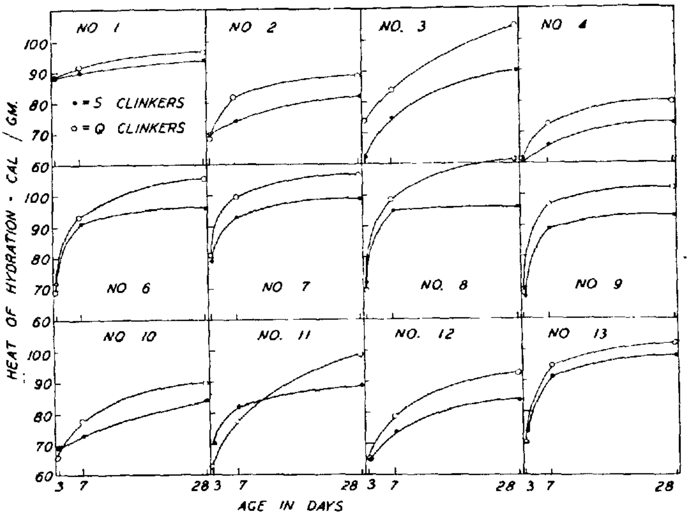

Fig. 9. The Heats of Hydration of Cements made from the slowly Cooled (*S*) and quickly Cooled (*Q*) Clinkers at 3, 7, and 28 Days.

This result should be expected because of the higher energy content of the glass. If the constituents, both as glass and as crystalline materials, hydrate to the same end products, the heat of hydration of the glass will be equal to the sum of the latent heat of crystallization of the glass and the heat of hydration of the crystalline compounds deriving from the glass. Consequently, the heat of complete hydration will be higher for a clinker containing glass than for one of the same composition which contains no glass. But at early ages the hydration has progressed only a short way towards completion, secondary reactions may have taken place, and the heat evolution will be affected by the relative rates of reaction of the phases present.

Other effects of the heat-treatment are under study, including resistance to sulfate action, the strengths of various types of specimens and the volume constancy of specimens stored in water and in air. When completed, this information will provide a very good beginning towards a better understanding of the effects on cement properties due to differences in the thermal history of the clinker and to accompanying differences in the glass content and compound composition.

Retrospect.

The advances that have been made during the past twenty years in our knowledge of the constitution of Portland cement clinker have come about through three well-recognized directions of effort: First, a continued patient study by many investigators of the phase relations of the components of clinker, particularly of the systems which include Fe_2O_3, MgO and the alkalies; second, a development of microscopic and X-ray technique in the identification and measurement of the phases observed; and third, a systematic study of the effects of each constituent, individually and collectively, on the properties of the cement, including especially such properties as heat of solution and hydration, resistance to sulfate attack, length changes under different conditions of exposure, and rate of development of strength.

During this period the concept of clinker as a mixture of phases, definitely determined by the composition and the heat-treatment, rather than as a mixture of hypothetically existing oxides, has become established. Recognizing the still incomplete information on these phases, their consideration, with prescribed limitations in interpretation, has been an important adjunct in the manufacture, specification and utilization of improved and special cements.

Perhaps of greatest interest at the moment is the information that is being obtained on the glass phase of clinker. Its composition in the four-component system CaO-SiO_2-Al_2O_3-Fe_2O_3 can be calculated and, with certain reservations, in more complex systems. Its nature has been found to be a metastable transition form between the random atomic orientation of a liquid and the periodic and atomic-selective structure of a crystal. Thermal and microscopic methods have been developed for its approximation. The time element in the crystallization of the liquid and lack of information on the course followed during the process precludes the setting up of precise equations for the calculation of constitution where a known amount of glass is present but, with certain postulations, equations have been developed for this purpose. These must be used with definite reservations in interpretation but their use, with such reservations, should still further elucidate the relationships between constitution and properties.

The presence of glass may change greatly not only the amounts but the ratios of the crystalline phases in the clinker and the properties of the cement may be expected to change accordingly. Thus, by way of illustration, the solution of magnesia in the glass may decrease or remove the Periclase which might otherwise give rise to serious expansions in concrete structures.

The alkali systems are now being studied intensively and already it is apparent that the small percentages in which they usually occur in commercial slurries may still be adequate to produce a profound effect on the percentages of the major constituents in the clinker.

All of this work leads to these ends: Increased security in the use of Portland cement, an enlarged field of service and the knowledge by which cement may be designed for the purposes which will not be known until tomorrow.

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Table 1. Theoretical Equilibrium Composition and Approximated Glass Content of Commercial Clinker treated as indicated.

S = clinker reheated and cooled slowly
P = plant clinker as received
Q = clinker reheated and cooled quickly

No.	A/F Ratio	Theoretical Equilibrium Composition[1]										
		C_3S	C_2S	C_3A	C_4AF	MgO	Free CaO			Glass Content		
							S	*P*	*Q*	*S*	*P*	*Q*
1	2.9	50	24	12	7	3.0	0.4	1.2	1.5	0	2	8
2	1.1	56	17	6	17	1.8	0.1	0.8	0.9	1	5	21
3	2.2	49	28	10	7	4.0	0.2	0.4	0.4	0	11	16
4	0.8	48	20	4	16	4.2	0.3	4.2	1.6	1	21	22
5	0.8	54	26	1	14	1.6	0.1	0.3	0.4	—	—	—
6	2.0	61	17	10	9	1.4	0	0.4	0.5	3	2	14
7	3.0	50	23	14	7	3.4	tr.	0.4	0.6	2	8	21
8	1.8	52	25	8	9	3.5	0.1	0.6	0.8	0	11	12
9	2.7	42	33	11	7	4.2	0.1	0.8	0.9	0	8	14
10	1.8	41	37	8	9	1.3	0.2	2.1	2.0	1	2	10
11	1.0	54	15	4	16	0.8	0.1	0.2	0.3	3	7	8
12	0.8	48	27	3	19	2.4	0	tr.	0.1	1	9	21
13	2.1	53	23	10	8	4.3	0.1	0.4	0.6	0	4	15
14	2.1	54	22	9	8	3.9	tr.	0.9	0.8	0	6	15
15	1.9	47	27	9	9	4.2	0.1	1.3	1.4	2	5	16
16	2.4	50	26	12	7	3.3	0	0.4	0.3	0	11	17
17	2.4	53	26	11	8	1.3	0.2	0.4	0.5	0	5	12
18	2.3	52	23	12	6	3.6	0.1	0.8	0.5	0	10	18
19	1.9	49	27	9	9	4.7	tr.	0.6	0.5	0	7	11
20	1.9	60	12	12	12	1.0	0.3	1.3	1.4	2	2	13
21	2.5	56	18	14	9	1.3	0.1	0.4	0.4	1	5	9
22	2.3	48	26	11	8	4.4	0	0.3	0.2	0	3	11
23	3.0	56	15	15	7	3.1	0.9	2.0	1.6	2	5	11

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[1] The usual abbreviations for the chemical symbols are used in TABLES and FIGURES. C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, M = MgO, N = Na_2O, K = K_2O. Hence, C_3A = $3CaO \cdot Al_2O_3$, etc.

Table 2. Comparison of Compound Contents.

%	Complete Equilibrium Crystallization	Crystallization at Eutectic Liquid gives Glass	Crystallization at Quintuple Line. Liquid gives Glass	Crystallization at Quintuple Line. Liquid crystallizes independently
I. $CaO = 68.0\ \%$; $SiO_2 = 23.0\ \%$; $Al_2O_3 = 6.0\ \%$; $Fe_2O_3 = 3.0\ \%$. A/F = 2				
C_3S.......	57.5	57.3	60.6	60.6
C_2S.......	22.5	19.5	15.8	20.3
C_3A.......	10.8	4.9	0	8.6
C_4AF.....	9.1	0	0	9.1
CaO......	0	0	0	0
C_5A_3......	0	0	0	1.5
Glass.....	0	18.3	23.4	0
II. $CaO = 68.0\ \%$; $SiO_2 = 23.0\ \%$; $Al_2O_3 = 7.0\ \%$; $Fe_2O_3 = 2.0\ \%$. A/F = 3.5				
C_3S.......	52.2	52.1	59.5	59.5
C_2S.......	26.5	24.5	15.7	21.0
C_3A.......	15.2	11.2	0	8.6
C_4AF.....	6.1	0	0	6.2
CaO......	0	0	0	0
C_5A_3......	0	0	0	4.7
Glass.....	0	12.2	24.7	0
III. $CaO = 66.0\ \%$; $SiO_2 = 24.0\ \%$; $Al_2O_3 = 7.5\ \%$; $Fe_2O_3 = 2.5\ \%$. A/F = 3				
C_3S.......	32.4	32.3	39.0	39.0
C_2S.......	44.5	42.0	34.8	40.4
C_3A.......	15.7	10.7	0	9.4
C_4AF.....	7.6	0	0	7.6
CaO......	0	0	0	0
C_5A_3......	0	0	0	4.4
Glass.....	0	15.3	27.1	0
IV. $CaO = 67.0\ \%$; $SiO_2 = 23.0\ \%$; $Al_2O_3 = 4.0$; $Fe_2O_3 = 6.0\ \%$[1]. A/F = 0.67				
C_3S.......	62.7	62.3	58.9	63.6
C_2S.......	18.6	18.4	18.1	18.1
C_3A.......	0.5	0	0	0.4
C_4AF.....	18.2	17.6	0	18.2
CaO......	0	0	0	0.2
C_5A_3......	0	0	0	0
Glass.....	0	1.5	22.6	0

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[1] In this case, free lime is produced when the liquid crystallizes independently. If this is estimated analytically, the Bogue calculation will give the values appearing under "Liquid crystallizes independently".

Table 2 (cont). *Comparison of Compound Contents.*

%	Crystallization at 1400° Liquid gives Glass	Crystallization at 1400° Liquid crystallizes independently	Crystallization at 1450° Liquid gives Glass	Crystallization at 1450° Liquid crystallizes independently
I. $CaO = 68.0\ \%$; $SiO_2 = 23.0\ \%$; $Al_2O_3 = 6.0\ \%$; $Fe_2O_3 = 3.0\ \%$. A/F = 2				
C_3S	59.6	59.6	59.6	59.6
C_2S	16.2	21.2	15.6	21.0
C_3A	0	8.9	0	9.8
C_4AF	0	9.1	0	9.1
CaO	0	0	0	0
C_5A_3	0	1.0	0	0.5
Glass	24.3	0	24.8	0
II. $CaO = 68.0\ \%$; $SiO_2 = 23.0\ \%$; $Al_2O_3 = 7.0\ \%$; $Fe_2O_3 = 2.0\ \%$. A/F = 3.5				
C_3S	60.6	60.6	59.4	59.4
C_2S	15.4	20.9	15.3	21.4
C_3A	0	9.4	0	9.7
C_4AF	0	6.1	0	5.9
CaO	0	0	0	0
C_5A_3	0	3.8	0	3.8
Glass	25.1	0	25.5	0
III. $CaO = 66.0\ \%$; $SiO_2 = 24.0\ \%$; $Al_2O_3 = 7.5\ \%$; $Fe_2O_3 = 2.5\ \%$. A/F = 3				
C_3S	38.2	38.2	38.5	38.5
C_2S	34.3	40.2	33.3	39.9
C_3A	0	10.5	0	10.6
C_4AF	0	7.6	0	7.6
CaO	0	0	0	0
C_5A_3	0	3.6	0	3.5
Glass	27.6	0	28.1	0
IV. $CaO = 67.0\ \%$; $SiO_2 = 23.0\ \%$; $Al_2O_3 = 4.0\ \%$; $Fe_2O_3 = 6.0\ \%$. A/F = 0.67				
C_3S	54.6	60.9	55.1	61.5
C_2S	20.2	20.2	19.4	19.4
C_3A	0	0.4	0	0.5
C_4AF	0	18.2	0	18.2
CaO	0	0.3	0	0.7
C_5A_3	0	0	0	0
Glass	25.0	0	25.5	0

Table 3. Potential Composition at Crystalline Equilibrium and Calculated Composition assuming Normal Crystallization to an Approximated Glass Content. Arranged in Order of increasing A/F Ratio.

No.	Condition	Type	Group	Series	A/F	Composition						Glass
						C_3S	C_2S	C_3A	C_4AF	MgO	Fr·CaO	
4Q	Potential	—	—	—	0.81	59.3	11.2	2.8	18.4	4.4	1.6	0
	Calculated	B	8b	45	—	55.8	10.6	0	4.6	3.1	1.6	22
11Q	Potential	—	—	—	0.95	67.0	13.7	3.5	13.2	0.8	0.3	0
	Calculated	B	9a	43	—	66.9	12.5	1.1	9.4	0.3	0.3	8
2Q	Potential	—	—	—	1.12	57.8	16.4	6.2	14.8	1.9	0.9	0
	Calculated	B	10b	44	—	59.4	11.1	0	5.0	0.6	0.9	21
8Q	Potential	—	—	—	1.65	52.0	26.1	7.9	9.0	3.5	0.8	0
	Calculated	A-1	2a	34	—	51.8	24.3	4.3	3.3	2.8	0.8	12
6Q	Potential	—	—		1.88	60.8	16.7	10.2	9.5	1.5	0.5	0
	Calculated	A-1	2a	34	—	60.6	14.6	6.0	2.9	0.7	0.5	14
3Q	Potential	—	—	—	2.60	51.6	25.6	10.3	6.0	4.0	0.4	0
	Calculated	A-1	2b	35	—	53.2	21.5	3.7	0	3.0	0.4	16
1Q	Potential	—	—	—	3.00	52.2	23.0	11.9	5.8	3.1	1.5	0
	Calculated	A-1	2a	34	—	52.1	21.8	9.5	2.0	2.6	1.5	8
7Q	Potential	—	—	—	3.47	51.2	22.2	14.7	6.0	3.5	0.6	0
	Calculated	A-1	2b	35	—	55.5	14.9	4.0	0	2.2	0.6	21

Appendix.

Equations for Calculating Phase Composition of Clinker with Normal Crystallization to an Estimated Glass Content, by Dahl (12). Types *A-1* and *B*.

The symbols A, B, C and D represent potential percentages of $3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$, $3CaO \cdot Al_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ respectively in any mixture or clinker under consideration. M is MgO and G is glass.

Where magnesia is to be considered, the estimated percentage of glass, containing MgO, is not G but may be designated as P. Then, if M is greater than 0.06P, G = 0.94P and free MgO = M—0.06P. If M is less than 0.06P, G = P—M and free MgO = O.

Classification Key-System C_3S-C_2S-C_3A-C_4AF.

Type

- C/D exceeds 0.64
  - B/D exceeds 0.32
    - C/D exceeds 3.33
      - B/D exceeds 2.40
        - B/C exceeds 0.72 .... *A-1*
        - B/C less than 0.72 ..... *A-2*
      - B/D less than 2.40 .... *A-2*
    - C/D less than 3.33
      - B exceeds (0.77C—0.17D) *A-1*
      - B less than (0.77C—0.17D) ... *A-2*
  - B/D between 0.28 and 0.32 .... *C-2*
  - B/D less than 0.28 .... *C-4*
- C/D less than 0.64
  - B/C exceeds 0.50 .... *B*
  - B/C between 0.43 and 0.50 .... *C-1*
  - B/C less than 0.43 .... *C-3*

Type *A-1*. (C_4AF the disappearing phase.)

Group 1. Crystallization at T_2

Equations to be applied when glass content is less than the quantity of liquid present when C_4AF disappears, as indicated in Groups 2 to 5.

Series

$$\left.\begin{array}{l} C_3S = A - 0.014G \\ C_2S = B - 0.162G \\ C_3A = C - 0.322G \\ C_4AF = D - 0.502G \end{array}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 34$$

Series

Group 2. C/D between 0.64 and 3.33

(a) G less than 1.99D

Use equations in Group 1.

(b) G between 1.99D and (1.12C+1.27D)

$$\left.\begin{aligned} C_3S &= A-1.19D+0.58G \\ C_2S &= B+1.05D-0.69G \\ C_3A &= C+1.14D-0.89G \end{aligned}\right\} \quad \cdots\cdots\cdots\cdots \quad 35$$

(c) G between (1.12C+1.27D) and (1.11C+1.37D)

$$\left.\begin{aligned} C_3S &= A+\frac{0.07G-0.16C}{D/C-0.12}+\frac{17.06C+10.15D-10.82G}{8.10-C/D} \\ C_2S &= B+\frac{0.05G+0.04C}{D/C-0.12}+\frac{2.72G-9.96C-2.05D}{8.10-C/D} \end{aligned}\right\} \quad \cdots\cdots \quad 36$$

(d) G between (1.11C+1.37D) and (1.16C+1.67D)

$$\left.\begin{aligned} C_3S &= A+\frac{0.31C-0.19G}{D/C+0.16}+\frac{5.86C-2.82D-0.58G}{C/D+6.34} \\ C_2S &= B+\frac{0.03G-0.15C}{D/C+0.16}+\frac{1.48C+9.16D-5.76G}{C/D+6.34} \end{aligned}\right\} \quad \cdots\cdots \quad 37$$

Group 3. C/D between 3.33 and 4.71

(a) G less than 1.99D

Use equations in Group 1.

(b) G between 1.99D and 5.00D

$$\left.\begin{aligned} C_3S &= A-1.19D+0.58G \\ C_2S &= B+1.05D-0.69G \\ C_3A &= C+1.14D-0.89G \end{aligned}\right\} \quad \cdots\cdots\cdots\cdots \quad 38$$

(c) G between 5.00D and (1.14C+1.19D)

$$\left.\begin{aligned} C_3S &= A-0.80D+0.50G \\ C_2S &= B+0.76D-0.63G \\ C_3A &= C+1.04D-0.87G \end{aligned}\right\} \quad \cdots\cdots\cdots\cdots \quad 39$$

(d) G between (1.14C+1.19D) and (1.10C+1.40D)

$$\left.\begin{aligned} C_3S &= A+\frac{0.46G-0.65C}{D/C-0.22}+\frac{10.62C+9.85D-9.00G}{4.49-C/D} \\ C_2S &= B+\frac{0.43C-0.24G}{D/C-0.22}+\frac{4.51G-7.13C-5.36D}{4.49-C/D} \end{aligned}\right\} \quad \cdots\cdots \quad 40$$

Group 3. C/D between 3.33 and 4.71 (cont.) Series

(e) G between $(1.10C+1.40D)$ and $(1.08C+1.92D)$

$$\left.\begin{aligned} C_3S &= A+\frac{0.07C-0.08G}{D/C-0.03}+\frac{31.3C-13.8D-4.5G}{32.6-C/D} \\ C_2S &= B+\frac{0.11G-0.10C}{D/C-0.03}+\frac{0.3C+46.4D-28.1G}{32.6-C/D} \end{aligned}\right\} \cdots\cdots\cdots 41$$

Group 4. C/D between 4.71 and 12.50

(a) G less than $(1.14C+1.19D)$

Use equations in Group 3 appropriate for the estimated value of G.

(b) G between $(1.14C+1.19D)$ and $(1.08C+1.92D)$

$$\left.\begin{aligned} C_3S &= A+\frac{0.07G-0.13C}{D/C-0.0865}+\frac{14.8C+7.10D-7.9G}{11.565-C/D} \\ C_2S &= B+\frac{0.01G+0.05C}{D/C-0.0865}+\frac{3.7G+4.45D-4.3C}{11.565-C/D} \end{aligned}\right\} \cdots\cdots\cdots 42$$

Group 5. C/D greater than 12.50

(a) G less than $5.00D$

Use equations in Group 3 appropriate for the estimated value of G.

(b) G between $5.00D$ and $(1.08C+1.92D)$

Use equations in Series 39.

Type *B*. (C_3A the disappearing phase.)

Group 6. Crystallization at T_2

Equations to be applied when glass content is less than the quantity of liquid present when C_3A disappears, as indicated in groups 7 to 10.

$$\left.\begin{aligned} C_3S &= A-0.014G \\ C_2S &= B-0.162G \\ C_3A &= C-0.322G \\ C_4AF &= D-0.502G \end{aligned}\right\} \cdots\cdots\cdots\cdots\cdots\cdots 43$$

Group 7. C/D less than 0.10

(a) G less than $3.10C$

Use equations in Group 6.

(b) G between $3.10C$ and $4.88C$

$$\left.\begin{aligned} C_3S &= A+0.98C-0.23G \\ C_2S &= B-0.88C+0.01G \\ C_4AF &= D+0.90C-0.78G \end{aligned}\right\} \cdots\cdots\cdots\cdots\cdots 44$$

Group 7. C/D less than 0.10 (cont.) Series

(c) G between 4.88C and 13.91C

$$\left.\begin{aligned} C_3S &= A + 0.60C - 0.25G \\ C_2S &= B - 0.43C + 0.03G \\ C_4AF &= D + 0.83C - 0.78G \end{aligned}\right\} \cdots\cdots\cdots\cdots\cdots \ 45$$

(d) G between 13.91C and (1.01C+1.29D)

$$\left.\begin{aligned} C_3S &= A + 0.34C - 0.23G \\ C_2S &= B - 0.13C + 0.01G \\ C_4AF &= D + 0.79C - 0.78G \end{aligned}\right\} \cdots\cdots\cdots\cdots\cdots \ 46$$

(e) G between (1.01C + 1.29D) and (1.04C + 1.37D)

$$\left.\begin{aligned} C_3S &= A + \frac{0.43G - 0.40C}{D/C + 0.36} + \frac{2.59C + 4.43D - 4.09G}{C/D + 2.81} \\ C_2S &= B + \frac{0.75C - 0.79G}{D/C + 0.36} + \frac{1.28G + 1.22C - 1.62D}{C/D + 2.81} \end{aligned}\right\} \cdots\cdots\cdots \ 47$$

(f) G between (1.04C + 1.37D) and (1.50C + 1.45D)

$$\left.\begin{aligned} C_3S &= A + \frac{4.33G - 3.67C}{D/C + 5.853} + \frac{0.23D - 1.18C - 0.22G}{C/D + 0.171} \\ C_2S &= B + \frac{9.52C - 10.18G}{D/C + 5.853} + \frac{0.05G + 2.35C - 0.06D}{C/D + 0.171} \end{aligned}\right\} \cdots\cdots\cdots \ 48$$

Group 8. C/D between 0.10 and 0.26

(a) G less than 4.88C

Use equations in Group 7 appropriate for the estimated value of G.

(b) G between 4.88C and (1.07C + 1.28D)

Use equations in series 45.

(c) G between (1.07C + 1.28D) and (1.04C + 1.37D)

$$\left.\begin{aligned} C_3S &= A + \frac{2.19C - 2.14G}{D/C - 0.32} + \frac{13.65C + 3.43D - 3.46G}{3.13 - C/D} \\ C_2S &= B + \frac{2.46G - 2.51C}{D/C - 0.32} + \frac{0.33G - 11.52C - 0.30D}{3.13 - C/D} \end{aligned}\right\} \cdots\cdots\cdots \ 49$$

(d) G between (1.04C + 1.37D) and (1.50C + 1.45D)

$$\left.\begin{aligned} C_3S &= A + \frac{4.33G - 3.67C}{D/C + 5.853} + \frac{0.23D - 1.18C - 0.22G}{C/D + 0.171} \\ C_2S &= B + \frac{9.52C - 10.18G}{D/C + 5.853} + \frac{2.35C + 0.05G - 0.06D}{C/D + 0.171} \end{aligned}\right\} \cdots\cdots\cdots \ 50$$

Group 9. C/D between 0.26 and 0.34 Series

(a) G less than 4.88C

Use equations in Group 7 appropriate for the estimated value of G.

(b) G between 4.88C and (1.07C + 1.28D)

Use equation in series 45.

(c) G between (1.07C + 1.28D) and (1.14C + 1.34D)

$$\left.\begin{aligned} C_3S &= A + \frac{4.74G - 4.69C}{D/C + 1.18} + \frac{3.68D - 1.91C - 3.09G}{C/D + 0.85} \\ C_2S &= B + \frac{5.87C - 5.92G}{D/C + 1.18} + \frac{2.24G + 3.76C - 2.83D}{C/D + 0.85} \end{aligned}\right\} \cdots\cdots\cdots 51$$

(d) G between (1.14C + 1.34D) and (1.50C + 1.45D)

$$\left.\begin{aligned} C_3S &= A + \frac{3.61C - 1.30G}{D/C + 3.437} + \frac{0.06G + 0.07C - 0.25D}{C/D + 0.291} \\ C_2S &= B + \frac{1.22C + 0.54D - 0.35G}{C/D + 0.291} - \frac{2.14G + 0.17C}{D/C + 3.437} \end{aligned}\right\} \cdots\cdots\cdots 52$$

Group 10. C/D between 0.34 and 0.64

(a) G less than 3.10C

Use equations in Group 6.

(b) G between 3.10C and (1.14C + 1.26D)

Use equations in series 44.

(c) G between (1.14C + 1.26D) and (1.14C + 1.34D)

$$\left.\begin{aligned} C_3S &= \frac{1.80G - 2.00C}{10D/C + 0.095} + \frac{2.22C + 1.58D - 1.60G}{C/100D + 1.05} \\ C_2S &= \frac{2.10C - 1.90G}{10D/C + 0.095} + \frac{0.55G - 1.16C - 0.53D}{C/100D + 1.05} \end{aligned}\right\} \cdots\cdots\cdots 53$$

(d) G between (1.14C + 1.34D) and (1.50C + 1.45D)

Use equations in series 52.

Discussion.

Mr. M. A. SWAYZE:[1]

Chemists and technologists in the American cement industry are following closely the investigations of the Portland Cement Association Fellowship Laboratory in Washington, and also the data on cement which come to us from European and other sources. The laboratory which I have the pleasure to represent is but one of many that are applying such information to plant processes and chemical control.

Our Company, known until recently as the International Cement Corporation, has been manufacturing high early strength Portland cement since 1927. This product, known as "Incor", is high in tricalcium silicate content, and our research department therefore is interested in the matter of scientific raw mix design. At first our chemical control was based on formulae which had to be varied somewhat from plant to plant to suit the individual case. Feeling that more accurate knowledge of our cement constitution was desirable, a study of clinker petrography was begun about three years ago. The petrographic work has been done by Dr. L. S. BROWN, formerly of Massachusetts Institute of Technology.

In the course of his work a number of apparent anomalies were found. Tricalcium aluminate was conspicuous by its absence in nearly all commercial clinker examined by thin section, although by calculation it should be found in amounts up to 15 %. Dicalcium silicate in the higher A:F-ratio mixes could not be found in quantities as calculated from the standpoint of complete crystallization, clinkers designed to contain 12—14 % of this compound often showing none present under the microscope. In lower A:F-ratio mixes, the iron-bearing interstitial material did not always agree in optical properties with C_4AF, but was distinctly not glass in the optical sense, as shown by its birefringence and other crystalline properties.

With these apparent contradictions in view, Dr. BROWN and the writer decided to enter into a more fundamental program of research than is usual for an operating research laboratory. Our first study was concerned with tricalcium aluminate in the binary, ternary and quaternary systems. This work was reported by BROWN in A. S. T. M. Proc. in 1937.

This investigation was followed by a study of the cement liquids as

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[1] Dr., Director of Research, Research Laboratory, Lone Star Cement Corp., Hudson, N. Y., U. S. A.

described by LEA and PARKER in their excellent paper on the quaternary system CaO-C_2S-C_5A_3-C_4AF. Our work on this subject has not been published. However, the chief item of interest to the cement chemist is that introduction of magnesia into this system displaces at least 2 % of lime from the liquids, making possible the conversion of more C_2S to C_3S than will be found by calculation from the DAHL formulae given in the APPENDIX of Dr. BOGUE's paper.

In all of these studies we found that wherever C_3A was associated with an iron-bearing liquid, it was rarely if ever in direct contact with true glass in quenched specimens. In the region of LEA and PARKER's point T_I pseudo-cubic crystals, yellowish-brown in colour, often appeared which were not C_3A and decidedly not C_4AF. Several indications led to the belief that this peculiar material belonged in the side plane CaO-C_5A_3-C_4AF of the quaternary diagram, and accordingly a restudy of this ternary system was begun late last year.

The original work on this system by Dr. BOGUE and his associates, in which the compound C_4AF was discovered, was done by means of heating and cooling curve studies, due to extreme difficulty experienced in obtaining quenches rapidly enough to prevent partial crystallization. A later study by H. F. MCMURDIE is described in the April 1937 Bureau of Standards Journal of Research. In this work MCMURDIE employed the quench method, but reported difficulty in preventing crystallization with mixes high in C_4AF (maximum mixture 63 % C_4AF). The C_3A-C_5A_3-C_4AF eutectic point and the CaO-C_3A-C_4AF invariant point were moved closer to C_4AF than as located in the original work.

Experimental Procedure.

In our work reagent materials were employed having very low magnesia and alkali contents, and with a fineness of practically 100 per cent through 200 mesh. Mixes were prepared by weighing the raw materials necessary for a 3.0 or a 1.5 g charge into a platinum crucible, wetting with distilled water to form a slurry, then stirring until the charge was homogeneous. The charge was dried at 110°, then remixed, after which it was ignited at 1 000° for at least 4 hours. The lightly sintered mass was then removed as completely as possible from the crucible and ground for 30 minutes in an agate mortar. These precautions were essential on account of the small size of our quench burns.

The quenching furnace consists of an alundum tube 15/16 in. inside diameter and 18 in. long, with a platinum-20 % rhodium winding over a length of 8 1/2 in. to 9 in. The heating element is insulated by special porous refractory brick set inside a 14 in. diameter by 16 in. high steel shell. The inner portion of the insulation next to the tube consists of fused, granulated C. P. alumina between 50 and 100 mesh in size, making removal of the tube and recovery of the winding very easy.

The temperature gradient of the tube interior is plotted for each new winding, and the hot junction of the thermocouple and the pan containing the charge are located at the center of the zone of maximum temperature. The charges and hot junction are placed as near to the centerline of the furnace tube as possible, and are never more than 1/8 in. apart horizontally and are at the same vertical level.

Several types of containers, weights of charges and methods of quenching were tried in the course of previous studies before a dependable technique was found which would give, first, uniform heat treatment of the entire charge, and second, quenching sufficiently rapid to preserve the phase relations in the state in which they existed at the furnace temperature. These requirements were finally met by using a slightly concave piece of platinum foil 0.025 mm thick and 6 mm square for the container, charges of 0.010—0.015 grams of material, and quenching in distilled water.

With this type of container and the small charge, uniformity in burned charges is very good, and quenching is exceedingly rapid. No difficulty has been encountered in obtaining 100 % true glass at temperatures 5°—10° above those for burns showing stable solid phases, even when as much as 75 % potential C_4AF is present.

With this procedure we have been able to plot primary phases rather closely. At the boundary curves for C_3A, a change of 1/2 % in lime content is sufficient to throw the primary phase into another field.

Results of the Investigation.

The C_3A-C_5A_3-C_4AF eutectic point has been found to be very close to the location assigned to it by BOGUE and his associates. The invariant point for CaO-C_3A-C_4AF, however, is even closer to C_4AF than as found by Mc MURDIE, and furthermore it lies slightly on the CaO-side of the C_3A-C_4AF-join, within 4 % Fe_2O_3 of the point where BOGUE's CaO-C_4AF-boundary crosses this join. The temperatures for this crossing point and our invariant point are the same—1 380°. FIG. 1 shows the revised phase diagram as plotted from more than 400 quench burns of 75 mixes.

A composition, such as No. 15 in this figure, is particularly well adapted to test the relative accuracy of phase relations as indicated in the three diagrams by BOGUE, MCMURDIE and ourselves. With this mix and with rising temperatures, liquid and CaO should appear simultaneously, according to the two previous diagrams, at either 1 345° (BOGUE) or 1 370° (MCMURDIE), and C_3A should disappear completely at this temperature. In the present diagram some liquid should appear and C_4AF disappear at about 1 380° at the intersection of the C_3A-C_4AF-boundary and the C_3A-C_4AF-join. Further heating should cause solution of C_3A until the intersection of the CaO-C_3A-boundary with the join is reached. Up to this point no CaO should appear.

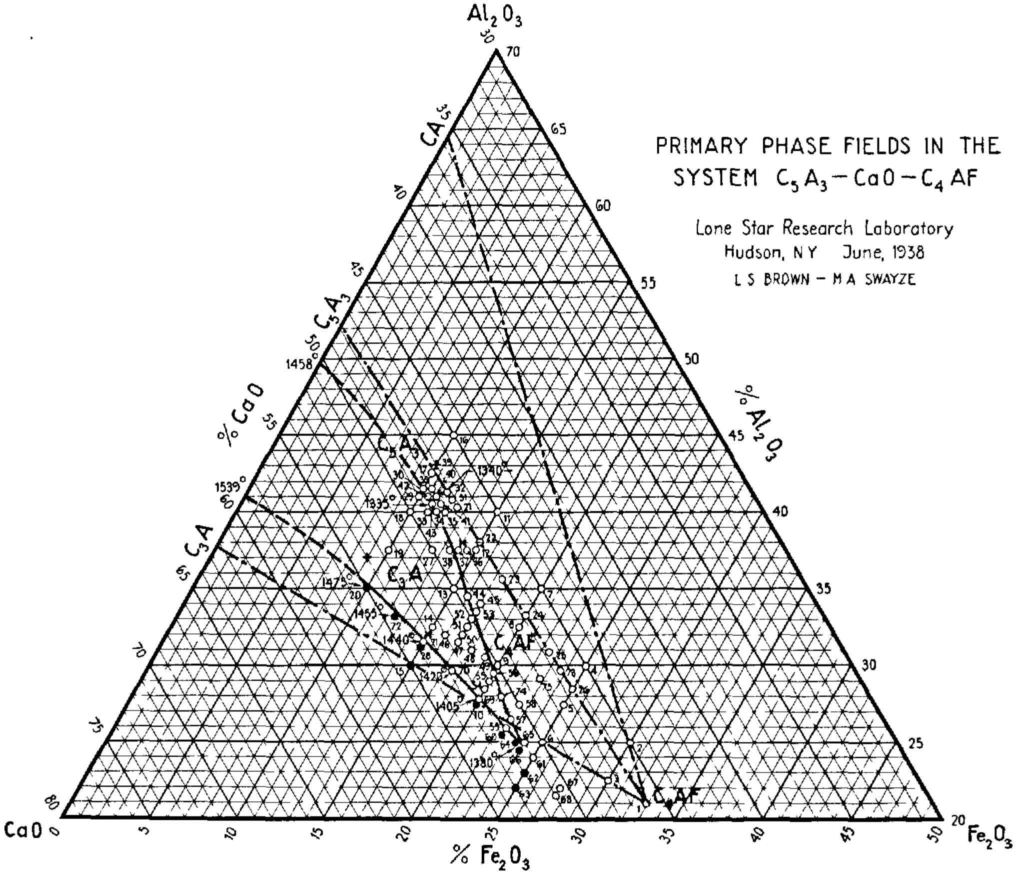

FIG. 1. Primary Phase Fields in the System C_5A_3-CaO-C_4AF.

Further heating should dissolve C_3A and deposit CaO until, at the point on the boundary in line with the mix composition and CaO, the charge will consist of CaO and liquid only.

Charges of this mix were burned at 1 360°, 1 390°, 1 420° and 1 440°. The first consisted of solid reaction products only, with no glass. CaO, C_4AF, C_5A_3 and C_3A were identified. The burn at 1 390° showed some glass, C_3A, a small amount of C_4AF, but no CaO. The 30-minute period of heating given was insufficient to reach equilibrium, which should have eliminated the C_4AF.

In the third charge (1 420°) much more glass was present, no C_4AF, and the relative proportions of C_3A and CaO were about as is indicated by the diagram. At 1 440° the quenched charge contained glass and CaO only.

In all of the mixes in the C_3A primary field, the C_3A-crystals were found to be surrounded by a border zone of more or less birefringent material. This border material or phase increases in thickness as the lime content of mixes is increased with the A:F-ratio constant. It also increases greatly in thickness as the invariant point is approached. It is also seen in the C_4AF-field around the C_4AF-grains in mixes near the C_3A-C_4AF-boundary.

Our object in presenting this description of our work is threefold: first to show the revision made in the CaO-C_5A_3-C_4AF-diagram by use of the special technique developed for burning and quenching charges; second, to direct attention to this border material or phase which is neither true glass, C_3A nor C_4AF, but which resembles the material referred to by Dr. BOGUE as the "metastable phase"; third, to interest other investigators in this problem.

We hope to publish our data on the work done in this system later in the year.

The following figures have been prepared as illustrations.

Crystallographic Figures.

Fig. No.	Burn No.	Temp. °C.	
2	G18u	*	C_5A_3: showing crystal habit—trigonal tristetrahedral. Note spears growing from apices—beginning of tetrahedral envelop. *Heated 1 370°—20 min. 1 345°—1 325°—60 min., held 1 335° 30 min. C_3A-C_4AF-C_5A_3 and glass present in quench.
3	G39s	1 335°	Glass + C_5A_3 inclosed in plate-like tetrahedral envelop.
4	G12e	1 360°	Glass + C_4AF—shows crystal habit: perfect orthorhombic crystals. All optical properties agree with published data except for original notation by HANSEN of slight extinction angle.
5	G36e	15 min. 1 360° 40 min. 1 340°	Normal prismatic form of C_4AF showing border growths as crystallizing from complete fusion.
6	G36d	30 min. 1 350°	Characteristic form of C_4AF in burns heated below liquidus is short, stubby crystals, usually with more or less heavy border. This view shows basal and prism orientation. Basal section gives excellent interference figures, Biaxial (—) with small axial angle.

Primary Phase Figures.

Fig. No.	Burn No.	Temp °C	
7	G18e	1 370°—30 min.	Glass + C_3A and thin borders. Index of C_3A, glass and Hyrax resin practically identical. C_3A stands out so boldly because of presence of border phase of considerably higher index.
8	G19h	1 410°—30 min.	Glass + C_3A with heavier borders, now distinct.
9	G20g	1 440°—30 min.	Glass + C_3A with still heavier borders. Good illustration crystal habit C_3A-combination of cube and octrahedon.
10	G14h	1 440°—30 min.	Glass + C_3A with much heavier borders. Perfect C_3A-crystal in growth of cubic development.
11	G55g	1 380°—30 min.	Glass + C_3A inside heavier border.
12	G55i_2	1 400°—15 min. 1 370°—40 min.	Glass + well developed, large crystals of C_3A with heavy borders.
13	G9f	1 370°—30 min.	1 % less lime than FIG 12; iron constant. Short, stubby crystals C_4AF—two in basal orientation—in glass.
14	G9h	1 390°—20 min. 1 370°—30 min.	C_4AF crystallizing from glass. Note border zones.
15	G59f	1 380°—30 min.	C_3A with very heavy border in glass.
16	G60g	1 390°—30 min.	Glass + CaO. (1/2 % higher CaO than FIG. 15.)
17	G57w	1 375°—30 min.	Glass + border phase only. (1/2 % lower CaO than FIG. 15.)

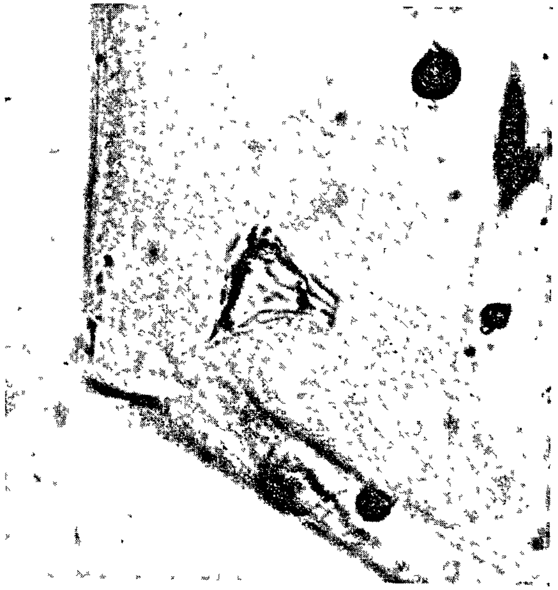

FIG. 2. Burn No. *G18u*. Heated 1 370°—20 min., 1 345°—1 325°—60 min, held 1 335° — 30 min. C_3A-C_4AF-C_5A_3 and glass present in quench. C_5A_3: showing crystal habit—trigonal tristetrahedral. Note spears growing from apices—beginning of tetrahedral envelop.

Magnification 600 ×.

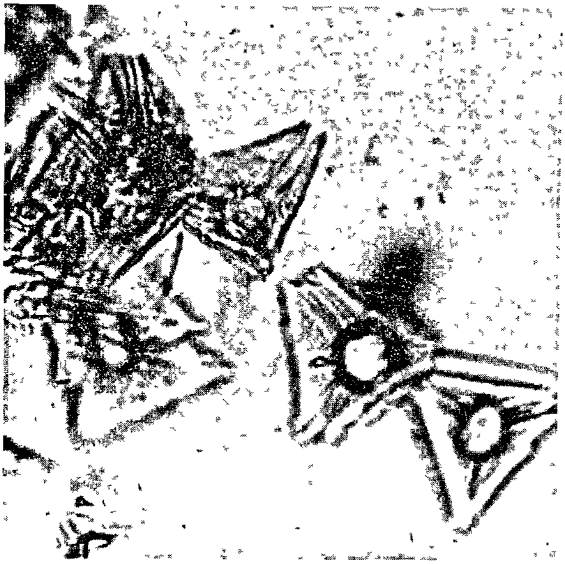

FIG. 3. Burn No. *G39s*, 1 335°.
Glass + C_5A_3 inclosed in plate-like tetrahedral envelop.
Magnification 600 ×.

Figs. 4 and 5 see p. 109.

FIG. 6. Burn No. *G36d*, 30 Min. 1 350°.
Characteristic form of C_4AF in burns heated below liquidus is short, stubby crystals, usually with more or less heavy border. This view shows basal and prism orientation. Basal section gives excellent interference figures, Biaxial (—) with small axial angle.
Magnification 300 ×.

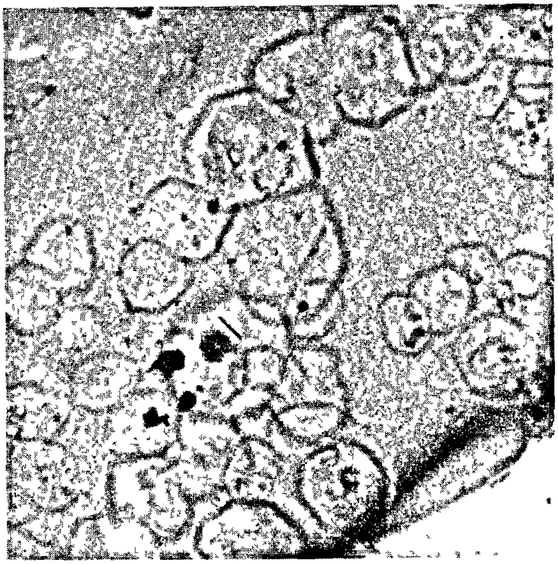

FIG. 7. Burn No. *G18e*, 30 Min. 1370°.
Glass + C_3A and thin borders. Index of C_3A, glass and Hyrax resin practically identical. C_3A stands out so boldly because of presence of border zone of considerably higher index.
Magnification 600 ×.

FIG. 8. Burn No. *G19h*, 30 Min. 1410°.
Glass + C_3A with heavier borders, now distinct.
Magnification 600 ×.

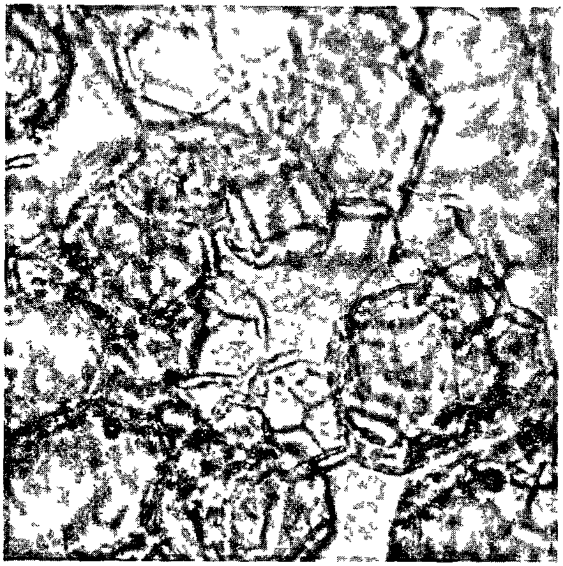

FIG 9. Burn No *G20g*, 30 Min 1440°
Glass + C_3A with still heavier borders Good illustration crystal habit C_3A-combination of cube and octahedron
Magnification 600 ×

FIG 10 Burn No *G14h*, 30 Min 1440°
Glass + C_3A with much heavier borders. Perfect C_3A-crystal in growth of cubic development
Magnification 600 ×.

FIG. 11. Burn No. *G55g*, 30 Min. 1 380°.
Glass + C_3A inside heavier border.
Magnification 600 ×.

Figs. 12—15 see pp. 110, 111.

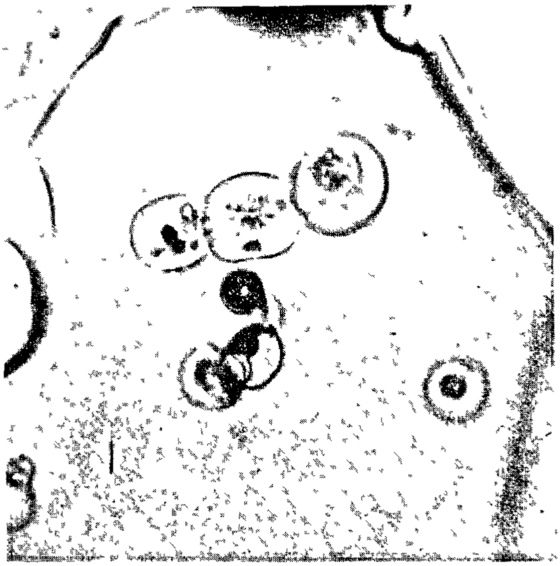

FIG. 16. Burn No. *G60g*, 30 Min. 1 390°.
Glass + CaO (½ % higher CaO than FIG. 15).
Magnification 600 ×.

FIG. 4. Burn No *G12e*, 1 360°
Glass + C_4AF—shows crystal habit, perfect orthorhombic crystals All optical properties agree with published data, except for original notation by HANSEN of slight extinction angle
Magnification 600 ×.

FIG 5 Burn No *G36e*, 15 Min 1 360°, 40 Min 1 340°.
Normal prismatic form of C_4AF showing border growths as crystallizing from complete fusion.
Magnification 300 ×.

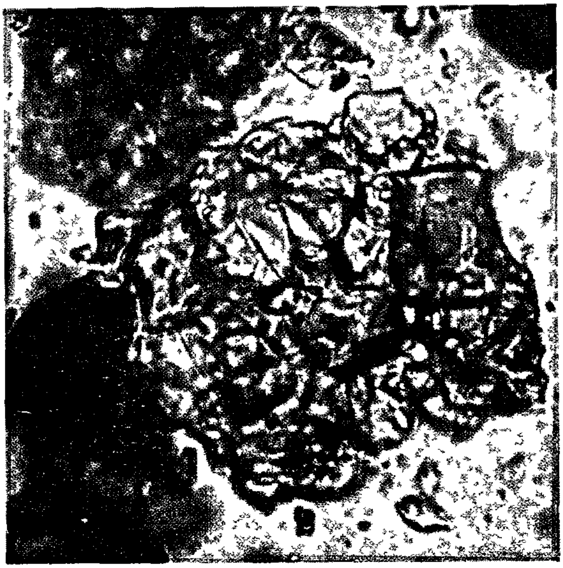

FIG 12 Burn No *G55i2* 15 Min 1 400°, 40 Min. 1 370°
Glass + well developed, large crystals of C_3A with heavy borders
Magnification 300 ×

FIG 13 Burn *G9f*, 30 Min 1 370°
1% less lime than FIG. 12, iron constant Short, stubby crystals C_4AF—two in basal orientation—in glass
Magnification 600 ×

FIG. 14. Burn No. *G9h*, 20 Min. 1 390°, 30 Min. 1 370°. C_4AF crystallizing from glass. Note border zones. Magnification 300 ×.

FIG. 15, Burn No. *G59f*, 30 Min. 1 380°. C_3A with very heavy border in glass. Magnification 600 ×.

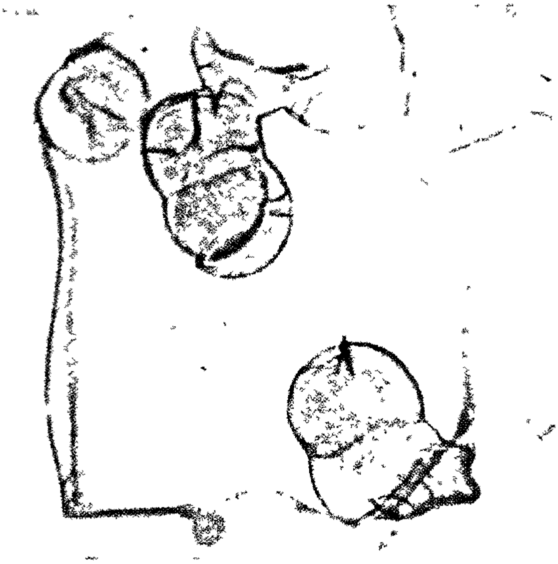

FIG 17. Burn No *G57a*, 30 Min 1375°
Glass + border phase only (½ % lower CaO than FIG. 15).
Magnification 600 ×.

Mr. T W. PARKER, *p. 113*

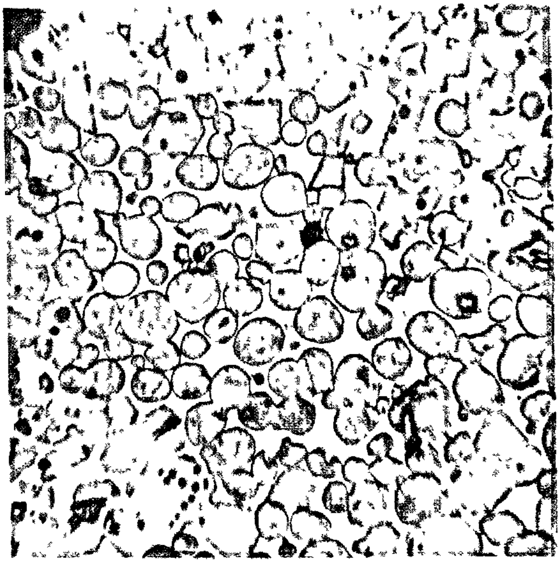

FIG. 6. Etched 30 Secs. with HF-Vapour.
Magnification 300 ×.

Mr. T. W. PARKER:[1]

The paper by Dr. BOGUE on the "Constitution of Portland Cement Clinker" sets out a composite account of the history of the various investigations during the past twenty years, together with the results of new work from the recent investigations of the Bureau of Standards. It is primarily with the latter that the present discussion is concerned.

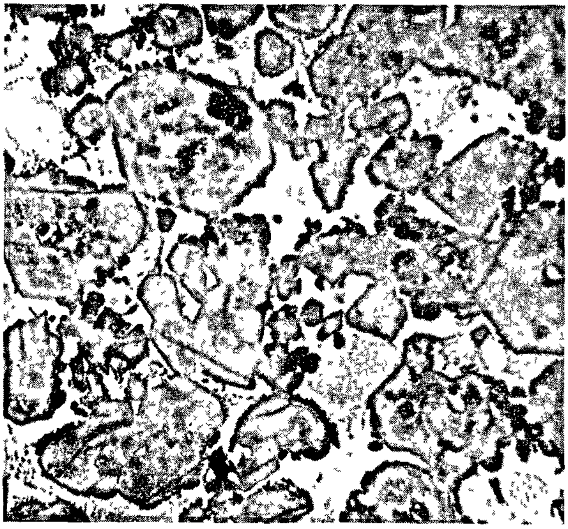

FIG. 1. Annealed Clinker. Etched 10 secs.; 1 : 3. Water: Alcohol. 5 secs.; $^1/_4$ % HNO_3 in Alcohol. Magnification 400 ×.

One of the objects of present day investigations is the solution of the problem of the composition of that portion of the clinker which is liquid at kiln temperatures. There are only two methods available for determining the *quantity* of each of the phases which may be formed when this liquid cools; direct counting under the microscope, or calculations derived from phase equilibrium studies, as for example those illustrated in DAHL's formulae. Neither method is free from objection. Discussing the latter first it will be noted that even if a preliminary estimate is made of the glass content by some experimental method (cf. pp. 77—80), the assumptions for determining the quantity of the various compounds which have crystallized from the residue depend always on a crystallization course for the residue based on equilibrium conditions. Yet it is very doubtful whether this is true under the cooling conditions in the rotary kiln. Once there is a departure from the slow cooling conditions necessary for equilibrium there is a possibility that crystalline phases may appear out of the order which would be expected on purely

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[1] M. Sc., Ph. D., A. I. C., Building Research Station, Garston, Herts, England.

phase equilibrium grounds. As a particular example, it will be agreed that there is a tendency for C_3A to crystallize more slowly than C_4AF and in consequence under fairly rapid cooling conditions the C_3A may fail to crystallize before C_4AF from residues in which it should, from phase equilibrium data, be the first to appear. In fact once supercooling has occurred the C_4AF may appear in such cases as the first crystalline phase from the residue, and the C_3A remain partially or entirely in the glass. This is of course recognized in Dr. BOGUE's paper and it was also a reason why formulae for only two extreme conditions were presented in Building Research Technical Paper No. 16. It is, however, well worth emphazising the point because it offers another possible basis for formulae for calculating compound contents. Such formulae would depend on the hypothesis that under normal kiln-cooling conditions a certain proportion, or a certain quantity, of C_4AF will crystallize; that an amount of glass (determined experimentally) remains; and that the residual material has crystallized under equilibrium conditions.

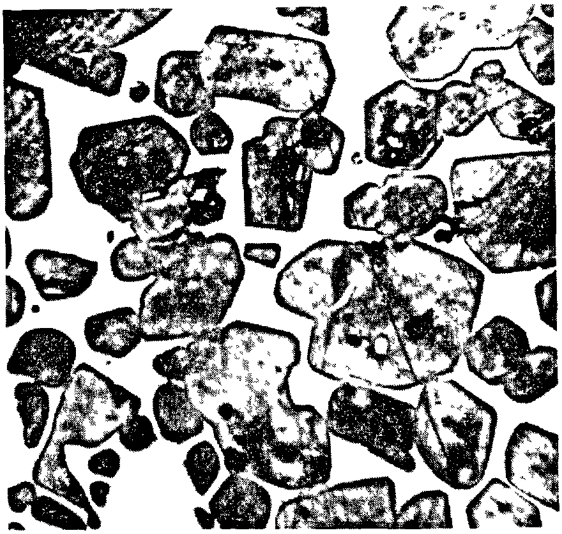

FIG. 2. Quenched Clinker. Etched as FIG. 1. Magnification 400 ×.

The error due to the assumption of equilibrium would thereby be reduced —in some cases to an appreciable extent. It is clear that more experimental work will be required to provide data on the order of crystallization under kiln-cooling conditions before even this limited extension can be applied. The measurement of the compound content by means of counts under the microscope may be made either with thin sections (cf. O. E. RADCZEWSKI and H. E. SCHWIETE, Zement, 1938, 27, 246—257, 275—280, 287—291) or with polished sections, but more accurate results can be obtained with the latter, since the clearer outlines of the crystal grains permit of better reproducibility of results by different observers, and also for other reasons given later. With polished sections it should usually be possible to make a quantitative estimate of C_3S, C_2S and "residue" by counting. The separation of the constituents of the "residue" is, however, a more difficult problem than might be inferred from Dr. BOGUE's paper. He notes that etch reactions produce a differentiation in the residue and, if the question of the alkali compounds be neglected, he concludes that C_4AF appears as a white, highly reflecting constituent, while a grey, etched constituent may be C_3A, or glass, or may be made up of both C_3A and glass. Investigations recently carried out at the Building Research Station verified that the C_4AF was white and highly reflecting and that the crystalline C_3A was etched grey or blue-grey, in fully crystalline clinkers. The method was to reheat a piece of clinker to 1 400°, cool slowly to 1 250°, anneal at this temperature for some hours to ensure crystallization, and to prepare a polished thin section from the specimen, for examination by both transmitted and reflected light.[1] Another polished and etched specimen was prepared from the clinker after it had been heated to 1 400° and quenched rapidly to convert the molten part to a glass. Examination of the latter by reflected light showed no differentiation in the "residue" (the matrix between the silicate grains) which was white and highly reflecting and yet must have been glass (see FIG. 2). Further investigation has provided an explanation of the apparent

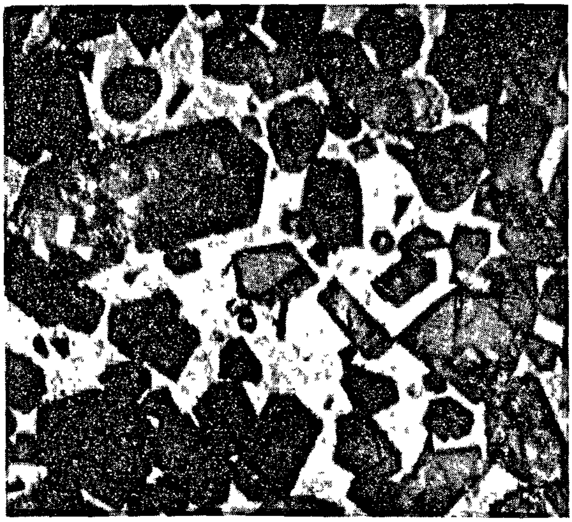

FIG. 3. Etched as FIG. 1. Magnification 400 ×.

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[1] See FIG. 1. It will be observed that the grey interstitial material has a tendency to a hexagonal outline, such as is sometimes assumed by C_3A in crystallizing from melts. The clusters of small spherical grains in the matrix have been identified as C_2S.

discrepancy between the results from the two laboratories. It would appear that the glass is etched when its composition is low in Fe_2O_3, such as may occur when C_4AF has crystallized from the molten liquid, but that the glass ceases to be etched when its Fe_2O_3-content becomes higher. No more definite data than this have yet been obtained but the following example will illustrate the effect. Two clinkers, containing only CaO, SiO_2, Al_2O_3 and Fe_2O_3, were prepared in the laboratory. The first had an Al_2O_3:Fe_2O_3-ratio higher than 1.38, the second lower than 1.38. Small quantities of each were enclosed in platinum foil and reheated in the quench furnaces at temperatures which from phase equilibrium data should have given, for the first, C_3S, C_2S, C_3A and liquid, and for the second, C_3S, C_2S, C_4AF and liquid. The specimens were rapidly quenched to convert the liquids to glasses and polished and etched specimens were prepared from each. Both showed a differentiation in the "residue" to grey and white constituents. In the first, (see FIG. 3) the grey must be placed as C_3A and the remaining white constituent must therefore be glass. In the second, (see FIG. 4) the white must be placed as C_4AF and the grey must therefore be glass. In examining a specimen of clinker from the kiln by the polished section method alone, the conclusion which may usually be drawn regarding the constituents of the "residue" can only be that the white material is C_4AF or glass and the grey material is C_3A or glass. If polished thin sections can be prepared from the specimen, it is sometimes possible to extend the identification, especially of the white material, which can, on occasion, be definitely assessed as C_4AF.

Returning to the question of clinker counts, there is occasionally an uncertainty on whether a crystal is C_3S or C_2S. Sometimes, also, C_3S-crystals have an altered border, probably caused by reaction with liquid during cooling. Evidence of this may be noted in FIG. 1. This border is most noticeable in polished sections; it may be missed altogether in thin sections. Errors in counting may arise as a result, but they can be reduced by using the polished section method with etch reagents which are specific for only one of the compounds of the clinker. At the Building Research Station a solution of ethylene glycol in alcohol is used as a specific etch reagent for C_3S. The reagent requires some hours to produce an etch. Quicker results may, however, be obtained with $MgSO_4$-solution. C_2S is etched in quite a distinctive way by holding the specimen over a concentrated HF-solution.[1]

It is hoped to present further details of this work in a paper to be published in the near future; it is, however, mentioned here as being a contribution which it is thought is sufficiently relevant to Dr. BOGUE's subject.

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[1] An example of the use of ethylene glycol to etch C_3S alone is given in FIG. 5, while FIG. 6 shows the blue colour produced on C_2S by etching with HF-vapour. Longer etching periods convert the C_2S to a red colour which is still distinctive although not so effective as the blue. The print is from a DUFAY-Chromex colour plate.

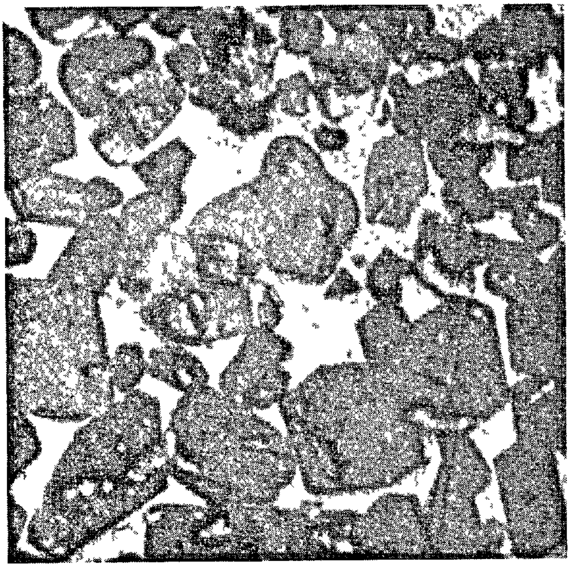

FIG. 4. Etched as FIG. 1.
Magnification 400 ×.

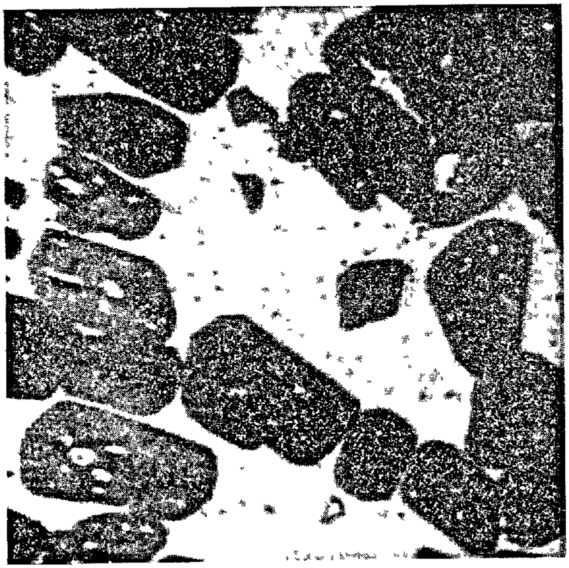

FIG. 5. Etched 4 Hours with 1 : 1 Ethylene Glycol: :Alcohol.
Magnification 400 ×.

Fig. 6, see p. 112!

Mr. B. TAVASCI:[1]

I.

I would like to ask the speaker: "How can you explain the equality (p. 64) of 'prismatic dark interstitial material' obtained by the adding of Na_2O and K_2O when in fact the aluminates relative to the 2 oxides ($8CaO \cdot Na_2O \cdot 3Al_2O_3$ and $K_2O \cdot Al_2O_3$) are different?"

We must evidently conclude that the fundamental substance of "prismatic dark interstitial material" is not composed of either one or the other of these compounds.

2.

How can the speaker explain the presence of the glassy phase (p. 64; Bibliography No. 27) slowly cooled in clinker mixtures (without Na_2O and K_2O)?

3.

Nature of the Glassy Phase - Metastable Phase (p. 72).

In the short time allowed I have once more prepared the two mixtures indicated on page 73 and made some observations under the metallographic microscope.

Mixture Nos.	CaO	Al_2O_3	SiO_2	Fe_2O_3	Observations
1 a	53·9	15·3	6.8	24	Quenched from 1 450° in Mercury
1 b	53·9	15·3	6.8	24	Quenched from 1 450° by floating in Mercury
2	45·9	—	7	47·1	Quenched from 1 550° in Mercury

Etching reagent—(etching convenient but not necessary): distilled water. The mixture No. *2* is but little attacked.

The mixture No. *1 a* is mainly homogeneous but at some points, however, it is possible to observe (FIG. 1 a) the beginning of crystallization. Where this is more advanced there becomes manifest a "dendritical" structure (FIG. 1 a, upper part).—This extends into the glassy mass—FIG. 1 a, lower part—in the shape of an irregular net.

In the mixture *1 b*, the process is much more developed (FIG. 1 b).

In the mixture No. *2*, although it is different in structure from the last, yet another net-like structure (FIG. 2) can be noticed.

Whatever the nature of the observed segregations may be we may nevertheless conclude that above mixtures are, despite the rapid cooling, not homogeneous and thus do not represent a unique phase.—I am therefore of opinion that it is not right to talk of "structural properties" of a "metastable phase" if this does not exist.

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[1] Dott.-Ing., Laboratorio Prove Materiali, R. Politecnico di Milano, Milano, Italy.

FIG. 1 a.
Magnification 500 ×.

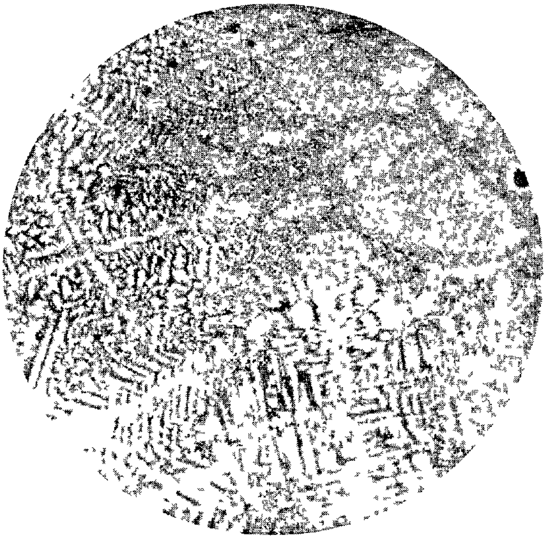

FIG. 1 b.
Magnification 500 ×.

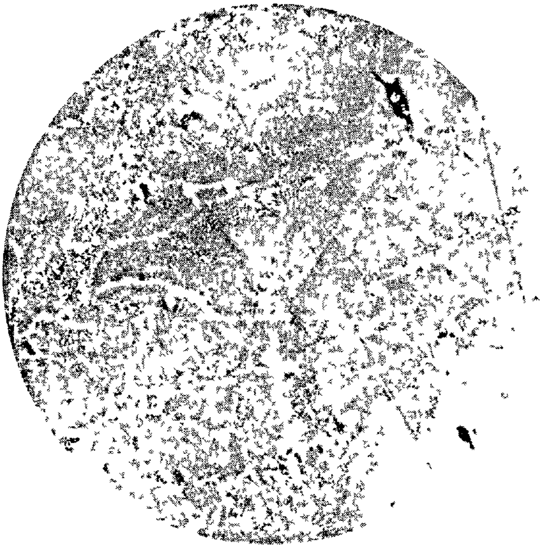

FIG. 2.
Magnification 500 ×.

Much more is this the case as regards the clinker, for which the cooling-off is much slower.

Especially may it be strongly doubted whether the "dark irregular interstitial material", supposedly homogeneous, really represents a non-crystalline phase.

4.

Glass content (p. 75).

INSLEY and MCMURDIE have found (Bur. Standards J. Research, NBS 1938, *20*, 173) that with a large number of clinkers under observation a noteworthy portion of them contained the "dark interstitial material" in the prismatic form. Evidently, in this case the "dark irregular interstitial material" ought to be negligible.

On the other hand, LERCH (diag. p. 76) found in all the clinkers studied "a glass content", which, if sometimes small, was never altogether negligible. Evidently, when the "dark interstitial material" is found in a prismatic and rectangular form the glass content should be practically annulled.

How can Dr. BOGUE explain that LERCH did not observe this fact in any clinker?

At this point I would like to call your attention to the fact *that also in the case when all the constituents are crystalline* when the clinker is rapid cooled off, their segregation, and this refers particularly to the last solidified constituents, may be by no means complete. We have, then, to deal with a lack of chemical equilibrium, which can be eliminated by annealing or slow cooling.

In this lack of equilibrium the thermal content of the clinker will, nevertheless, be different from that of the clinker slowly cooled.

Of course all the constituents of the clinker and not only those of the "celite" will generally participate in such a transformation.

Although the heat of transformation may be small as the whole clinker is here involved, it may turn out that the total development of heat is of the same order of magnitude as that relative to devitrification (assuming this to happen) of the "dark irregular interstitial material". If this is so, the question posed to Dr. BOGUE is promptly answered. It follows further that the determination of the "glass content" is on the whole deceptive.

5.

It is much more satisfactory to us, to have a unitory conception of the nature of the different constituents of the clinker and in particular of the "dark interstitial material".

The conditions of equilibrium being known, the chemical forces always tend to this equilibrium. (They are much more sensible than mankind!). Accidental circumstances can, however, displace it according to their importance, or only modify the external appearance.

The phase rule requesting 4 phases for 4 components, it is difficult to understand how, in the conditions of equilibrium under consideration, the presence of the two forms of different constitution of the "dark interstitial material" can be found in clinker mixtures not containing alkali (p. 64, Bibliography No. 27).

Just as a small force can provoke only a small alteration in the motion of a body, so it is difficult to conceive how a small addition of alkali can modify in a general way the nature of any phase of the clinker in such a way as to be considered different from the initial one.

We suppose, then, of course, that the said alkali enters in solid solution in such a way, that the number of the phase remains unchanged and that the quantity of the single phases is not too small.

We have seen before that the force of crystallization is remarkable, so that a not too rapid cooling will be able to modify the phases in their quantitative composition but not in their intrinsic nature.

In conclusion, we find more satisfactory the idea of a unique "dark interstitial material" with properties and external aspect more or less altered but similar in nature to the one corresponding to the equilibrium.—*(Translated from Italian.)*

Mr. N. SUNDIUS:[1]

Referring to the paper by Dr. BOGUE on the constitution of the Portland cement clinker I would say some words about the question of the disilicate. TÖRNEBOHM distinguished two species of cement minerals which he named belite and felite, but he states also that they may be chemically related as they substitute one another in different clinker samples. Later RANKIN—WRIGHT stated that the compound disilicate exists in three different modifications stable at different temperatures. This statement seems to have been made on account of thermal relations, at least concerning the both high modifications, because the mineralogical properties as given by them are very similar. But evidently they must have found an apparent thermal effect at the points of changes.

Some years later I re-investigated the old slides of TÖRNEBOHM and verified the existence of the two species distinguished by him. Also γ-disilicate is present in some cases. The properties of the two species were determined in the clinker and compared with the compounds in pure artificial melts. The α- and β- disilicate differ in the following respects:

1. A higher double refraction in the β-form.
2. The axial angle is great in the β-form but small in the α-form
3. The α-form is characterized by a peculiar cross-twinning, the β-form has a single twinning system.

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[1] Phil. Dr., Geological Survey of Sweden, Stockholm, Sweden.

4. The α-form is distinguished through the content of a brown pigment, probably small particles of ferrite-aluminate or ferrite which never are found in the β-form.

The disilicate has been studied by means of X-rays by BRANDENBERGER, who found that α- and β-disilicate are different though the atomic arrangement must be rather similar. Later INSLEY found that the α- and β-forms give identical spectra. From this INSLEY according to Dr. BOGUE concluded that both forms are identical and only at different temperatures give rise to different twinning formations. This would be a rather uncommon case mineralogically, because we must conclude that the double refraction and the axial angle also change on account of the different twinning. It would also nullify the statements of RANKIN alluded to above.

I think this conclusion may not be right and as I think we have also in the continuation to reckon with the existence of three modifications of the mineral, though possibly the atomic structure of the two high-temperatured forms is very similar.

Mr. E. BRANDENBERGER:[1]

I should like to discuss shortly the picture of the *metastable phase* given by Dr. BROWNMILLER in the Am. J. Sci. (5) 35 (1938) 241, especially in FIGS. 8 and 9. The metastable phase is there considered as a continuous structure consisting of an oxygen network, with the cations Si, Al, Fe in the centers of the oxygen polyhedra, the Ca atoms as inactive cations in holes of the network. I think, that at high temperatures, also here, Ca becomes active and lies therefore as an active center of co-ordination in the same or in a similar position as Si, Al, Fe, *i. e.* in the center of an oxygen polyhedron. For silicates formed at high temperatures such an uniform behaviour of all cations is characteristic, so that the differences existing between different cations at normal temperature disappear.

Mr. W. EITEL:[2]

1. I would like to make another small contribution to the great work of Dr. BOGUE, which may interest those of you who are working on the *microscopy of cement minerals*. It has struck me that in clinkers of the most varying

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[1] Dr., Eidgenössische technische Hochschule, Zürich, Switzerland.

[2] Professor, Phil. Dr., Kaiser-Wilhelm-Institut für Silikatforschung, Berlin-Dahlem, Germany.

nature, tricalcium silicate, even superficially, often appears to be of very different forms. In the wonderful photos of Dr. TAVASCI (in reflected light), I have so far certainly only met with the normal type, which we all know from, for instance, rotary furnace clinker. TÖRNEBOHM's original thin sections, which Dr. SUNDIUS has again described so wonderfully, reproduce typical shaft furnace clinker. But I am thinking also of some other clinkers, sent me by the courtesy of Dr. H. E. SCHWIETE, obtained by the French Basset-process. They show a quite peculiar coarse-grained formation of tricalcium silicate, which I have never before seen in normal rotary furnace clinker. I have, in addition, quite recently come across a clinker produced in a rotary grate process. I assume that most of you know the proposals made to discard entirely the principle of rotary furnaces, and to calcinate the raw material on a travelling grate. That process thus reverts to the old way of manufacturing shaft furnace clinkers to the extent that coal is added to the crude powder, and the mixture fired; the mixture will then burn into clinker of a peculiar, slag-like appearance. The morphological formation of this clinker is quite different from the normal formation of tricalcium silicate, as we have up to now learnt to know it from the rotary furnaces. You will in the first place note its very marked zonal structure, which is so far not known in normal rotary furnace clinker. This may possibly be due to the formation of compound crystals, perhaps with ferrites, or else with aluminates or the like. The clinker from the travelling grate struck me also because, contrary to the type of tricalcium silicate with thick lamellae you all know, its lamellae are quite thin, so that it in cross section appears to be composed of only thin needles.

2. I felt compelled to look for some system, by the aid of which, instead of the theoretical investigations of phases on a static basis hitherto used, we might by *quicker* crystallization easily obtain equilibrium of the phases concerned. This is actually possible by the addition of strongly acting *mineralizers*. It is an old technical experience that fluorides have an excellent effect on the clinker-forming process. The fundamental system that I examined in this respect was the Ca_2SiO_4-CaO-CaF_2-system. In this system we can very clearly see that the primary crystallization of tricalcium silicate is only possible within a quite definite range of concentrations and temperatures. According to FIG. 1., tricalcium silicate can only crystallize in the narrow, crescent-shaped field between the maximum temperature 1 900° (acc. to RANKIN) and 1 250° (acc. to CARLSON). With fluoride, the reactions are so quick and smooth that even under ordinary cooling conditions, *e. g.* in only one hour while cooling down from 1 450° to 1 200°, there is a quantitative breaking-up of tricalcium silicate. The tricalcium silicate, which is thus obtained as primary crystallization only if definite precautions are taken,

and above all at higher concentrations, is of a remarkably peculiar type, which I have so far never met with in clinker, being of the pronouncedly pseudo-hexagonal, low symmetrical character of tricalcium silicate. So far, the researches of GUTTMANN and GILLE, and some work of American colleagues, have always made us regard tricalcium silicate as a hexagonal crystal. Actually, it can only be said to be of *pseudo*-hexagonal structure. Tricalcium silicate is probably of monoclinic or even triclinic symmetry. I have further seen some very interesting twin formations, reminiscent of the pseudo-hexagonal twinning of Chrysoberyl or calcium sulphate.—*(Translated from German.)*

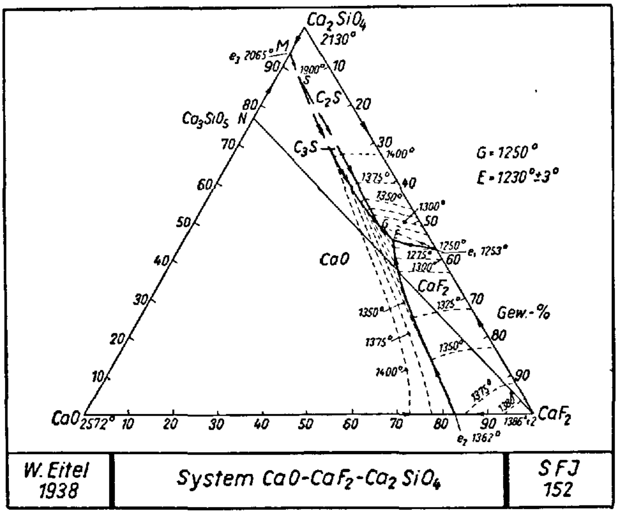

FIG. 1.

Mr. R. G. FRANKLIN:[1]

I should like to mention one point on Dr. BOGUE's paper regarding the estimation of the glass in clinker by the heat-of-solution method. Dr. BOGUE estimates the glass content by comparing the heats of solution of the clinker as received and after annealing to effect complete crystallization and dividing the difference between the two figures by the value for the latent heat of crystallization of the glass found in separate determinations on pure glass of approximately similar composition.

In an attempt to determine the glass content of technical clinker we have tried an alternative method, which is to determine the heats of solution of

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[1] Imperial Chemical Industries (Fertilizer & Synthetic Products) Ltd, Billingham, England.

the clinker in three conditions, quenched, as received, and fully annealed. From these figures it should be easy to calculate how much crystallization of the liquid phase has taken place but in practice the results obtained were anomalous. With your permission, Mr. Chairman, I would ask Dr. Lea to continue the discussion of this point, since the work was actually carried out by him at the Building Research Station.

Mr. F. M. Lea:[1]

Dr. Bogue in his paper has given a most interesting account of the recent advances in knowledge of the constitution of Portland cement clinker. The problems now remaining to be solved in this field fall into two main groups, associated respectively with the effects of partial crystallization and with the influence of the minor components.

My colleague Dr. Parker has in another communication discussed the uncertainties which arise in the calculation of compound content from the insufficiency in our knowledge of the effects of partial crystallization.

The time now appears ripe for some preliminary consideration to be given to the effect of magnesia, alkalies and titania on the maximum lime content and compound content.

Under the assumption of quenched equilibrium the maximum amount of lime which can be combined in the clinkering of Portland cement is determined by the composition and amount of the liquid phase which is formed. At the clinkering temperature the original mix becomes divided into a solid part, consisting of C_3S, or C_3S and C_2S, and a liquid which is more acidic. When the maximum amount of lime which can be combined is present, the mix is, at the clinkering temperature, made up of C_3S and a liquid. In the system $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}Fe_2O_3$ this liquid is too acidic to yield C_3S, C_3A and C_4AF alone and, if it crystallizes on cooling, it gives C_3S, C_2S, C_3A and C_4AF when the $Al_2O_3:Fe_2O_3$-ratio is between 0.9 and 1.7, and C_2S, C_3A, C_5A_3 and C_4AF when this ratio is above 1.7.

The maximum lime content which can be present in this four-component system, without free lime appearing as a solid phase at the clinkering temperature, is represented closely by the plane connecting the composition of the CaO, C_3S, C_3A invariant point in the system $CaO\text{-}Al_2O_3\text{-}SiO_2$ with the points C_3S and C_4AF. It is expressed by the equation to this plane which is:

$$CaO = 2.8SiO_2 + 1.18Al_2O_3 + 0.65Fe_2O_3 \quad [1]$$

The introduction of minor components can, apart from the purely arith-

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[1] D. Sc., F. I. C., Building Research Station, Garston, Herts, England.

metical reduction necessarily caused in the amounts of the main components, influence the maximum lime content in two ways.

1. By the formation at the clinkering temperature of solids containing the minor components.
2. By changing the relative proportions of CaO, Al_2O_3, SiO_2 and Fe_2O_3 in the liquid phase which exists in *equilibrium with* C_3S *at the clinkering* temperature, and also by altering the amount of liquid formed.

As is shown in Dr. BOGUE's paper MgO will be present as a solid phase at the clinkering temperature if it is present in more than certain proportions. Since, however, it then exists as free crystalline MgO, and is not combined with the acidic components, this will not reduce the maximum amount of lime which can be combined. Dr. BOGUE stated that very recent work in his laboratory had shown that the alkalies probably form compounds of the type $x(2CaO \cdot SiO_2) \cdot y(R_2O \cdot Al_2O_3)$. These alkali-containing compounds are found amongst the interstitial material in clinker, indicating that they are formed by crystallization of the liquid and that they are not present as solids at the clinkering temperature. The same is probably true also of the titania compounds. We may, therefore, when these minor components are present, still assume that the maximum lime content of the mix is represented by a point on a line connecting the C_3S-composition with the liquid composition, *i. e.* if at the clinkering temperature x per cent liquid and $(100 - x)$ per cent C_3S is formed the maximum lime content of the mix is:

Maximum % CaO $= 0.737\ (100 - x) + \frac{x \cdot y}{100}$ where y is the percentage CaO in the liquid.

Now there is evidence (cf. LEA and PARKER, Building Research Technical Paper No. 16, 1935) that the amount of liquid formed on clinkering is only increased, when minor components are added to a CaO-Al_2O_3-SiO_2-Fe_2O_3-mix, by an amount roughly equivalent to the additions made. The amount of C_3S, $(100 - x)$, suffers therefore on this account only a purely arithmetical decrease corresponding roughly to the reduction in the total amount of the major components present. More important is the effect of possible changes in the composition of the liquid. The introduction of Fe_2O_3 into the system CaO-Al_2O_3-SiO_2 causes the composition of the liquid present at clinkering temperatures to move towards the C_3S-C_3A-C_4AF-plane. The addition of MgO to CaO-Al_2O_3-SiO_2-mixes has however the reverse effect, as may be seen from the data of MCMURDIE and INSLEY (Bur. Standards J. Research 1936, *16*, 467), and moves the clinker liquid composition further away from the C_3S-C_3A-MgO-plane to more acidic regions. Nothing is at present known of the effect of alkalies and titania on these liquid compositions.

Considering only the oxides $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}MgO$ the maximum lime content can in this system be represented by the plane through the compositions of the three points *(1)* C_3S, *(2)* CaO, C_3S, C_3A invariant point in the ternary system $CaO\text{-}Al_2O_3\text{-}SiO_2$, *(3)* CaO, C_3S, C_3A, MgO invariant point in the quaternary system $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}MgO$. The equation to this plane, which can be calculated with the aid of the data for point *(3)* given by McMURDIE and INSLEY, is as follows:

$$CaO = 2.8SiO_2 + 1.18Al_2O_3 - 0.93MgO \ldots\ldots\ldots\ldots \quad [2]$$

This equation indicates that the addition of MgO to $CaO\text{-}Al_2O_3\text{-}SiO_2$-mixes reduces the maximum percentage of lime which can be combined—altogether apart from the purely arithmetical reduction caused by the lowering of the total Al_2O_3 and SiO_2 present—and this is due not to replacement of CaO by MgO in silicate or aluminate compounds, but to the change in the composition of the clinker liquid.

It seems, however, that no such large effect can occur when MgO is added to the $CaO\text{-}Al_2O_3\text{-}SiO_2$-system for, if this were so, the maximum lime content which can combine with SiO_2, Al_2O_3 and Fe_2O_3 would be reduced by nearly 1 per cent for each per cent MgO present.

Now earlier work (LEA and PARKER, Building Research Technical Paper No. 16, 1935) has shown that the equation [1] for maximum lime content deduced from the system $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}Fe_2O_3$ does represent closely the maximum combined lime found in commercial cements. It is, however, of interest to examine this point a little further. Data are shown in TABLE 1 on commercial cements selected as containing high combined lime contents and varying magnesia contents. The combined lime, derived from the total CaO-content of the cement after correcting for free lime and lime present as $CaSO_4$, is shown in Column IV, and the maximum lime which could be combined according to formula [1] in Column V. Column VI shows the excess (+) or deficiency (—) of the combined lime found compared with that calculated. The negative values may of course, despite the presence of free lime, merely indicate that the amount of lime combined has not reached the maximum possible and, for the moment, it is the positive values which will be considered. Positive values are found with Nos. 110, 6, 18 and 19, but apart from No. 19 the excess is within the sum of possible analytical errors. No. 19 is anomalous suggesting either rather large analytical errors or some abnormality in method of production. With this one exception the formula represents satistactorily the maximum lime content found combined. If, however, the presence of magnesia were to have an effect comparable with that produced in the system $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}MgO$, as indicated by formula

[2], a considerable reduction in the theoretical combined lime content would occur, and cements Nos. 79, 72, 110, 20, 16, 6, 17, 8, 15, 18 and 19 would all have found combined lime contents from 1 to 3 per cent above the theoretical value.

Table 1. Combined Lime Content of Some High-Lime Portland Cements.

I	II	III	IV	V	VI	VII
Cement No.	Lime—Lime in $CaSO_4$	Free CaO	Combined CaO Found	Maximum Combined CaO calculated LEA and PARKER Formula	Found Combined CaO—Maximum calculated	MgO-Content of Cement
20	62.7	6.4	56.3	57.8	— 1.5	3.7
22	61.8	1.0	60.8	63.3	— 2.5	3.6
16	62.0	0.6	61.4	62.3	— 0.9	3.5
79	61.2	2.0	59.2	59.2	0	3.27
5	61.7	0.4	61.3	63.9	— 2.6	2.9
9	64.6	1.0	63.6	65.1	— 1.5	2.5
72	63.15	1.9	61.2	62.4	— 1.2	2.72
6	64.5	1.1	63.4	62.8	+ 0.6	2.2
17	64.2	1.1	63.1	63.7	— 0.6	1.8
8	64.5	0.3	64.2	64.5	— 0.3	1.7
15	64.6	3.5	61.1	61.5	— 0.4	1.6
78	63.96	2.8	61.1	62.2	— 1.1	1.47
71	59.9	0.5	59.4	59.6	— 0.2	1.12
11	64.1	0.8	63.3	65.0	— 1.7	1.0
18	64.2	0.3	63.9	62.9	+ 1.0	0.9
19	66.0	1.6	64.4	62.1	+ 2.3	0.9
110	63.7	0.4	63.3	63.0	+ 0.3	0.72
74	65.55	2.9	62.6	63.2	— 0.6	0.65

Data for cements Nos. 71—110 taken from Building Research Station analyses. Data for cements Nos. 5—22 taken from C. R. GAUSE. Bur. Standards J. Research 1935, *15*, 421.

It is of interest, however, to consider further the negative values shown in Column VI of the table. Most of these cements are of the rapid-hardening type in which an attempt has probably been made to obtain as high a combined lime content as possible. Data on commercial cements are not of course satisfactory for obtaining any precise information, but the negative values do give some indication that the presence of magnesia may cause some reduction in the maximum possible combined lime content, though it is less than that suggested by equation [2], amounting probably to appreciably less than one half of that indicated by the magnesia factor in this equation. It is in any case uncertain if any such correction for magnesia can be applied as a direct additive term, for the effect of magnesia in moving the C_3S-field towards more acid regions may vary with the Al_2O_3:Fe_2O_3-ratio of the cement.

In these commercial cements the effect of the remaining minor components is, of course, superimposed on that of the magnesia.

The effect of magnesia, and the other minor components, on the compound content of cement cannot at present be at all closely assessed, but some general indication of the changes caused can be obtained. In the CaO-Al_2O_3-SiO_2-Fe_2O_3-mixes the C_3S-content under conditions of frozen equilibrium becomes progressively greater than the BOGUE value as the $Al_2O_3:Fe_2O_3$-ratio increases. In so far as the addition of MgO raises slightly the content of silica, and reduces that of lime, in the clinker liquid it will increase the ratio of C_3S to C_2S in the solid present at the clinkering temperature. This will raise the C_3S-content somewhat except in the case of mixes saturated, or almost saturated, with lime for which the increase of the silica in the liquid phase will involve a slight reduction in C_3S-formation. The results of some microscopic counts on polished and etched surfaces of laboratory clinker containing magnesia and alkalies offer some confirmatory evidence, for the C_3S-contents so measured tend to be several per cent above those calculated from the LEA and PARKER values derived from the CaO-Al_2O_3-SiO_2-Fe_2O_3-system, and of course still further above the BOGUE values.

We have what is at first sight the somewhat contradictory result that the presence of magnesia and alkalies probably reduces slightly the maximum combined lime content of the mix yet raises the C_3S-content a little (apart from cements in which little or no C_2S exists). The explanation is of course that the greater acidity of the clinker liquid results in an increased $CaO:SiO_2$-ratio in the solids present at the clinkering temperature.

The products obtained from the clinker liquid, if it crystallizes, will also be affected by the presence of minor components. Thus combination of alkalies with alumina in a compound $x(2CaO \cdot SiO_2) \cdot y(R_2O \cdot Al_2O_3)$ will make available for other purposes more lime than is required to satisfy the requirements of the titania present. This may form $3CaO \cdot 2TiO_2$ or $CaO \cdot TiO_2$, the latter being the more probable in cements yielding any C_5A_3. As an example we may consider a cement which contains 0.7 per cent K_2O, 0.3 per cent Na_2O and 0.3 per cent TiO_2, and which gives a liquid crystallizing to C_2S, C_3A, C_5A_3 and C_4AF. The K_2O and Na_2O will together require 1.25 per cent Al_2O_3 and thus release 1.1 per cent CaO which would have been required to combine with it to form C_5A_3. The 0.3 per cent TiO_2 requires 0.2 per cent CaO to form $CaO \cdot TiO_2$ leaving 0.9 per cent CaO available for other purposes. This is sufficient to convert 2.4 per cent C_5A_3 to 3.3 per cent C_3A. The presence of alkalies and titania[1] in such proportions, which are typical values, will thus result in a reduction of the C_5A_3 and an increase

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[1] If the alkalies combine with titania to any extent the general effect on the compound content will remain of the same type, but quantitatively there may be differences.

in the C_3A-content, while any excess lime available above that required for this purpose will result in crystallization of some C_3S in place of C_2S. For a liquid normally crystallizing to C_3S, C_2S, C_3A and C_4AF the 1.25 per cent Al_2O_3 taken up by the alkalies will release 2.05 per cent CaO which would have been required to combine to form C_3A. After correcting for titania as before we have 1.85 per cent CaO available which is sufficient to convert 5.7 per cent C_2S to 7.5 per cent C_3S. Superimposed on these effects there will of course also be those resulting from any changes produced by the minor components on the ratios of $CaO:Al_2O_3:SiO_2:Fe_2O_3$ in the clinker liquid. The magnitude of these changes cannot be estimated, but as shown earlier, they will probably be such as to act in the reverse direction to those discussed above and so, more or less, to offset or reverse them.

In connection with the heat-of-solution method for determination of glass content, we have, as Mr. FRANKLIN has mentioned, found some difficulty. Some three years ago an attempt was made to develop a "bracketing" method in which the heat of solution of a clinker as received was determined and also after (1) annealing the clinker to crystallize it completely and (2) quenching the clinker from a temperature of 1 400°—1 450°. The results were disappointing. The method seemed to work reasonably satisfactorily on laboratory clinkers, but it broke down when applied to commercial clinkers. Sometimes the clinker as received gave a lower value for the heat of solution in the nitric-hydrofluoric acid solvent than the annealed material. It seems that some change was occurring during the reheating of the clinker, but no explanation of the nature of this change was found.

Mr. SWAYZE in his contribution to the discussion on Dr. BOGUE's paper has mentioned a "border phase" surrounding crystals of tricalcium aluminate. As is well known, quench growths form very readily in the system CaO-Al_2O_3-Fe_2O_3 and we must I think be cautious before we assume that this "border phase" is a true primary phase.

In reply to Mr. F. M. LEA, Mr. M. A. SWAYZE has made the following additional remarks:

Neither Dr. BROWN nor myself consider the material which we find surrounding the C_3A-crystals to be quench growths for several reasons. Some of these are given in my original discussion.

First, while our charges are extremely small, a cross section of them is nevertheless much thinner at the edge than at the centre. In some charges in the C_3A primary phase field which are high in iron, and, therefore, have a liquid of relatively high specific gravity, the C_3A-crystals tend to collect around the edges and at the centre of the melt. If the material surrounding

C_3A-crystals were a quench growth, we should expect it to be thicker in the centre of the charge than at the edges where quenching must be the most rapid. However, the thickness of the borders seems to be about the same throughout the section.

Second, the material does not have the fibrous structure which we find in charges which are more slowly cooled and in which crystallization has begun due to the slower drop in temperature.

Another reason for considering the material to be something else beside a quench growth is its occurrence in contact with C_4AF-crystals. We have found by heating mixes in the primary phase field of this compound and then slowly cooling for a few degrees, but quenching the charge while it still contains only one solid phase, that the C_4AF-crystals have grown during the slow cooling process by additions at the long end of the crystal. These additions are often in the form of very fine fringe-like growths, which, under anything but high magnification, present a very fibrous appearance. On the other hand, in similar charges quenched without the initial pre-cooling period, the border material is distinctly non-fibrous in appearance and appears to be of approximately an even thickness on all sides of the crystal.

Another reason for considering the material to be a stable substance is that along the portion of the C_3A-C_4AF-boundary curve near the invariant point, the material has been found to exist by itself with C_3A and C_4AF seed crystals both absent. Charges of this sort have been held for hours in the furnace at a temperature 5° to 10° below that required for complete fusion, and the material has exactly the same appearance which it possesses in charges heated at the same temperature for only thirty minutes or so.

Regarding the optical properties of the material, its index is always higher than C_3A, but less than C_4AF. However, the index varies with the composition of the charge, increasing with the iron content. Its index is also higher than any of the glasses with which it is in contact. The material also has a variable birefringence, which, coupled with its varying index, would preclude the assumption that it might be a new compound.

Considering all of the observations which we have made, the exact nature of this substance, which we have referred to as the "border growth" or "border phase", is still obscure. However, the fact remains that the iron-bearing interstitial material in many of our Portland cement clinkers bears a striking resemblance to this substance. We, therefore, hope that you and others will re-examine evidence which you may have, from the viewpoint that there may be something more to this material than a quench growth.

Mr. L. FORSÉN:[1]

From Dr. BOGUE's most valuable and comprehensive report I am very much delighted to gather that the principal questions are settled with regard to the constitution of the Portland cement clinker.

For the technical production of cement another question has also been of great interest, and that is to establish the upper permissible limit of lime and also to find the reason why this, in spite of good raw materials and careful processing, often has a lower value than that calculated from the formula for final equilibrium. My suggestion that this lower value is the result of a frozen equilibrium, or, to use BOGUE's expression, an arrested crystallization—with as a consequence higher C_3S-content and less lime in the glass than is required for C_3A—has been verified through LEA's excellent investigation of the quaternary system $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}Fe_2O_3$ and through BOGUE's careful determinations of the glass content under various heating conditions.

For the calculation of the maximum content of combined lime I have given a formula with a factor "f" that indicates the amount of CaO which is combined with that amount of Al_2O_3 which exceeds C_4AF. From RANKIN's diagram the following formula—with "f" = 1.18—can be read:

$$3CaO,\ SiO_2 + x(2.15CaO,\ Al_2O_3)$$
$$\%\ CaO = 2.8 \cdot \%\ SiO_2 + 1.18 \cdot \%\ Al_2O_3$$

For technical cement clinker I found that "f" varies from 1 to 1.65 corresponding to the formula:

$$3CaO,\ SiO_2 + x(4CaO, Al_2O_3, Fe_2O_3) + y(nCaO,\ Al_2O_3)$$
$$\%\,CaO = 2.8 \cdot \%\ SiO_2 + 1.4 \cdot \%\ Fe_2O_3 \qquad + f\,(\%\,Al_2O_3 - 0.64 \cdot \%\ Fe_2O_3)$$

In clinker with comparatively low A:F "f" could be raised to 1.65 whereas at high A:F-ratio "f" was about 1.

LEA has shown, that, at frozen equilibrium in the quaternary system $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}Fe_2O_3$, the maximum amount of combined lime can be expressed by the following formula:

$$\%\ CaO = 2.8 \cdot \%\ SiO_2 + 0.65 \cdot \%\ Fe_2O_3 + 1.18 \cdot \%\ Al_2O_3.$$

If this formula is recalculated to compounds we obtain:

$$3CaO,\ SiO_2 + x(4CaO, Al_2O_3, Fe_2O_3) + y(2.15CaO,\ Al_2O_3) \text{ or } \%\ CaO =$$
$$= 2.8 \cdot \%\ SiO_2 + 1.4 \cdot \%\ Fe_2O_3 \qquad + 1.18\ (\%\ Al_2O_3 - 0.64 \cdot \%\ Fe_2O_3).$$

This formula is valid for completely arrested crystallization without crystallization of the glass. LEA's formula accordingly gives in some cases lower limit for the lime content than the one given by me for technical conditions,

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[1] Dr.-Ing., Chief Chemist, Skånska Cementaktiebolaget, Limhamn, Sweden.

The reason why, at low A:F-ratio, final equilibrium is reached even under technical conditions appears to be that primarily crystallized CaO is readily absorbed in such systems.

I also wish to take the opportunity to touch upon a question of nomenclature. The clinker minerals are formed in a similar way to many natural ones, and we know that these generally are contaminated with impurities. We also know that alite differs somewhat from pure C_3S with regard to X-ray pattern—maybe on account of a certain content of aluminate, that belite can be yellowish—possible on account of a certain iron content—and that celite probably contains some MgO. Furthermore, a certain difference in reaction velocity also seems to exist between pure C_3S and alite in Portland cement. In autoclave tests we found that C_3S liberated lime rather slowly (about 0.3 mol. CaO after 48 hours at 170°) whereas alite in Portland cement reacts very rapidly (complete conversion to $C_2S \cdot Aq.$ after 8 hours at 170°).

It appears to me that the existing differences between the pure clinker components and the minerals present in clinker—especially between C_3S and alite—argue in favour of retaining the old names alite, belite and celite for the clinker minerals and reserving the chemical formulae for the synthetic compounds in the same way as we distinguish between the names of the natural minerals and of the corresponding pure chemical compounds.

Mr. R. H. BOGUE (*author's closure*):

Mr. SWAYZE has made an important contribution in demonstrating an extended field for $3CaO \cdot Al_2O_3$ in the CaO-Al_2O_3-Fe_2O_3-system, and giving a revised location for the invariant point for CaO, $3CaO \cdot Al_2O_3$ and $4CaO \cdot \cdot Al_2O_3 \cdot Fe_2O_3$.

There is, however, some question in my mind with respect to the identification of the "border phase". This phase has been found by Dr. WARD in our laboratory to show a wavy or shadow extinction under crossed Nicols and, under favorable conditions, it appears to develop into spherulites. These observations suggest that the phase may be a quench growth. An X-ray diffraction pattern, furthermore, has given only the structure of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ with no evidence of the cubic ($3CaO \cdot Al_2O_3$) pattern which BROWNMILLER found to be typical of the "metastable" phase.

It is readily agreed that a differentiation between glass on the one hand and $3CaO \cdot Al_2O_3$ or $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ on the other hand is not altogether satisfactory by our present polished section technique. In our own laboratory, the procedure adopted by Dr. WARD is to etch the specimen for 5 seconds with distilled water, rinse in alcohol and dry. Using reflected light and a yellow-green filter, the $3CaO \cdot Al_2O_3$ appears almost black whereas the glass is gray. Subsequent treatment for two seconds with 1 per cent nitric acid in alcohol virtually destroys the dark etch of the $3CaO \cdot Al_2O_3$ but leaves the glass still gray and distinctly outlined.

Greater difficulty is experienced in distinguishing between $3CaO \cdot Al_2O_3$ and the dark prismatic phase, since they etch to the same dark color. In this case, the prismatic structure is the distinguishing characteristic.

For differentiating between $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ and a high-iron (light reflecting) glass, TAVASCI's reagent for $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ (1 part 10 per cent Na_2HPO_4 with 4 parts of 10 per cent sodium hydroxide) has shown best results. Definite differentiation has been found by use of this reagent in some clinkers where no glass could be observed by the usual methods although a considerable amount had been indicated by the heat-of-solution method.

I find that I have difficulty in understanding the questions raised by Professor TAVASCI; perhaps it is a mutual difficulty due to differences in our languages. I will, however, try to read my own interpretation and answer them as best I can.

1. I think Professor TAVASCI wishes to know why the soda and the potash give, apparently, an identical phase in clinker, whereas the known compounds of those oxides in the cement systems are quite different. That is a question which has challenged us since the discovery of the prismatic dark interstitial phase and has led us to set forth repeatedly that solution of the alkali systems with the silica component must be awaited before we can state the nature of the alkali compounds in commercial clinker. Such studies are under way and it seems probable that an understanding of the nature of the alkali phases will soon be reached.

2. Professor TAVASCI asks how the glassy phase can be present in a slowly-cooled, alkali-free laboratory clinker described by INSLEY. I have talked with Dr. INSLEY on this matter and he tells me that probably no glass was present but that the irregular form of the dark interstitial material in this case was due to residual crystallization of $3CaO \cdot Al_2O_3$ in the pattern determined by the silicates.

3. Professor TAVASCI argues that we should not speak of "structural properties" of a "metastable phase" if this does not exist and he cites, in proof of the non-existence of this phase, observations made by him which indicate that a "dendritical" structure is formed. A dendritical structure, he argues, shows that the material is not homogeneous and because it is

not homogeneous there can be no "unique" phase, and hence no "metastable" phase. I do not understand that inhomogeneity rules out the possible presence of one or more phases. I do not understand that an inhomogeneous specimen may not be made up of, let us say, unoriented glass, a partially oriented transition phase and a completely oriented crystal phase. The X-ray evidence which, in the present case, is most striking, indicates a form of symmetry that invites an explanation. We have suggested an hypothesis which we submit, not as an established truth, but as a step in our reasoning which, with the aid of the combined interest of other investigators, we hope will lead to an ultimate understanding.

4. Professor TAVASCI assumes that, where a prismatic dark interstitial phase is found, the irregular dark interstitial phase (glass) ought to be negligible, and he asks why no commercial clinker (containing the prismatic phase) was found with a zero glass content. I do not understand why the presence of the prismatic phase should preclude the possibility of the presence of glass. In this connection I may point out that several commercial clinkers have been examined which have shown, in polished section, the presence of both of those phases in definitely significant amounts.

We recognize, and have repeatedly stated, that the heat-of-solution method for determining glass content is not a precision process, due to many indeterminate conditions as stated in the original paper, but we feel that a conservative interpretation of data so obtained provides us with a further tool for gaining an understanding of the state of equilibrium in a given clinker.

5. The phase rule applies only to a system in equilibrium. In the case of clinkers containing glass, we are definitely postulating a state of unequilibrium. This being the case, there is no contradiction to theory in stating the presence of phases in excess of those that may be present at equilibrium according to the Phase Rule.

I cannot agree that a small force may not provoke a large change in the motion of a body nor that a small amount of alkali may not produce a large change in some of the phases of clinker. To illustrate this point, let us assume (which very likely is not correct) that soda in clinker enters into combination as $8CaO \cdot Na_2O \cdot 3Al_2O_3$ according to the reaction: $3\ 3CaO \cdot Al_2O_3 + {} + Na_2O \rightarrow 8CaO \cdot Na_2O \cdot 3Al_2O_3 + CaO$. Suppose we add 0.5 per cent Na_2O to an alkali-free clinker. This would be capable of interacting with 6.5 per cent $3CaO \cdot Al_2O_3$ to form 6.6 per cent $8CaO \cdot Na_2O \cdot 3Al_2O_3$ and liberating 0.4 per cent CaO which would raise the $3CaO \cdot SiO_2$ 1.8 per cent and decrease the $2CaO \cdot SiO_2$ 1.4 per cent. If we assume further that the $3CaO \cdot Al_2O_3$-content of the clinker, with alkalies, excluded, is 10 per cent, the $3CaO \cdot Al_2O_3$ remaining after the formation of $8CaO \cdot Na_2O \cdot 3Al_2O_3$ would be 3.5 per cent but this would enter into solid solution with the

$8CaO \cdot Na_2O \cdot 3Al_2O_3$ to form 10.1 per cent of a new solid solution phase. Thus the insignificant (?) amount of 0.5 per cent Na_2O might change the constitution of the clinker under discussion by adding 10 per cent of a new phase, eliminating completely the $3CaO \cdot Al_2O_3$, and raising the $3CaO \cdot SiO_2$ and lowering the $2CaO \cdot SiO_2$ by amounts between 1 and 2 per cent.

Professor TAVASCI finds more satisfactory "the idea of a unique 'dark interstitial material' with properties and external aspect more or less altered but similar in nature to the one corresponding to the equilibrium". But it has been shown by an abundance of evidence by LEA and PARKER, by FORSÉN, by ourselves and others that the liquid present at clinkering temperatures, and consequently the undercooled liquid or glass, has a composition markedly different from that of either of the phases that have crystallized at that temperature or the clinker as a whole. This being the case, I cannot understand how the glass can be "similar in nature to the one corresponding to the equilibrium". Indeed, if equilibrium were attained, there could be no dark interstitial material except $3CaO \cdot Al_2O_3$ (omitting alkalies) whereas, if glass were present, it must contain a considerable proportion of iron, as well as silica and magnesia, and a mixture of low $Al_2O_3 : Fe_2O_3$ ratio would contain at equilibrium no dark interstitial material at all.

In reply to the discussion of Dr. SUNDIUS on the identity of the α- and β-dicalcium silicate, I give herewith a few comments by INSLEY:

"As I showed in Bur. Standards J. Research, NBS 17, 353—362 (1936), RP 917, difference in index of refraction values of alpha- and beta-$2CaO \cdot SiO_2$ both in the determinations of WRIGHT and of SUNDIUS are practically within the limits of precision given by them. In measuring index of refraction of a finely twinned grain by matching against a liquid of known index the apparent value for the index of refraction is an average of the indices for the individual members of the twin. Because the interference figure is formed by interference of light rays from all parts of the field of view, the optic axial angle of the figure depends also upon the angular relation of individual members of a twinned grain.

If the plane of the optic axes and the acute bisectrix are approximately normal to one of the twinning planes and the light passes through more than one member of the twin, then the interference figure observed is a composite of the figures in the members of the twins. In general, this will result in a lessening of the apparent optic axial angle. The same is true of apparent double refraction. The production of twinning as a result of inversion is not a new phenomenon. It is cited by LE CHATELIER ("The Constitution of Hydraulic Mortars", McGraw-Hill Book Co., New York, 1905, p. 53) and has been assumed by some to be the cause of complex twinning in Microcline."

Replying to Dr. BRANDENBERGER, BROWNMILLER believes that any experimental evidence confirming the existence of oxygen polyhedra surrounding calcium cations in silicate liquids at high temperatures certainly must be evaluated in a complete theory for the constitution of such liquids. The existence of such groups would introduce a new conception in the theory of the ultimate structure of glasses as presented in the Am. J. Sci., 1938, (5) 35, 241.

The work reported in that paper did not attempt to reveal the ultimate structure of the liquid but proceeded with a review of certain theories which undoubtedly will have to be altered in the light of new evidence. The experimental work reported there was interpreted as showing that the ions or groups of ions did not agglomerate directly on cooling to the form of the equilibrium compounds but passed through an intermediate state of definite orientation, of indefinite, but limited, composition. A variation of the amount of certain cations in the composition did not alter the structure as revealed by the X-ray so that the interpretation of an oxygen framework with the other ions within this lattice, seemed logical.

The existence of calcium ions at the centers of oxygen polyhedra as proposed by Dr. BRANDENBERGER would not change the interpretation of the new experimental work in that paper, but would supplement the review of the theory of the constitution of liquids and glasses, and on the basis of confirmed experiments should have been included in the theoretical discussion.

The needle-like crystals of $3CaO \cdot SiO_2$ described by Professor EITEL are a form which we have never observed in commercial clinker and in only one investigation with synthetic preparations. DYCKERHOFF had, however, observed a needle-like form of $3CaO \cdot SiO_2$ in some commercial clinkers and found it in mixtures of CaO, Al_2O_3 and SiO_2 which had been heated in an oxyhydrogen flame. By use of this method we have obtained $3CaO \cdot SiO_2$ in this form in the primary phase region of both the system $CaO\text{-}Al_2O_3\text{-}SiO_2$ and the system $CaO\text{-}Fe_2O_3\text{-}SiO_2$. (J. Phys. Chem., 1927, 31, 607; Portland Cement Association Fellowship Paper No. 6). It is interesting that Professor EITEL has now found this form in the system $CaO\text{-}CaF_2\text{-}SiO_2$.

Dr. FRANKLIN has referred to a determination of the glass content of clinkers from heat-of-solution data on the clinker under the three conditions—quenched, as received, and fully annealed. I assume that latent heat of crystallization of the liquid phase is not determined separately, nor made use of in the calculations. The principle of the two methods is substantially the same but two objections occur to me to the method suggested by Dr. Franklin. In practice, great difficulty is experienced in attaining complete freezing of the liquid phase except by the use of very small charges quenched by instantaneous submergence in mercury. Where charges of the liquid phase alone are used, it is not usually difficult to observe microscopically if the charge is completely in the glassy state but where a commercial clinker is used, the crystallization of a part of the liquid cannot easily be detected. Hence the suggested method, first, requires an additional operation, accomplished with difficulty and, second, assumes a condition of the clinker that is not easily verified and may introduce significant errors. Inasmuch as differently composed clinkers crystallize with different rapidity, it would seem probable that errors of varying magnitude would be introduced which might account for the anomalous results obtained.

I have asked Mr. Dahl to read the comments of Dr. Lea on my paper and he has given me a discussion of the technical lime limit as developed by Dr. Lea. Inasmuch as this discussion amplifies the equations of Lea, I am giving it in full below.

"Dr. Lea defines the technical lime limit by the following equation, which appeared also in Building Research Technical Paper No. 16.

$$CaO = 2.80SiO_2 + 1.18Al_2O_3 + 0.65Fe_2O_3 \ldots\ldots\ldots\ldots\ldots\ldots \quad [1]$$

This equation represents a plane in the space model of the quaternary system, passing through the C_3S- and C_4AF-points, and through the CaO, C_3S, C_3A invariant point on the $CaO\text{-}Al_2O_3\text{-}SiO_2$-phase. This invariant point has the composition 59.7 % CaO, 32.8 % Al_2O_3, 7.5 % SiO_2.

Since the plane represented by equation [1] passes through the C_3S- and C_4AF-points, an equation for the plane expressed in terms of components of the system $C_3S\text{-}C_2S\text{-}C_3A\text{-}C_4AF$ will lack C_3S- and C_4AF-terms, representing only a relation between C_2S and C_3A. The equation may be set up readily in determinant form, as shown below:

$$\begin{vmatrix} C_3S & 100 & 0 & -34.35 \\ C_2S & 0 & 0 & 47.42 \\ C_3A & 0 & 0 & 86.93 \\ C_4AF & 0 & 100 & 0 \end{vmatrix} = 0$$

The second, third, and fourth columns of the determinant are the potential compound compositions of C_3S, C_4AF and the CaO, C_3S, C_3A invariant points. Evaluating the determinant,

$$86.93\,C_2S - 47.42C_3A = 0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad [2]$$

This equation reduces almost exactly to the equation,

$$11C_2S - 6C_3A = 0 \quad [3]$$

From equation [3] it is seen that a composition is on the plane representing Dr. LEA's technical lime limit if the potential C_2S is 6/11 of the potential C_3A, regardless of what the values of C_3S and C_4AF may be. If the C_2S is less than $6C_3A/11$, the technical lime limit is exceeded.

An expression for estimating the amount by which the lime content of a mixture falls short of the technical lime limit may be obtained by multiplying equation [3] by a factor which will make the coefficient of C_2S equal to mol. wt. CaO/mol. wt. C_2S. This factor is 0.0296. By this procedure the following equation is obtained.

$$\text{Lime deficiency} = 0.33C_2S - 0.18C_3A \quad [4]$$

Equations [2—4] are identical in significance to Dr. LEA's equation [1], provided that the C_2S is computed without allowance for free CaO. Besides being convenient to use when potential compositions are calculated for other purposes, they serve to show the fact that as the C_3A is reduced the minimum C_2S which is safe is also reduced. Thus in low C_3A-compositions a higher C_3S may be secured without passing the technical lime limit than in high C_3A-compositions."

I hasten to correct the impression gained by Dr. FORSÉN that we regard the principal questions on the constitution of Portland cement clinker as settled. On the contrary, we feel that, through the painstaking investigations of FORSÉN, of LEA and PARKER, and others who have been interested in the state of equilibrium attained in commercial clinker, we are for the first time provided with some of the basic data by which we may now extend our research to include the glassy phase. But at the outset it is apparent that the new problems presented require new technique and new methods of approach. The polished section petrography is in process of development and the difficult study must be undertaken (and is now under way) on the course of crystallization in the cement systems. The phase relations of the alkalies must be determined.

But at every stage in the process I feel that it is both permissible and desirable that we examine our results by methods of mathematical and statistical analysis and compare such theoretical findings with observed phases and properties. By so doing we uncover new leads which show the direction of required further study and note the progress that is being made towards the ultimate goal of precise predictability and predetermination of behavior.

There is something to be said in favor of Dr. FORSÉN's suggestion that the old nomenclature for the phases of cement be retained. Personally, however, I feel that the chemical names are to be preferred even though the phases referred to are not pure. If generally recognized mineral names for these compounds were used, there could be no objection, as Periclase to designate free magnesia. But no one unfamiliar with the early cement literature would have any idea what was meant by alite, belite, etc. and, unless these terms were defined chemically in each paper used, they would be confusing to the uninitiated reader.

X-RAYS AND CEMENT CHEMISTRY[1]

BY

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Introduction.

The theme indicated by "X-Rays and Cement Chemistry" contrasts a method of investigation with a field of research. It may be said to deal, therefore, perhaps just as much with the methodical research into the assistance given by X-rays to the investigation of cement, as with the results achieved up to now by this method in cement chemistry. Under present circumstances it is of course the description of results that are of major interest. These results, therefore, comprise the principal part of this report. But as the amount of positive knowledge at our disposal is only slight in comparison with what still remains to be discovered, and a further penetration into this unexplored territory is in part only possible by means of improved methods, a little epilogue has been added which will deal with a few of these standpoints.

Results of X-Ray Research in Cement Compounds and their Hydrates.

The aim of X-ray research in cement chemistry is, above all, the complete explanation of the structure of cement compounds and their relationship to the entire physico-chemical procedure. As an introduction into the process of thought underlying structure-chemistry a few fundamental principles may be briefly outlined.

Fundamental Principles of Crystal Chemistry.

The fundamental principles of crystal chemistry (18) have been deduced from very numerous experiments dealing with the volume of ions in crystal lattice. It was found that the volume of the individual ions was relatively a

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[1] Translated from German.

constant one, represented by the contents of spheres of action which, for the separate ions, were derived from simple series of crystallized compounds. Nearly all simple structures could be explained, or predicted, as the closest packing of ionic particles, having regard at the same time to a favourable saturation of the cation and anion charges, for all the lattice points in question. The tendency towards closest packing with simultaneous valence saturation is responsible for the fact that every cation surrounds itself with a definite number of anions in a definite configuration, and vice-versa, this configuration depending upon the radius-ratio of the cations and anions. That is to say, for a certain kind of anion, every cation has a definite number of co-ordinated anions, which are grouped around them always in an identical, or very nearly identical, geometrical configuration. As the first approach one may deduce this configuration from the fact that practically all anions are in contact with one another and with the cation. If we confine ourselves only to oxygen compounds, we find the co-ordination number 3 applies, in the case of very small cations for instance to boron with the ionic-radius 0.2 Å or C, also with 0.2 Å, with the cation situated in the middle of a plane anion triangle. For somewhat larger cations, for instance Be (I. R. = 0.34 Å; Si = 0.39 Å; S = 0.3 Å), as well as for Al with 0.57 Å, the co-ordination number 4, with the grouping of the anions in the form of a regular tetrahedron around the cation applies. For still larger cations Mg, Ti, Fe, with a I. R. of 0.6—0.8 Å the octahedron surrounding is preferred (co-ordination number 6), whereas for cations which in their extension approach the anion itself (O= 0.82 Å), for instance Ca 1.06 Å, surroundings result with the co-ordination number 8 and more. Stress must be laid here on two things. The first is that with a rising co-ordination number the co-ordination force grows less; in complicated structures the surrounding of the larger cations is often far removed from its ideal form, which may be best illustrated by explaining that, given the same charge, the attracting and directing forces of a large cation on its anion surrounding are less than those of a small cation. The second fact is that the frontiers between the different co-ordination-groups are not sharply defined; there are a number of cations whose ionic-radius is transitory and which sometimes appear in the group with the smaller co-ordination number and sometimes in that with the larger. To these belong Mg, and, in particular, Al.

Let us now examine the gathering of such polyhedrons to a space lattice. It is of course understood that only in the rarest cases here does the co-ordination number tally completely with the stoichiometric ratio of the cations to the anions. Therefore, a crystal lattice cannot be created merely by the juxtaposition of co-ordination polyhedrons. There must ensue a kind of "condensation" of these polyhedrons with a resultant formation of bridges, in such a manner that several polyhedrons together possess common oxygen atoms (bridge oxygen). For instance, if we examine the silicates, we find them characterized by the Si-ion with its strong co-ordination force and a resultant tetrahedral co-ordination, without exception. A Si:O-relationship of the metasilicates (disregarding for the moment the cations present beside Si) can only materialize if every SiO_4-tetrahedron possesses two free corners and two in common with others; half of the oxygen atoms are bridge oxygen. In the orthosilicates the SiO_4-groups make an appearance as independent radicals; these structures contain no bridge oxygens.

With the silicates, we have already arrived at those compounds which contain two kinds of cations. Here we can find an important differentiation. As already mentioned, the co-ordination power of the large cations is considerably less than that of the small cations. A comparison of the systematically varied series of structures reveals that for the composition of a structure in the first place the small high-charged cation is decisive, while the big cations with lesser charges serve in the first place only to fill up cavities and to saturate electric valencies. We will describe the small cations, in particular therefore silicium and aluminium as cations of the first category, and the large (alkali etc.) ions as cations of the second category, or, according to BRANDENBERGER (5) the first as active and the second as inactive cations. Of course this division is not inflexible; sometimes the same ion can function as active and sometimes as inactive. A very good example of a structure with active and inactive cations is the Perovskite (3), a structure to which $3CaO \cdot Al_2O_3$, so important to cement chemistry, belongs, to which reference will be made later. Cations of the first category are here the Ti-ions which in 6 co-ordinations of oxygen are surrounded by octahedrons; every oxygen is a bridge oxygen and belongs to two Ti-ions.[1] For the saturation of the charge the cations of the second category (Ca^{++}) have been introduced in the cavities between the TiO_6-octahedrons. That these cations of the second category are fairly unimportant to the structure may be gauged from the fact that they may partly or wholly be dispensed with if there is some other means of saturating the electric charges. This occurs in Na-W-bronzes belonging to the perovskite type merely by substituting five-valency wolfram by six-valency, according to the suppression of Na-ions, until the combination attains the $NaO \cdot 3WO_3$. In the case of rheniumoxide ReO_3 (38) whose ReO_6-octahedron net-work is electrically neutral through the six-valency of the rhenium, the inactive cation of the second category can be dispensed with altogether; the oxide crystallizes in spite of it in the perovskite type!

We have arrived at the supposition that the compounds of this kind are to be regarded as packings of oxygen-polyhedrons, in which the fundamental structure in the first place is derived from the striving after co-ordina-

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[1] See also FIG. 1 a.

tion of the cations of the first category and the stoichiometric relation of the cations of the first category to anions of the first category, while cations and anions of the second category are used for the saturation of surplus valencies, but only in the second place, and only in a negative sense, by reason of their repulsive power when they co-operate in a lattice construction.

Crystal Chemistry of Cement Compounds.

General Observations.

The cement compounds are in general so complicated in their stoichiometric composition and symmetry that any prediction of their structure deduced from the general principles just laid down is not possible. We are dependent upon exact experimental investigations which take a good single-crystal material for granted. This has not yet been possible to obtain, owing to the different melting-points of many of these materials, or too large a number of germs, or other reasons. In spite of this, there is sufficient experimental data based upon some important combinations which warrant closer discussion. We can, therefore, even if we approach our subject to a certain degree from a speculative standpoint, debate the question of what makes the cement compounds appear structurally remarkable at the outset and what it is possible to say in this respect even without special knowledge of the individual structures.

The characteristic feature of the cement compounds, possessed by all of them, even if in a different manner and different strength, is their ability to react with water and to harden. This instability where water is concerned must be conditioned already in the crystal formation, since in the last analysis every quality of any solid material is to be explained by its atomic construction.

BRANDENBERGER (5) who was the first to concern himself with this problem, propounded the hypothesis that this instability as regards water was connected with the dual part played by calcium. We have already seen that the calcium ion is normally embedded as a cation of the second category (perovskite lattice). At a high temperature, though, beside this inactive interstratification, the active manifestation of calcium as a co-ordinating centre is also possible. We can quote as an extreme example of this the combination $(Ca \cdot SiO_4)Na_2$ (38), when the Ca-ion is said to possess a surrounding of 4 oxygen ions only, instead of the normal 8- and 12-fold co-ordinations (4). Quite apart from this question, whether the co-ordination number of 4 for calcium as indicated in this case is the right one or not (35), we must suspect in general that with a higher temperature the tendency to a lower co-ordination number and therefore to a "more active" manifestation really does exist. Thermal oscillations tend to create a perceptible rising of the ionic-radius; if the elongations of oxygen are greater than those of the heavy cations a shifting of the radius-ratio may ensue, in the sense that a lower co-ordination number would prove more stable. The co-ordinations that resulted at a high temperature are unstable at a lower one. This might become manifest in a polymorphic transformation —that is to say, the compound without the addition of any further medium has become substituted by a modification more stable at a lower temperature.

Besides this transformation in a homogeneous phase there is still the possibility of a heterogeneous transformation through contact with another phase, such as water. By drawing new particles from this medium (OH-groups, H_2O-molecules) the stable co-ordinations of the lower temperatures can be achieved.

We can thus gain some idea, if not a strictly scientific one, of why just the lime silicates and lime aluminates formed at very high temperatures are capable of reacting with water. The active manifestation of the lime as a cation of the first category at a high temperature is not in accordance with the co-ordination claims of this ion at room temperature. The groupings formed at a high temperature are, in so far as they contain active lime, unstable, and undergo either polymorphic transformations, or split hydrolytically on contact with water and are changed into stable lime silicate, lime aluminate, or lime alumo-silicate hydrates with inactive calcium ions.

These two kinds of transformation into a condition stable at the lower temperature are particularly apparent in dicalcium silicate. The two very similar modifications α and β, both formed and both stable at a high temperature, obviously contain the calcium ion in an active form. This is particularly apparent from the fact of their both being closely packed, which composition has in this case been attained at the cost of considerable distortions of the individual groups and the lowest symmetry. The relatively close packing is recognizable in particular by the low volumes available per oxygen atom ($c = 21.8$ Å^3) and from the light refractivity (1.717—1.733). It is significant that on account of the $Si:O = 1:4$ relationship the co-ordination of the Ca-ion must consist of oxygen ions which have already been completely claimed for the formation of the Si-co-ordination; the two high temperature modifications of C_2S are formed, so to say, from a rivalry of the two effective cations of the first category in connection with the formation of a polyhedron association. The formation thus created is unstable at room temperature. Only two things can happen; either there must ensue the technically undesirable spontaneous *transformation into the γ-C_2S, in* which case by producing a considerably looser packing (Vol. per O atom = 23.9 Å^3!) the Ca manifestly passes over from the rôle of a cation of the first category to that of a cation of the second category and the compound no longer possesses any reacting qualities, or it can—and this is the technically desirable process—on contact with the mixing-water result in a hydrolysis followed by the formation of a stable hydrate with inactive calcium ions.

Conditions are somewhat different in the case of C_3S, the most essential compound for Portland cement. Although we do not yet know its structure, we are able to assume from the stoichiometric composition ($Si : O = 1 : 5$) of the constantly confirmed validity of the co-ordination number 4 for silicium that oxygen atoms which are only co-ordinated with the Ca must exist in this structure. It is clear, that the calcium forms an active co-ordination centre with a few, probably 6, oxygen ions, of which one part has combined with silicium but another only with calcium. In this lies the reason for the reactivity.

Stress need not be laid upon the fact that beside the lime co-ordination there might be other reasons for the instability and hydrolysis of a compound. One must remember that aluminium (39) can also appear in two forms of co-ordination (4 and 6). It is the aim of the following exposition to test by the structures already examined how far this hypothesis of the unstable co-ordinations, in particular this hypothesis of the "active" lime, is actually applicable.

Special Structures of Cement Compounds.

$3CaO \cdot Al_2O_3$, (C_3A).

The tricalcium aluminate is the quickest reacting of all cement compounds. For this reason, therefore, the "activity" of lime, viewed structurally, must be most clearly apparent.

The first comprehensive X-ray examination of C_3A was made by STEELE and DAVEY (50). They declared after investigations based on powder diagrams, the unit cell length to be 7.624 Å and the space-group to be O_h^1; $Pm3m$. Their cell is characterized by AlO_6-octahedrons and in plane AlO_4-groups (squares). Of the Ca-ions contained in the cell one is situated without an anion envelope in the immediate vicinity of other cations while in the middle of the cell an O_6-octahedron is without a central cation. The result of this disposition is an extraordinarily bad electrical valency saturation, which makes the structure appear impossible for this reason alone. The structure proposition of STEELE and DAVEY met with lively criticism; HERMANN (23) made a noteworthy suggestion for improvement. According to this the 6 oxygen ions situated in the middle of the cell must be removed and grouped with the Ca-ions found in the corner of the cell. This measure alone makes the valency saturation considerably better even if atom distances still appear unusual and the remaining planary quadratic configuration around the one category of Al-ions seems rather impossible.

The direction taken by a final improvement of the old STEELE—DAVEY-structure propositions emerged first from the new measurement of lattice dimensions made by WESTGREN, LAGERQVIST and WALLMARK (32) according to which the length of the unit should not be given as 7.624 Å, but twice this figure, namely 15.22 Å. In our Institute a direct single crystal investigation of C_3A was made by A. EITEL and the present writer, which, however, was not carried out on C_3A itself but on the isomorphic tristrontium aluminate and essential results of which may already be touched upon here. By melting tristrontium aluminate single crystals were prepared from the resultant compound which was recognizable as such by the assistance of LAUE-diagrams, and could be used for further diagrams. It was gathered from the LAUE-diagrams that the X-ray symmetry of this compound belongs to the symmetry group

$$T_h.$$

A rotation diagram confirmed the unit length of 15.79 Å diagnosed by WESTGREN and his collaborators from the powder diagrams. SCHIEBOLD—SAUTER-diagrams of the equator (100) were also made, on which the two planes of symmetry of the symmetry group T_h were also plainly recognizable. Of the space-groups of the two classes in question, T and T_h, all except the groups

$$T_h^6,\ T^4 \text{ and } T^1 \text{ and } T_h^1$$

could be definitely excluded.

It appears at first to be fairly hopeless to try and localize the 264 atoms present in the unit cell of these space-groups of the lowest cubic symmetry. In spite of this we made an attempt at an approximate localization since we had made a chance observation that indicated the broad outlines of the structure. In the course of working with Perovskite we ascertained that the main spectral lines of C_3A are extraordinarily like those of Perovskite as regards position and intensity; according to these signs the atomic position in both cases should display a similar striking likeness. Since the improvement proposed by HERMANN indicated a structure that is directly derived from the perovskite structure, we attempted, by applying the suggestions of HERMANN to the new unit cell and space-group to achieve as exhaustive sta ructure explanation as possible. The space-group T_h^6 was used as a foundation, as this

1 a.

1 b.

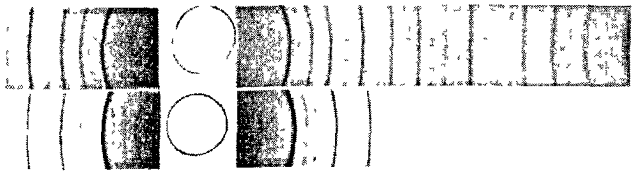

FIG. 1 a. Perovskite. 1 b. $3CaO \cdot Al_2O_3$.

seemed to accord best with the extinction laws based upon the SCHIEBOLD—SAUTER-diagrams. The same structure with slight deformations materializes as well in the space-group T^4 or in the trigonal sub-groups C_{3i}^2 and C_3^2.

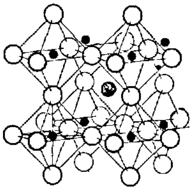

FIG. 2 a. Perovskite.

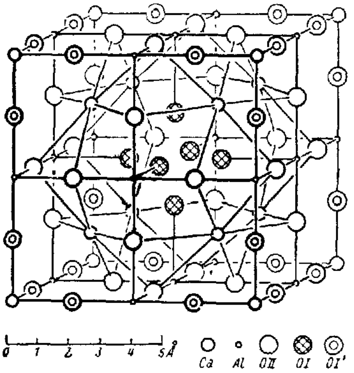

FIG. 2 b. $3CaO \cdot Al_2O_3$ ($^1/_8$ of the unit cell).

The structure is derived from the perovskite structure by quadrupling the original unit length of 3.8 Å and removing all the Al-atoms situated in the corners and in the centre of the cube with half the unit cell (Vol. = $^1/_8$), to which must be added the 48 oxygen atoms which were grouped round the Ti-atoms in the middle of this cube.[1] In these eight positions the structure displays larger cavities. The group of AlO_6-octahedra,[2] which have been transformed by the abolition of the 48 oxygen atoms into planary AlO_4-squares have been deformed into flat tetrahedra. The place in the corners of the cube $^1/_8$ left vacant by the suppression of the Ti have been occupied by Ca.

The structure is therefore to be described as a polyhedron-net-work of AlO_4-, AlO_6- and CaO_6-groups, in which further Ca-ions are embedded as cations of the second category. The surface of contact of the individual polyhedra is such that octahedra and tetrahedra are only in contact at the corners, and every oxygen bridge ion belongs either to one octahedron and tetrahedron or to two different octahedra.

The Ca embedded in the place of Al has the co-ordination number 6 and is, since it is substituted for Al, to be described as "active" Ca. The remaining Ca is, however, close by, not "active" in an incomplete co-ordination, since it is lying, so to say, in oxygen baskets which are open on one side, namely towards the centre of the cube. The co-ordination number is 6, though if the somewhat further removed oxygen atoms are included it is 9. The AlO_4-tetrahedra must also be regarded as unstable factors of the structure; they display unusually large spaces.

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[1] In FIG. 2 b the oxygen-atoms OI.
[2] In FIG. 2 b the oxygen-atoms OII.

Table 1. Analogy between Perovskite, C_3A, C_8NA, C_2F, and C_4AF.

Oxide Formula	Gross Formula	Symm.	a (Å)
$CaO \cdot TiO_2$	$Ca_8 \quad Ti_8^{VI} \quad O_{24}$	O_h	3.8
$3CaO \cdot Al_2O_3$	$Ca_8 \ (Ca^{IV}Al_6^{IV, VI}) \ O_{18}$	T_h	$4 \cdot 3.8$
$8CaO \cdot Na_2O \cdot Al_2O_3$	$Ca_8 \ (Na_2^{VI}Al_8^{IV, VI}) \ O_{18}$	C_3 ?	$4 \cdot 3.8$?
$2CaO \cdot Fe_2O_3$	$Ca_8 \ (Fe_4^{IV}Fe_4^{VI}) \ O_{20}$	V_h	$\sqrt{2} \cdot 3.8$
$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	$Ca_8 \ (Fe_4^{IV}Al_4^{VI}) \ O_{20}$	V_h	$\sqrt{2} \cdot 3.8$

We are enabled to understand the reactivity of the combination structurally 1. owing to the presence of "active" lime with adjoining octahedra, and 2. the presence of large holes which are bounded by incomplete co-ordinations of the remaining lime- as well as the tetrahedric Al-ions.

The Compound $8CaO \cdot Na_2O \cdot 3Al_2O_3$.

After discussing C_3A, the compound discovered by BROWNMILLER and BOGUE (8) $8CaO \cdot Na_2O \cdot 3Al_2O_3$ next occupies our attention, as this is possibly the carrier of the alkali found in cement compounds. Although this compound has not yet been individually investigated, a plausible theory of its structure can already be propounded on the data given by BROWNMILLER and BOGUE. We can gather from the DEBYE—SCHERRER-diagrams supplied by these authors that the compound structurally completely resembles C_3A. This is easy to understand from the structure of C_3A if we presume that an Na is substituted for Ca, which in C_3A possesses the 6 co-ordination, while the other comes into the cavities of the structure (middle of the cube).

The lattice is obviously distorted to trigonal symmetry owing to the Na-ions in the middle of the cubes (the holes of the C_3A-lattice) trying to obtain a suitable co-ordination. Whether the space-groups C_{3i}^2 or C_3^2, the sub-groups of the space-groups T_h^6 of C_3A materialize can only be ascertained by an accurate single-crystal investigation of the compound in which the structure hypothesis mentioned above must be tested in detail.[1]

$12CaO \cdot 7Al_2O_3$, ("$5CaO \cdot 3Al_2O_3$").

BÜSSEM and EITEL (10) have prepared a complete structural analysis of this compound. It was derived, from melting the composition 5 : 3, single

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[1] Attention must be called here to the work of LERCH and BROWNMILLER (33) who derived a composition with perovskite lines from a glass free from alumina. There obviously exists a ferrite (silicate?) with a perovskite structure.

crystals allotted the unit cell dimensions of 11.95 Å. The Laue-symmetry of the compound is the cubic-holoedric, the probable space-group T_d^6. The density of the substance was examined again, and found to be 2.69, less than is usually given. As this density does not permit of a whole number of molecules being calculated per unit cell by the formula C_5A_3, this cannot be used; but a whole number can be calculated very accurately according to the formula $C_{12}A_7$ ($z = 2.00$), which can be used as bases for the true composition of the further analysis.

The lattice presents a spatial net-work of AlO_4-tetrahedra, partially connected by bridge-oxygen atoms. Bridge oxygens are 48 to 64 (66) O-atoms. The tetrahedra round 16 Al are distorted to pyramids, the tetrahedra round 12 Al to bi-sphenoids. The Ca-ion has the co-ordination number 6; the 6 oxygen atoms again form a species of basket which opens into the open cavities in the structure of position 12 *b*.

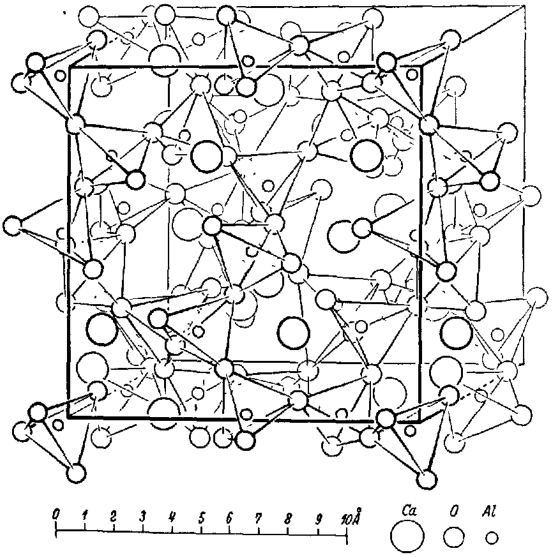

Fig. 3. 12 CaO · $7Al_2O_3$, (C_5A_3).

The structure has a strong analogy to lime-alumina-garnet and to tricalcium aluminate hexahydrate (see below).

The lime cannot be regarded as "active" although it possesses the co-ordination number 6; the unsymmetrical one-sided oxygen surrounding (basket) must be considered as the unstable factor. This, as in C_3A, is open towards the structure cavities.

Westgren and his collaborators (32) have discussed the question as to whether another formula instead of $C_{12}A_7$ might not be possible. They have

Table 2. Analogy between Garnet, C_3AH_6 and $C_{12}A_7$.

Oxide Formula	Gross Formula	Symm.	a (Å)
$3CaO \cdot Al_2O_3 \cdot 3SiO_2$	$Ca_{12}\ (Si^{IV}_{12}\,Al^{VI}_8)\ O_{48}$	O_h	11.83
$3CaO \cdot Al_2O_3 \cdot 6H_2O$	$Ca_{12}\ Al^{VI}_8\ (OH)_{48}$	O_h	12.55
$12CaO \cdot 7Al_2O_3$	$Ca_{12}\ (Al^{IV}_6\,Al^{IV}_8)\ O_{33}$	T_d	11.95

debated whether the two oxygen atoms statistically disposed over the cell can be omitted, so that an oxygen number compatible with the space-grouping 64 could be obtained. In this case there must be $1^1/_3$ aluminium atoms per cell statistically omitted as well, so that the gross composition of the compound would now be 9:5. Although the theoretical possibility of such a defective structure must in no way be dismissed, many reasons can be brought forward against this theory: 1. With the formula C_9A_5 there is a density of 2.62 g/cm³. The departure from the experimental density of 2.69 is considerable. The supposition of WESTGREN and his colleagues that the preparations of BÜSSEM and EITEL, of which they determined the density, might still contain appreciable quantities of glass, is improbable. The combination crystallizes very well and an extremely quick cooling is necessary to maintain it glassy. It is practically impossible that the given density of 2.69 could have been falsified owing to the presence of glass (with the density of 2.87). 2. The composition 9 : 5 is almost exactly the same as that given by American research workers (46) for the eutectic composition C_5A_3-C_3A. It would be very strange if the compound had been so inaccurately determined that a minimum melting-point should have been discovered exactly at the point where in reality the maximum lies. 3. The eutectic composition (9 : 5) has been subjected to X-ray examination by ourselves several times, and the existence of two phases has always been distinctly visible. 4. According to THORVALDSON and GRACE (54) the thermic decomposition of tricalcium aluminate hexahydrate isolates lime and this maximally at 26.6 %. This is based upon the reaction

$$3(3CaO \cdot Al_2O_3 \cdot 6H_2O) \rightarrow 5CaO \cdot 3Al_2O_3 + 4CaO + 18H_2O.$$

But according to this 27.67 % CaO must ensue. This discrepancy does not exist if, instead of C_5A_3, the composition $C_{12}A_7$ is assumed.

$$7(3CaO \cdot Al_2O_3 \cdot 6H_2O) \rightarrow 12CaO \cdot 7Al_2O_3 + 9CaO + 42H_2O.$$

According to this reaction the maximum 26.9 % CaO must appear, which accords very well with the 26.6 % obtained. This finally excludes the composition 9 : 5.

$CaO \cdot 2Al_2O_3$, ("$3CaO \cdot 5Al_2O_3$").

This compound, which, according to SOLACOLU (47) is responsible for the reaction and hardening of the alumina cements of the second category, has, like 5 : 3, a different composition from that originally credited to it in the system. WESTGREN and his collaborators (32) analysed it lately, with the result that in single crystals the monoclinic symmetry of the space-group was C_{2h}^6 or C_s^4. The unit cell is characterized by the following values: $a = 12.82$ Å; $b = 8.84$ Å; $c = 5.42$ Å; $\beta = 107.8°$. For the formula 3 : 5 the density would be 1.82, whereas the experimental density is 2.90 g/cm³. With the formula 1 : 2, on the other hand, the result is $s = 2.78$, and this accords considerably better with the experimental value. As proof of the composition 1 : 2, it must be indicated more particularly that it was only when this was used that the preparations were homogeneous when examined by X-ray. It may also be mentioned here, that TAVAŞCI, using another method (52), at the same time made the existence of the compound 1 : 2 appear probable.

The prospect of a further structural explanation of the combination 1 : 2 has been held out by the Swedish investigators: they point out that there is perhaps a certain likeness to the Diopside $Si_2O_6Mg^{VI}Ca^{VIII}$, although here the deviation of the stoichiometric combination would present difficulties. Moreover the *a*-axis is very different from that of the Diopside (12.82 against 9.71 Å). Before further investigations have been carried out nothing can as yet be said about the presence of "active" lime in the structure.

Gehlenite, $2CaO \cdot Al_2O_3 \cdot SiO_2$.

Gehlenite is an ingredient of aluminous cement of the second category (according to SOLACOLU) but it differs from the compounds analysed up to now in not reacting with water. This is all the more interesting because, as will be shown later, it presents a hydratic compound of the composition $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot xH_2O$, which is the most important result of the chemical reactions in the quaternary system CaO-SiO_2-Al_2O_3-H_2O. Gehlenite must therefore be distinguished by an atomic structure which, in contrast to the compounds already described, presents a very stable configuration in respect to water and, according to BRANDENBERGER, contains lime in an inactive form. This is actually the case.

The structure investigation of Gehlenite was made by RAAZ (42). He isolated single crystals and determined tetragonal symmetry. The unit cell is determined by the edge lengths, $a = 7.69$ Å and $c = 5.10$ Å. Space-grouping V_d^3.

The lattice is characterized by a two-dimensional net-work of SiO_4- and AlO_4-tetrahedra which with the corners are connected by bridge oxygens forming slightly curved layers. The layers are held together in a space lattice by Ca-ions. The co-ordination number of the Ca-ion is 8!

In complete accordance with the BRANDENBERGER hypothesis of "active" lime it can be established that in this compound the lime actually does exist in "inactive" form, *i. e.* in 8 co-ordination. Viewed structurally, therefore, the lack of reaction in Gehlenite must be put down to this fact.

$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, ($C_4AF$).

The compound was identified by X-ray for the first time by HANSEN, BROWNMILLER and BOGUE (21), later on by SOLACOLU (48), a single-crystal investigation has been made by BÜSSEM (11). This was carried out on small laminar single crystals formed in melting, in which the rhombic symmetry was definitely determined by LAUE-diagrams. The unit cell was analysed by rotary diagrams: $a = 5.34$ Å; $b = 14.44$ Å; $c = 5.52$ Å. The unit cell is therefore pseudo-tetragonal with the *ac*-plane as basis plane. The probable space-group is V_h^{28} Imma. The unit cell contains 2 molecules $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. The lattice, like that of C_3A, can be characterized as a three-dimensional net-work of octahedra and tetrahedra. A rhombic layer of FeO_4-tetrahedra, which in the *a*-direction are one-dimensionally connected with one another, is above and below connected by oxygen bridges with a tetragonal layer of AlO_6-octahedra at a distance of $^1/_4$ *b*. The Ca-ions are situated between the octahedric and the tetrahedric layers; they possess an incomplete co-ordination of 6 O-atoms and somewhat farther away another 4 O-atoms.

This compound, which reacts with water, displays again an incomplete and unsymmetrical co-ordination of only 6 direct anions of contact; the CaO_6-polyhedron is open again towards the cavities of the structure (which are situated in the Fe-layer); the unusual Ca- and Fe-co-ordination is in all probability the structural reason for the reactivity.

The compound is able to form, with the $2CaO \cdot Fe_2O_3$ an unbroken series of mixed crystal; this occurs simply by substituting for the Al-ions in the layers with $b = 0$ and $b = {}^1/_2$ Fe-ions. As a result of this, the octahedra having been enlarged by the bigger iron-ion and the adjoining FeO_4-tetrahedrons connected by bridge oxygen having consequently become just as enlarged, space strains ensue, which manifest themselves in a relative instability of this combination in comparison with C_4AF. The same strains would follow, if all the iron of the C_2F were exchanged. The $2CaO \cdot Al_2O_3$ as final member of the series of mixed crystals emanating from C_2F is in any case not stable. A slight Al-embedding in the C_4AF-lattice is possible (36).

The combination mentioned by HANSEN and BROWNMILLER (22), $4CaO \cdot 2MgO \cdot Al_2O_3 \cdot Fe_2O_3$ does not exist; this does away with the mixing possibilities to C_2F and C_4AF, which would have been, to this extent, difficult to understand. On the other hand, a slight intraposition of magnesia, such as SCHWIETE and ZUR STRASSEN (45) have found maximally at 2 % is very plausible; the structure has still enough room in the Fe-layer to make such an intraposition possible without change of lattice. From the fact that this intraposition must take place in the iron layer we are able to explain why the MgO-embedding to the given extent brings about a change of colour of the C_4AF from yellow-brown to olive-green, which indeed greatly influences the colour of the cement compound. The strongly polarizable Fe-ion becomes involved in the unsymmetrical Mg- and O-intraposition, which takes place in its immediate vicinity and thus leads to the change of colour.

$3CaO \cdot SiO_2$, (C_3S).

There is, unfortunately, as yet no definite X-ray data on the most important compound for Portland cement, the C_3S. A few general crystal-chemical observations pertaining to it have already been made in our introduction. Besides very numerous identifications by the DEBYE—SCHERRER-method, there are two single-crystal descriptions made by GUTTMANN and GILLE (20) and ANDERSON and LEE (1) in which at least the unit cell and the symmetry have been approximately determined. The C_3S, according to these results, possesses a hexagonal or pseudo-hexagonal unit cell of the size $a_h = 7$ Å and $c = 25.0$ Å. A further space-group and structure analysis is still to be made.

An attempt has been made by some investigators to analyse the immixing in the C_3S-lattice in regard to both quality and quantity. In analyses up to the present SCHWIETE and BÜSSEM (44) discovered the possibility of introducing of a slight amount of C_3A (maximally 4 %) in solid solution. The latter problem has been attacked again lately by JANDER and WUHRER (27). They found that in the course of the reaction of the C_3S-formation from $CaCO_3$ and kaolin the C_3A originally formed was strongly absorbed by the C_3S in process of formation, and this to a greater degree than the research of SCHWIETE and BÜSSEM had led them to expect.

The same investigators are studying the C_3S-formation from $CaCO_3$ and C_2S. They have made the interesting observation that the C_3S in process of formation is in an "active" state which is made manifest by a lattice expansion. They attribute this lattice expansion to the compound possessing a lime deficiency, so that it might be possible to speak of a formation of solid solutions between C_3S and C_2S (40, 15)—though only in connection with these active states. In accordance with this SOLACOLU (49) assumes, on the basis of X-ray examination, a mixed crystal formation of this kind, but with the lattice of the C_2S above 1 900° when such "active" conditions occur as well ("Meta-alite").

$2CaO \cdot SiO_2$, (C_2S).

We know least about the three calcium orthosilicates. The reason for this is that these three compounds are of very low symmetry and that it seems practically impossible to obtain single crystals of them. The two high-temperature modifications at which one might possibly obtain crystals of larger size from the melt disintegrate at room temperature, and this all the more quickly the bigger they are. But the γ-C_2S, on the other hand, is practically only obtainable when the high temperature modifications have been reached, so that here, too, the prospects are very slight. The most likely possibility is to obtain big enough crystals of one kind or the other from the ternary or polynary systems and to stabilize them. The general observations on this subject that without special knowledge it is possible to make have been made in our introduction; we can add here that a relationship of calcium orthosilicate to Rhenanite has lately been ascertained by Schleede, based on its similarity to the Debye—Scherrer-diagrams. Perhaps by these means the production of single crystals may be successful and with them the structure problem be solved.

According to an observation made by zur Strassen, which I owe to him personally, a similarity exists as well between the β-C_2S and the Merwinite, $3MgO \cdot CaO \cdot 2SiO_2$.

X-Ray Characteristics of the Lime-Alumina-Silica-Ironoxide-Hydrates.

Calcium Hydroxide and Alumina Hydrates.

Just as important as is the structure of cement compounds for the process of reactivity is the structure of the hydrates and hydroxides formed by the wetting for the process of hardening. Unfortunately, our knowledge of this does not go very far, principally because here again the compounds in question can not easily be obtained in single crystals which are absolutely necessary for a conclusive X-ray analysis.

$Ca(OH)_2$.

This compound, which has been known for a long time (34), crystallizes in the hexagonal space-group D^3_{3d} with the lengths of unit $a = 3.58$ Å and $c = 5.03$ Å. The lattice must be regarded as a hexagonal maximally close packing of the OH-group with Ca embedded, or according to polyhedron conceptions as an agglomerate of $Ca(OH)_6$-octahedra, in which each OH-group belongs to 3 octahedra and the octahedra are arranged in plane layers.

Hydrargillite, $Al(OH)_3$.

The Hydrargillite (Gibbsite) crystallizes (37) in the monoclinic space-group C^5_{2h}-$P_{2_1/n}$. The lengths of unit are: $a = 8.6236$ Å; $b = 5.0602$ Å; $c = 9.699$ Å; $\beta = 85°26'$. All the atoms are to be found in the general position. The oxygen atoms again form a, certainly distorted, very close hexagonal packing, in which the Al-ions are embedded. In polyhedron terms the lattice is built up of $Al(OH)_6$-octahedra which are arranged in parallel layers (001); every octahedron has one side in common with its neighbouring octahedron. Every OH-group belongs therefore to two $AlOH_6$-octahedra.

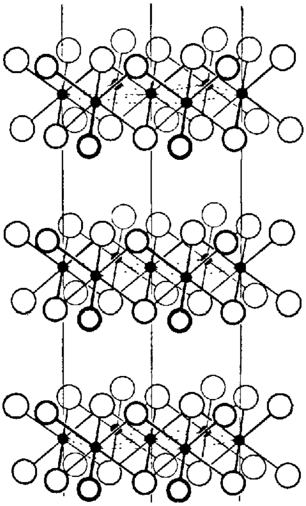

FIG. 4. $Ca(OH)_2$.

Diaspor, AlOOH.

Diaspor crystallizes (13) in the rhombic space-group $D^{16}_{2h}Pbnm$. The axes' lengths are $a = 4.40$ Å; $b = 9.38$ Å, and $c = 2.83$ Å. In this lattice, also the OH- or O-ions form the closest hexagonal packing with the Al-ions situated in their octahedric spaces. Of the twelve sides of every octahedron four are common to every two octahedra; this results in a chain of particularly closely knit octahedra in the c-direction. Every O- or OH-ion belongs to three octahedra.

Besides these alumina hydrates there exist the modifications Böhmite, Bayerite and other compounds which yet lack a definite X-ray characterization.

Calcium Aluminate Hydrates.

$Ca_3\,[Al\,(OH)_6]_2$.

The compound crystallizes on analogy with the calcium-aluminium-garnets in the cubic space-group $O^{10}_h Ia3d$; it arises from these if the Si-ions are omitted and the O-atoms substituted by OH-groups. The spatial radical union of the SiO_4- and the AlO_6-groups is dissolved by the removal of the Si-atoms so that in this structure the $Al(OH)_6$-groups appear as free radicals, which are held together by the Ca-ions embedded as cations of the second category. The lattice constant according to THORVALDSON, VIGFUSSON and GRACE (55) is 12.576 Å, according to KÖBERICH (30) 15.542 Å, and according to BRANDENBERGER 15.56 Å (6).

In connection with the structure defined by BRANDENBERGER, whose exact parameter values are not yet available in detail, it is interesting to go into particulars of the results of THORVALDSON and GRACE (54) regarding the dehydration of this compound. THORVALDSON and GRACE found that the compound first begins to loose its water at a relatively high temperature, that the dehydration then proceeds to a hydration degree of about $1.5H_2O$, during which period according to the EMLEY-method no free lime occurs. If the temperature be increased, so that the last $1.5H_2O$ are released as well, free lime appears to an extent that leads to the conclusion of the combination 12 : 7 (see above). These results have been absolutely confirmed by KÖBERICH (30), who used the eudiotensimetrical method. KÖBERICH discovered two completely different dehydration territories: a zeolithic dehydration whose static steam tension at 200° lies between 45 mm for $6H_2O$ and 4 mm for $1.8H_2O$. All the products of this dehydration area absorb the dehydrated water again down to the hexahydrate within a short period of time (*e.g.* 3 days for 16.5 mm for H_2O). The second dehydration area is found between 1.8 and 0 mol. H_2O; it is characterized by very small disintegrating steam tensions, which only attain the height of 45 mm at 390°. The disintegration is irreversible; free lime appears; in a steam-atmosphere of 16.5 mm there is no re-formation of the hexahydrates. The dehydration products formed in the first dehydration area were subjected to X-ray tests; they display the original lattice type, which has, however, undergone big disturbance. The lattice constant diminishes in proportion to the dehydration and at $3.75H_2O$ attains the value of 12.37 Å, and at $1.5H_2O$ the value of 11.94 Å.

How is one to imagine the dehydration while the structure is retained? We have ventured to suppose that a transformation of the $Al(OH)_6$-groups into $Al(OH)_4$- and AlO_4-groups takes place. If one assumes this, one obtains a hydrate $3CaO \cdot Al_2O_3 \cdot 2H_2O$, which is in very close accordance with the degree of about $1.8H_2O$ to be ascertained from the KÖBERICH curves.

Hydrocalumite, $4CaO \cdot Al_2O_3 \cdot 12H_2O$.

The compound crystallizes according to TILLEY, MEGAW and HEY (57) in the monoclinic space-group $C_2^2P2_1$ with $a = 9.6$ Å; $b = 11.4$ Å; $c = 16.84$ Å; $\beta = 69°$. Number of molecules in the cell = 4. A structure is suggested in which Ca occurs in 6-co-ordination, Al in 4- or 6-co-ordination.

The Hexagonal Calcium Aluminate Hydrates.

THORVALDSON, GRACE and VIGFUSSON (55) have studied the $3CaO \cdot Al_2O_3 \cdot 8H_2O$ prepared at low temperatures and belonging to the hexagonal system for X-ray examination, and using the HULL-method they found the following lattice constants: $a_{hex} = 5.711$ Å; $c_{hex} = 6.453$ Å. With this cell, however, the number of molecules in the cell = 1.5, so that the authors suggest that the c-axis should be doubled. This would make the number of molecules in the cell $= 3$, the calculated X-ray density $= 2.07$ as opposed to an experimental density of 2.13. The higher hydrates are, when examined by X-ray, very similar to 8-hydrate.

SALMONI (43) gave the X-ray characteristic of dicalcium aluminate hydrates as $5\text{-}9H_2O$, as $3H_2O$ and $1H_2O$. The hydrate degrees of 5, 7, and $9H_2O$ are very alike in their X-ray pictures, also the 1- and 3-hydrates are mutually somewhat alike, too, while the group of the 5-9-hydrates is markedly dissimilar from the 1-3-hydrates.

A comprehensive study of composition, degree of stability, and X-ray characteristics of all calcium aluminate hydrates has been made by ASSARSSON (2). He found the following, mostly hexagonal or pseudo-hexagonal combinations:

$5CaO \cdot Al_2O_3 \cdot 34H_2O$
$4CaO \cdot Al_2O_3 \cdot 14H_2O$ (α)
$4CaO \cdot Al_2O_3 \cdot 14H_2O$ (β)
$4CaO \cdot Al_2O_3 \cdot 12H_2O$
$3CaO \cdot Al_2O_3 \cdot 12$ (?) H_2O
$2CaO \cdot Al_2O_3 \cdot 9H_2O$
$CaO \cdot Al_2O_3 \cdot 10H_2O$

To these must be added $Ca(OH)_2$, the cubic $3CaO \cdot Al_2O_3 \cdot 6H_2O$, and four different aluminium hydrates, among them obviously Hydrargillite, Bayerite, and two unknown hydrates.

All the calcium aluminates of the hexagonal type have a certain family likeness. This led BRANDENBERGER (6) to the hypothesis that all hexagonal calcium aluminates might be built up from hexagonal $Ca(OH)_2$- and $Al(OH)_3$-layers, which, according to the description given above, does not appear impossible, since both have a sphere packing of maximum density of the OH-groups. The lattice constants certainly differ individually very strongly from one another so that only a complicated coalescing mechanism comes into the question. The principle of the growth in layers built up of alternating simple strata is often met with in nature; one needs only recall the Chondrodite (53) formation where through alternating coalescence of Brucite and Olivine layers the composition and structure of four minerals can be explained. The clay minerals offer an important example of this. In these Hydrargillite layers of $Al(OH)_6$ and SiO_4-tetrahedric layers are knitted together either on one side (kaolinite type) or on both sides (montmorillonite type). Through this the structure and stoichiometric composition are determined (Kaolinite $Al_2O_3 : SiO_2 = 1 : 2$; Montmorillonite $Al_2O_3 : SiO_2 = 1 : 4$). The BRANDENBERGER hypothesis appears thus to be a likely one. The hydrates would therefore have to be designated by the formula

$$m\mathrm{Ca(OH)_2} \cdot n\mathrm{Al(OH)_3} \cdot p\mathrm{H_2O}$$

in which case p represents the number of the H_2O-molecules escaping at over 100°. For instance, $2CaO \cdot Al_2O_3 \cdot 5H_2O$ would have $m = 1$, $n = 1$, $p = 0$. Hydrates of the C_2A under 5, such as the 3- and 1-hydrates according to SALMONI could not be built up according to this principle of construction.

Calcium Silicate Hydrates.

The calcium silicate hydrates possess a special interest as the final production of the hardening reaction of Portland cement.

Regarding those combinations which occur in nature reference must be made to the studies of DOELTER (14) and VIGFUSSON (58). The X-ray characteristics of Hillebrandite and Foshagite will also be found there. The native conditions of the very numerous compounds and their identity with the synthetic ones discovered in the laboratories or in the hydration of Portland cement have by no means been established.

A unit-cell analysis has hitherto only been made by GOTTFRIED on natural Afwillite (19). This gives the unit lengths of the mineral monoclinic as $a = 11.39$ Å; $b = 5.47$ Å; $c = 13.09$ Å; $\beta = 98°26'$, density: 2.630. Number of molecules in the unit body = 4. The extinctions indicate very strongly the holohedric space-grouping C_{2h}^5 5, but the space-group $C_2^2 P2_1$ is assumed on account of the piezo-electrical proof.

Xonotlite has been prepared by hydrothermal methods followed by X-ray identification in comparison with a well defined natural product. The synthesis was performed by NAGAI (41) from the hydrothermal treatment of a mixture of one part CaO with one part SiO_2 at 180°—200°. As comparative product, a mineral from Tetela de Xonotla in Mexico was used containing 49.02 % SiO_2, 0.47 % Al_2O_3, 0.11 % Fe_2O_3, 44.77 % CaO, 0.2 % MgO, 0.08 % K_2O, 0.18 % Na_2O, 0.58 % MnO, 0.40 % CO_2 and 3.99 %H_2O (theor. 46.5CaO, 49.8SiO_2, 3.7H_2O). Fräulein Dr. M. BENDIG was kind enough to carry out the analysis. Synthetic and natural products were proved identical according to the photographs made by our Institute.

The tests made by NAGAI, beginning with the proportions 2 : 1 (experimental numbers 17 and 10), which according to his statements were to consist chiefly of Afwillite, resulted in X-ray diagrams which approached very closely a compound $2CaO \cdot SiO_2 \cdot H_2O$ first identified by VIGFUSSON, BATES and Thorvaldson. It must be noted that these investigators published optical data, which agreed almost completely with those for Afwillite.

$n_\alpha = 1.614$, $n_\beta = 1.620$, $n_\gamma = 1.633$, $2V = 68°$

For Afwillite $n_\alpha = 1.617$, $n_\beta = 1.620$, $n_\gamma = 1.634$, $2V = 55°$

As the identification of the products of Nagai took place microscopically the results of Nagai are completely to be understood. But after the combination $2CaO \cdot SiO_2 \cdot H_2O$ has been satisfactorily isolated and identified by Vigfusson, Bates and Thorvaldson, Nagai's results must be so interpreted that in the hydrothermal synthesis with a mixture proportion $CaO : SiO_2 = 2:1$ a dicalcium silicate monohydrate actually appears, which is not identical with Afwillite. The striking identity of the optical data for Afwillite and dicalcium silicate monohydrate must be carefully noted in later analyses. The Nagai product 40, beginning with mixture proportions 3:1 to 5:1, which, according to his own opinions contains Hillebrandite, resulted in an X-ray picture poor in line, whose eight lines can be identified with the Hillebrandite diagram given by Vigfusson (58). On the whole, the Nagai experiments may be so interpreted that, with a mixture proportion $CaO : SiO_2 = 1:1$ at 180°—200° Xonotlite, with mixture proportions of 3:2 to 2:1 the dicalcium silicate monohydrate similar to Afwillite, and with mixture proportions of 3:1 to 5:1 Hillebrandite or the compound reported by Vigfusson, Bates and Thorvaldson as similar to Hillebrandite, results.

Köhler (31) has re-examined the experiments of Nagai. The formation of Xonotlite from $CaO : SiO_2$-mixtures in the proportion 1:1 at temperatures of 150°—290° has been confirmed by chemical analyses and microscopic examination. The X-ray diagrams given by Köhler accord fairly closely with the diagram of Xonotlite.

Köhler does not agree with Nagai with regard to the other results as he obtains from mixtures of $CaO : SiO_2$ reaction products higher than 1:1 which he can not identify as Afwillite or Hillebrandite. He prefers to call the formation from $CaO : SiO_2$ (quartz) $= 2:1$ at 290° a monocalcium silicate hydrate, which is said to agree with that which is formed from the proportions 1:1. When he takes gel as the original substance he obtains other results which he cannot identify further. From dicalcium silicate and tricalcium silicate he obtains by hydrothermal methods the formation of Hillebrandite.

Of late, Mlle Foret (17) has studied these hydrothermal syntheses and again obtained different results. First she analysed the mixtures with the initial proportions 1:1. She found two differing crystalline formations according to whether she was working under 140° or over 140°. The product obtained under 140° she identified by X-ray with the monocalcium silicate hydrate produced by Chassevent (see below) at room temperature, whereas the formations at a higher temperature prove to be a crystalline monocalcium hydrate which, according to the X-ray diagram, is obviously identical with Xonotlite. All the investigators up to now (Nagai, Köhler, and Foret) agree therefore that, with an initial mixture of $CaO : SiO_2 = 1 : 1$ in a hydrothermal synthesis between 140°—290°, a silicate hydrate results corresponding to the natural Xonotlite.

In another experiment (17) Mlle Foret used other initial mixtures. At temperatures below 130° she obtained a mixture of calcium hydroxide and the "monocalcium silicate hydrate" of Chassevent. At temperatures above 130° no free lime can be found chemically but in spite of this she obtained from this product an X-ray diagram corresponding to the β-monocalcium silicate hydrate (Xonotlite). As regards the mixing proportions 2 : 1 (quartz) this fact accords with the results of Köhler. Mlle Foret prepares di-, tri- and tetracalcium silicate hydrates which all give the same X-ray diagram. It need not be stressed that such combinations are very difficult to imagine with variable lime-and variable water-content. Vigfusson, Bates and Thorvaldson found in the study already mentioned (59) that, from CaO + silica gel in mol. proportions 4 : 1 at 170°, a dicalcium silicate of $1.34\text{-}1.5H_2O$ is obtained whose X-ray diagrams are like those of Hillebrandite, but really different from it.

Under the same conditions from saturated lime-water and quartz as well as from Portland cement mortar a compound resulted that differed only slightly in the composition but gave in the structure a completely different hydrate $2CaO \cdot SiO_2 \cdot 1.14\text{-}1.25H_2O$.

Strätling (51) obtained by hydrothermal treatment of the dicalcium silicate a dicalcium silicate hydrate with $1.03H_2O$ whose X-ray characteristics are in complete accordance with the hydrothermal products of Vigfusson, Bates and Thorvaldson.

A new dicalcium silicate with $1H_2O$ has been described by Keevil and Thorvaldson (29); it is very different both from the natural mineral Hillebrandite and the two other hydrates already described. This hydrate displays the peculiarity that, while maintaining its structure, it may obviously be dehydrated to the content of 0.3 mol. H_2O when the refraction index diminishes slightly; when heated to 900° this compound is transformed like the two others into β-dicalcium silicate.

The important fact is established, therefore, that four dicalcium silicate hydrates exist with one molecule of water, each different in their structure, whose origins have not been fully explained. The results up to now serve to indicate, however, that these four combinations are only formed under hydrothermal conditions.

Keevil and Thorvaldson have produced by hydrothermal methods a tricalcium silicate hydrate with 1.3—2 molecules of water. This compound differs in its construction completely from the four dicalcium silicates. In this compound the splitting up is remarkable; when heated to 900° it disintegrates into free lime and dicalcium silicate, which indicates clearly the instability of the tricalcium silicate at this temperature.

If a hydrolysis of the tricalcium silicate can take place, it is not the hydrate $C_3S \cdot 2H_2O$ that is formed, but calcium hydroxide and dicalcium silicate monohydrate. This was obviously the case in the experiments by Köhler, who in his hydrothermal treatment of C_3S carried out X-ray observations of the formation of Hillebrandite.

The experiments described up to now confine themselves entirely to hydrothermal formations, the knowledge of which is important for theoretical and practical reasons (steam-hardening). With regard to the products formed at room temperature which correspond to the actual conditions of normal hydration, it was assumed formerly that in the reaction of lime with silica or silica gel only amorphous gel-like products originated to which the formula $3CaO \cdot 2SiO_2 \cdot xH_2O$ was generally attributed. Several new experiments have shown, however, that this opinion was false.

Chassevent (12) demonstrated that precipitations derived from the admixture of lime and silica solutions provided X-ray diagrams after only two hours. On the ground of former experiments by Jolibois and Chassevent (28), this crystalline product is called by Chassevent a monocalcium silicate hydrate. The composition of the precipitations after being kept some time with a lime surplus is a lime: SiO_2-proportion of 3 : 2.

Strätling (51) carried out experiments of this kind with precipitations of silica and CaO (initial mol. proportion $CaO : SiO_2 = 2 : 1$) which in the course of a few months at 20° resulted quantitatively in the compound $3CaO \cdot 2SiO_2 \cdot xH_2O$, which gave rise to a defined X-ray spectrum, though with broadened lines. The compounds made by Chassevent and by Strätling when examined by X-ray are so similar to these that they must have the same basic structure. According to the experiments carried out by Strätling the compound must be regarded as a 3 : 2-silicate, which corresponds with the investigations of Thorvaldson and Vigfusson (56) who came to a similar conclusion owing to the splitting-up of C_3S and C_2S, which they describe as the compound richest possible in lime with a statically saturated lime solution. It is satisfactory that there should exist a 1 : 1-hydrate structurally related to the 3:2-hydrate since the hydrolysis curves of Thorvaldson and Vigfusson indicate the existence of such a compound.

Strätling demonstrated that the compound designated by him as 3 : 2 appears as a new formation if normal Portland cement is shaken up with water. The light voluminous products are automatically separated from the dark components. The X-ray diagram indicated the presence of the 5 characteristic lines of the compound 3 : 2.

Later on BRANDENBERGER (7) carried out a similar separation of new formed compounds in a shaken-up Portland cement and came to a like conclusion. The combination 3 : 2 (or according to CHASSEVENT 1 : 1) is therefore the most important crystalline hardening product of Portland cement.

Calcium Alumo-Silicate Hydrates.

The interest taken in natural and synthetic pozzolanas gave rise to the question as to whether the reaction of lime, silicium dioxide, alumina and water always leads to calcium silicate hydrates and calcium alumina hydrates or whether or not calcium alumo-silicate hydrates might not also exist. The work of STRÄTLING (51) has given proof that as a quaternary compound in the system CaO-SiO_2-Al_2O_3-H_2O, the compound $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot xH_2O$, does indeed exist. This compound ensues, for instance together with the 3:2-hydrate mentioned above at the reaction of lime-water with dehydrated kaolin and also when C_3S and C_3A are precipitated in water. The compound does not result through the reaction of Gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$) with water as Gehlenite does not directly react with water (no active lime) although there is a hydrate of the same composition. The circumstances here are the same as those in Wollastonite, which does not react directly, although there are corresponding hydrates.

In the same way the compound does not arise from dicalcium silicate hydrate if this, together with $3CaO \cdot Al_2O_3 \cdot 6H_2O$ is precipitated in water.

It is probable that in the reaction of Portland cement with water this compound is formed as well; experiments made up to now could not confirm this supposition as the combination was obviously not formed in either shape or quantity so as to be apparent by X-ray.

Lime Ferrite Hydrates.

The most important compound is that of $3CaO \cdot Fe_2O_3 \cdot 6H_2O$, isomorphic to the compound $3CaO \cdot Al_2O_3 \cdot 6H_2O$, which was discovered by EIGER (16). Lattice constants $a = 12.71$ Å; X-ray density 2.790. The dehydration process of the compound corresponds again entirely to the $3CaO \cdot Al_2O_3 \cdot 6H_2O$, the 2-hydrate degree is distinctly outlined.

Whether a series of mixed crystals exists with the aluminate has not yet been investigated. HOFFMANN (24) has described two tetracalcium ferrite hydrates with 14 or 7 water as possible compounds of which the latter compound displays similarities to the $3CaO \cdot Fe_2O_3 \cdot 6H_2O$. The often suspected compound $CaO \cdot Fe_2O_3 \cdot xH_2O$ has not yet been found by X-ray work.

Methodical Improvements of the X-Ray Process.

The solution of many of the problems left open to debate in the preceding exposition will tax the X-ray methods to their highest degree of efficiency. There are a number of problems which up to now appear either unsolvable, or only solvable with insufficient precision; it is only necessary to mention the problem of the proof of hydratic new formations in slight concentration, the problem of "active" conditions and the problem of the slight solubility of crystalline compounds.

The possibilities of increasing the efficiency of X-ray methods lie, as far as is to be seen to-day, in two directions. Firstly, there must be an improvement in the precision of linear measurement. A number of good precision processes have been developed to this end; for cement investigation the processes above all to be considered are those which enable the first lines to be calculated with great precision. Cement compounds, and in particular their hydrates, very often only possess lines with small reflecting angles and, therefore, those precision processes based upon the lines with large reflecting angles ("Rückstrahlverfahren") are not of great importance. The most suitable procedures appear to be those which give very sharp lines with a small exposure; these are in particular the focussing processes according to Seeman—Bohlin and Brentano. It is superfluous to say that such an improved diagram, which would be expressed in the lowering of the line-breadth measured in degrees is also suitable for the separation of the line systems of crystals of lower symmetry in compounds (C_3S+C_2S).

The second possibility of improvement in X-ray methods lies in an increase of the precision with which the *intensity* of the X-ray lines can be registered and measured. One of the principal defects of the X-ray method is often said to be its lack of sensitiveness; this sensitivity leaves much to be desired when small quantities are to be looked for. As an improvement in this respect is greatly to be desired, the possibilities of compassing it will be briefly examined.

We may take it for granted that the X-ray lines of a crystal compound will appear, in connection with a certain procedure with a certain relative intensity; every line has its maximal value if the crystal compound is present to the extent of a hundred per cent. If the content of a crystal compound be lessened, the intensity of all lines will lessen in proportion to the percentage. The weaker lines sink farther and farther below the surface of vision, in small percentages only the heaviest line is just recognizable. (Test limit.) Brownmiller and Bogue (9) gave the following limits for cement compound tests: C_3S 8 %, β-C_2S 15 %, C_3A 6 %, C_4AF 15 %, MgO 2.5 %, CaO 2.5 %.

The test limit of the last line depends upon the intensity ratio of this line to its background (contrast) in which the transition is also lost sight of. It is characteristic of the X-ray interference process that the background scattering is relatively strong in comparison with the line scattering. If one considers a spot of the background near to the interference line, all the atoms of the irradiated body are assisting towards this intensity with all the wave-lengths contained in the primary beams (to which must be added fluorescence and COMPTON-radiation) whereas only the atoms belonging to the crystal in the reflecting position contribute to the interference line rising above the background and then only with one single wave-length. If one imagines the contents of the crystal compound in question to be decreased bit by bit, the intensity of the associated interference line will diminish equally, but the intensity of the background remains constant because in the place of the atoms removed from the crystal other substances appear which adopt their background scattering. By constantly decreasing line intensity and an approximately constant background, the contrast soon attains the test limit $L : U \sim 0.05$,[1] at which even under the most favourable physiological conditions (blackening-in of the background $S = \sim 1.0$) the line can no longer be deciphered with certainty. It is to be seen from this that the proof of any compound present in a sample may be calculated in advance from a diagram of the pure substance. If x is the percentual content of a substance in a sample and $a_{100\%}$ the intensity ratio of the line intensity : background for the 100 % substance, a_{min} the $L : U$-ratio-limit, then the proof limit is:

$$X_{min}\,\% = \frac{a_{min} \cdot 100}{a_{100\%}}\,\%;\ (a_{min} \sim 0.05).$$

In highest radiating cubic substances the highest value $a_{100\%} \sim 5$; therefore ~ 1 % can still be proved. With reference to this relationship the way in which sensitiveness may be increased can be considered. As the numerator a_{min} is physiologically limited the demonstrability of a crystal compound can only be rendered more favourable by increasing the denominator. If we consider this more closely we find the value for line intensity not very capable of being influenced. Something might be accomplished by decreasing the temperature and lowering the heat vibrations which, however, is not very efficacious with the compounds in question, as they are analysed very far below their melting-point. It is clear, moreover, that only the background U is able of being strongly influenced. The background radiation is very complex; it contains: 1. the monochromatic coherent scattering part of the substance under consideration. Besides this it contains: 2. the monochromatic scattering part of the by-substances, 3. the polychromatic part of the principal substance, 4. the polychromatic part of the by-substances (to which may be added, the air in the room, the edges of the slit, substance of the apparatus, etc.), and further 5. the fluorescence radiation of all the parts, 6. the COMPTON-radiation. The possibilities of

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[1] L is the intensity of the X-ray line, U the intensity of the background under the line.

a decrease of the background are therefore as follows: 1. the use of a strictly monochromatic X-ray light by reflection in a crystal (*e. g.* NaCl). This measure is the most important as, by this, besides parts 3 and 4, part 5 can be strongly reduced as well as part 6. As a further measure the use of vacuum chambers, good shutter construction and an elimination of all superfluous holders etc.

It will be useful to enumerate clearly the success which these measures might have, and the sacrifices they entail. Let us suppose then that it has been possible to reduce the background scattering by a third. Now, a compound with an L/U-value of $a_{100\,\%} = 3$ under normal circumstances will obtain an L/U-value of 9. Whereas normally only about 1.7 % is demonstrable, another 0.6 % can now be demonstrated. In the normal procedure an exposure of 20 *min.* was necessary so that line and background created the blackening 1 (in 100 % substance). But if the percentual content is reduced by 0.6 %, the line intensity diminishes to the 150th part; it is therefore negligible in comparison with the background, which, it is assumed, shall remain stable without monochromatization. Through the monochromatization then, the background will be reduced to a third part and at the same time the exposure raised by the factor 6 as of course the primary intensity of the monochromator is about six times smaller. Altogether, then, the exposure must be $4 \cdot 3 \cdot 6 = 72$ times, that is to say, 24 hours, so that L and U create the blackening 1.

It is seen, therefore, that the problem of increasing the sensitivity of the X-ray process depends very much upon the development of X-ray technics. The practical materialization of any such improvements necessitates stronger X-ray tubes and more sensitive films.

Summary.

1. The report contains introductory remarks concerning the co-ordination principle as basic and order principle of crystal chemistry. A description is given of the Brandenberger hypothesis according to which the active co-ordination of the Ca^{++}-ion at high temperatures is the cause of the reactivity of cement compounds.

2. In a detailed examination of the already studied cement compound structures (C_3A, $C_{12}A_7$, C_4AF, C_2AS), this principle has been several times confirmed, as well as other structural factors (cavities) are recognized as the cause of reactivity.

3. The construction principles of hydrates, as far as is known, have been briefly described. In most of the compounds the X-ray analysis is still in its first stage: the attempt at a completely satisfactory identification. The lime-silica-hydrates are still highly debatable. Besides their bad crystallizing capacity the salient fact is to be reckoned with that these compounds obviously

possess a complicated principle of construction. This leads to chemically different bodies presenting an identical X-ray diagram.

4. In conclusion, certain suggestions have been offered which might lead to an improvement in the accuracy and sensitiveness of the X-ray analysis.

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Fig. 2a has been taken from (5)
» 2b » » » » (23)
» 3 » » » » (10)
» 4 » » » » (5).

Discussion.

Mr. G. E. Bessey:[1]

Some work is being carried out at the Building Research Station on the structure, as determined by X-ray, of the hydrated calcium silicates and aluminates. Whilst insufficient experimental data is as yet available to put forward any detailed structures some classification of the aluminates and the related double salts may be attempted from the available X-ray data and a consideration of the properties of these compounds.

The suggested classification is shown in Table 1.

Table 1. Classification of Calcium Aluminates by Crystal Form and Structure.

I. Cubic Group	$Ca_3Al_2(OH)_{12}$	Garnet structure. Relatively inactive and stable.
II. Hexagonal or Pseudo-hexagonal Group (plate habit).	(a) $Ca_4Al_2(OH)_{14} \cdot 6H_2O \cdot$ $\cdot Ca_4Al_2(OH)_{12} \cdot R'' \cdot xH_2O$ where $R'' = SO_4$, CO_3 $x = 5 - 7$ $Ca_4Al_2(OH)_{12} \cdot R'_2 \cdot yH_2O$ where $R' = Cl$, NO_3, etc. $y = 2 - 4$	Layer structure. Rather unstable.
	(b) $Ca_3Al_2(OH)_{12} \cdot 6H_2O$ (c) $Ca_2Al_2(OH)_{10} \cdot 3H_2O$ (d) $CaAl_2(OH)_8 \cdot 6H_2O$	Layer structure. More unstable than group II a.
III. Hexagonal or Lower Symmetry Group (needle habit).	$Ca_3Al_2(OH)_{12} \cdot 12H_2O$ $Ca_5Al_2(OH)_{16} \cdot 24H_2O$ $Ca_6Al_2(OH)_{12} \cdot R''_3 \cdot 24H_2O$. where $R'' = SO_4$, CrO_4, CO_3, etc.	No structure suggested, but probably all related. Varying in stability.

The tricalcium aluminate hexahydrate is the only compound with cubic symmetry; the garnet structure suggested by Brandenberger gives reasonable values for intensities of the observed lines when parameters very close to those for calcium garnet are assumed. The stability and relative inactivity of this compound are in agreement with its structure.

The group of compounds having hexagonal or pseudo-hexagonal symmetry, with a hexagonal plate crystal habit, is a large one. Apart from the examination

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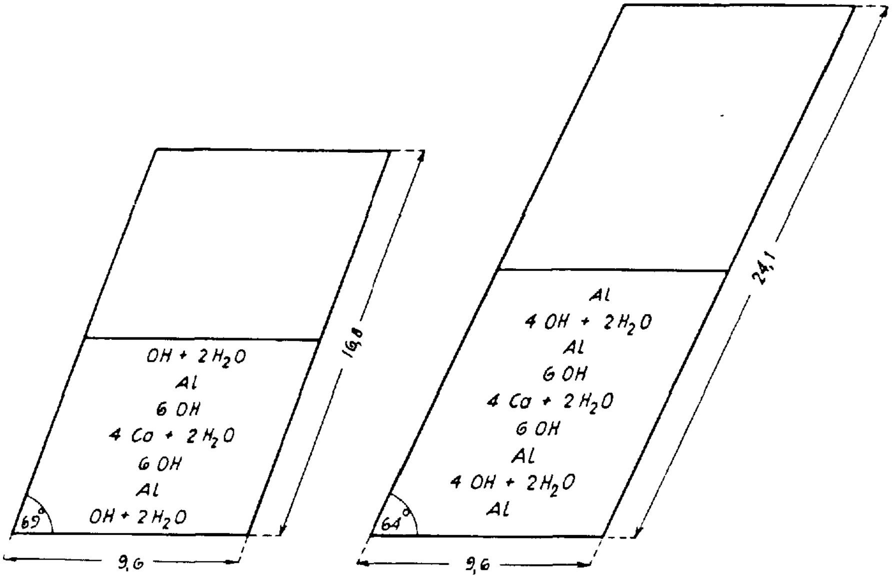
of the natural compound Hydrocalumite by TILLEY, MEGAW and HEY (2), only powder patterns have so far been obtained on any of this group. These compounds show, however, a marked resemblance which, taken in conjunction with their similarity in optical properties and their similarly limited stability, suggests closely similar structures.

The structure suggested for Hydrocalumite ($4CaO \cdot Al_2O_3 \cdot 13H_2O$) whilst admittedly only tentative, may, in default of evidence to the contrary be considered as probably correct. Attempts have been made by the present writer to relate the structures of the other compounds of this group to that given by TILLEY, MEGAW and HEY; the structures derived are hypothetical, but if an approximation to the structures can be found which fits available X-ray data, and conforms to the known physico-chemical properties, the results may be of some assistance in the interpretation of the relationships between the various compounds, and provide some basis for further investigation.



A. $Ca_4Al_2(OH)_{14} \cdot 6H_2O$.
¼ Unit cell. (1 Molecule)

B. $Ca_2Al_2(OH)_{10} \cdot 3H_2O$.
¼ Unit cell. (2 Molecules.)

FIG. 1. Projection in (010) Plane showing Approximate Arrangements suggested for Tetracalcium and Dicalcium Aluminate Hydrates.

One example of the possible structures derived may be given here. The dicalcium compound $Ca_2Al_2(OH)_{10} \cdot 3H_2O$ is one of the more metastable compounds in the system $CaO\text{-}Al_2O_3\text{-}H_2O$; in contact with its saturated solution in water it is converted to the tetracalcium compound without recrystallization or change in crystal form, but with liberation of hydrated alumina. In contact with solutions of higher lime concentration it is converted to the similar tri- or tetracalcium compounds, again without disturbance of the existing crystals. The general structure of the natural tetracalcium compound, according to TILLEY and MEGAW, is shown in FIG. 1 A, which represents a pseudo-quarter cell based on the pseudo-halvings for *hkl* (k odd, very weak, $h + \frac{k}{2}$ odd, very weak) and *hol* (h or l odd, very weak).

The cell dimensions are given as:

$$a = 9.6 \qquad b = 11.4 \qquad c = 16.84 \qquad \beta = 69^\circ,$$

with 4 molecules to the unit cell.

A simple method of deriving the dicalcium compound from the given tetracalcium compound, with the minimum of modification of the structure, is shown in FIG. 1 B. The only changes in the pseudo-quarter cell are the completion of the two half layers ($OH + 2H_2O$) at positions 0 and 1 to give the six group ($4OH + 2H_2O$) required for the full layer, and the introduction of two Al-atoms between each new pair of ($4OH + 2H_2O$)-layers. This gives the quarter cell with two molecules of $Ca_2Al_2(OH)_{10} \cdot 3H_2O$.

The conversion of the two half layers to two full layers at positions 0 and 1 must necessarily involve an increase in the value of c by something probably greater than $^1/_4$ c of the original cell. The increase in c would therefore probably be about 5—6 Å, giving a new value of c of about 22—24 Å. The introduction of further layers with only weakly electropositive Al-atoms between may also tend to increase the lateral a- and b-dimensions of the cell very slightly and would tend, according to PAULING's rule, to make the compound relatively unstable, as it indeed is.

Only powder diffraction patterns are available for the dicalcium compound. An attempt has been made to fit the simpler planes of a cell of the form indicated to the stronger lines of the observed powder patterns for this compound, and an approximate fit has been obtained with the cell dimensions.

$$a = 9.65 \qquad b = 11.6 \qquad c = 24.1 \qquad \beta = 64^\circ.$$

The volume of this cell would be 2 420 Å^3. The observed density of $Ca_2Al_2(OH)_{10} \cdot 3H_2O$ is 1.95, whence the molecular volume is 303 Å^3. Eight molecules required for the above cell according to the structure suggested would occupy 2 424 Å^3, in agreement with the value above.

The calculated spacings for the (*hoo*), (*oko*), and (*ool*) planes are given in TABLE 2 together with the observed lines and intensities according to three independent observations. No attempt has been made to fit other observed lines to the less simple planes of the lattice, as with a cell of this size the

Table 2. Observed and Calculated Spacings for $Ca_2 \cdot Al_2(OH)_{10} \cdot 3H_2O$.

Calculated		SALMONI		Observed ASSARSSON		B. R. S.	
Plane	d_{hkl}	d_{hkl}	I	d_{hkl}	I	d_{hkl}	I
001 4	5·4	5·33	s	5·44	s	5·3	s
						4·75	w
100 2	4·3					4·35	w
010 3	3·87					3·85	m
001 6	3·6			3·63	s	3·56	w
		3·42	m				
010 4	2.9)	2.86	vs	2.89	vs	2.85	vs
100 3	2.88)			2.81	m		
001 8	2.7	2.66	m	2.71	s	2.67	w
				2.57	s	2.54	m
		2.46	vs	2.50	m	2.45	m
				2.40	m		
				2.30	w	2.31	w
		2.23	vw	2.26	w		
001 10)	2.15			2.16	w		
100 4)				2.11	s	2.11	vw
				2.02	m	2.03	w
010 6	1.93	1.95	vw	1.97	s		
001 12	1.80	1.83	w	1.85	m	1.84	w
				1.78	w		
				1.74	w		
				1.71	w		
		1.65	s	1.67	vs	1.66	vs
				1.65	m		
100 6	1.60	1.62	w	1.60	s	1.58	vw
010 8	1.45	1.51	vw	1.52	w		
				1.45	m		
100 6	1.44	1.43	m	1.43	vw	1.44	w
001 16	1.35	1.36	vw	1.38	m		
				1.092	m		
001 20)	1.08	1.08	m	1.080	m	1.087	m
100 8)							

probability of finding a fit would be high and the result would have little significance.

Similar structures have been derived for other members of this group, the complex double salts being regarded as tetracalcium aluminate with the acid radicles substituted for hydroxyl, possibly by insertion in the Ca-layer with a consequent redistribution of OH- and H_2O-groups. A lower water content with those salts having two monovalent radicles than those with one bivalent radicle, as is found, would thus be expected.

The compounds of Group III, do not show any close similarity to each other in their diffraction patterns, but from their similar large water contents, crystal habits and optical properties, it seems likely that they are structurally related. No attempt has been made at structure determinations on any of the artificial compounds of this group, but the natural mineral calcium sulpho-aluminate, Ettringite, has been investigated by Bannister (1); the structure suggested is of a layer type somewhat similar to that of the compounds of Group II.

Bibliography.

1. Bannister, F. A. — Mineralogical Mag., 1936, *23* (153), 324—329.
2. Tilley, C. E., Megaw, H. D. and Hey, M. H. — Mineralogical Mag., 1934, *23* (146), 607—615.

Mr. A. Eiger:[1]

The tricalcium ferrite hydrate stated by Dr. Büssem is a compound C_3F with 6 mols. water. I came to the idea to look for this compound for two reasons. First because of the analogy of Al- and Fe-compounds, and, besides this, I thought the hydration of Brownmillerite to proceed in a somehow different way than it is usually described. My idea was, and I am very happy to have found it in Prof. Schläpfer's paper, that this reaction runs as follows:

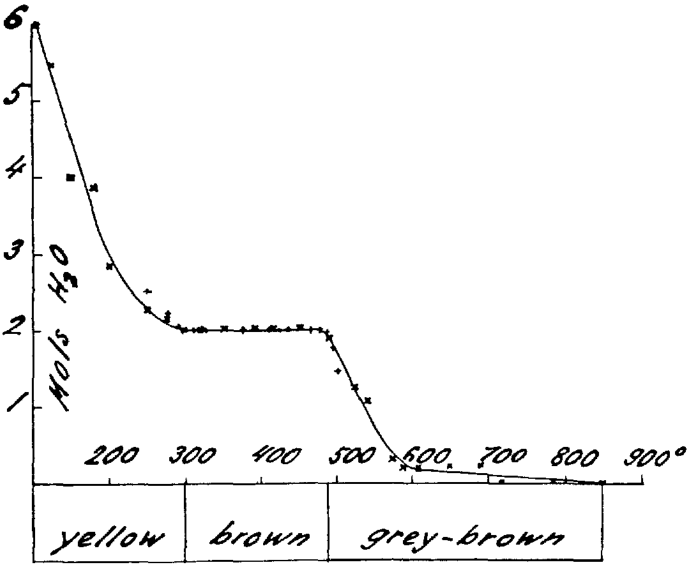


Fig. 1. Dehydration of Tricalcium Ferrite Hydrate.

$$C_4AF + 10H = C_3AH_6 + FH_3 + CH$$

then the iron hydroxide combining with hydroxide of lime from the supersaturated solution

$$FH_3 + 3CH = C_3FH_6$$

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[1] Inz. Dr. n. t., Mazowiecka 7, Warszawa, Poland.

It is evident that it is only possible for free iron hydroxide to appear in hydrated cement as it does if the reaction goes this way. The structure of C_3FH_6 has been found by Dr. LEA and Mr. BESSEY, who kindly examined this compound, to be very similar to the structure of C_3AH_6 differing fairly by the lattice constant, which is 12.71 Å—a little bit larger than the aluminate.

If we start dehydrating this compound it begins losing water about 105°, the dehydration proceeds uniformly till 300° are reached. This temperature corresponds to two mols. of H_2O, and in full analogy to C_3AH_6 a stop occurs up to about 480°.

The full process is shown on FIG. 1. The compound C_3FH_6 is stable against a lime concentration of 250 mg/l. Below this concentration it goes over in C_2FH_5 of orange colour, which is hydrolysed up to a concentration of 15 mg/l CaO. This reaction is reversible, the hydrate of dicalcium ferrite giving C_3FH_6 in saturated lime solutions in about fifteen hours, which might be a reason for C_3FH_6 existing in ordinary hydrated cement. Using large quantities of water, C_3FH_6 can be hydrolysed as to leave FH_3. When this hydroxide is acted upon with a saturated lime solution it reacts giving a silky glance, which was observed by MANN during his synthesis of C_4AH_7 starting with colloidal AH_3 and lime solutions. The ultimate product is again C_3FH_6.

The dehydrated compound shows a composition of C_3F. Dr. BRANDENBERGER, who kindly examined it by X-rays, concluded for the possibility of a cubic lattice without being able to give a definite statement due to the impurity of the sample.

The dehydrated compound is slowly decomposed by water, changing its dark-brown colour to orange. In saturated lime solution no change could be observed.

Glycol dissolves about 10 % CaO and small quantities of iron out of C_3FH_6, the dehydrated ferrite losing only about 1 % CaO, while treated with glycol.

Further researches concerning the lattice of C_3F, the presumed C_2FH_5, the reactions occurring when heating C_3F and the possibility of obtaining complex salts are under execution.

(FIG. 1 is made by Mr. J. GOTLIEB in Prof. Dr. ZAWODSKI's Institute of Inorganic Technology in Warzaw.)

Mr. E. BRANDENBERGER:[1]

Dr. BÜSSEM has pointed out some very interesting relations of the structures of certain cement compounds to the perovskite type. He has found lattice-constants, which are multiples of 3.8 Å, *i. e.* the unit length of the

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[1] Dr., Eidgenössische Technische Hochschule, Zürich, Switzerland.

perovskite cell. The distance 3.8 Å. E., however, has a more general significance: $3.8/\sqrt{2}$ is 2.7 Å, the distance of two neighbouring O-atoms. Indeed, all calcium silicates have in their X-ray diagrams strong interferences with spacings between 2.6—2.8 Å given by the diameter of an oxygen atom (2.64 Å).

Mr. T. THORVALDSON:[1]

I would like to contribute to the discussion of Dr. BÜSSEM's paper but as the hour is very late I will take time to consider only one point.

When dealing with the formula of the so-called "5:3"-calcium aluminate, Dr. BÜSSEM cites the experiments of Dr. GRACE and myself on the maximum liberation of lime from the cubic hexahydrate of tricalcium aluminate when it is dehydrated as evidence in favor of the formula $C_{12}A_7$ as against C_5A_3. When we published the results of our experiments we had no idea that our data might be used as evidence on a very important question of this type. It would therefore be well to consider critically the applicability and the probable accuracy of the data. There is the question of the purity of the original sample of tricalcium aluminate, the completeness of hydration, the completeness of dehydration, the absence of recombination of the free lime and the "5:3"-aluminate at the temperature used for dehydration and the accuracy of the determination of free lime.

As to the purity of the original sample of tricalcium aluminate, I would say that this was prepared in platinum crucibles from highly purified lime and alumina and that the final product contained no free lime and the correct ratio of lime to alumina as determined by careful analysis. The hydration was apparently complete as the theoretical amount of water was absorbed and the hydrated material was isotropic and of uniform refractive index.

The absence of error due to incompleteness of dehydration or recombination of the free lime is not so certain. By referring to our original data [THORVALDSON and GRACE, Can. J. Research, 1929 (1), 10, Table VI], it is apparent that the maximum values for free lime were obtained when the product still contained from 1.1 to 1.6 per cent water, and that when dehydration was carried further by increasing the temperature or the duration of heating, recombination apparently did occur, giving lower values for the free lime. If one were to assume that the 1.1 per cent of moisture held indicated incomplete destruction of the crystal lattice and that the formula of the compound involved is $3CaO \cdot Al_2O_3 \cdot 2H_2O$, then the value for the lime liberated should be 2.3 per cent less than the theoretical for complete decomposition. The average value obtained by dehydration between 700° and 850°, is actually only 1.3 per cent too low. It does, however, seem likely that the crystal

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[1] Professor, Phil. Dr., University of Saskatchewan, Saskatoon, Canada.

lattice is completely destroyed by 12 to 16 hours heating at 700° to 850°, and that the moisture was held by adsorption. On the other hand, there is no positive evidence that there is not some recombination of lime and "5:3"-calcium aluminate at the temperatures used, thus causing low values for free lime.

The determinations of free lime were made by the original method of LERCH and BOGUE, an equivalent weight of freshly ignited pure lime being used for standardization. The low results could hardly be attributed to a constant analytical error.

It seems to me that before one accepts the evidence as conclusive, it would be necessary to study further the effect of completeness of dehydration on the lime liberated and to exclude the possibility of recombination under the conditions used for dehydration.

Mr. W. BÜSSEM (*author's closure*):

As regards Professor THORVALDSON's remarks, I would like to say that a resumption of his and Mr. GRACE's experiments in the dehydration of C_3AH_6 would certainly be interesting; an attempt might then be made to avoid every error of the kind indicated by him, or at least to determine the magnitude of the probable errors. Apart from the analytical error in determining the amount of free lime, particular attention would, as Professor THORVALDSON himself has said, have to be given to the error arising through the free lime again combining. This error might perhaps be ascertained by determining the rapidity of the reaction $C_{12}A_7$ $(C_5A_3) + C = C_3A$ at some higher temperatures, and so it might be possible to extrapolate its lower limit or at least its order of magnitude at the temperature used for dehydrating C_3AH_6. From the results of these and similar experiments it must be decided whether the argument, which among so many other arguments has been adduced for the existence of $C_{12}A_7$, that there is a deficiency of lime in the breaking-up of C_3AH_6, can be considered conclusive.

The remarkable dehydration behaviour of C_3AH_6, first discovered by Professor THORVALDSON, moreover still offers enough unsolved problems, especially of a structural nature, to make it seem worth while again to reconsider this problem.

This also applies to the compound C_3FH_6, closely related to C_3AH_6, reported on by Mr. EIGER. What is particularly interesting is that the step in the dehydration curve comes exactly at 2 mols. H_2O, which agrees well with the description of the mechanism of the dehydration process of these compounds suggested in the paper.

I would like to underline the observation of Dr. BRANDENBERGER about the significance of the universal constant 3.8 in the perovskite series (see TABLE 1). It shows the important part played by oxygen in the building-up of all these compounds. Further, the structures mentioned are of course related to one another, not only with reference to the oxygen atoms, but also by a far-reaching analogy of the arrangement of the cations.

With reference to the interesting observations of Mr. BESSEY on the classification of the calcium aluminate hydrates, I only wish to say that his suggestions for the structural description of dicalcium aluminate hydrate are all very likely right, but will naturally have to be reexamined with regard to intensity. As this would probably at present be rather difficult, one must meanwhile be satisfied with such models. — *(Translated from German.)*

THE CALCIUM ALUMINATE AND SILICATE HYDRATES

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Introduction.

The two series of compounds considered in the present paper have been investigated by numerous workers, some forty or fifty in the case of the aluminates and for the silicates an even larger number. It is the purpose of this paper to consider the knowledge available from this large amount of work, and to attempt some explanation and classification of the results.

Both series of compounds have been studied for some years at the Building Research Station, Watford, by Dr. F. M. LEA and the present author. The main results of this work are at present being analysed and prepared for publication; certain of the results, and conclusions, are discussed in the course of the present Report and have also previously been mentioned in Annual Reports of the Building Research Board (5) during recent years.

The discussion will be limited to the two ternary systems CaO-Al_2O_3-H_2O and CaO-SiO_2-H_2O, as no data are available for the quaternary system CaO--Al_2O_3-SiO_2-H_2O.

In order to economize in space in the text, the shorthand method of using the initial letter of each oxide instead of the full formula, which is in general use for the anhydrous cement compounds, will be extended here by using H for H_2O, thus:

$$C_3AH_6 = 3CaO \cdot Al_2O_3 \cdot 6H_2O.$$
$$C_2SH = 2CaO \cdot SiO_2 \cdot H_2O.$$

Naturally Occurring Compounds.

The relatively high basicity of most of the hydrated calcium silicates and aluminates, their solubility, and the ease with which they are hydrolysed render their occurrence in nature somewhat rare.

The only recorded occurrence of a hydrated calcium aluminate is that described by TILLEY and MEGAW, in altered intrusive contact-rocks in Ireland.

Table 1. Naturally Occurring Minerals in Systems $CaO\text{-}Al_2O_3\text{-}H_2O$ and $CaO\text{-}SiO_2\text{-}H_2O$.

Mineral	Formula	Crystal System	Habit	Elongation	Refractive Indices			Optical Character	Density
					α	β	γ		
System $CaO\text{-}Al_2O_3\text{-}H_2O$									
Hydrocalumite......	$4CaO \cdot Al_2O_3 \cdot 12H_2O$	Monoclinic (Pseudo-hexagonal)	—	—	1.535	1.553	1.557	Biaxial.negative	2.15
System $CaO\text{-}SiO_2\text{-}H_2O$									
Okenite...........	$CaO \cdot 2SiO_2 \cdot 2H_2O$	Orthorhombic	Fibrous	γ	1.512	1.514	1.515	Biaxial.negative	2.28
Centrallasite........	$4CaO \cdot 7SiO_2 \cdot 5H_2O$	Orthorhombic	Fibrous	γ	1.535	—	1.549	Biaxial.negative	2.43
Gyrolite...........	$2CaO \cdot 3SiO_2 \cdot 2H_2O$	Rhomb.	Lamellar	—	1.535	—	1.545	Uniaxial.negative	2.43
Reyerite...........									
Crestmoreite........	$2CaO \cdot 2SiO_2 \cdot 3H_2O$	Monoclinic?	Fibrous	γ	1.593	1.603	1.607	? negative	2.22
Riversideite.........	$2CaO \cdot 2SiO_2 \cdot H_2O$	?	Fibrous	γ	1.595	1.600	1.603	? ?	2.64
Xonotlite..........	$5CaO \cdot 5SiO_2 \cdot H_2O$	Orthorhombic?	Fibrous	γ	1.583	1.583	1.593	Biaxial.positive	2.70
Afwillite...........	$3CaO \cdot 2SiO_2 \cdot 3H_2O$	Monoclinic	Prismatic	β	1.617	1.620	1.634	Biaxial.positive $2V = 55°$	2.63
Hillebrandite.......	$2CaO \cdot SiO_2 \cdot H_2O$	Orthorhombic	Fibrous prism.	γ	1.605	1.610	1.612	Biaxial.negative $2V = 70°$	2.69

Table 2. Artificially Prepared Compounds.

Name	Formula	Observed and reported by	Form
System CaO-Al_2O_3-H_2O			
Pentacalcium aluminate hydrate	$5CaO \cdot Al_2O_3 \cdot (34)H_2O$	Assarsson	Hex. prisms
Tetracalcium aluminate 13-hydrate	$4CaO \cdot Al_2O_3 \cdot 13H_2O$	Le Chatelier, Assarsson (two forms), Mylius	Hex. plates
Tricalcium aluminate 18-hydrate	$3CaO \cdot Al_2O_3 \cdot 18H_2O$	Travers & Sehnoutka, Mylius	Needles
Tricalcium aluminate (11-12)-hydrate	$3CaO \cdot Al_2O_3 \cdot 11\text{-}12H_2O$	Thorvaldson, Grace & Vigfusson, Mylius	Hex. plates
Tricalcium aluminate hexahydrate	$3CaO \cdot Al_2O_3 \cdot 6H_2O$	Allen & Rogers, Thorvaldson	Cubic
Dicalcium aluminate (7-9)-hydrate	$2CaO \cdot Al_2O_3 \cdot 7\text{-}9H_2O$	Lafuma, Mylius, Salmoni	Hex. plates
Monocalcium aluminate hydrate	$CaO \cdot Al_2O_3 \cdot 10H_2O$	Assarsson	Plates
System CaO-SiO_2-H_2O			
Monocalcium disilicate hydrate	$CaO \cdot 2SiO_2 \cdot xH_2O$	Flint & Wells, Schläpfer & Niggli	Gel Crystals
Monocalcium silicate hydrate	$CaO \cdot SiO_2 \cdot xH_2O \cdot (0.2\text{-}1.0)H_2O$	Flint & Wells, Foret	Gel Crystals
Tricalcium disilicate hydrate	$3CaO \cdot 2SiO_2 \cdot xH_2O$	Various, Bessey	Gel Needles
Dicalcium silicate monohydrate	$2CaO \cdot SiO_2 \cdot H_2O$	Thorvaldson & co-authors, Bessey	Plates and lathes Needles
Tricalcium silicate dihydrate	$3CaO \cdot SiO \cdot (1\tfrac{1}{2}\text{-}2)H_2O$	Keevil & Thorvaldson, Bessey	Needles

The mineral which was named "Hydrocalumite" gave analyses corresponding to the formula $4CaO \cdot Al_2O_3 \cdot 12H_2O$, but with about 1.8 per cent carbon dioxide present. The optical properties and density are given in Table 1. The compound was found by X-ray study to be pseudo-hexagonal with a monoclinic cell having the dimensions:

$$a_0 = 9.6,\quad b_0 = 11.4,\quad C_0 = 16.84 \text{ and } \beta = 69^\circ,$$

with four molecules to the unit cell, and a possible structure was suggested.

A much larger number of hydrated silicates are known, although all of them must be regarded as rare minerals. The formulæ and properties of these minerals, as described by Vigfusson, are shown in Table 1. Another mineral, Foshagite, was listed by Vigfusson but subsequently shown by him to be most probably an altered form of Hillebrandite. The compositions given by Vigfusson are not in all cases generally agreed. Berman (2) gives Centrallasite as $Ca_4Si_6O_{15}(OH)_2 \cdot 5H_2O$ and Crestmoreite as $CaSiO_3 \cdot 2H_2O$ and considers that Centrallasite and Gyrolite are probably identical, whilst

LARSEN and BERMAN (19) give Centrallasite as $4CaO \cdot 7SiO_2 \cdot 3H_2O$, Crestmoreite as $4CaO \cdot 4SiO_2 \cdot 7H_2O$, Riversideite as $2CaO \cdot 2SiO_2 \cdot 3H_2O$, and Gyrolite as $4CaO \cdot 6SiO_2 \cdot 5H_2O$.

The list of mineral hydrated calcium silicates shown is a long one, but it seems that most of them at least are true mineral species; the list does not include all the compounds that have been prepared artificially. The structure of certain of these compounds has been examined by X-ray crystal analysis and will be referred to later.

Artificially Prepared Compounds.

The artificially prepared compounds which have been observed and whose identity appears to be established are shown in TABLE 2. Compounds other than those shown have been reported in the literature, but their existence has not been confirmed and the original evidence for their existence was inadequate. The aluminates, owing to their higher solubility, are nearly always obtained in crystalline form, but the silicates occur more frequently as gels, which, owing to their colloidal properties, differ in some important respects from the crystalline forms.

The investigations dealing with the preparation, properties and phase equilibria of these compounds are described in the following pages for each of the ternary systems separately.

THE SYSTEM CaO-Al_2O_3-H_2O.

Introduction.

The system CaO-Al_2O_3-H_2O has been found very difficult to elucidate. The difficulties lie mainly in the existence of a large number of compounds, all of which have a relatively low solubility and most of which are metastable but, once formed, persist almost indefinitely. Investigations have been complicated, moreover, and have sometimes given erroneous results, through the difficulty of excluding traces of carbon dioxide from the materials; the importance of this is even greater here than with the silicates, since complex compounds are formed containing carbonate and the presence of even small amounts may influence the results very seriously.

Methods of Preparation.

A number of methods have been used for obtaining preparations of the hydrated aluminates. They may practically all be included under the three headings of Direct Synthesis, Hydration of the Anhydrous Calcium Aluminates, and Precipitation Methods.

Direct Synthesis.

Direct synthesis has been attempted both from aluminium metal and calcium hydroxide solutions and from aluminium hydroxide and calcium hydroxide. The reaction with the metal was studied by Assarsson (2) at various temperatures. At the lower temperatures (below 22°) he obtained compounds approximating to the formula C_4AH_{12-13}, and C_3AH_{11-12}, usually together with some AH_3, whilst at higher temperatures, up to 90°, the cubic compound C_3AH_6 was formed. The method may be used, as was done by Mylius (21), for obtaining a fairly pure preparation of C_3AH_6, but this is never quite free from traces of the other compounds.

The synthesis from aluminium hydroxide and lime-water has not been widely used, owing to the difficulties of preparing pure aluminium hydroxide, of obtaining complete reaction, and of controlling the product of reaction. This method was used by Mylius (21) for preparing C_2AH_{7-9}, by MacIntyre and Shaw (20) for C_3AH_{10-11} and C_3AH_6 (contaminated with some alumina), and by Lafuma (14) for a tetracalcium aluminate hydrate.

Hydration of the Anhydrous Calcium Aluminates.

The direct hydration of the anhydrous aluminates has been widely studied. The hydration products have been found to vary to some extent according to the anhydrous compound used and to the conditions of hydration. The results observed may conveniently be considered for each of the anhydrous compounds in turn.

Tricalcium Aluminate, $3CaO \cdot Al_2O_3$. At temperatures in the range 0°—25° and with high water : solid ratios this compound hydrates fairly rapidly, particles up to about 50 μ being completely hydrated within a few days. The products of hydration are usually mixtures of the hexagonal plate compounds. Thorvaldson (35) prepared an apparently homogeneous tricalcium compound of the formula $3CaO \cdot Al_2O_3 \cdot 11\text{-}12H_2O$. Some other workers have also reported hydrated tricalcium compounds of varying water contents obtained in this way, but have not apparently established the homogeneity of their products, whilst others have definitely found mixtures of di-, tri- and tetracalcium compounds. It seems probable that the compounds formed are largely a matter of chance, depending perhaps upon the first crystal nuclei formed.

At temperatures above about 25° any of the above compounds may be formed, but the cubic compound $3CaO \cdot Al_2O_3 \cdot 6H_2O$ is also formed and predominates at the higher temperatures. There is no definite temperature above which the cubic compound is formed and there does not appear to be any transition temperature. It seems probable, therefore, that the series of plate-forming compounds are all metastable with respect to the cubic compound at all temperatures down to 0°. Thorvaldson and Grace (34) used the direct hydration in steam under pressure to prepare the cubic compound and obtained a fairly pure preparation; it has, however, been found difficult by other workers to obtain it in an absolutely pure state in this way.

Pentacalcium Trialuminate, $5CaO \cdot 3Al_2O_3$, and *Monocalcium Aluminate*, $CaO \cdot Al_2O_3$. These compounds (the former of which is now considered by some workers to have the formula $12CaO \cdot 7Al_2O_3$) hydrate in a somewhat different manner from the tricalcium compound. They both dissolve appreciably in water, forming metastable solutions (WELLS, ASSARSSON), and then precipitate out a mixture of aluminium hydroxide and hydrated aluminates. ASSARSSON (2) made a study of the nature of these precipitation reactions and found that a monocalcium aluminate hydrate CAH_{10} was formed at the lower temperatures. He was able to isolate this compound and determine certain of its properties. SALMONI (30) also concluded that such a compound was formed from aluminous cements in the same manner. The crystalline compound has not been observed by other workers, but an amorphous material of similar refractive index has been observed by the author, in the presence of other hydrated aluminates and alumina.

At higher temperatures or at longer ages ASSARSSON (2) found that dicalcium aluminate hydrate C_2AH_{7-9} was precipitated and that other compounds, including the cubic C_3AH_6, may be formed at the same time or subsequently. A useful method of preparation of the dicalcium compound, suggested by KOYANAGI (11) and successfully used by the present author, is that of shaking a fine flour of aluminous cement with water for a given period and then passing the suspension through a fine sieve. Any unhydrated cement, aluminium hydroxide, and other products of hydration pass the sieve and leave behind the compound $2CaO \cdot Al_2O_3 \cdot 7\text{-}9H_2O$ as small spherulithic crystals. The separation is almost perfect, but the yield varies with different aluminous cements.

Precipitation Methods.

Two types of precipitation methods have been used, one making use of the supersaturated and metastable calcium aluminate solutions and the other using potassium or sodium aluminate solutions.

Precipitation from Calcium Aluminate Solutions. This method was used by ASSARSSON (2) by mixing metastable calcium aluminate solutions with lime solutions in various concentrations and proportions at controlled temperatures. The maximum concentration of alumina found in these metastable solutions is about 2.5 g Al_2O_3 per litre (ASSARSSON); the ratio of solid aluminate surface to water, the vigour of shaking, the time and the temperature, all have an important effect upon the concentration found. The precipitates found by ASSARSSON (2) were usually mixtures of the various aluminates with or without hydrated alumina, but, from suitable concentrations, the compounds C_4AH_{12-13} (stated to occur in two forms), C_3AH_6, C_2AH_{7-9}, CAH_{10} and C_5AH_{31-35} were prepared in a sufficiently pure state for examination. The two last compounds have not been reported by any other workers. LE CHATELIER, WELLS (41) and MYLIUS (21) also used a similar method.

Precipitation from Potassium Aluminate Solutions. The precipitation of potassium aluminate solutions with calcium hydroxide and calcium salt solutions was suggested by TRAVERS and SEHNOUTKA (39) and has also been used by MYLIUS (21). By this means the former authors were the first to prepare the compound C_3AH_{18-21}, occurring in long needles. Mixtures of the hexagonal plate compounds were also obtained.

Properties of the Hydrated Calcium Aluminates.

The difficulty of preparing the individual hydrated aluminates in a pure condition has led to some lack of agreement in their observed properties, and the data are somewhat incomplete.

Crystal Forms, Optical Properties and Density.

In TABLE 3 the crystal forms, optical properties and density, where known, are given.

Only values on apparently homogeneous materials of determined composition are included in TABLE 3.

Penta-calcium aluminate hydrate, $5CaO \cdot Al_2O_3 \cdot 34H_2O$, has only been observed by ASSARSSON (2). In spite of its high basicity and large water content its existence as a metastable compound is not unlikely if it be regarded as related in structure to calcium sulpho-aluminate $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 30H_2O$.

The refractive index data on *the tetracalcium aluminate hydrates* suggest, as pointed out by ASSARSSON (2), that at least two forms exist. These appear to be an

$$\alpha\text{-form with } \omega = 1.537 \pm 0.003$$
$$\varepsilon = 1.520 \pm 0.003,$$

and a

$$\beta\text{-form with } \omega = 1.535 \pm 0.003$$
$$\varepsilon = 1.507 \pm 0.003.$$

Both sets of indices have been observed by various workers, including the present author, and both have similar water contents, approximating to $13H_2O$.

Table 3. Physical Properties of the Hydrated Calcium Aluminates.

Formula of Compound	Crystal Form		Water Content (Mols.)	Refractive Indices ω	Refractive Indices ε	Optical Character	Observed by	Density
$5CaO \cdot Al_2O_3 \cdot 34H_2O$	Hexagonal prisms (Prism & basal planes)		34.3—34.4	1.487	1.480	Uniaxial.negative	ASSARSSON	—
$4CaO \cdot Al_2O_3 \cdot 12\text{-}13H_2O$	(Pseudo?) hexagonal plates	α-form	13.7—14.3	1.535—9	1.520	Biaxial.negative $2V = 10°$	ASSARSSON	—
			12.5—13.6	1.533	1.522	Uniaxial.negative	MYLIUS	
		β-form	13.7—14.0	1.535	1.507	Biaxial.negative $2V = 14°$	ASSARSSON	
			12.0±0.5	1.532±0.005	1.505		WELLS	
		(?) γ-form	12.6—13.1	1.549	1.527	? negative	ASSARSSON	
			12.1	1.549	1.533	Uniaxial.negative	MYLIUS	
$3CaO \cdot Al_2O_3 \cdot 18H_2O$	Long needles		17.7—18.0	$\alpha = 1.479$ $\beta = 1.489$ $\gamma = 1.495$		Biaxial.negative	MYLIUS	—
$3CaO \cdot Al_2O_3 \cdot 11\text{-}12H_2O$	Hexagonal plates		10.9—12.5	1.529±0.002	1.506±0.002	Uniaxial?negative	THORVALDSON	2.04 (with 10.5 H_2O)
			10.1—11.8				MYLIUS	
$3CaO \cdot Al_2O_3 \cdot 6H_2O$	Cubic (100) (110) (111) (211)		6.0	1.605±0.002		Isotropic	THORVALDSON Numerous other authors	2.522
$2CaO \cdot Al_2O_3 \cdot 7\text{-}9H_2O$	Hexagonal plates (usually in spherulithic clusters)		8.6—9.1	1.520±0.002	1.505±0.003	Biaxial.negative $2V = 7°$ approx.	ASSARSSON	1.95
			6.8—8.8				MYLIUS	
			—				SALMONI	
			7.8—8.5				LEA & BESSEY	
$CaO \cdot Al_2O_3 \cdot 10H_2O$	Plates		9.4—10.3	Mean = 1.48		Negative elongation	ASSARSSON	—

A third form was observed by ASSARSSON (2) with the indices $\omega = 1.549$, $\varepsilon = 1.527$, with a slightly smaller water content. The author has observed similar indices on preparations approximating to the formula $4CaO \cdot Al_2O_3 \cdot 12H_2O$, but containing appreciable amounts of carbon dioxide. The compound $4CaO \cdot Al_2O_3 \cdot CO_2 \cdot 11H_2O$ (tetracalcium carbonato-aluminate), which has also been observed by the author, has the indices $\omega = 1.552 \pm 0.003$, $\varepsilon = 1.532 \pm 0.003$, and it seems likely that a small amount of this compound may, by solid solution formation, influence the structure of the tetracalcium aluminate hydrate and give the indices observed. The existence of this third form in a pure state thus requires confirmation. The indices of the natural mineral Hydrocalumite are of interest in this connection since they are similar ($\alpha = 1.535$, $\beta = 1.553$, $\gamma = 1.557$), and the mineral contains 1.8 per cent carbon dioxide.

The density of the tetracalcium compounds has not been determined; the values would be useful to confirm the different forms indicated by the refractive indices.

Tricalcium aluminate 18-hydrate has only been observed in precipitation experiments in which ions other than those of the calcium aluminates were present, and it is possible that it is never formed by hydration of the anhydrous calcium aluminates. The author has found it difficult to obtain free from impurities and only a rough check of the refractive indices has been made.

It is difficult to prepare the *tricalcium aluminate (11-12)-hydrate* in a pure state. THORVALDSON, GRACE and VIGFUSSON's (35) preparation by direct hydration of tricalcium aluminate has been found by other workers to give mixtures of the plate hydrates. MYLIUS (21) was successful in preparing it by precipitation from potassium aluminate solutions.

Tricalcium aluminate 6-hydrate, the most stable of the hydrated aluminates, is readily prepared and its properties have been fully checked. Its variety of crystal form is of interest; cubes, octahedra, dodecahedra and icositetrahedra and all combinations of these are observed. KOYANAGI (11) has observed that the predominant form is influenced by the lime concentration of the solution from which the compound crystallizes.

The preparation of the *dicalcium aluminate (7-9)-hydrate* by various workers, using a variety of methods, has given material with consistent optical properties. The density was determined by LEA and BESSEY (15).

The *monocalcium aluminate hydrate* has only been observed definitely by ASSARSSON as amorphous or finely crystalline material, and only a mean refractive index was recorded.

Water Contents and Dehydration.

The water content of the hydrated aluminates is not known accurately in all cases, as a portion of the water is readily lost at relatively high humidities. Part of the water is undoubtedly present in the crystal structure as hydroxyl and part as water, loosely co-ordinated to the Ca^{++}- and Al^{+++}-atoms. The course of dehydration at reduced vapour-pressures or at elevated temperatures gives some evidence of the structure by indicating the number of molecules of water which are more firmly combined.

The results of drying the aluminates at room temperatures under different conditions, together with the refractive indices of the products, where observed, are shown in TABLE 4.

TABLE 5 shows the water contents retained at various temperatures up to 350°. The results of LEFOL (18) are taken from continuous heating curves in which the whole range of temperature was covered in about five hours; they cannot, therefore, be considered as in equilibrium. THORVALDSON, GRACE and VIGFUSSON's (35) results were obtained by heating for one to three hours at each temperature, whilst MYLIUS's (21) results at 105° were obtained with much longer periods of heating. NACKEN's (22) results were obtained by use of a HÜTTIG-eudiotensimeter with vapour-pressures of 0—5 mm Hg. The results quoted are interpolated from the curves given. The somewhat sluggish rate of loss found by MYLIUS with the compounds C_4AH_{13} and C_2AH_8 probably indicate that some part of the loosely combined water lies in positions in the crystal lattice from which it cannot so readily escape as the remainder.

The tetracalcium compound in a nearly saturated atmosphere appears to contain 13 mols. of water (C_4AH_{13}); it very easily loses one molecule at ordinary temperatures to give C_4AH_{12}, and from MYLIUS's results, appears to lose a further 5 mols. at 105° to give C_4AH_7. This suggests that the structural formula may be $Ca_4Al_2(OH)_{14} \cdot 6H_2O$.

The tricalcium compound occurring as needles, which has initially 18 mols. of water (C_3AH_{18}), loses only 8.5 mols. at low humidities at ordinary temperatures but 10—12 mols. at 105°. NACKEN indicates breaks in the loss curve at 15, 9, 6, 4, and 2 mols. H_2O retained. The break at $6H_2O$ above 100° suggests $Ca_3Al_2(OH)_{12} \cdot 12H_2O$ as the correct formula.

The tricalcium compound with an initial water content of 11—12 mols. has, according to both THORVALDSON and MYLIUS, a number of stages of dehydration at room temperatures. The results do not, however, establish definitely the composition of the hydrates. This is indicated by the curve in FIG. 1 which shows THORVALDSON's water contents in molecules H_2O plotted against vapour-pressure. This curve might be interpreted as indicating either that the true compound is C_3AH_{11} and that the remaining water is adsorbed under very high humidity conditions, or that the normal hydrate contains 12 mols.,

Table 4. Dehydration of the Aluminates at Room Temperatures.

Compound	$4CaO \cdot Al_2O_3 \cdot mH_2O$	$3CaO \cdot Al_2O_3 \cdot xH_2O$	$3CaO \cdot Al_2O_3 \cdot yH_2O$	$3CaO \cdot Al_2O_3 \cdot zH_2O$	$2CaO \cdot Al_2O_3 \cdot nH_2O$
	$m =$	$x =$	$y =$	$z =$	$n =$
Condition of Drying:					
Humidity 18.1 mm; 21° C	—	—	12.5 (Thorvaldson) $\omega = 1.527$ $\varepsilon = 1.505$	6.0 (Thorvaldson)	—
Humidity 13.5 mm; 17° C	—	—	—	—	8.3 (Lea & Bessey) $\omega = 1.520$ $\varepsilon = 1.505$
Washed with alcohol & ether and dried few minutes in vacuo over $CaCl_2$	12.8—13.6 (Mylius) $\omega = 1.533$ $\varepsilon = 1.522$	17.7—17.9 (Mylius)	10.1—11.8 (Mylius) $\omega = 1.528$ $\varepsilon = 1.508$	5.9 (Mylius)	6.8—7.3 (Mylius) $\omega = 1.522$ $\varepsilon = 1.502$
Washed with alcohol & ether	12.6—14.3 (Assarsson)	—	—	—	8.6—9.1 (Assarsson) $\omega = 1.519$ $\varepsilon = 1.506$
Humidity 16.1 mm; 21° C	—	—	10.9 (Thorvaldson) $\omega = 1.530$ $\varepsilon = 1.510$	—	—
Over $CaCl_2$	11.7 (Mylius) $\omega = 1.549$ $\varepsilon = 1.533$	—	10.1 (Mylius)	—	—
Humidity 3.7 mm; 21° C	—	—	10.5 (Thorvaldson)	—	—
Humidity 2.8 mm; 17° C	—	—	—	—	7.6 (Lea & Bessey) $\omega = 1.521$ $\varepsilon = 1.512$
Humidity 2.2 mm; 21° C	—	—	9.6 (Thorvaldson)	—	—
Humidity 0.8 mm; 21° C	—	—	9.4 (Thorvaldson)	—	—
Over CaO; 17° C	—	—	—	—	5.0 (Lea & Bessey) $\omega = 1.535—1.549$ $\varepsilon = 1.530—1.540$
Over CaO; 21° C	—	—	8.0 (Thorvaldson) $\omega = 1.538$ $\varepsilon = 1.520$	6.0 (Thorvaldson)	—
Over P_2O_5 without vacuum	12.0 (Mylius)	—	9.7 (Mylius)	—	—
Over P_2O_5 in vacuo	11.0—13.2 (Assarsson)	9.4 (Mylius)	—	—	5.2 (Mylius)

Table 5. *Dehydration of the Aluminates at Elevated Temperatures.*

Temperature of Drying	$4CaO \cdot Al_2O_3 \cdot \cdot mH_2O$			$3CaO \cdot Al_2O_3 \cdot \cdot xH_2O$			$3CaO \cdot Al_2O_3 \cdot yH_2O$				$3CaO \cdot Al_2O_3 \cdot zH_2O$				$2CaO \cdot Al_2O_3 \cdot nH_2O$				
°C	$m =$			$x =$			$y =$				$z =$				$n =$				
	Lefol	Mylius	Nacken	Lefol	Mylius	Nacken	Thorvaldson	Mylius	Nacken	Lea & Jones	Lefol	Mylius	Nacken	Thorvaldson	Lefol	Mylius	Nacken	Lea & Jones	Salmoni
<50	12.2	12.8	14	> 24 (moist)	17.9	18	12.5	11.8	11.5	—	6.0	5.9	6	6.0	7.3	7.3	9 8 (40°—80°)	8	9
100	10.5	—	9	> 24	—	7.5	6.9	—	10	8—9	6.0	—	6	6.0	6.5	—	5	5	5
105	—	7.3	—	—	6.4	—	—	6.6	—	—	—	5.9	—	—	—	4.9	—	—	—
150	9.0	—	7	7.9	—	6.5	—	—	6	6	5.8	—	6	6.0	5.0	—	4	4	—
200	5.6	—	7	6.5	—	6	—	—	4	5	5.3	—	4	5.9	4.6	—	4	3.5	3
250	4.9	—	5	5.2	—	4	—	—	4	4	5.2	—	2	—	4.1	—	2	2.5	—
300	3.8	—	3	4.0	—	4	—	—	4	2.5	1.9	—	1.8	1.5	3.3	—	2	1	1
350	3.4	—	3	3.4	—	4	—	—	2	2	1.5	—	1.3	—	1.2	—	1	—	—

one of which is very readily lost; this ready loss of one mol. is common also to the compounds C_4AH_{13} and C_2AH_8. The breaks at lower water contents are of doubtful interpretation. The $9.5H_2O$ break shown by THORVALDSON, GRACE and VIGFUSSON is supported by MYLIUS's results and by NACKEN, who also finds breaks at higher temperatures at 10, 6, 4, and 2 H_2O. The water retained at temperatures slightly over 100° suggests that the formula should be expressed as $Ca_3Al_2(OH)_{12} \cdot 6H_2O$.

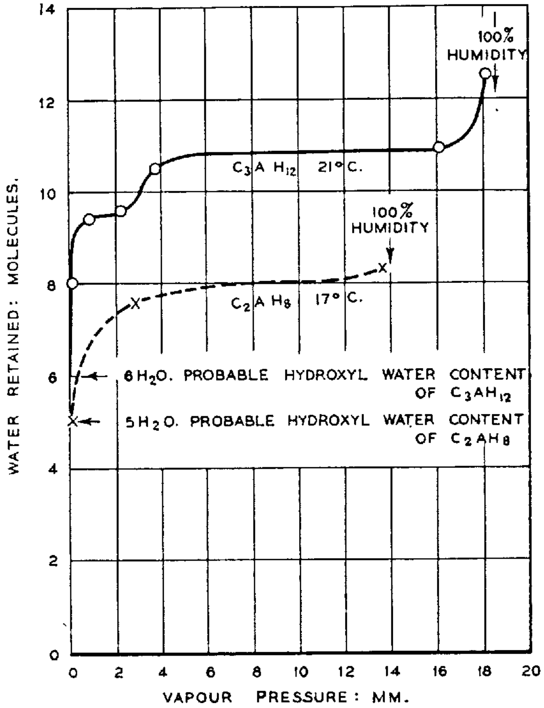

FIG. 1. Water Content of Tricalcium Aluminate Hydrate (Hexagonal Plate) at 21° (THORVALDSON) and Dicalcium Aluminate Hydrate (Hexagonal Plate) at 17° (LEA & BESSEY).

The cubic compound, C_3AH_6, is stable and does not lose water under any conditions at room temperature, or when heated to temperatures below 200°. It may thus be considered as a hydroxide containing no water molecules, *i. e.* as $Ca_3Al_2(OH)_{12}$. NACKEN (22) finds that, in common with 18- and 12-H_2O compounds, it has two definite breaks in the loss curve at higher temperatures at $4H_2O$ and $2H_2O$.

The dicalcium aluminate hydrate has been variously considered as normally having 7, 8 or 9 mols. of water. The results of LEA and BESSEY on the water content under controlled humidity conditions (FIG. 1) suggest that the most probable value is 8, but this result requires further check. Nacken suggests breaks in his loss curve for this compound at 8, 7, 6, 5, 4, 3, 2, and $1H_2O$; the more definite breaks, however, lie apparently at 8, 5, 4, 2, and $1H_2O$. The position of the $5H_2O$ break at temperatures slightly above 100° agrees with results at low humidities at ordinary temperatures and indicates $Ca_2Al_2(OH)_{10} \cdot 3H_2O$ as the structural formula. Nacken gives refractive indices of the material at different stages of dehydration. The material with 7, 8, or $9H_2O$ gave similar values ($\omega = 1.520 \pm 0.003$, $\varepsilon = 1.508 \pm 0.003$), material with 6, 5, or $4H_2O$ gave a second set of values ($\omega = 1.549 \pm 0.003$, $\varepsilon = 1.535 \pm 0.005$), and material with 3, 2, or $1HO_2$ a third set ($\omega = 1.575 \pm$ ± 0.005, $\varepsilon = 1.565 \pm 0.005$). The individual points obtained within these groups varied, but only within the range indicated. These refractive index determinations should be of assistance in considering the crystal structures of the compound.

Constitution and Crystal Structure.

Forsén first considered the constitution of the hydrated aluminates as co-ordination compounds. He based his suggestions upon 4- or 6-co-ordinated Al-atoms, and 0-, 2-, or 4-co-ordinated Ca-atoms. Whilst this gave an idea of the type of structure of these compounds, which is probably not far from the truth in principle, it seems unlikely that the co-ordination numbers of the Ca and Al in the crystal vary to the extent indicated, since the compounds are so similar in character. Forsén's (8) co-ordination formulæ are, nevertheless, an extremely useful attempt to relate the structures of these compounds with each other and with other allied complex compounds, but require checking by X-ray analysis of the crystal structures. The generalized structures agree with the results of dehydration data. Brandenberger (4) further suggests that all the hydrated calcium aluminates may be expressed by the general formula $m\mathrm{Ca(OH)_2} \cdot n\mathrm{Al(OH)_3} \cdot p\mathrm{H_2O}$. It will be observed that the various structural formulæ, which are shown below, all contain, with one doubtful exception, a number of water molecules which is a multiple of three. This is probably associated with the co-ordination requirements of the Ca- and Al-atoms.

$Ca_5Al_2(OH)_{16} \cdot 26H_2O$ (?24)
$Ca_4Al_2(OH)_{14} \cdot 6H_2O$
$Ca_3Al_2(OH)_{12} \cdot 12H_2O$
$Ca_3Al_2(OH)_{12} \cdot 6H_2O$
$Ca_3Al_2(OH)_{12}$
$Ca_2Al_2(OH)_{10} \cdot 3H_2O$
$CaAl_2(OH)_8 \cdot 6H_2O$.

BRANDENBERGER (4) has also suggested that the series of compounds occurring as hexagonal plates (C_4AH_{13}, C_3AH_{12}, C_2AH_8, and possibly CAH_{10}) may be built up of layers of $Ca(OH)_2$ and $Al(OH)_3$, and points out their similarity in symmetry and form to calcium hydroxide, and also the formation of overgrowths which has been observed. This view is supported by the structure worked out by TILLEY and MEGAW (36) for the natural tetracalcium aluminate hydrate, Hydrocalumite.

The X-ray data concerning these compounds and the many allied compounds are at present very incomplete and much experimental work is required to enable structures to be worked out. The elucidation of their structural relations will be of considerable value, however, in assisting our knowledge and understanding of their chemical relations. Powder X-ray patterns have been determined by ASSARSSON, THORVALDSON, SALMONI, and the present author for these compounds, but further checking of the results is required, with line intensity measurements and, if possible, single-crystal measurements. The subject of X-ray studies is considered elsewhere in this Symposium and need not therefore be pursued further here.

Solubility and Phase Equilibria.

The solubility data in this system are somewhat confusing and apparently often contradictory. The methods used for attempting to attain equilibria are essentially those described earlier in this Report for preparing the hydrated materials, together with direct solubility determinations on the prepared hydrated compounds. Few of the more important investigations carried out on the system have, however, been concerned with the phase equilibrium relations but have dealt rather with the properties of the individual hydrated compounds (*e. g.* THORVALDSON, MYLIUS) or the course of the immediate hydration reactions of the anhydrous compounds [*e. g.* KLEIN and PHILLIPS (9), LERCH and BOGUE (19), WELLS (41)]. ASSARSSON, whose studies of the products of precipitation reactions provide useful data with regard to the equilibrium, suggests that the phase rule can, however, only be applied with the greatest caution both to his own and other workers' experimental data. LAFUMA (14), KÜHL, THILO and CHI YÜ (12), POLHEIM (27), ERCULISSE and SAPGIR (16), and NACKEN and MOSEBACH (23) have each attempted to assign the limits of concentration over which particular compounds are stable at given temperatures (*i. e.* the isothermal invariant points). Their conclusions have been based in all cases upon the results of experiments of one type only and are therefore open to criticism. Only by approaching equilibrium in a number of different ways can any conclusive result be obtained in a system of this type where a number of metastable phases occur, and it is essential that the identity of the solid phases be established not only by analysis but also by their optical properties when dried under accurately controlled conditions.

LAFUMA (14) found, by repeated extraction of C_4AH_{13} with excess lime initially present, that a halt in the lime solution concentrations was obtained at 1.08 g CaO per litre. The solid phase above this point was C_4AH_{13} (C_4AH_{12} according to LAFUMA). A further halt was obtained at 0.16 g CaO per litre with 0.05 g Al_2O_3 per litre also in solution; analysis of the solid before reaching this concentration (*i. e.* at 0.4 g CaO per litre) gave a composition of C_2AH_7. LAFUMA therefore suggests that this first halt was the invariant point C_4AH_{12}-C_2AH_7, and the second halt the invariant point C_2AH_7-AH_3. The existence of an invariant point at 1.08 g per litre has been suggested by the results of other workers [NORTH (25), CANDLOT, LEA and BESSEY]. There is, however, considerable doubt whether LAFUMA's tetracalcium aluminate was pure since he states that, on placing it in water, it gave a solution concentration of 1.08 g per litre. No subsequent work has confirmed this, and it is considered that only material with free lime present would give such a concentration. The lower halt at 0.16 g CaO, 0.05 g Al_2O_3 per litre, is, it must be noted, in the neighbourhood of the solubility of the compound C_3AH_6 in water (0.15—0.18 g CaO, 0.09—0.12 g Al_2O_3 per litre), or of the carbonato-aluminate (0.14 g CaO, 0.07 g Al_2O_3 per litre). ERCULISSE and SAPGIR failed to repeat these results.

KÜHL, THILO and CHI YÜ (12), from the apparent equilibrium attained with monocalcium aluminate and a dilute lime solution in about ten weeks, indicate 0.360 g CaO, 0.109 g Al_2O_3 per litre as the invariant point C_2AH_8-AH_3. Actually, the solution concentration of alumina found was 0.163, but from the results of potentiometric and conductivity data they calculate that a portion of the alumina is present as AH_3 in a colloidal condition; these calculations appear to be open to criticism. No optical examination of the solid is given and there is no evidence, therefore, of the solid phases actually present.

POLHEIM (27) studied the solution concentrations obtained with C_3A and with C_5A_3 on shaking with water or with lime-water for various periods at 20° and at 37°. As a result he suggests values for invariant points as follows:

C_4AH_{13}-C_3AH_{12} · 0.107 g CaO, $<$ 0.003 g Al_2O_3 per litre,
C_3AH_{12}-C_2AH_8 · 0.056 g CaO, 0.080 g Al_2O_3 per litre,

and considers that his results confirm the invariant point for C_2AH_8 suggested by KÜHL, THILO and CHI YÜ (12). The evidence for any of these points appears to be very limited and the results lack confirmation by any positive identification of the solid phases. It is to be noted that the transition point at 0.107 g CaO per litre is similar to that of LAFUMA; there is, however, no definite evidence whether it is the invariant point C_4AH_{13}-C_3AH_{12} or C_4AH_{13}-C_3AH_6.

NACKEN and MOSEBACH (23) recognized that certain of the compounds must be metastable. Their experimental work was, however, limited to studies of the apparent equilibrium obtained on shaking anhydrous tricalcium aluminate with water and lime solutions, and no positive identification of the solid phases, other than distinction between the cubic C_3AH_6 and plate hydrates, is given. In view of the mixed nature of the plates normally formed by hydration of tricalcium aluminate in this way, solubility data of this type taken alone must be interpreted with the greatest caution. These authors take the point obtained on shaking C_3A with water and yielding almost exclusively C_3AH_6 as the solubility of the latter compound. The value so obtained (0.42 g CaO, 0.26 g Al_2O_3 per litre) is much greater than the value obtained by other workers for the solubility of this compound, and is probably near to the solubility of one of the metastable plate hydrates which had been present, but was almost entirely transformed to C_3AH_6 in their experiment. The compound C_3AH_6 is regarded by these authors as stable and congruently soluble, C_2AH_8 as stable over a narrow field of concentration, but incongruently soluble, and C_4AH_{13} as metastable. Whilst these general conclusions are probably correct in part, the particular solubility points indicated have not necessarily the meanings attributed to them.

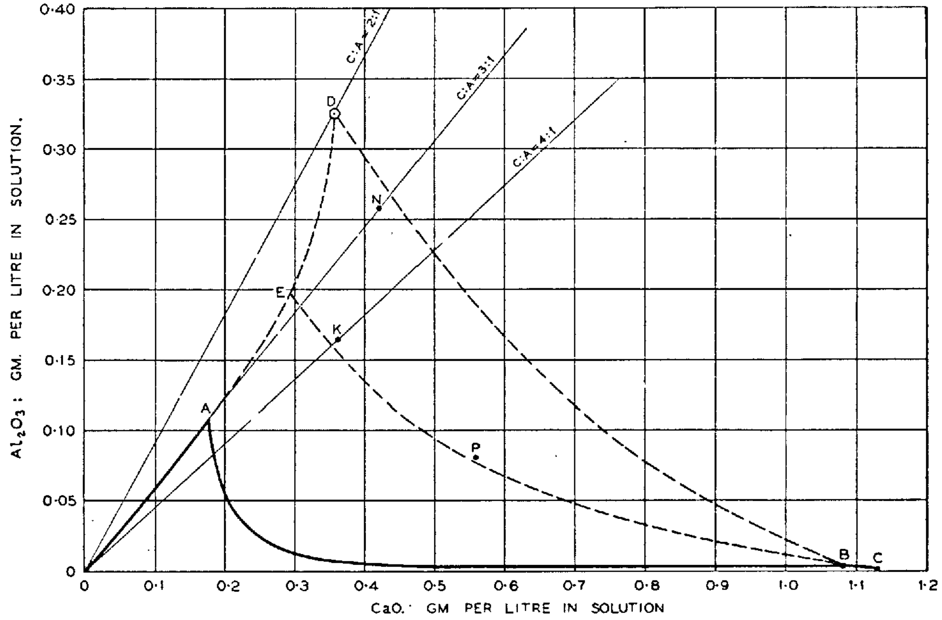

FIG. 2. Solubility Relations in the System $CaO-Al_2O_3-H_2O$ at 25°.

THORVALDSON, GRACE and VIGFUSSON (35) found the solubility of the cubic compound C_3AH_6 to be 0.0246 g C_3A per 100 cc (equivalent to 0.0153 g CaO and 0.0093 g Al_2O_3) at 21° and 0.0268 g (equivalent to 0.0167 g CaO and 0.0101 g. Al_2O_3) at 40°, and therefore congruent. They stated that supersaturated solutions are formed if the finer particles are not removed by washing.

The present author, in collaboration with LEA, has carried out an extensive investigation at the Building Research Station, Watford, of the equilibria in this system, mainly at 25°. In this work, attempts have been made to attain equilibrium by all the methods which have been considered in the present Report. Much of the earlier part of this work, similarly to that of other workers, was rendered of little value by failure to differentiate the individual compounds and by the absence of knowledge of the effect of small amounts of carbonate. These factors have, however, been fully considered in the later parts of the work, carried out over a period of several years, and the general relations in the system can now be outlined. In FIG. 2 the portions of the solubility curves which are considered to be established are shown. The curves and points marked are as follows:

OA. Stable solubility curve of $Al_2O_3 \cdot Aq$.

A. Congruent solubility of the compound $3CaO \cdot Al_2O_3 \cdot 6H_2O$ and invariant point $Al_2O_3 \cdot Aq$.—$3CaO \cdot Al_2O_3 \cdot 6H_2O$ (THORVALDSON, LEA and BESSEY).

AB. Stable solubility curve of compound $3CaO \cdot Al_2O_3 \cdot 6H_2O$ (LEA and BESSEY).

B. Invariant point.
Either $3CaO \cdot Al_2O_3 \cdot 6H_2O$—$4CaO \cdot Al_2O_3 \cdot 13H_2O$,
or $3CaO \cdot Al_2O_3 \cdot 12H_2O$—$4CaO. Al_2O_3 \cdot 13H_2O$.
LAFUMA (14), POLHEIM (27), LEA and BESSEY (15).

BC. Solubility curve.
Either a continuation of the solubility curve *AB* of $3CaO \cdot Al_2O_3 \cdot \cdot 6H_2O$,
or the stable solubility curve of $4CaO \cdot Al_2O_3 \cdot 13H_2O$. Both compounds are found in this range and the two solubility curves are practically superimposed; which of the two is the stable and which the metastable phase has not yet been established.

C. Solubility of calcium hydroxide in water. BASSETT (3), LEA and BESSEY (15).

OD. Metastable solubility curve of $Al_2O_3 \cdot Aq$. It is not certain whether this actually passes through *A* or whether it is an entirely separate curve, possibly of a different hydrate of alumina. LEA and BESSEY (15).

D. Approximate solubility of $2CaO \cdot Al_2O_3 \cdot 8H_2O$, apparently congruent, in water, and metastable invariant point $2CaO \cdot Al_2O_3 \cdot \cdot 8H_2O—Al_2O_3 \cdot Aq$. LEA and BESSEY (15).

DEB. Area in which solubility curves of the following compounds lie:

$4CaO \cdot Al_2O_3 \cdot 13H_2O$
$3CaO \cdot Al_2O_3 \cdot 12H_2O$
$2CaO \cdot Al_2O_3 \cdot 8H_2O$
$3CaO \cdot Al_2O_3 \cdot 18H_2O$

(LEA and BESSEY).

All these compounds are metastable in this area, the tetracalcium compound being the only one which may possibly have a stable solubility curve (*BC*). The data relating to the metastable solubility curves have not yet been fully analysed; in view of their closeness and the extreme difficulty in obtaining equilibrium, it may not be found possible to trace them individually with any accuracy.

The point *P* corresponds with the invariant point suggested by POLHEIM, $4CaO \cdot Al_2O_3 \cdot 13H_2O—3CaO \cdot Al_2O_3 \cdot 12H_2O$. Evidence in LEA and BESSEY's work points also to the presence of an invariant point close to this point, but its significance is still uncertain.

K is KÜHL's suggested invariant point $2CaO \cdot Al_2O_3 \cdot 8H_2O—Al_2O_3 \cdot Aq$. *N* is NACKEN and MOSEBACH's apparent solubility of $3CaO \cdot Al_2O_3 \cdot 6H_2O$ in water. Both of these last two points appear to have some significance, although not that assigned to them by these authors.

The two compounds C_5AH_{34} and CAH_{10}, described by ASSARSSON, are not considered in FIG. 2. If they exist at 25° in contact with lime solutions they are likely to have solubilities greater than any shown in the figure, since they are probably the least stable at this temperature.

A few solubility determinations at other temperatures have been carried out by LEA and BESSEY, but the only general conclusion that can be drawn is that the solubility of the cubic compound C_3AH_6 does not change very rapidly with temperature, that the curve *BC* disappears with rising temperature, and that the other compounds all become less stable.

THE SYSTEM CaO-SiO_2-H_2O.

Introduction.

The major sources of difficulties in this system are the almost negligible solubility of the hydrated calcium silicates in water, and the formation of gels. The difficulty of eliminating atmospheric carbon dioxide in preparing and investigating these compounds is again important, but no carbonate compound other than Calcite ($CaCO_3$) has been observed.

The hydrated silicates formed at normal temperatures are almost invariably amorphous or gel materials, and, consequently, they must be considered separately from the crystalline materials which have been prepared mainly by hydrothermal processes. Most workers have confined their attentions to either the crystalline or the gel substances and there is very little information available concerning the relation between the two.

Methods of Preparation.

Direct synthesis, hydration of anhydrous silicates, and precipitation methods have all been used for the preparation of the hydrated silicates.

Direct Synthesis.

Crystalline silica (Quartz) does not react with lime at a measurable rate at ordinary temperatures, although it has been stated [BRINTZINGER and BUBAM (3) and others] that reaction occurs over long periods in lime-sand mortars in the absence of carbon dioxide, but the rate becomes perceptible at temperatures approaching 100°. Even at this temperature, however, it is too slow.to serve as a method of preparation of the silicates, and the reaction can only be carried out satisfactorily in the autoclave.

THORVALDSON (35) and his collaborators observed that a dicalcium silicate hydrate (C_2SH), occurring as rhombic lathes and plates, was formed when a saturated lime solution and quartz crystals were subjected to prolonged exposure to saturated steam at 170°; a second compound of similar composition, but occurring as thin needles and giving a different X-ray pattern, was formed by a mixture of silica gel with excess lime under similar conditions. NAGAI (29), using powdered quartz and calcium oxide in various proportions, reported compounds of the compositions, C_2SH, $C_3S_2H_8$, C_3S_2H, and C_4S_4H. FORET (9) prepared the monocalcium compound CSH_x in two forms, α and β, with the water content x, in both cases between 0.25 and 0.80. The two forms were distinguished by X-ray examination.

THORVALDSON'S crystalline materials were obtained with long periods of autoclaving; the present author has found that with the shorter periods of autoclaving such as are used in sand-lime brick manufacture, crystallization only occurs in some cases, and is influenced by the sand and lime used. It is believed that the degree to which crystals or amorphous material are formed depends mainly upon the activity of the surface of the quartz; tests of dye sorption by different types of sand tend to confirm this. The crystals observed in sand-lime bricks are needles of low birefringence with a mean refractive index of about 1.58.

Direct synthesis is possible at ordinary temperatures by the use of silica gel or colloidal silica solution. This reaction has been studied by many investigators, including LE CHATELIER (21), SHAW and MACINTYRE (33), VAN DER BURGH (5), JOLIBOIS and CHASSEVENT (12), MAFFEI (24), and the present author. Some of these investigators consider that the first reaction is an adsorption, but all agree that a hydrated calcium monosilicate is formed. This compound was found to exist in equilibrium with a solution containing 0.052 g CaO per litre by LE CHATELIER and 0.08 g by MACINTYRE and SHAW. At higher lime concentrations further lime is taken up, LE CHATELIER obtaining a maximum CaO : SiO_2-ratio of 1.7 : 1. This further reaction is treated by MACINTYRE and SHAW as an adsorption and they give the following equation for the adsorption isotherm

$$x = 2.34\, C^{0.1818}$$

where x is the molar ratio of C : S and C is the equilibrium concentration of lime in solution expressed as g CaO per litre.

Hydration of Anhydrous Calcium Silicates.

The hydration of $3CaO \cdot SiO_2$ and of β-$2CaO \cdot SiO_2$ at ordinary temperatures follows a similar course, differing only in the rate of reaction and in the amount of $Ca(OH)_2$ produced. It is generally agreed that the reaction is of the form

$$3CaO \cdot SiO_2 + Aq. \rightarrow mCaO \cdot nSiO_2 \cdot xH_2O + (3\text{-}m)Ca(OH)_2$$

but the composition of the gelatinous hydrated silicate produced is still in doubt. THORVALDSON and VIGFUSSON (35) found a solid CaO : SiO_2-ratio of 1.5 : 1 in lime solutions approaching saturation and indications of the monocalcium compound in lower lime concentrations. TAVASCI (34) by repeated extraction of hydrated tricalcium silicate with water found breaks in the extraction curve which were considered to indicate the existence of compounds with CaO : SiO_2-ratios of 5 : 3, 1 : 1, and 1 : 2, but no evidence is given of the homogeneity of the products. NACKEN (27) found compounds with CaO : SiO_2-ratios of 2 : 1, 3 : 2, and 1 : 1 in equilibrium with progressively lower solution lime concentrations, and KÜHL and MANN (17) also considered the compounds formed had compositions between the limits 2 : 1 and 1 : 1. KOYANAGI (16) investigated the gel obtained by shaking coarse Portland cement particles with water or lime-water. The gel was separated by decantation from unhydrated material and the more coarsely crystalline calcium hydroxide. After allowing for the entrained calcium hydroxide, by estimation by the glycerol method, and for lime combined with alumina, the composition of the gel corresponded to CSH_2. It is questionable, however, whether free lime determinations by this or similar methods on such gels have any real meaning, since lime which may be present in excess of a 1 : 1 lime : silica ratio is apparently in a weak state of combination and is likely to react with glycerol or other reagents in a manner similar to free lime. The ratio of total lime to silica in KOYANAGI's gels lay between 1.3 and 1.6 suggesting that the silicate present could not have a $CaO : SiO_2$-ratio above 3 : 2. The method of investigation is one which might profitably be pursued further.

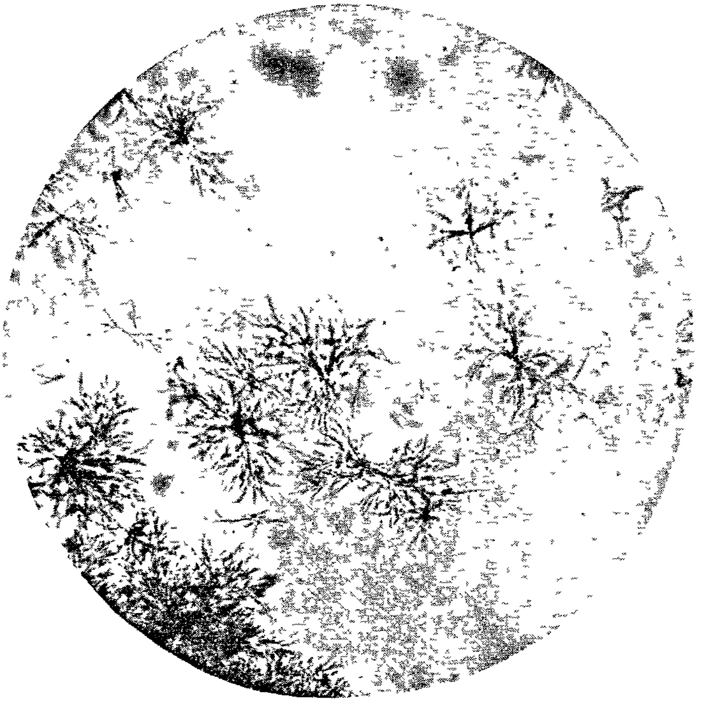

FIG. 3. Dicalcium Silicate hydrated One Year on Microscope Slide with Large Excess of Water.
Magnification 150 ×.

FLINT and WELLS (8), in their investigation of this system at 30°, did not attempt to isolate the compounds formed, and were concerned rather with the solution-solid equilibria. Their results, however, indicated the existence of compounds with lime: silica ratios of 2 : 1, 3 : 2, 1 : 1, and 1 : 2, and suggest that the 2 : 1 compound is formed by direct hydration of C_3S and β-C_2S. Their results show also that unstable supersaturated solutions are formed in the early stages of hydration of these compounds.

All the above authors have observed only gel products from the hydration at ordinary temperatures. PULFRICH and LINCK (31) observed the formation of needles with refractive indices $\alpha = 1.498$, $\gamma = 1.500$ on hydration of C_3S, but gave little further information. Le CHATELIER (21), KEISERMANN (14) and TIPPMANN (36) also claimed to have observed the formation of needles. The formation of crystallized material in this way is rare, but has also been observed by the author, by hydration of β-dicalcium silicate on slides with a large excess of water (FIGS. 3 and 4). Hydration of tricalcium silicate under similar conditions gave no crystalline material other than calcium hydroxide; it is probable that the presence of the calcium hydroxide suppresses the solubility of the hydrated silicate so completely as to prevent crystal growth. The requisite conditions are apparently slow hydration in the presence of a large excess of water. Insufficient of this crystalline material has so far been obtained for its composition to be determined, but the apparent absence of calcium hydroxide on the slides suggests that it is a dicalcium silicate hydrate.

FIG. 4 Dicalcium Silicate hydrated Two Years on Microscope Slide with Large Excess of Water. Magnification 400 ×.

It can be concluded that the hydrated silicate formed by the hydration of C_3S or β-C_2S, when none of the products of hydration are removed has a lime: silica ratio between 3 : 2 and 2 : 1, but no final composition can yet be given.

The present author, however, has found that gel with compositions approximating to the 3 : 2-ratio are in apparent equilibrium with lime solutions containing 1.1 g CaO per litre at 17°; at concentrations between this and saturation (1.3 g CaO per litre) the ratio approaches 2 : 1 and it seems probable that a compound of this composition is stable only in contact with solutions approaching saturation with lime at this temperature.

The hydration of C_3S and β-C_2S in steam under pressure has been shown by several investigators to yield crystalline hydrates. From C_3S, KEEVIL and THORVALDSON (13) prepared the compounds C_3SH_2 and C_2SH, while with β-C_2S three compounds all of the composition C_2SH, but with different crystalline form, optical properties and X-ray diffraction patterns, were obtained. KÖHLER (18) found only one compound C_2SH from C_3S or β-C_2S, but the present author has independently observed the C_3SH_2-compound and two of the modifications of the C_2SH-compounds.

Precipitation Methods.

Apart from the use of colloidal silica solutions mentioned earlier, certain investigators have studied other precipitation reactions.

KLASSE and KÜHL (15) used solutions of sodium silicate and calcium nitrate and obtained solids with lime: silica ratios varying between 1.6 : 1 and 1 : 1.8. The ratios obtained clearly depended upon the $Na_2O : SiO_2$-ratio in the sodium silicate used, and it is probable that the solids formed were mixtures which, when first precipitated, probably contained free silica. The present author has also prepared gels in this manner, using a sodium silicate solution of low soda : silica ratio and adding sodium hydroxide as required before adding the calcium salt, to obtain any given lime : silica ratio in the precipitate. Gels obtained in this way were similar in all respects to those obtained by direct synthesis or by hydration of tricalcium silicate.

An accidental preparation by the author of crystalline material is of some interest. A number of different batches of sand-lime bricks was stored for some months in a tank of water; at the end of this period a growth of silicate upon some of the bricks was observed. This was in some cases apparently a gel, but on one or two bricks it had a crystalline appearance. On drying over calcium chloride this material was found to consist of weakly birefringent parallel or fibrous growths, having a refractive index of about 1.51 and a composition approximating to $3CaO \cdot 2SiO_2 \cdot xH_2O$. The mechanism of its formation appeared to be solution of silicate from some bricks containing no free lime, and a slow precipitation or crystallization on bricks containing free lime.

FLINT and WELLS (8) found that a true silica solution, metastable, but able to persist for long periods, could be prepared by boiling silica gel with very dilute calcium hydroxide solution. By mixing such a solution with a calcium hydroxide solution, allowing it to come to equilibrium under controlled temperature conditions, filtering and analysing the solutions, they were able to determine the equilibrium solubility curves of the gels formed. The compositions of the gels were determined by difference, and no examination of the properties of these solids was reported.

Properties of the Artificial Hydrated Calcium Silicates.

There is only a limited amount of data available on the properties of the individual artificial silicates, and the greater part of this deals with the crystalline compounds which have been prepared at higher temperatures.

Crystal Forms, Optical Properties and Density.

The crystal forms and optical properties, where observed, are shown in TABLE 6. The only published density determination is that of the dicalcium silicate hydrate occurring as orthorhombic prisms (α-C_2SH), which is given as close to 2.8 by VIGFUSSON, THORVALDSON and BATES (38). The density of the tricalcium silicate hydrate with 1.6 mols. water was found to be 2.56 and that of a sample of the monocalcium silicate hydrate, with 0.35 molecules of water, 2.67, by the present author.

The three forms of the dicalcium compound, C_2SH, are marked as α-, β-, and γ-forms in the table; these letters are not intended to show any relation to the anhydrous dicalcium silicate modifications with the same prefixed letters, and are only given for convenience in reference.

The compounds prepared by hydrothermal processes are included in the subject of another report in the present Symposium and their properties will not therefore be discussed further here.

Water Contents and Dehydration.

The water content of the hydrated silicates is much lower than that of the aluminates, and there is, therefore, rather less doubt about the degree of hydration of the crystalline compounds. As in the aluminates, part of the water is probably present in the structure as hydroxyl and part as loosely combined water molecules. Insufficient work has been carried out upon any of the compounds, however, to indicate the proportions of hydroxyl or water molecules present.

A certain amount of data has been accumulated by the present author, but the results are at present incomplete. They indicate that the crystalline compounds in general do not vary widely in water content with the humidity at which they are dried; the effect upon the gels is of course much greater. Fig. 5 shows as an example, the water contents of the monocalcium silicate crystal and gel respectively dried in different humidities at 17°. The curves suggest that the gel contains a definite hydrate and that it is different in structure from the crystalline material. It is possible that the gel is related to the natural mineral Crestmoreite or Riversideite, whilst the observed crystalline form is similar to Xonotlite.

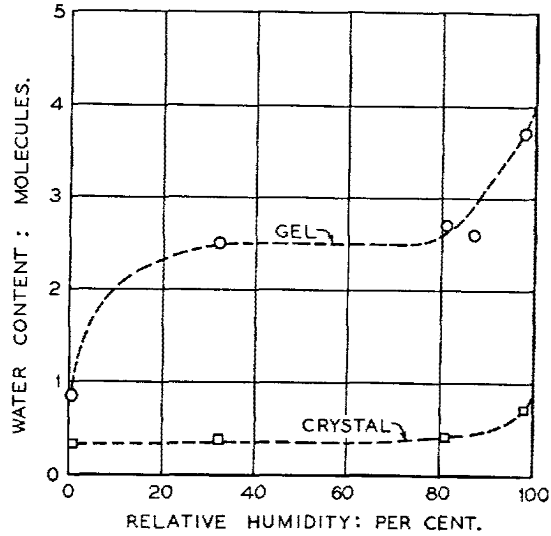

Fig. 5. Variation of Water Content of Monocalcium Silicate Hydrate with Vapour-Pressure at 17°.

Lefol (22) has examined the water retained by a gel of 1.2—1.3 : 1 lime : silica ratio with varying humidity and temperature and found breaks in the curves at about one and two molecules H_2O.

Constitution and Crystal Structure.

The constitution of silicates has been very widely studied during recent years by X-ray methods, and it has been concluded that they can generally be regarded as structures depending essentially upon SiO_4-tetrahedra, linked in different ways, with the anions and other groups usually occupying positions which do not determine the main structure. The composition and characterist-

Table 6. Crystal Form and Optical Properties of the Artificial Hydrated Calcium Silicates.

Formula of Compound	Crystal Forms	Water Content (Mols.)	Refractive Indices			Optical Character, etc.	Observed by
			α	β	γ		
$3CaO \cdot SiO_2 \cdot (1\frac{1}{2}\text{-}2)H_2O$	Prismatic needles	1.5—2.0	1.589	—	1.597	Parallel extinction	Keevil & Thorvaldson
			(1.59 mean)				
		1.5—2.0	1.589	—	1.598	Positive elongation	Bessey
			(1.592—1.602 mean in different samples)				
$2CaO \cdot SiO_2 \cdot H_2O$	Orthorhombic lathes and prisms	1.2	1.614	1.620	1.633	Positive elongation Parallel extinction	Vigfusson, Bates & Thorvaldson
		0.9—1.1	1.614	1.621	1.635	Biaxial. positive 2 V=68°	Bessey
$2CaO \cdot SiO_2 \cdot H_2O$	Very fine needles or fibrous growth or radiating growth	1.3—1.5	—	1.597	—		Vigfusson, Bates & Thorvaldson
		1.2	—	1.590	—	Positive elongation	Bessey
$2CaO \cdot SiO_2 \cdot H_2O$	Irregular grains and masses	0.3—1.0	1.62—1.64			—	Keevil & Thorvaldson unconfirmed
$3CaO \cdot 2SiO_2 \cdot 8H_2O$	—	—	—			—	Nagai, unconfirmed
$3CaO \cdot 2SiO \cdot (1\text{-}3)H_2O$	—	—	—			—	Nagai
	Fine needles variable composition	1.8—2.6	1.585—1.60			Positive elongation Birefringence 0.005±0.003	Bessey
$CaO \cdot SiO_2 \cdot (0.20\text{-}0.50)H_2O$	Fine needles	0.5				Low birefringence	Vigfusson, Bates & Thorvaldson
	» »	0.35—0.5	1.575—1.580			Straight extinction	Bessey

ics of the compound depend largely upon the manner in which the tetrahedra are linked. The existence of independent tetrahedra, for example, gives SiO_4, double tetrahedra Si_2O_7, ring structures and chain structures SiO_3, Si_3O_8, Si_4O_{11} etc., and sheet structures Si_2O_5.

BERMAN (2), in classifying the natural silicates on this basis has given the following constitutional formula to the natural silicates:

Disilicate Type (Sheet structure)	Okenite	$Ca_2\,Si_4O_{10} \cdot 4H_2O$
	Centrallasite	$Ca_4Si_6O_{15}(OH)_2 \cdot 5H_2O$
	Gyrolite	$Ca_4Si_6O_{15}(OH)_2 \cdot 3H_2O$
Metasilicate Type (Chain structure)	Crestmoreite	$CaSiO_3 \cdot 2H_2O$
	Riversideite	$Ca_2Si_2O_6 \cdot H_2O$
	Xonotlite	$Ca_3Si_3O_8(OH)_2$
	Afwillite	$Ca_3Si_2O_6(OH)_2 \cdot 2H_2O$
	Hillebrandite	$Ca_2SiO_3(OH)_2$.

The only experimental evidence adduced for these structures lies in the fibrous nature of the metasilicate group, indicating probably a chain structure, and a very limited amount of X-ray data. They are, however, probably substantially correct and await only confirmation by X-ray analysis. The only artificial compound which is not included in the above list of formulæ, is the tricalcium compound. This can probably be regarded as a pyrosilicate with the formula,

$$Ca_6Si_2O_7(OH)_6.$$

In addition to the above, however, it is possible that alternative structures for the same empirical formulæ exist, such as may be required for the different forms of $2CaO \cdot SiO_2 \cdot H_2O$, for example.

FLINT and WELLS (8), from considerations of the results of electrometric measurements of the solutions, regard all the compounds falling within the range of the gel system as salts of orthosilicic acid as follows:

$$\begin{array}{ll}
Ca_2SiO_4 & nH_2O. \\
Ca_3(HSiO_4)_2 & nH_2O. \\
CaH_2SiO_4 & nH_2O. \\
Ca(H_3SiO_4)_2 & nH_2O.
\end{array}$$

It is doubtful whether the results of measurements upon solutions can be applied in a case of this type to the constitution of the solids, and the presence of OH-groups attached directly to Si, as would be required by this type of structure, is found to be uncommon in mineral silicates. Nevertheless, the possibility of this type of structure existing in the amorphous or gel material precipitated rapidly from solutions should not be overlooked. It is conceivable that the structures of the crystalline compounds and the amorphous material are very different.

X-ray examination of the hydrated silicates have been reported as follows:

Hillebrandite	Vigfusson (37)
Afwillite	Gottfried (10)
Xonotlite	Berman (2)
Artificial $3CaO \cdot SiO_2 \cdot 2H_2O$	Keevil and Thorvaldson (13)
» α-$2CaO \cdot SiO_2 \cdot H_2O$	Vigfusson, Bates and Thorvaldson (38)
» β-$2CaO \cdot SiO_2 \cdot H_2O$	Vigfusson, Bates and Thorvaldson (38)
» $CaO \cdot SiO_2 \cdot (0.2\text{-}1.0)H_2O$ (two forms).	Foret (9)

Observations of patterns given by freshly formed and aged gels have also been made by Chassevent (6).

Solubility and Phase Equilibria.

Very few solubility determinations have been carried out in the system lime-silica-water, owing to the extremely low solubilities involved, and in most studies of the equilibria, only lime concentrations have been determined.

Flint and Wells's study of the system at 30° by precipitation of silica sols. with lime-water, is certainly the most useful work yet published in this connection. They obtained equilibrium solubility curves, part of which, as is indicated later, appear to be metastable, by this precipitation method, and were also able to obtain points approaching parts of the same curves by the action of water on the anhydrous silicates and by the reaction of diatomaceous silica or silica gel and lime solutions. Their curve, showing the lime and silica contents of the solutions, and the solids precipitated at the various points along the curve, is reproduced in Fig. 6.

One transition point has been reported frequently sometimes as a transition point and sometimes as the solubility of the hydrated silicate in water, *i. e.* the invariant point $CaO \cdot SiO_2 \cdot xH_2O$— $SiO_2 \cdot Aq$. The solution concentrations given for this point are as follows:

	CaO g per Litre	SiO_2 g per Litre
Le Chatelier (21)	0.052	—
Michaëlis (25)	0.047	0.038
Weisberg (17°)	0.046	—
Flint and Wells (8) (30°)	0.049	0.046
Bessey (unpublished work, 17° & 25°)	0.050—0.055	0.035—0.050

The value here attributed to Flint and Wells is not quoted by them for this invariant point, but is taken from the approximate location of the point *F* in Fig. 6.

It appears from the above figures for the lime and silica concentrations at the invariant point that the solution is incongruent with respect to the monocalcium silicate hydrate. This is confirmed by the experiments carried out by Lerch and Bogue (23), who found that on shaking either anhydrous tricalcium or dicalcium silicates with water and repeatedly replacing the water every few days, at least 95—99 per cent of the total lime could be removed, in solution, with only about half of the total silica; the residue was almost pure hydrated silica. This incongruent solution of the silicate, with formation of hydrated silica requires that the silicate shall be in equilibrium with silica at this point; it is, therefore, the invariant point with silica and the upward prolongation of the curve to *E* in Fig. 6 can only be metastable. A stable silica solubility curve from *F* to approximately the zero point should exist but has not been definitely observed.

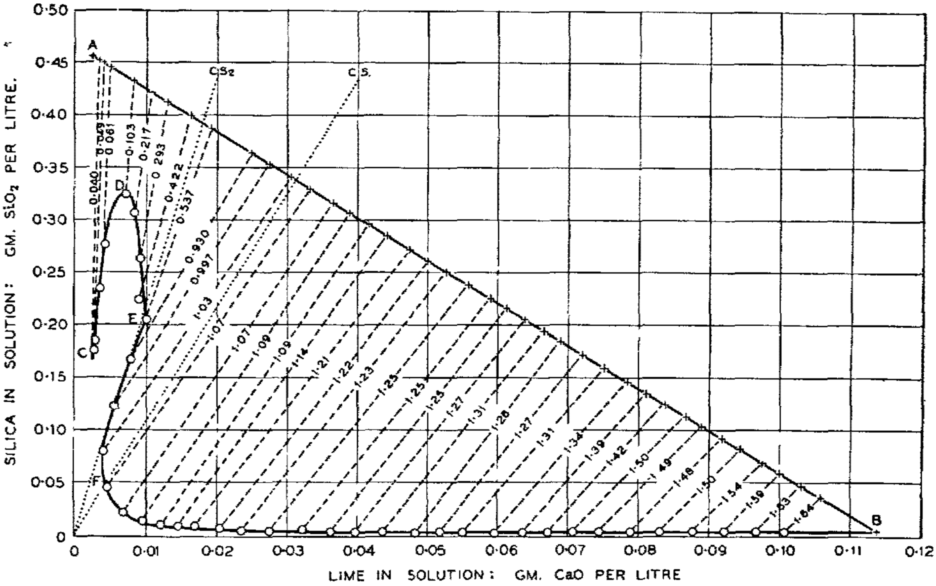

Fig. 6. Solubility Curves in the System CaO-SiO_2-H_2O. According to Flint & Wells.

With increasing lime concentration above point *F*, the silica solubility falls rapidly. At 0.12 g CaO per litre for example, it has been found by the present author to be less than 0.01 g per litre; Flint and Wells's results at the same lime concentration indicate a silica concentration of about 0.015 g. The former result is by direct solubility determination and the latter by precipitation of unstable solutions. At concentrations above 0.02 g CaO per litre, the solubility is of the order of 1—2 milligrams per litre.

The solids in equilibrium with points along this curve have, according to FLINT and WELLS, compositions varying from 1.00 at the invariant point *F* up to 1.85 with a lime concentration of 1.159 g CaO per litre (*i. e.* very nearly saturated lime solution). There is no indication in FLINT and WELLS's results of very marked breaks in the composition curve, although there is an apparent tendency for the lime : silica ratio to remain constant at 1.25 : 1 between 0.2 and 0.4 g CaO per litre and at 1.50 : 1 between 0.7 and 0.85 g CaO per litre. Other workers have also found continuously varying compositions in this range of lime concentrations, and give values for the maximum CaO : SiO_2 ratio of the solid up to 1.7: 1.

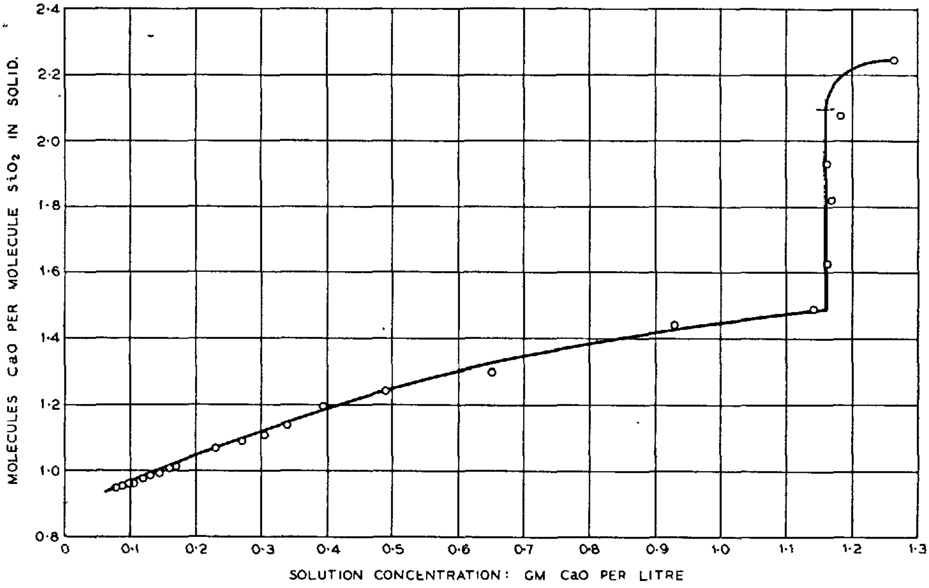

FIG. 7. Equilibrium between Calcium Silicate Gel and Lime Solutions.

Studies of the equilibrium attained with gel silicates in contact with lime solutions at 17°, prepared by all the methods previously discussed, have been made by the present author. The attainment of true equilibrium has been found difficult, but the results, from whatever source the gel was obtained, and whether equilibrium was reached by giving up or absorbing lime from the solutions, have been found to be approximately the same. FIG. 7 shows the solid lime : silica ratios of gels in apparent equilibrium with lime solutions from 0.08 g CaO per litre up to the saturation point of lime solution. The gel used for the experiment shown in the figure was obtained by precipitation of sodium silicate by calcium nitrate. It contained, initially, free calcium hydroxide observable under the microscope and had a composition corresponding to the ratios $2.33CaO : 1SiO_2 : 3.3H_2O$. 15 g of this material treated with a lime solution of 0.05 g CaO per 100 cc, allowed to come to equilibrium and repeatedly diluted to the above concentration, gave the curve shown. The final material was found by analysis to have a composition, after drying *in vacuo* at 17° and about 80 per cent relative humidity, corresponding to $0.97CaO \cdot SiO_2 \cdot 2.8H_2O$. The above results are all corrected for CO_2 and CaO present as calcium carbonate impurity.

The results of this work have shown that these gels have, as found by other workers, compositions varying continuously from $CaO \cdot SiO_2 \cdot nH_2O$ at the lower invariant point $CaO \cdot SiO_2 \cdot mH_2O—SiO_2 \cdot nH_2O$, to $3CaO \cdot 2SiO_2 \cdot xH_2O$ in a solution of about 1.1 g CaO per litre. Above this point, which is below the saturation concentration for calcium hydroxide, the lime: silica ratio of the solid increases sharply, indicating a transition point. The closeness of this point to the saturation point of calcium hydroxide, together with the known difficulty of defining very precisely the solubility of the latter, on account of the effect of particle size and the tendency for supersaturation, has made it impossible so far to determine the composition of the solid above 1.1 g CaO per litre. There appear to be three possibilities:

1. That this is the invariant point
   $2CaO \cdot SiO_2 \cdot mH_2O—3CaO \cdot 2SiO_2 \cdot nH_2O$.
2. That a solid solution series between $Ca(OH)_2$ and $3CaO \cdot 2SiO_2 \cdot nH_2O$ exists above this point.
3. That the solubility of calcium hydroxide itself is lowered to this point by the silicate.

Whilst the data are insufficient to decide definitely which of these explanations is true, there is some evidence tending to eliminate possibilities 2 and 3. The variation in composition above the transition point would be gradual if 2 were true; actually, it is always abrupt at the point, although small apparent variations in the actual point are found with different materials. The third possibility seems unlikely, for when free calcium hydroxide was definitely identified a higher solubility was obtained. It thus seems probable that a dicalcium silicate hydrate exists over the very narrow range of lime solubility between about 1.1 g CaO per litre and 1.3 g CaO per litre at 17°. The effect of temperature upon this transition point has not yet been determined, but it seems probable that the region of stability of the dicalcium compound may disappear completely with increasing temperature and diminishing solubility of $Ca(OH)_2$.

The curve *CDEF* in Flint and Wells's diagram (Fig. 6) may now be considered. It has already been suggested that this area must be metastable since an incongruent solution is obtained at *F*. The existence of these metastable curves have, however, been amply confirmed by results of other workers, the significance of which were not fully understood at the time. Shaw and Mac Intyre (33), for example, using silica gel and lime solutions, obtained a silica solubility of 0.206 g SiO_2 per litre with a lime concentration of 0.100 g CaO per litre and a P_H of 10.53 corresponding very closely toFlint and Wells's point *E*, and two different silica solubilities with a lime concentration of 0.083 g CaO, of 0.245 and 0.033 g SiO_2 per litre, with P_H of 10.00 and 11.31 respectively, corresponding to points on Flint and Wells's curves *DE* and *FB*. The solid phases in this work were not apparently homogeneous and the solids in equilibrium on these curves could not therefore be deduced. Cummins and Miller (7), in examining the reaction of diatomaceous earth with lime solutions found, like Flint and Wells, considerable amounts of silica in solution of low lime concentrations. The present author has determined the solubility of the monocalcium silicate gel in contact with silica gel as 0.21 g SiO_2 and 0.08 g CaO per litre, in satisfactory agreement with Flint and Wells's point *E* for this invariant point.

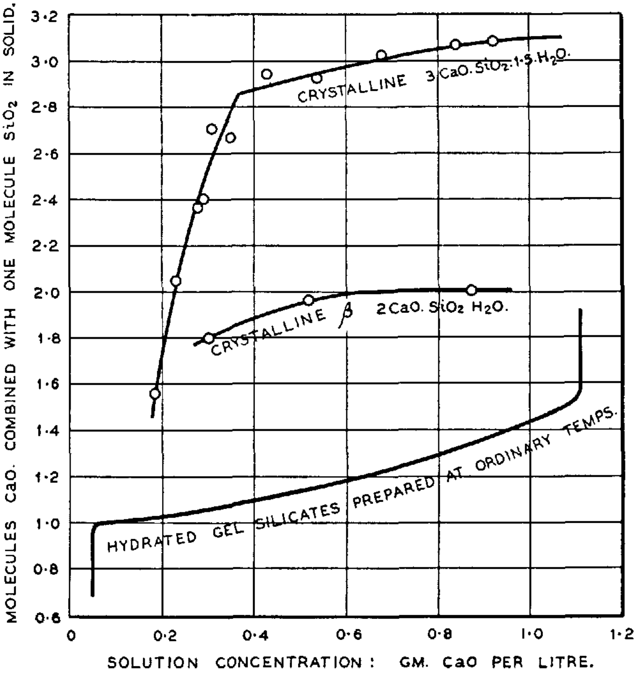

Fig. 8. Lime Extraction Curves of Hydrated Calcium Silicates.

No other work has been reported which provides any check upon the composition of the solid along the curve *DE* in Fig. 6. The solids found along this curve vary, as shown in the figure from 0.22 to 0.54 : 1 lime: silica ratio, and Flint and Wells consider that it is probably the solubility curve of $CaO \cdot 2SiO_2 \cdot xH_2O$. Confirmation of this seems to be required. The curve *CD* represents apparently the metastable solubility of $SiO_2 \cdot nH_2O$ in water and its form and extent are of little real importance or meaning. The whole of this metastable area above *F* in the figure is outside the range of cement chemistry and can only apparently be obtained in the presence of hydrated free silica and is therefore of little immediate practical importance.

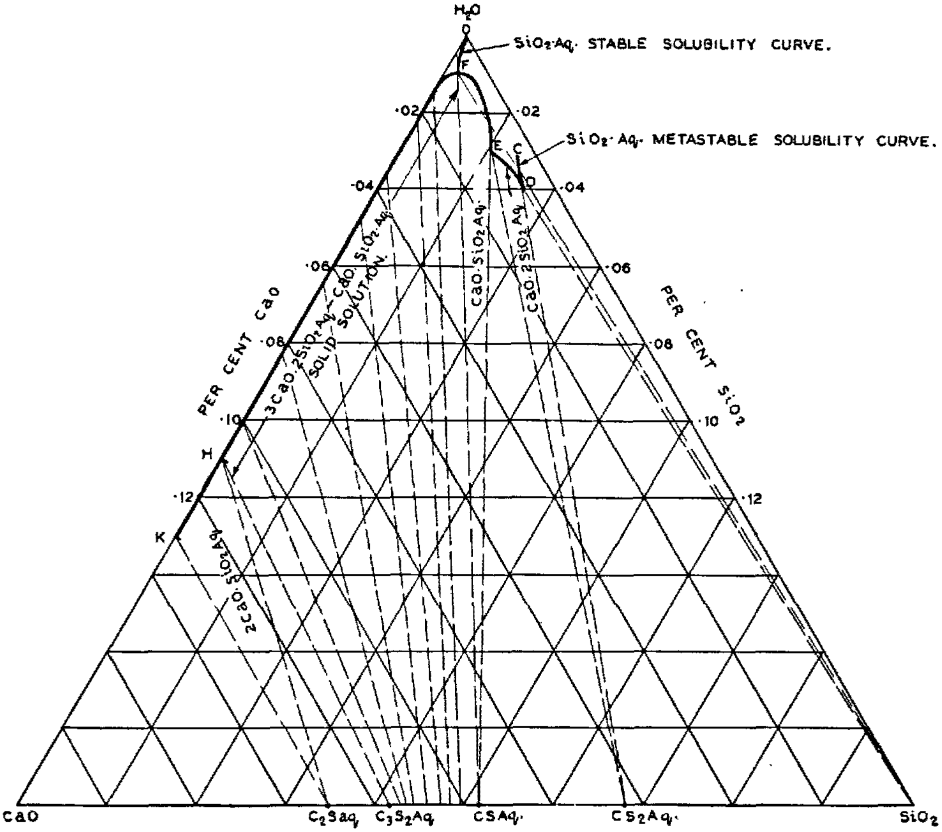

Fig. 9. Suggested Ternary Diagram of System Lime-Silica-Water (Gel Hydrates).

No reference to the equilibrium of the crystalline hydrated silicates has been found in the literature, apart from a statement by Keevil and Thorvaldson (13) that the hydrolysis curves of the tricalcium and dicalcium silicate hydrates are similar to those of the anhydrous compounds, and show hydrolysis to the composition $C_3S_2H_x$ in solutions approaching saturation with lime-water and to CSH_x in more dilute solutions. These authors state, moreover, that equilibrium is more quickly attained with the hydrated compounds than with the anhydrous compounds. The present author's experience differs in this; no appreciable hydrolysis has been observed either with the tricalcium or the β-dicalcium silicate hydrates in contact with lime solutions containing more than about 0.4 g CaO per litre. FIG. 8 shows some results of attempts to attain equilibrium between these compounds and lime solutions and a similar curve for the gel materials over the same range of lime concentrations. It is thought probable that these results are due to great inactivity of the crystalline compounds rather than any difference in true equilibrium from the gel substances, despite the fact that some of the points shown represent the result of shaking with the solution for 70 to 100 days. The view is supported by the results of similar tests with the crystalline monocalcium compound which, for example, absorbed only 3.6 per cent CaO in 15 days, and only 5.0 per cent in 110 days in contact with lime solution containing 0.90 g CaO per litre, though an absorption of about 20 per cent is found under the same conditions with the gels. It is of course likely that certain of the crystalline bodies may be metastable with respect to the material formed at ordinary temperatures or vice versa, but until further evidence is available, it does not appear possible to indicate any definite relation between the crystalline and the gel materials.

The ternary diagram of the system is shown in FIG. 9, only the amorphous or gel solid compounds and the solutions in equilibrium with them being considered, and the most probable values in the light of the foregoing discussion being assigned. The solid phases are all shown with the same percentage water content and the scale of the solubilities exaggerated to make the diagram clear.

The suggested probable solubility curves and invariant points are as follows:

CD. Metastable $SiO_2 \cdot Aq.$ solubility curve.

C. Indefinite.

D. Invariant point $SiO_2 \cdot Aq.$—$CaO \cdot 2SiO_2 \cdot Aq.$ 0.070 g CaO, 0.326 g SiO_2 per litre.
(FLINT and WELLS).

DE. Metastable $CaO \cdot 2SiO_2 \cdot Aq.$ solubility curve.

E. Invariant point $CaO \cdot 2SiO_2 \cdot Aq.$—$CaO \cdot SiO_2 \cdot Aq.$ 0.08—0.100 g CaO, 0.21 g SiO_2 per litre.
(FLINT and WELLS, BESSEY).

EF. Metastable $CaO \cdot SiO_2 \cdot Aq.$ solubility curve.

F. Invariant point $SiO_2 \cdot Aq.$—$CaO \cdot SiO_2 \cdot Aq.$ 0.05 g CaO, 0.04 g SiO_2 per litre.
(Various investigators).

OF. Stable $SiO_2 \cdot Aq.$ solubility curve.

FH. Stable $CaO \cdot SiO_2 \cdot Aq.$—$3CaO \cdot 2SiO_2 \cdot Aq.$ solid solution solubility curve.

H. Invariant point $3CaO \cdot 2SiO_2 \cdot Aq.$—$2CaO \cdot SiO_2 \cdot Aq.$ 1.1 g CaO < 0.002 g SiO_2 per litre (17°).
(BESSEY).

K. Invariant point $2CaO \cdot SiO_2 \cdot Aq.$—$Ca(OH)_2$, probably very close to the solubility of $Ca(OH)_2$ in water.

No information is available with regard to the effect of temperature upon the solubilities and phase equilibria in this system.

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Discussion.

Mr. B. TAVASCI:[1]

In "The System CaO-SiO_2-H_2O" of his paper, dealing with hydrated calcium silicates obtained by hydration of anhydrous silicates, Mr. BESSEY, referring to a paper published by the author (2), speaks of the lack of evidence for the homogeneity of hydrated silicates obtained, thus implicitly raising a doubt as to the correctness of the results.

It will therefore be useful to elucidate this point and, in particular, to define the significance of the term "homogeneity".

It is obvious that the term "homogeneity" assumes two distinct meanings in the case of hydrated calcium silicates obtained by hydrolysis, and whose composition varies almost continuously with the variation of the CaO-contents in solution.

The first significance of the term, which we shall describe as *external homogeneity*, refers to the presence or absence of foreign substances mixed with the basic substance. In our case, crystallized calcium hydrate, particles of silicates not yet hydrated, and the impurities consisting of calcium carbonate due to absorption of carbon anhydrite are to be considered as such foreign substances. The second significance, described here as *internal homogeneity*, refers to the identity or lack of identity in the chemical composition of the various points of the same grain of hydrated silicate.

External homogeneity.

If we have ascertained the quality and the quantity of the external substances present, it is evident that the lack of external homogeneity cannot influence the computation of the chemical composition of the hydrated silicate.

In the hydrolitic decomposition of tricalcium silicate, this compound being in the anhydrous state, the hydrate and the carbonate of calcium may be readily identified as to quality by microscopic observation of a drop of the suspension. On the other hand, their quantitative determination is practically impossible except as regards the carbonate. The quantity of the latter in the various stages of the investigation may be approximately calculated on the basis of the analysis of the final product. It is, furthermore, obvious that calcium carbonate, being practically insoluble, does not modify the equilibrium

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of the hydro-silicate and the liquid phase (at least when the hydro-silicate is sufficiently rich in CaO). In the last analysis, in the case of hydrolysis of a calcium silicate by means of gradual substitution of water for the liquid phase, the absorption of carbon dioxide is equivalent in its effects to removal of $Ca(OH)_2$ with this water.

It is also evident that the presence of anhydrous tricalcium silicate mixed with hydrated silicate may change the conditions of equilibrium. The same applies to solid calcium hydroxide, unless the latter is in equilibrium with the two other phases (the tricalcium silicate never is in equilibrium with these phases).

It is to be added in particular that *also in those cases where this is allowed by the chemical nature of the hydrated silicate in decomposition*, the presence of anhydrous tricalcium silicate in all probability impedes sudden variations in CaO-concentration of the liquid phase, when in the case of mixture of three phases: — solid $Ca(OH)_2$, solid hydrated silicate, and liquid phase, — the firstmentioned phase is decomposed by gradual washing with water.

This drawback is obviously due to gradual hydration of anhydrous silicate.

Conversely it may be said that when such a sudden variation in concentration is observed, not only solid $Ca(OH)_2$ *is decomposed, but it is also found in the absence of tricalcium silicate not yet hydrated and, therefore, under the conditions of equilibrium.*

(Assuming naturally that the other conditions necessary for this equilibrium are verified.)

Examining now the paper by the author (2) we find immediately from FIG. 1 and TABLE 3 that the conditions of equilibrium have been ascertained. The agreement of our results with those obtained in a different way by LE CHATELIER should also be noted.

Internal homogeneity.

It is easy to remove the lime of a hydro-silicate, but it is not equally easy to have it re-absorbed. This is convincingly shown by LE CHATELIER's investigations (1).

It follows that in such hydrated silicates having zones of variable CaO-content, the equalization of the chemical composition will necessarily be a very slow process. For instance, in particles of a hydrated silicate richer in CaO in the interior than in the exterior, an excess of internal lime will be able to pass into solution (assuming a certain permeability of the particle) without being absorbed, wholly or in part, by the external zone. When an anhydrous or hydrated silicate is treated with an excess of water or with a solution of $Ca(OH)_2$ too much diluted, the external zone of the solid particles will be decalcified to a considerable depth. Thus, the hydro-silicate obtained will not at all be homogeneous in its parts and not in the state of chemical equilibrium. After that the re-establishment of equilibrium will require very long time.

It follows that when studying the hydrolysis of a calcium silicate we must, apart from taking other precautions, try to avoid the above-mentioned drawback, *viz., we must operate in the beginning with as high a ratio of silicate to water as possible and in the sequel substitute water for the liquid phase from time to time, in such proportions as to vary the concentration of CaO in the liquid as little as possible.*

In this way the internal homogeneity of the hydro-silicate will be ensured. Some investigations have been carried out without taking into account these precautions. Hence the lack of agreement between the results in the various parts of the same investigation.

Examining now the author's paper (2) it will be clearly seen that the above-mentioned conditions have been fulfilled. — *(Translated from Italian.)*

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Mr. T. THORVALDSON:[1]

Mr. BESSEY has done a very excellent service in summarizing and adding to the data on the solubility of the hydrated calcium aluminates. The apparent disagreement of the results obtained by different experimenters suggests that further work is required. Perhaps the large discrepancies met with are mainly due to working with mixtures of the different hydrates, that is, due to difficulty in obtaining a strictly homogeneous "Bodenkörper".

Mr. BESSEY has found it difficult to prepare the cubic hydrate of tricalcium aluminate in an absolutely pure state by the direct hydration of the aluminate in steam under pressure. While I cannot offer an explanation of the difficulty in reproducing our early results, I would like to mention the experience of one of my students.

Mr. J. M. HUMPHRYS prepared from very pure materials several samples of tricalcium aluminate. Analysis showed that they were slightly deficient in alumina, containing from 0.1 to 0.3 per cent excess of calcium oxide. On prolonged autoclaving none of these samples took up the theoretical 40 per cent of water required to form the hexahydrate and a small amount of anisotropic material was always present. On the other hand, when he used two samples

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of tricalcium aluminate prepared by Dr. N. S. GRACE, one of which contained exactly the right ratio of lime to alumina, the other a slight excess of alumina, treatment in the autoclave resulted in rapid absorption of the theoretical 40 per cent of water, giving an apparently homogeneous isotropic product. Further work is being done to attempt to explain the results.

The experimental results on the hydrolysis of the silicates may appear to some extent contradictory, but I think that on the whole they are beginning to present a rather definite picture. There appears to be little doubt that when anhydrous β-dicalcium silicate is placed in contact with pure water, the silicate dissolving at first is completely hydrolysed and that the production of a hydro-silicate occurs through a re-alignment of the products of hydrolysis. If the ratio of water to silicate is high, the final equilibrium may represent the presence of an inappreciable or a very small quantity of calcium hydrosilicate low in lime, but, as this ratio is decreased, the solid or gel phase becomes richer in lime. Possibly there is hydrated monocalcium silicate formed but this can hardly be considered to be definitely established. For ratios of lime to silica in the gel phase between 1:1 and 3:2, the curve for the distribution of the calcium between the liquid and gel phases is almost a straight line so that there is no evidence that the gel phase over this range is actually a mixture of the hydrated 1:1- and 3:2-calcium silicates. When the silicate is hydrated in saturated lime water it appears that the lime: silica ratio in the gel phase reaches 2:1 or even somewhat higher.

It must be remembered that the equilibria involved are heterogeneous, changes being effected by diffusion which may take place very slowly. When the silicate is placed in pure water, the reactions do not take place uniformly throughout the solid. This results in the production of mixtures, the particle sizes involved being of colloidal dimensions. True solubility equilibria may, therefore, be almost impossible to attain.

Two of my students, Mr. J. L. MORRISON and Mr. R. B. HARVEY, have been studying the behaviour of pastes of β-dicalcium silicate by conductivity methods during the last four years. They have found that the conductivity of the paste rises rapidly to a value corresponding to approximately a saturated solution of calcium hydroxide and then remains constant for a long time while hydration proceeds. The pastes never show an appreciable amount of free calcium hydroxide when analysed by the method of LERCH and BOGUE. Thus it appears that the surface hydration of the particles of β-dicalcium silicate occurs by the mechanism of hydrolysis but that recombination to form a hydro-silicate prevents the solution from exceeding saturation and therefore no solid calcium hydroxide is deposited. On account of the small amount of water present, the total amount of free calcium hydroxide at any time is very small and the hydrated silicate therefore must have a lime: silica ratio of 2:1.

Mr. BESSEY's results on the equilibrium between the crystalline hydrates of β-dicalcium silicate and tricalcium silicate and lime solutions are very interesting. There appears to be a discrepancy between his results and those of KEEVIL and THORVALDSON, which perhaps is due to differences in experimental conditions. In our experiments the autoclaved hydro-silicates were shaken with water which, to begin with, contained no lime. However, as we made only a few experiments, our general statement may be too broad and therefore possibly in error. As Mr. BESSEY suggests, experiments of longer duration would be desirable. There is also the question of the containers used in such experiments. In these experiments we used glass vessels protected by paraffin. We have found, however, that the use of any kind of glass vessels is unsatisfactory and that protective coatings on the glass, while helpful, break down before long-time experiments are completed.

Mr. G. ASSARSSON:[1]

When certain properties of a compound are to be investigated, the methods of its preparation, of the chemical analysis, etc., determine the degree of control of the purity of the preparations. It is very important thoroughly to have studied these conditions. Some points of this kind will be discussed shortly in connection with Mr. BESSEY's paper.

Micro-analysis simplifies the work of the estimation of the compositions of the compounds. The preparations can be reliably controlled, the analyses are surely and quickly, small volumes of the preparation solutions can be selected, good, pure, and large-crystalline preparations are obtained. I have in this manner investigated very good preparations of most aluminate hydrates. I have always found the micro-analysis to be extremely superior to the macro-methods; the former method should be used exclusively in scientific investigations of calcium aluminate hydrates.

In my preparations I have found the water content of the tetra- and dialuminates to be higher than those mentioned by LE CHATELIER and ALLEN and ROGERS. Later, MYLIUS, SCHWIETE and SALMONI also found higher water values; SCHWIETE and SALMONI the same composition of the dialuminate as I found. The two α- and β-tetraaluminates have proved to contain 14 molecules of water, the dialuminate 9 molecules. All MYLIUS's preparations show a smaller water content; these preparations, however, always consist of very diminutive crystals.

The variations in the composition can be considered of very little importance; but it may be mentioned that the composition proved with good analyses must

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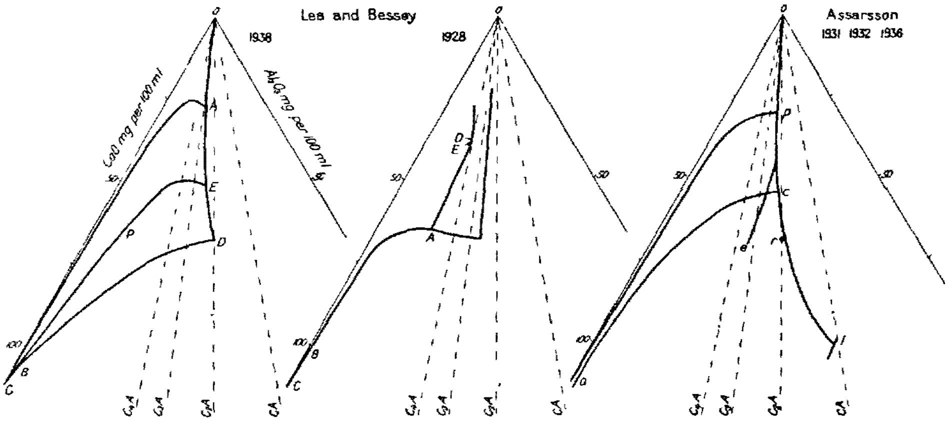
be the basis of the discussion of the structure of the crystals. Structure calculations and also writing of formulae (according to Dr. FORSÉN) must be made with regard to the composition really proved. Most of these calculations are made on the supposition that the crystals are hexagonal as per Miss MEGAW's determination of the structure of the monocline mineral Hydrocalumite. The two α- and β-tetraaluminates are not hexagonal, nor would the dialuminate appear to be, as I demonstrated in 1931.

The other methods used for the identification of the compounds, the optical and the X-ray ones, must also be used with caution. When, for instance, the preparations consist of large and thick crystals, the optical determination is rather reliable. When the optical values of two substances approach each other some difficulties arise. The tricalcium aluminate 12-hydrate is a compound of this kind. Its refractive indices lie between those of the tetra- and dialuminates. In addition the X-ray examination yields powder photographs too little different from the powder photos of the other aluminates. The powder photos of the hexagonal trialuminate so far measured contain no characteristic lines with the aid of which the presence of the composition in question can be proved. The methods for the preparation of good samples of the hexagonal trialuminate are very vague. Mr. BESSEY mentions that MYLIUS was successful when using aluminate and lime solutions (the alumina cement solutions are only mentioned by MYLIUS; all his experiments were made with alkali aluminate solutions). When the preparations are studied, the proportion of lime and alumina in the mixed solutions (according to MYLIUS) is always 3 to 1; MYLIUS also emphasizes that a not insignificant excess of alkali must always occur. In this way all the alumina present must be precipitated



1a 1b 1c

FIG. 1. Triangular Diagrams on the Properties of the Calcium Aluminate Solutions according to BESSEY's Diagram (FIG. 2) and Some Diagrams Earlier published.

together with the lime by the alkali. Apart from the unsuitability of using alkali aluminate solutions for the preparation of lime aluminates (often emphasized by me), the many experiments carried out by me and my assistant, Mr. BORGSTEDT, have led us to the conclusion that the hexagonal tricalcium aluminate 12-hydrate prepared in this way perhaps does not exist.

There are two compounds that have been prepared by me. It seems to be impossible to prepare the pentacalcium aluminate without any trace of sulphate. Mr. BORGSTEDT and I have studied the properties of the pentaaluminate; our results will be published in connection with other investigations. It may be mentioned that the powder photographs show that the most reflex lines always have their fixed position; a small number of them, however, change their positions successively as the sulphate increases. The refractive indices also change successively. These properties may also appear when the tricalcium aluminate 18-hydrate is carefully examined (cf. Mr. BESSEY's paper p. 182).

The monocalcium aluminate 10-hydrate plays a certain part in the hydration of high alumina cement. When a pure monocalcium aluminate solution is brought to crystallize at low temperatures the solid formed precipitates as a white powder. It is not gelous. It can very easily be made free from solution. Hitherto it has not been possible to get sufficient crystals large enough for a careful examination. However, the conditions of the formation and the uniformity of the properties of the preparations warrant the existence of the monoaluminate. Upon being subjected to microscopical examinations, the "poorly crystalline material"[1] (according to Mr. BESSEY) is found to be very homogeneous. If another calcium aluminate should occur, that would be dialuminate; also hydrated alumina. The powder photographs of these two compounds do not agree with the photograph of the monoaluminate. Thus the existence of the monoaluminate needs no confirmation. On the other hand, a certain experience is necessary for its preparation. Mr. BORGSTEDT and I experienced no difficulties in getting good preparations nor in examining them. The preparation with alkali aluminate and lime-water was not tried by us. One new result may be mentioned. It appears very probable that the monoaluminate hydrate has not hexagonal crystals, but crystals of a lower symmetry and a rather large axial angle.

Another compound may be mentioned shortly. I also found a tetraaluminate hydrate of a little lower water content than the other tetraaluminates. The crystallization conditions indicate that it probably is a new compound (γ-tetraaluminate according to Mr. BESSEY); preliminarily I mentioned this compound as a dehydrated α-tetraaluminate. It would not appear very likely that it is a carbonato-aluminate.

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[1] This phrase is used in Mr. BESSEY's paper earlier; it has been corrected there after my contribution to the discussion.

When we try to determine certain properties of a compound we must always make sure that the properties are always uniform and completely independent of accidental circumstances. Mr. BESSEY and Dr. LEA have taken up the problems as to whether the solubility of the lime aluminate hydrate is stable or metastable, have investigated its equilibrium, etc. Such attempts have previously been carried out by POLHEIM, NACKEN and MOSEBACH, myself, and several others. It seemed to me that the difficulties in most cases were not to show the metastability qualitatively and to obtain an approximate value, but to get results to which no objections could be raised. In these experiments the results more than otherwise depend on the preparation conditions. The precariousness of preparing pure aluminates with using alkali-aluminates shall not be further emphasized. On the other hand, I might mention the circumstances that contributed to the interruption of my experiments along these lines. I always used preparations made only by mixing solutions of calcium aluminate and of lime. When determining for instance the solubility, this was found to decrease when the aluminate was stored for some time. The transformation of an aluminate poor in lime into another rich in lime depends also on the way in which it is prepared. MYLIUS's method generally yields less reactive preparations. As a consequence of these circumstances we must suppose the formation of a deactivating surface on crystals of the calcium aluminate hydrates. Sometimes these surfaces can be so thick that they can be observed microscopically. As regards the cubic trialuminate 6-hydrate, I mentioned already in 1932 that the crystals sometimes were covered with stronger refracting layers, the refraction being about 1.625 instead of 1.605. I have observed deactivation phenomena in mono-, di-, and tetraaluminates and also in hydrated high alumina cement. Because of difficulties in the preparation methods we must ask what are the conditions of the determination of the maximum, metastable solubility.

Here I shall only touch upon some questions concerning the equilibrium relations presented in the diagram, FIG. 2 in Mr. BESSEY's paper. I have made a sketch of this figure in the shape of a triangular diagram and have connected it with other diagrams. The first diagram is the new FIG. 2, the second is the diagram published in Building Research's Report 1928.[1] The difference between these two diagrams must be referred to the influence of traces of carbon dioxide (according to BESSEY). However, the difference is too great to be explained in this way. The line *O—A—B* should represent the maximum

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[1] "During the year, this research reached the point at which *it is possible to denote the main characteristics of the system at 25°*" (1928). "It will be anticipated that this investigation *will be completed* in the ensuing year" (1929). "The present work is limited to the determination of the composition of the solid phase in equilibrium with the various solubility curves *previously traced out*" (1930). — Rept. Bldg. Research Board.

solubility of the cubic trialuminate 6-hydrate; this compound would then be the only one that is dissolved "congruently". The other aluminate hydrates, the di-, tri-, and tetraaluminates, should then correspond to the area *E—B—D* and should be metastable, probably also the penta- and monoaluminates.

When we select a point between the lines *AB* and *EB*, such solutions should yield cubic trialuminate as solid. However, my own experiments, very often repeated, show that no cubic crystals are formed but pseudohexagonal tetraaluminate crystals which should be referred to the area *E—B—D* in Mr. BESSEY's diagram. This cannot be ascribed to the occurrence of a small trace of carbon dioxide, as the experiments have always been made on condition that carbon dioxide has been carefully avoided. The *composition and the optical properties of the crystals are exactly those of the tetraaluminate* but not those of the carbonato-aluminate; these two properties can be determined very easily and exactly.

In my own experiments I found that the diluted solutions yield only tetraaluminate, the more concentrated solutions at first tetraaluminate, later also solids containing chiefly dialuminate mixed with tetraaluminate. The limit between these two kinds of solutions lies approximatively on the line *a—c* (FIG. 1 c), which is nearly identical with limit *B—P—E* (FIG. 1 a).

Point *r*, FIG. 1 c (maximum solubility of dialuminate according to ASSARSSON 1936) is also identic with the maximum solubility, found by BESSEY (point *D*, FIG. 1 a). When solutions after the crystallization of the solids containing dialuminate are separated and mixed with a little diluted lime-water (in this way the solutions can be made absolutely CO_2-free), they yield tetraaluminate but no cubic trialuminate; the more diluted solutions yield also always tetraaluminate (ASSARSSON). The solubility of the tetraaluminate agrees very nearly with the line *a—p* (ASSARSSON 1931). It is much smaller than the solubility of the tetraaluminate corresponding to the line *B—P—E* (FIG. 1 a) supposed by Mr. BESSEY. The difference between the temperatures used (25° by Mr. BESSEY and 20° and 22° by me) cannot cause *all these differences and accordances.*

Mr. BESSEY's diagram is open also to other objections. The difficulties encountered in treating these problems are great. The crystals that are really stable against the most diluted solutions are not yet conclusively proved. This point I strongly emphasized in my monograph of 1936. We know all very well that metastability of certain substances always must occur. Most of the problems connected with the calcium aluminates and their solutions, however, must be treated by using quite other points of view.

Mr. A. TRAVERS:[1]

A Simple Method for Preparing Hexahydrate of Tricalcium Aluminate, and a Study of its Dehydration.

The methods described for the preparation of this compound permit one to obtain conveniently only very small quantities of the order of a gramme (KLEIN and PHILLIPS, PULFRICH and LINCK, THORVALDSON and GRACE).

I succeeded in obtaining it in a *homogeneous* medium, employing *solutions* of the raw materials; these are:

1. A solution of calcium phenate (shaking, with protection from CO_2, of an aqueous solution of phenol—6 %—in the presence of an excess of pure CaO, obtained from the oxalate). Care is taken that all the phenol is well neutralized; in the affirmative a drop of 5 %-solution of potash gives a precipitate, $[Ca(OH)_2]$. The P_H of the solution is in the region of 11.

2. A concentrated solution of potassium aluminate, crystallized $K_2O \cdot Al_2O_3 \cdot 3H_2O$ of known strength, with an addition of excess of alkali, calculated according to the quantity of phenol formed in the reaction:

$$3(C_6H_5O)_2\,Ca + K_2O \cdot Al_2O_3 + 8H_2O = 3CaO \cdot Al_2O_3 \cdot 6H_2O + 2C_6H_5OK + 4C_6H_5OH.$$

The solution 1. is brought to boiling-point in a flask surmounted by a vertical cooler and furnished with a CO_2-guard; the aluminate solution is poured in drop by drop. Very pure and abundant crystals of tricalcium aluminate hydrate are immediately precipitated.

The solution of potassium phenate assures the conditions of stability of the tricalcium aluminate (P_H 11.3). The composition of the salt obtained is, at 1/300, the theoretical composition; one easily obtains in a single operation 15 to 20 g of the compound.

I have verified in this hydrate a series of properties described in detail by THORVALDSON and his collaborators.

1. *Congruent* dissolution of the salt (0.316 g of anhydrous salt per litre at 17°).
2. Stability with the time of these solutions.
3. Recrystallization from solutions, at $t > 25°$.

Dehydration.—On the other hand, I do not agree with the data of the literature concerning dehydration.

According to THORVALDSON and GRAGE (1) the dehydration takes place by stages; as long as the water content remains less than $1.5H_2O$ no lime will be liberated; above this, free lime will be formed.

I heat the salt *in a current of nitrogen:* no loss of weight is shown before 275°. Between 275° and 450° 67 % of the water is given off, which corresponds approximately to the formation of the hydrate with $2H_2O$.

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It is only towards 1 000°—as for $Al(OH)_3$—that the dehydration is complete. *But in any case we obtain no free CaO.* To control this I employed the method already described by my pupil P. LEDUC (Thesis, Nancy 1934) (heating of the product in a boiling alcoholic solution of NH_4Cl; no giving-off of NH_3 is observed).

Thus all the water contained in the hydrate is constitutional water; the formula

$$Ca_3[Al(OH)_6]_2$$

confirms this perfectly.

The dehydration *in a current of inert gas* involving no hydrolysis, one thus obtains a simple and elegant method for preparing anhydrous tricalcium aluminate, which it is difficult to obtain by the dry process because of the decomposition of this salt before its point of fusion. — *(Translated from French.)*

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1. THORVALDSON, T. and GRACE, N. S. — Can. J. Research, 1929, 45.

Messrs. A. TRAVERS[1] and A. ZAHABI:[2]

On the Crystallized, Hydrated Monocalcium Aluminate.

While the anhydrous aluminate with congruent fusion is easily prepared by fusion, employing the theoretical proportions, of Al_2O_3 and CaO, the *crystallized* hydrate of this salt has not been described.

ASSARSSON (1) has obtained an amorphous mass—to which he has given the composition of a hydrate of $CaO \cdot Al_2O_3$—by cooling to 5° the solution, saturated at 20°, of the anhydrous salt.

As the solubility of this body increases with the temperature, while nevertheless remaining rather weak, it would seem advantageous *a priori* to begin with a solution made *à chaud* (50° for example), while preventing hydrolysis by the addition of potassium phenate.

50 g of anhydrous aluminate are shaken for 15 minutes in a litre of water at 50°; this is then centrifuged, and to the filtrate is added 100 cc of a normal solution of C_6H_5OK. A crystalline precipitate is immediately produced, and this is accentuated on cooling. The precipitate, dried over sulphuric acid, corresponds to the formula

$$CaO \cdot Al_2O_3 \cdot 4H_2O.$$

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It gives no reaction with the solution in *absolute* alcohol of NH_4Cl (2) and is, then, akin to the cubic aluminate of THORVALDSON, $3CaO \cdot Al_2O_3 \cdot 6H_2O$; actually two of the molecules of water are water of crystallization and are only eliminated in a current of nitrogen above 150°.

It corresponds, then, to monocalcium ortho-aluminate $Ca(AlO_3H_2)_2$, analogous to $Ca(PO_4H_2)_2$. Its solutions, stabilized by potassium phenate, keep for months without any trouble.

It is scarcely probable that this compound is formed in the setting of aluminous cements; for its solution, in the absence of a stabilizer, is very unstable, like that of the anhydrous aluminate; it deposits alumina and hydrates of aluminate richer in lime. — *(Translated from French.)*

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1. ASSARSSON, G. — Z. anorg. allgem. Chem., 1931, 200, 385; 1932, 205, 335; 1935 222, 321.
2. Reaction described by one of us in collaboration with P. LEDUC.

Mr. G. E. BESSEY *(author's closure)*:

The reference in the report to the lack of evidence of homogeneity of the products obtained by Dr. TAVASCI by extraction of tricalcium silicate was intended to refer only to internal homogeneity of the hydrated silicates formed. Is is agreed that the experiment in question was carried out under suitable conditions for obtaining satisfactory equilibrium, but complete equilibrium throughout particles of the gel silicates is difficult to obtain and it is unsafe to infer, without other evidence, that such equilibrium was actually obtained.

A doubt is expressed by Professor THORVALDSON whether the formation of a monocalcium silicate hydrate by hydrolysis of dicalcium silicate can be considered to be definitely established. The curve shown in FIG. 7 in the report has been found by the author to be of similar form for gel silicates prepared either by hydration of tricalcium silicate, by reaction of lime and silica, or by precipitation from sodium silicate solutions, and points on the curve can be obtained either from solids of higher or lower lime:silica ratio by shaking with the appropriate lime solutions. There appears therefore to be little doubt of the equilibrium as far as gel material is concerned, and the presence of inflections in the curve (FIG. 8) at about 0.05 g per litre with the solid composition corresponding to $CaO \cdot SiO_2 \cdot xH_2O$ indicates, with little room for doubt, the existence of this compound. The solid between 0.05 g per litre and 1.1 g per litre is most probably a solid solution of CSH_x and $C_3S_2H_y$; it is difficult to place any other interpretation upon the data with regard to the equilibria between solids and lime solutions. Owing to the slowness with which equilibrium can be obtained with β-dicalcium silicate, compositions of the solids in equilibrium with lime solutions have not yet been accurately determined, but if the values with the other gel materials are correct, the final equilibrium must be the same for this compound.

The results of studies of the conductivity of pastes of β-dicalcium silicate mentioned by Professor THORVALDSON are in agreement with the author's conception of the hydration process of this compound. At normal temperatures and in the absence of other components there seems to be little doubt that the gel product is a dicalcium silicate hydrate.

Professor THORVALDSON also mentions the important question of vessels used for long period equilibrium experiments on hydrated silicates and aluminates. The author has found that the use of glass vessels of any type for establishing equilibria was undesirable. In the solubility work on the calcium aluminates, gold-plated copper vessels have been used, and in work on the silicates, stainless steel vessels. The latter have been found to be the more convenient as gold plating is readily damaged and requires renewal. No corrosion has been found with the stainless steel.

Professor THORVALDSON's observations with regard to the hydration of different tricalcium aluminate samples in the autoclave are interesting, and may provide the explanation of difficulties which have sometimes been found in obtaining perfectly pure samples of the hexahydrate in this way. The method of preparation of the latter compound described by Professor TRAVERS is a very useful one, having the advantages of avoiding the previous preparation of the anhydrous aluminate, and of giving high yields without difficulty. The utilization of this compound to prepare anhydrous tricalcium aluminate by direct ignition was suggested by THORVALDSON, GRACE and VIGFUSSON, and the method described by Professor TRAVERS for its preparation makes it possible to utilize that suggestion.

The de-activated layer on the surface of crystals of some samples of tricalcium aluminate hexahydrate, mentioned by Dr. ASSARSSON, has not been observed by the author. It is difficult to understand what this layer can be unless two forms of the compound exist; the matter is clearly one which requires further study.

Dr. ASSARSSON raises a number of points in connection with the methods used in investigations of the hydrated aluminates. The use of micro-analysis for determination of the composition of solids and solutions has undoubted advantages, and the use of such methods of analysis in Dr. ASSARSSON's own work has been a notable example of their value. The dangers of contamination by carbon dioxide during the determination of solubilities are, however, probably increased when working with very small amounts of materials.

The exact water content of these compounds remains a debatable point. It depends very much upon the temperature and humidity at which the samples are dried. Dr. ASSARSSON has used samples washed with alcohol or acetone and ether, without further drying, for his analyses; the present author has used samples dried *in vacuo* over a saturated ammonium sulphate solution in most cases, and considers that drying under standard conditions of vapour-pressure is preferable to washing; other investigators have used various other drying conditions. It is admittedly difficult to determine whether physically occluded moisture is completely removed by washing, or whether small amounts of very loosely combined water may not be removed by drying even under high vapour-pressures. It is for this reason that determination of structure by X-ray methods may assist in deciding finally the true water content; in structure determination, symmetry and other considerations may decide the correct formulae when, as in the present cases, the chemical analyses leave some doubt.

The difficulties of identification of the individual compounds, owing to the similarity of their optical characteristics, are rightly stressed by Dr. ASSARSSON, and there is no doubt that much of the confusion in the past has been due to this difficulty. The X-ray powder photographs also have so much in common that the published patterns have not been of any great assistance in identification.

The conclusion of Dr. ASSARSSON that the tricalcium aluminate 12-hydrate may not exist is interesting. THORVALDSON and his co-workers and MYLIUS have both claimed its preparation in a pure state; the present author has only identified it in mixtures by the indices assigned to it by these authors, and has not prepared it in a state sufficiently pure to affirm without doubt that it exists with the formula given.

The observations made by Dr. ASSARSSON with regard to the pentacalcium aluminate hydrate are of interest in connection with the suggestion, put forward by the present author in the discussion on Dr. BÜSSEM's paper, that the pentacalcium aluminate hydrate, the tricalcium aluminate 18-hydrate and the high sulphate calcium sulpho-aluminate are closely related in structure. The fact that the pentacalcium compound cannot be prepared free from sulphate and that solid solution, as evidenced by slight changes in the X-ray powder pattern with increasing sulphate content, exists, is in agreement with such a similarity in structure.

The monocalcium aluminate hydrate prepared by Dr. ASSARSSON is apparently formed in the system CaO-Al_2O_3-H_2O only at low temperatures. Failure to observe its existence by the present author, who has worked mainly at 25°, and by other investigators is probably due to this. The method of preparation now reported by Professor TRAVERS and Dr. ZAHABI of a monocalcium compound with the formula $CaO \cdot Al_2O_3 \cdot 4H_2O$ is entirely novel; whether this compound is the same as that described by Dr. ASSARSSON, or whether it is an entirely new compound, is not clear. If it is the same as Dr. ASSARSSON's compound it would appear that the latter must, in the presence of the potassium phenate, be stable at much higher temperatures than when in contact with the pure aluminate solutions.

Dr. ASSARSSON does not agree with the phase equilibria diagram[1] as given by LEA and BESSEY. The disagreement is too complete for adequate discussion at this stage, and the arguments in favour of the curves shown can only be given when the complete data are published. The principal point of difference experimentally between Dr. ASSARSSON's data and those of LEA and BESSEY is the precipitation according to the former, of tetracalcium aluminate in the area which, according to FIG. 2, should only precipitate C_3AH_6. It is interesting to note that in Dr. ASSARSSON's work at 20° solutions of high initial concentration, however long they were left to attain equilibrium, never gave concentrations lying below the curves $OEBC$; the only solutions which gave precipitates in the area below these curves were those starting below and precipitating only a few milligrams of material. However great the care in excluding carbon dioxide it is felt that there must be some risk of contamination of such small amounts of solid, and that, in view of the effect of carbonate upon this system, which has been observed by the author (the solubility of the carbonato-aluminate being lower than that of the compound C_3AH_6), the results require checking with determination of carbonate content.

With Dr. ASSARSSON's contention that Phase Rule conceptions are not the most suitable for dealing with the problem of the calcium aluminates and their solutions the author cannot agree. It is his opinion that the elucidation of the phase equilibria in this and allied systems, together with a knowledge of the paths by which the equilibria may be attained, should provide the surest means of attaining an understanding of the hydration of cements.

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[1] The diagram 1 b reproduced by ASSARSSON from the 1928 Annual Report of the Building Research Board was a preliminary one based on a short initial survey of the system and it in no way represented any final conclusion.

THE CALCIUM ALUMINATE COMPLEX SALTS

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Introduction.

Until within the past ten years, knowledge of the complex calcium aluminates has been confined to the high sulphate form of calcium sulpho-aluminate, and calcium chloro-aluminate containing one mol. of $CaCl_2$. The separation of a low sulphate form of calcium sulpho-aluminate, reported in 1929 by LERCH, ASHTON and BOGUE (15), and the investigation by FORSÉN (6) of the effect of water-soluble calcium salts in retarding the setting time of cements, has been followed by the isolation of a number of complex salts of inorganic and organic acids by FORET (5) and by FORSÉN (7) and MYLIUS (18). In the following report, the available data are selected and summarized to give a brief survey of the field.

The only naturally occurring complex compound of those described is the high sulphate form of calcium sulpho-aluminate, Ettringite. This was originally found by LEHMANN (14) in 1874 lining the cavities of metamorphosed limestone inclusions near Ettringen, Rhineland, and recently has been found by TILLEY (20) in association with "Hydrocalumite" ($4CaO \cdot Al_2O_3 \cdot 12H_2O$) in Ireland.

The following abbreviations are used:

$$C = CaO, \quad A = Al_2O_3. \text{ Thus}$$

$$C_3A \cdot 3CaSO_4 \cdot mH_2O = 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot mH_2O.$$

List of Reported Compounds.

The compounds which have been prepared are listed in TABLE 1. Nos. 2—9, 16—19, 20—21 inclusive have been described only by the authors FORET (5), FORSÉN (7) and MYLIUS (18). Except for Nos. 20 and 21, the compounds may be assigned to two series, of empirical formulae:

$$\begin{array}{ccc} \text{I} & & \text{II} \\ C_3A \cdot 3CaX \cdot mH_2O & & C_3A \cdot CaX \cdot nH_2O \\ \text{or} & \text{and} & \text{or} \\ C_3A \cdot 3CaY_2 \cdot mH_2O & & C_3A \cdot CaY_2 \cdot nH_2O \end{array}$$

where X = bivalent acid radical; SO_4, CrO_4, SeO_4, CO_3,

Y = monovalent acid radical; Cl, Br, I, NO_3, NO_2, MnO_4, ClO_3, IO_3, HCO_2, $CH_3 \cdot CO_2$, $C_2H_5 \cdot CO_2$.

The maximum water contents appear to be $m = 30$—$32H_2O$, $n = 10$—$12H_2O$. Corresponding compounds of these types containing 3 and 1 mols. respectively of the same calcium salt have been obtained only in four cases for SO_4, ClO_3, CH_3CO_2 and CO_3.

Table 1. List of Reported Compounds.

Series	No.	Formula	Observers
I $C_3A\cdot 3CaX\cdot mH_2O$	1	$C_3A\cdot 3CaSO_4\cdot Aq.$	Michaëlis (17) & many others
$C_3A\cdot 3CaY_2\cdot mH_2O$	2	$C_3A\cdot 3CaCrO_4\cdot Aq.$	Foret (5)
	3	$C_3A\cdot 3CaSeO_4\cdot Aq.$	» (5)
	4	$C_3A\cdot 3Ca(MnO_4)_2\cdot Aq.$	» (5)
	5	$C_3A\cdot 3Ca(ClO_3)_2\cdot Aq.$	» (5)
	6	$C_3A\cdot 3Ca(IO_3)_2\cdot Aq.$	» (5)
	7	$C_3A\cdot 3Ca(HCO_2)_2\cdot Aq.$	» (5)
	8	$C_3A\cdot 3Ca(CH_3\cdot CO_2)_2\cdot Aq.$	
	9	$C_3A\cdot 3Ca(C_2H_5\cdot CO_2)_2\cdot Aq.$	
	10	$C_3A\cdot 3CaCO_3\cdot Aq.$	Bessey (2)
II $C_3A\cdot CaX\cdot nH_2O$	11	$C_3A\cdot CaSO_4\cdot Aq.$	Lerch, Ashton & Bogue (15), Forsén (7), Mylius (18)
$C_3A\cdot CaY_2\cdot nH_2O$	12	$C_3A\cdot CaCl_2\cdot Aq.$	Friedel (8), Wells (21), Lafuma (11), Forsén (7), Mylius (18)
	13	$C_3A\cdot CaBr_2\cdot Aq.$	Foret (5), Forsén (7), Mylius (18)
	14	$C_3A\cdot CaI_2\cdot Aq.$	Foret (5), Forsén (7), Mylius (18)
	15	$C_3A\cdot Ca(NO_3)_2\cdot Aq.$	Foret (5), Forsén (7), Mylius (18)
	16	$C_3A\cdot Ca(NO_2)_2\cdot Aq.$	Foret (5)
	17	$C_3A\cdot Ca(ClO_3)_2\cdot Aq.$	Forsén (7), Mylius (18)
	18	$C_3A\cdot Ca(CH_3\cdot CO_2)_2\cdot Aq.$	» (7), » (18)
	19	$C_3A\cdot CaCO_3\cdot Aq.$	Bessey (2)
Other compounds	20	$C_4A\cdot Ca(IO_3)_2\cdot Aq.$	Forsén (7), Mylius (18)
	21	$C_5A\cdot Ca(IO_3)_2\cdot Aq.$	» (7), » (18)

Methods of Preparation.

Two methods of preparation, both involving crystallization from solution, have been chiefly used.

1. Precipitation from Calcium Aluminate Solutions: This consists essentially in the mixing of solutions of calcium salt and lime-water with a metastable calcium aluminate solution.

2. Precipitation from Aluminium Salt Solutions: A simple method is to add lime-water to a solution of the appropriate aluminium salt. Since the complex compounds are not in general congruently soluble in water, appropriate additions of excess lime and Ca-salt are required to provide a solution from which the desired compound may crystallize as a single stable phase.

A modification of the first method is to use a potassium aluminate solution in place of calcium aluminate.

Table 2. Crystal Form and Optical Properties.

No.	Formula	Crystal Form	Refractive Indices		Optical Character	Observers
			ω	ε		
1	$C_3A \cdot 3CaSO_4 \cdot 31$—$33H_2O$	Needle-like tetragonal prisms			—	MICHAËLIS
		Hexagonal, needle-like prisms	1.464	1.458	Uniaxial negative	LERCH, ASHTON & BOGUE
		Prisms	1.465	1.461	»	KOYANAGI (8)
		Long needle-like hexagonal prisms	1.463	1.459	»	FORSÉN, MYLIUS
2	$C_3A \cdot 3CaCrO_4 \cdot 30H_2O$	Needles, crystallizing badly	Not determined			FORET
3	$C_3A \cdot 3CaSeO_4 \cdot 30H_2O$	At first gelatinous in appearance. Slowly becomes crystalline. No typical needles shown in photo x 450	»			»
4	$C_3A \cdot 3CaMnO_4 \cdot 30H_2O$	Photo x 450 shows indefinite material	»			»
5	$C_3A \cdot 3Ca(ClO_3)_2 \cdot 30H_2O$	Not stated	»			»
6	$C_3A \cdot 3Ca(IO_3)_2 \cdot 30H_2O$	Not stated	»			»
7	$C_3A \cdot 3Ca(HCO_2)_2 \cdot 30H_2O$	Needles	»			»
8	$C_3A \cdot Ca(CH_3 \cdot CO_2)_2 \cdot 30H_2O$	Crystallizes badly	»			»
9	$C_3A \cdot 3Ca(C_2H_5 \cdot CO_2)_2 \cdot 30H_2O$	Photo x 600 shows ill-defined needles	»			»
10	$C_3A \cdot 3CaCO_3 \cdot 27H_2O$	Needles	Close to No. 1		—	BESSEY
11	$C_3A \cdot CaSO_4 \cdot 12H_2O$	Hexagonal plates, often in spherulitic groups	1.504	1.488	Uniaxial negative	LERCH, ASHTON & BOGUE
12	$C_3A \cdot CaCl_2 \cdot 10H_2O$	Irr. hexagonal plates	—	—	—	FRIEDEL
		Hexagonal plates	1.550	1.535	Uniaxial negative	WELLS
		Hexagonal plates, often in spherulitic groups	1.552	1.533	»	FORSÉN, MYLIUS
	$C_3A \cdot CaCl_2 \cdot 18H_2O$	Small, birefringent crystals	—		—	LAFUMA (11)

Table 2 (Contd.).

No.	Formula	Crystal Form	Refractive Indices	Optical Character	Observers
13	$C_3A \cdot CaBr_2 \cdot 10?H_2O$	Hexagonal plates, mostly in spherulitic groups	1.556 1.546	Uniaxial negative	FORSÉN, MYLIUS
14	$C_3A \cdot CaI_2 \cdot 8H_2O$	Hexagonal plates in spherulitic groups	1.575 1.572	»	»
15	$C_3A \cdot Ca(NO_3)_2 \cdot 10H_2O$	Hexagonal plates, mostly in spherulitic groups	1.502 1.532	Uniaxial	»
16	$C_3A \cdot Ca(NO_2)_2 \cdot 10H_2O$		Not determined		FORET
17	$C_3A \cdot Ca(ClO_3)_2 \cdot 10H_2O$	Hexagonal plates, mostly in spherulitic groups	1.519 —1.521 1.521	—	FORSÉN, MYLIUS
18	$C_3A \cdot Ca(CH_3 \cdot CO_2)_2 \cdot 8H_2O$	Thin, soft, hexagonal plates, mostly in spherulitic groups	1.549 1.538	Uniaxial negative	»
19	$C_3A \cdot CaCO_3 \cdot 11H_2O$	Hexagonal plates	1.550 1.530	—	BESSEY
20	$C_4A \cdot Ca(IO_3)_2 \cdot 22H_2O$	Long needles probably hexagonal	1.521 1.496	Uniaxial negative	FORSÉN, MYLIUS
21	$C_5A \cdot Ca(IO_3)_2 \cdot 33H_2O$	Long needle-like prisms, probably hexagonal	Very feebly birefringent. Mean index 1.471	»	»

MICHAËLIS (17) prepared $C_3A \cdot 3CaSO_4 \cdot Aq.$ by (*2.*), LERCH, ASHTON and BOGUE (15) by (*1.*) and (*2.*). The compound $C_3A \cdot CaSO_4 \cdot Aq.$ was prepared by the latter by modifying (*1.*), first mixing lime-water and calcium aluminate solution, filtering off the precipitate, and then adding a solution of calcium sulphate to the filtrate. WELLS (21) prepared $C_3A \cdot CaCl_2 \cdot Aq.$ by (*2.*), FORET (5) almost entirely used (*1.*), FORSÉN (7) and MYLIUS (18) used both methods, and employed LERCH, ASHTON and BOGUE's modification for $C_3A \cdot CaSO_4 \cdot Aq.$ and the potassium aluminate solution for $C_3A \cdot Ca(CH_3 \cdot CO_2)_2$ and $C_4A \cdot Ca(IO_3)_2$. BESSEY (2) has prepared $C_3A \cdot 3CaCO_3 \cdot Aq.$ in admixture with $CaCO_3$ by mixing a calcium aluminate solution with lime-water and ammonium carbonate solution and $C_3A \cdot CaCO_3 \cdot Aq.$ by using a similar mixture together with KOH-solution.

Properties of the Complex Aluminates.

Crystal Form, Optical Properties, Density.

Density values have been obtained for the sulphates only. LERCH, ASHTON and BOGUE (15) reported the values 1.48 for the $3CaSO_4$-compound ($31H_2O$), probably a misprint for 1.78, and 1.95 for the $1CaSO_4$-compound ($12H_2O$). The present writer obtained 1.73 for the $3CaSO_4$-compound ($32H_2O$) compared with a value for the natural Ettringite of 1.75 ($33H_2O$) [LEHMANN (14)], 1.78 ($32H_2O$) [BANNISTER (1).]

The available data for crystal form and optical properties are given in TABLE 2. FORET has not given optical properties.

Water Contents and Dehydration.

The available data for dehydration at room temperature and above are given in TABLES 3 and 4 respectively. The water contents over anhydrous $CaCl_2$ are taken from analytical data given by the authors. There is some uncertainty about the precise water contents in many cases. FORSÉN (7) and MYLIUS (18) distinguish between loosely combined water retained over $CaCl_2$ and firmly combined water, retained over P_2O_5 or after drying at 105°. It is stated that after drying over anhydrous $CaCl_2$ the $CaBr_2$-compound contained 8—8.5H_2O, and appeared optically as a mixture of two hydrates, of indices $\omega = 1.556, \varepsilon = 1.546$ and $\omega = 1.570, \varepsilon = 1.558$. This is considered to be a mixture of $10H_2O$- and $8H_2O$-hydrates. The $CaCl_2$-compound could be obtained only as a $8H_2O$-hydrate. FORET (5) obtained values up to 8.65H_2O, supporting FORSÉN's and MYLIUS's hypothesis of the existence of an unstable $10H_2O$-compound.

Table 3. Dehydration Data at Room Temperature.

No.	Compound	Molecules H_2O retained under Stated Drying Conditions			
		Anhydrous $CaCl_2$	P_2O_5	Other Conditions	
1	$C_3A \cdot 3CaSO_4 \cdot 31—33H_2O$	31.5 (FM)[1]	7.5 (FM)	31.2 (LAB)	Dried to constant weight in air after washing with alc. and ether.
		29.9 (F)	0.8 (LE)		
				30.5 at 14.5 mm 29 » 2.2 » 11.5 » 0.8 » (LE)	Over H_2SO_4 - solns. at 20°
				32 » 14 » (J)	Over sat. $(NH_4)_2SO_4$ at 20°
				32 » 0.7 »	» H_2SO_4-soln. at 20°
				8 » 0.2 »	» $CaO — Ca(OH)_2$
2	$C_3A \cdot 3CaCrO_4 \cdot 30H_2O$	29.4 (F)	—		
3	$C_3A \cdot 3CaSeO_4 \cdot 30H_2O$	29 (F)	—		
4	$C_3A \cdot 3CaMnO_4 \cdot 30H_2O$	26 (F)	—		
5	$C_3A \cdot 3Ca(ClO_3)_2 \cdot 30H_2O$	—	—		
6	$C_3A \cdot 3Ca(IO_3)_2 \cdot 30H_2O$	—	—		
7	$C_3A \cdot 3Ca(HCO_2)_2 \cdot 30H_2O$	27.31 (F)	—		
8	$C_3A \cdot 3Ca(CH_3 \cdot CO_2)_2 \cdot 30H_2O$	—	—		
9	$C_3A \cdot 3Ca(C_2H_5 \cdot CO_2)_2 \cdot 30H_2O$	—	—		
10	$C_3A \cdot 3CaCO_3 \cdot 27H_2O$	—	—	27 (B)	Over sat. $(NH_4)_2SO_4$ at 20°

Table 3 (Contd.).

No.	Compound	Molecules H_2O retained under Stated Drying Conditions			
		Anhydrous $CaCl_2$	P_2O_5	Other Conditions	
11	$C_3A \cdot CaSO_4 \cdot 12H_2O$	11.5 (FM)	8 (FM)	12.2 (LAB)	Dried to constant weight in air after washing with alc. and ether.
12	$C_3A \cdot CaCl_2 \cdot 10H_2O$	10 (FM)	7 (FM)	10 at 14.5 mm	(Le) Over H_2SO_4-solns. at 20°
		10.3 (F)	6.5 (Le)	9.9 » 2.2 »	
		10 (FM)	—	9.9 » 0.8 »	
	$C_3A \cdot CaCl_2 \cdot 18H_2O$	18 (La)	—		
13	$C_3A \cdot CaBr_2 \cdot 10H_2O$	8—8.5 (FM)	6 (FM)		
		9.3, 9.7 (F)	—		
		8 (FM)	—		
14	$C_3A \cdot CaI_2 \cdot 8H_2O$	8.45, 8.65 (F)	—		
15	$C_3A \cdot Ca(NO_3)_2 \cdot 10H_2O$	9—10 (FM)	6 (FM)		
		9.6, 9.85 (F)	—		
16	$C_3A \cdot Ca(NO_2)_2 \cdot 10H_2O$	10.0, 10.7 (F)	—		
17	$C_3A \cdot Ca(ClO_3)_2 \cdot 10H_2O$	8—9 (FM)	6 (FM)		
18	$C_3A \cdot Ca(CH_3 \cdot CO_2)_2 \cdot 8H_2O$	8 (FM)	—		
19	$C_3A \cdot CaCO_3 \cdot 11H_2O$	—	—	11 (B)	Over sat. $(NH_4)_2SO_4$ at 20°
20	$C_4A \cdot Ca(IO_3)_2 \cdot 22H_2O$	22.2—22.4 (FM)	6.5 (FM)		
21	$C_5A \cdot Ca(IO_3)_2 \cdot 33H_2O$	33 (FM)	—		

[1] FM = FORSÉN and MYLIUS, F = FORET, LAB = LERCH, ASHTON & BOGUE, LE = LEFOL, LA = LAFUMA, B = BESSEY, J = JONES

The $Ca(ClO_3)_2$-compound giving 8—$9H_2O$ is also stated by Mylius (18) to be optically a mixture, though the indices were close, and only a mean value could be determined.

Constitution and Crystal Structure.

The problem of the constitution of the complex compounds is naturally related to that of the hydrated aluminates. The ideas of Werner in the representation of such compounds have been applied by Forsén (7), the compounds being represented as derived from the ortho-aluminate ion $Al(OH)_6$. The formulae suggested present a coherent picture, and offer an explanation for the behaviour observed on dehydration, the loosely combined water being regarded as H_2O-groups co-ordinated to Ca or the acid radical, and the firmly combined water as OH-groups co-ordinated to Al. Thus Forsén writes:

$$1.\quad [Ca(OH_2)]_4\,[Al(OH)_6]_2\,[Cl_2] \xrightarrow{\substack{\text{over}\\ P_2O_5}} Ca_4\,[Al(OH)_6]_2\,[Cl_2]$$

$$i.\,e.\quad C_3A\cdot CaCl_2\cdot 10H_2O \xrightarrow{\substack{\text{over}\\ P_2O_5}} C_3A\cdot CaCl_2\cdot 6H_2O$$

$$2.\quad [Ca(OH_2)]_4\,[Al(OH)_6]_2\,[SO_4\cdot 2H_2O] \xrightarrow{\substack{\text{over}\\ P_2O_5}} Ca_4\,[Al(OH)_6]_2\,[SO_4\cdot \tfrac{1}{2}H_2O]$$

$$i.\,e.\quad C_3A\cdot CaSO_4\cdot 12H_2O \xrightarrow{\substack{\text{over}\\ P_2O_5}} C_3A\cdot CaSO_4\cdot 6\tfrac{1}{2}H_2O$$

$$3.\quad [Ca(OH_2)_4]_6\,[Al(OH)_6]_2\,[SO_4\cdot 2H_2O]_3 \xrightarrow{\substack{\text{over}\\ CaCl_2}} [Ca(OH_2)_4]_6\,[Al(OH)_6]_2\,[SO_4\cdot \tfrac{1}{2}H_2O]_3$$

$$4.\quad \xrightarrow{\substack{\text{over}\\ P_2O_5}} Ca_6\,[Al(OH)_6]_2\,[SO_4\cdot \tfrac{1}{2}H_2O]_3$$

$$i.\,e.\quad C_3A\cdot 3CaSO_4\cdot 36H_2O \xrightarrow{\substack{\text{over}\\ CaCl_2}} C_3A\cdot 3CaSO_4\cdot 31\tfrac{1}{2}H_2O$$

$$\xrightarrow{\substack{\text{over}\\ P_2O_5}} C_3A\cdot 3CaSO_4\cdot 7\tfrac{1}{2}H_2O$$

Mylius (18) has presented evidence for the existence of $10H_2O$- and 8 H_2O-compounds of the type $C_3A \cdot CaCl_2 \cdot 10H_2O$ and $8H_2O$, and formulates the $10H_2O$-compounds as $Ca_4(Cl_2)\,[Al(OH)_6]_2\cdot 4H_2O$. In connection with the $36H_2O$-hydrate of calcium sulpho-aluminate formulated above, he has reported a hydrate with $34H_2O$, obtained by recrystallization of $C_3A \cdot 3CaSO_4 \cdot 31\tfrac{1}{2}H_2O$ from lime-calcium sulphate solution. Another hydrate with $12H_2O$ reported by Michaëlis (17) is formulated as $Ca_6[(Al(OH)_6]_2\,(SO_4 \cdot 2H_2O)_3$.

Whilst such formulae throw some light on the constitution of these compounds, the only way open to a clear picture of structure is that of X-ray

Table 4. Dehydration Data above Room Temperature.

No.	Compound	Mols. H_2O retained at Temperature stated in °C									Observers
		50	100	105	110	150	200	250	300	350	
1	$C_3A \cdot 3CaSO_4 \cdot 31\text{-}33H_2O$	28.8	26.5	25	24	8.5	5.2	4.0	3.1	2.5	LEFOL (13)[1]
		29	8.8	8.5	8.0	6.9	5.2	3.5	2.3	1.6	JONES
		—	—	7.5	—	—	—	—	—	—	FORSÉN, MYLIUS
		—	—	—	7	—	—	—	—	—	LERCH, ASHTON & BOGUE
11	$C_3A \cdot CaSO_4 \cdot 12H_2O$...	—	—	6.5	—	—	—	—	—	—	FORSÉN, MYLIUS
		—	—	—	6	—	—	—	—	—	LERCH, ASHTON & BOGUE
12	$C_3A \cdot CaCl_2 \cdot 10H_2O$....	10.0	9.8	9.8	9.7	7.5	5.6	5.6	4.6	1.8	LEFOL[2]
		—	—	6	—	—	—	—	—	—	FORSÉN, MYLIUS
13	$C_3A \cdot CaBr_2 \cdot 10\ ?\ H_2O$.	—	—	decomp.	—	—	—	—	—	—	»
15	$C_3A \cdot Ca(NO_3)_2 \cdot 10H_2O$	—	—	6	—	—	—	—	—	—	»
17	$C_3A \cdot Ca(ClO_3)_2 \cdot 10H_2O$	—	—	decomp.	—	—	—	—	—	—	»

[1] Continuous heating. [2] Not equilibrium values.

analysis. BRANDENBERGER (4) has emphasized its importance, and points out that analysis of the structure of hydrated C_3A leads to a representation in the solid state different from the complex formulation suggested by FORSÉN. Some brief discussion of FORSÉN's and BRANDENBERGER's views is given by BESSEY (3), and will not be further pursued here.

The only reliable X-ray data available on the complex aluminates is that from a rotation photograph of the natural Ettringite reported by BANNISTER (1). The rotation photograph showed a hexagonal lattice and unit cell dimensions $a = 11.24 \pm 0.02$; $c=21.45 \pm 0.05$ Å; $a:c = 1:1.908$. The density was found to be 1.772. It was concluded that the unit cell contains $12CaO \cdot 2Al_2O_3 \cdot 6SO_3$ and probably $64H_2O$. A structural formula of zeolitic type was suggested with $48H_2O$ located in the channels parallel to the c-axis, such a structure changing to $Ca_{12}Al_4(OH)_{24}(SO_4)_6 \cdot 4H_2O$ on dehydration. This was, however, not altogether satisfactory and BANNISTER states that it is hoped to make a further analysis.

Solubility and Phase Equilibria.

Examination of solubility and phase equilibria in the case of these complex salts extends the study of the system lime-alumina-water to include a fourth component, the calcium salt of the acid radical involved. Little work has as yet been published dealing with these quaternary systems. Limited data for the solubility in water at various temperatures have been reported by a few workers, and LAFUMA (11), FORET (5), and NACKEN and MOSEBACH (19) have published data covering restricted portions of the systems.

In general, the compounds dissolve incongruently in water. Published data for "solubility" at room temperature are given in TABLE 5.

Both LAFUMA and FORET have determined at room temperature the concentrations of solutions obtained when $C_3A \cdot 3CaSO_4 \cdot Aq.$ is placed in lime- and calcium sulphate solutions of various concentrations. LAFUMA has reported only the lime- and calcium sulphate concentrations. The results of these authors together with data obtained by the present writer at the Building Research Station, are given in FIG. 1. The latter data were obtained in the determination of the CaO-, Al_2O_3- and SO_3-contents of solutions obtained by shaking 2 grams of the salt with 250 cc of water, or lime- or calcium sulphate solution, for varying periods at 21° and finally allowing to stand for 1 day in a thermostat at 25°. They are therefore open to some criticism in that it is doubtful whether 25° equilibrium was attained, the data lying within the range 21°—25°. In the representation of the quaternary system CaO-$CaSO_4$-Al_2O_3-H_2O, the concentrations of the CaO- and $CaSO_4$-components may be plotted along two axes at right angles as in FIG. 1. The concentrations of the Al_2O_3-component may then be shown along a third axis at right angles to the plane of the paper. The curve plotted in Fig. 1 is thus a projection of the true data on to the water-lime-calcium sulphate face shown. Since the equilibrium solutions contain alumina, such a partial representation is

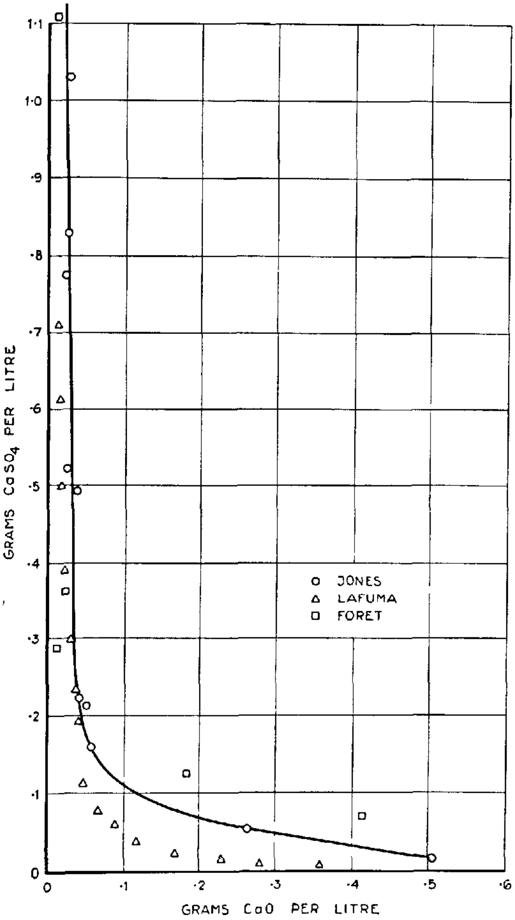

Fig. 1. Solutions formed with $C_3A \cdot 3CaSO_4 \cdot Aq.$ & Lime- and Calcium Sulphate Solutions.

of limited usefulness. The significance of the true curves depends upon the solid phases present in equilibrium with the solution. Lafuma (11) and Foret (5) have incorrectly assumed that with two solid phases, the quaternary system is bivariant. Two solid phases in contact with a solution phase in a condensed isothermal quaternary system gives an univariant system, whilst three solid phases can co-exist only with a solution of definite concentration, the system then being invariant. The writer is at the present time investigating

Table 5. "Solubility" in Water at Room Temperature.

No.	Compound	g per Litre			Mols. per Litre			Observers
		CaO	Al_2O_3	Ca-Salt	CaO	Al_2O_3	Ca-Salt	
1	$C_3A \cdot 3CaSO_4 \cdot 31$—$33H_2O$	0.010	0.012	0.085	0.00018	0.00012	0.00063	LERCH, ASHTON & BOGUE
		0.045	0	0.11	0.00080	—	0.00081	LAFUMA
		—	0.017	—	—	0.00017	—	FORSÉN, MYLIUS
		0.022	0.016	0.363	0.0004	0.00016	0.00267	FORET
		0.049	0.032	0.155	0.00087	0.00031	0.00114	MAC INTYRE & SHAW (16)
		0.044	0.035	0.215	0.00079	0.00034	0.00158	JONES
2	$C_3A \cdot 3CaCrO_4 \cdot 30H_2O$.....	0.084	—	0.515	0.0015	—	0.0033	FORET
3	$C_3A \cdot 3CaSeO_4 \cdot 30H_2O$.....	0.028	0.025	3.85	0.0005	0.00025	0.02101	»
7	$C_3A \cdot 3Ca(HCO_2)_2 \cdot 30H_2O$..	0.280	—	2.56	0.005	—	0.0197	»
8	$C_3A \cdot 3Ca(CH_3 \cdot CO_2)_2 \cdot 30H_2O$	0.280	—	9.16	0.005	—	0.058	»
9	$C_3A \cdot 3Ca(C_2H_5 \cdot CO_2)_2 \cdot 30H_2O$	0.168	—	7.07	0.003	—	0.038	»
11	$C_3A \cdot CaSO_4 \cdot 12H_2O$.......	—	0.089	—	—	0.00087	—	FORSÉN, MYLIUS
12	$C_3A \cdot CaCl_2 \cdot 10H_2O$........	—	0.073	—	—	0.00072	—	» »
		0.280	0.194	0.311	0.005	0.0019	0.0028	FORET
		0.16	—	0.1	0.00285	—	0.00090	LAFUMA
13	$C_3A \cdot CaBr_2 \cdot 10\ ?\ H_2O$.....	—	0.074	—	—	0.00073	—	FORSÉN, MYLIUS
		0.286	0.204	0.700	0.0051	0.002	0.0035	FORET
14	$C_3A \cdot CaI_2 \cdot 8H_2O$.........	—	0.075	—	—	0.00074	—	FORSÉN, MYLIUS
		0.308	0.642	0.882	0.0055	0.0063	0.003	FORET
15	$C_3A \cdot Ca(NO_3)_2 \cdot 10H_2O$....	—	0.085	—	—	0.00083	—	FORSÉN, MYLIUS
		0.308	—	0.476	0.0055	—	0.0029	FORET
17	$C_3A \cdot Ca(ClO_3)_2 \cdot 10H_2O$....	—	0.076	—	—	0.00075	—	FORSÉN, MYLIUS
18	$C_3A \cdot Ca(CH_3CO_2)_2 \cdot 8H_2O$	—	0.044	—	—	0.00043	—	FORSÉN, MYLIUS

Values by LAFUMA and FORET at "room temperature".
FORSÉN and MYLIUS at 19°.
JONES at 25°.

Table 6. Equilibria Data for $C_3A \cdot 3CaSO_4 \cdot Aq.$ in Salt Solutions.

Solution	Composition of Solution g per Litre			Temperature, °C	Observers
	CaO	Al_2O_3	SO_3		
3 % NaCl........	0.295	0.115	0.230[1]	25	JONES
	0.258	0.085	0.169[2]	room	LERCH, ASHTON & BOGUE
	0.235	0.07	0.18	room	LAFUMA
3 % $Na_2SO_4 \cdot 10H_2O$	0.220	0.081	—	room	LERCH, ASHTON & BOGUE
5 % Na_2SO_4......	0.185	0.065	—[3]	25	JONES

[1] Shaken 35 days at 25°.
[2] Standing 3 weeks.
[3] Shaken 17 days at 25°.

the system lime-alumina-calcium sulphate-water at 25°. This involves a determination of the various boundary curves (two solid phases) and invariant points (three solid phases) in the system. The solid phases present are being determined by microscopic examination. Whilst the work is fairly advanced, it is premature to discuss the results obtained.

Both LAFUMA (11) and FORET (5) have published data for $C_3A \cdot CaCl_2 \cdot Aq.$ similar to those discussed above, but they are not in good agreement, and LAFUMA gives no alumina values. FORET's conclusion that the data represent equilibria of three solid phases with solution cannot be correct. LAFUMA's data which are reproduced in FIG. 2, show three distinct portions. As before, the curves are projections of the true curves. These must either be boundary curves for two solid phases, or curves lying within and tracing a portion of a field for one solid phase. LAFUMA assumes certain decomposition reactions which are not necessarily true. The precise meaning of these curves can only be settled by microscopic identifications of the solid phase or phases present. NACKEN and MOSEBACH (19) have also examined a portion of the $CaO\text{-}Al_2O_3\text{-}CaCl_2\text{-}H_2O$-system at 30°. Anhydrous C_3A was shaken with $CaCl_2$-solutions up to N/10 concentration, with analysis of the solutions and microscopic examination of the solid phases. Only two phases were formed, $C_3A \cdot CaCl_2 \cdot 10H_2O$ and $C_3A \cdot 6H_2O$(cubic). The solutions always contained lime and alumina in the ratio 3CaO to $1Al_2O_3$. The data could thus be represented in the ternary system $CaCl_2\text{-}C_3A\text{-}H_2O$. Within this system

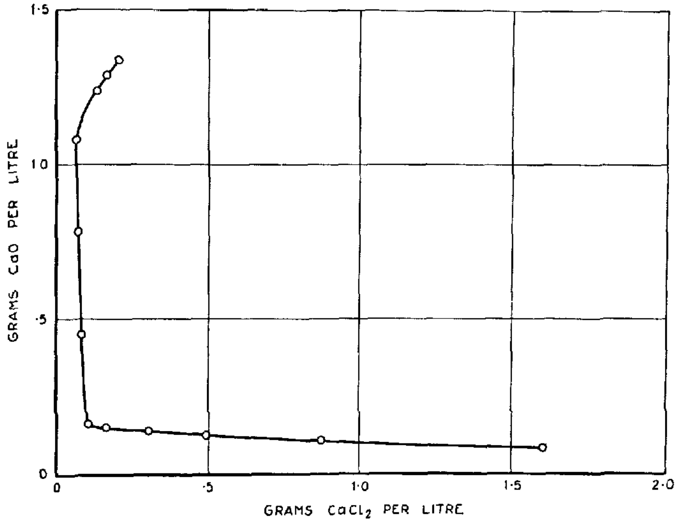

FIG. 2. Solutions formed with $C_3A \cdot CaCl_2 \cdot Aq.$ and Lime- & Calcium Chloride Solutions (LAFUMA).

they obtained curves for the separate phases $C_3A \cdot 6H_2O$ and $C_3A \cdot CaCl_2 \cdot 10H_2O$, and an invariant point for mixtures of the two compounds.

A few authors have observed behaviour in aqueous solution at higher temperatures. MYLIUS (18) states that all the complex compounds prepared by him are decomposed by boiling water to give cubic $C_3A \cdot 6H_2O$. LAFUMA (11) states that partial decomposition of $C_3A \cdot 3CaSO_4 \cdot$ Aq. occurs in boiling water and that the solution contains 0.12 g CaO, 0.27 g $CaSO_4$, 0.1 g Al_2O_3 per litre. KÜHL and ALBERT (10) found that lime-water and aluminium sulphate when mixed together at temperatures above 40°, formed $C_3A \cdot 3CaSO_4 \cdot$ Aq. and hexagonal crystals stated to be $Ca(OH)_2$. LEDUC (12) heated $C_3A \cdot 3CaSO_4 \cdot$ Aq. with a small amount of water for 3 hours at 100° without finding appreciable alteration. At 150° in the autoclave, rapid transformation to well-formed hexagons and large rods of calcium sulphate occurred. The hexagons in turn gave place to cubes. LEDUC considered the hexagons to be the hexagonal form of $C_3A \cdot$ Aq. The writer has found that on shaking 0.5 g $C_3A \cdot 3CaSO_4 \cdot 32H_2O$ with 100 cc water for 7 days at 99°, partial conversion to well-formed large hexagonal plates took place. These had the refractive indices $\omega = 1.503$, $\varepsilon = 1.489$, corresponding to the low sulphate form $C_3A \cdot CaSO_4 \cdot 12H_2O$. It seems probable that the hexagonal plates observed by KÜHL and ALBERT, and by LEDUC, were this compound, and that it is stable within certain limits of concentration above room temperature. The method of preparation of $C_3A \cdot CaSO_4 \cdot 12H_2O$ at room temperature requires a high lime concentration and the writer has so far not identified it as a stable phase in the quaternary system. Either its field of stability is very small or it is metastable at 25°. This accounts for the difficulty of preparing the compound in a pure state. It is hoped that it will be possible later to examine the systems at higher temperatures and to establish the conditions of stability. It is possible that similar effects of temperature on the stability of the 3- and 1-mol. compounds are to be found in the other quaternary systems. It has been indicated that corresponding compounds containing 3 and 1 mols. respectively of the same calcium salt have been obtained in four cases only. It may prove possible to prepare missing members of a pair by suitably modifying the conditions, a high calcium salt concentration and lowering of temperature leading to the 3-mol. compound, and a high lime concentration and raising of temperature leading to the 1-mol. compound.

In the determination of the stability in salt solutions (other than calcium) of the complex compounds of direct interest in cement chemistry, again only a very limited amount of work has been done. LERCH, ASHTON and BOGUE (15) placed $C_3A \cdot 3CaSO_4 \cdot$ Aq. in various salt solutions, and found that greater hydrolysis occurred in NaCl- and Na_2SO_4-solutions than in pure water. In $MgSO_4$- and Na_2CO_3-solutions complete decomposition occurred, the former depositing gypsum crystals and amorphous material, whilst the latter yielded $CaCO_3$ as the only crystalline phase. The low sulphate form, examined similarly, was converted to the high sulphate form in NaCl- and Na_2SO_4-solutions, and was decomposed in $MgSO_4$- and Na_2CO_3-solutions. LAFUMA (11) also determined the effect of NaCl-solution on $C_3A \cdot 3CaSO_4 \cdot$ Aq. and found increased decomposition. The writer has also found increases in concentration in NaCl- and Na_2SO_4-solutions. The data are given in TABLE 6. Such data are of interest in indicating the greater concentrations required for stabilizing the complex compound, but considerably more work from the standpoint of the phase rule appears necessary in order satisfactorily to elucidate behaviour in such solutions, involving as they do additional components and greater complexity.

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PORTLAND CEMENT AND HYDROTHERMAL REACTIONS

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Introduction.

The main interest of the cement chemist lies in the synthetic processes involved in the manufacture of cements or in the preparation of the anhydrous cement substances at high temperatures and in the reactions of these substances with water at ordinary temperatures. He is also interested, though perhaps to a less degree, in the direct synthesis of the products formed on hydration of the compounds present in cements. Due to a desire to speed up these synthetic and hydrolytic processes and to obtain the products in crystalline form, he has been led to make his studies at higher temperatures and has thus been brought into the field of hydrothermal and pneumatolytic alterations and syntheses, which formerly was chiefly of interest to the Geochemist. The cement chemist has thus become interested in the hydrothermal study of the various systems composed of the oxides CaO, SiO_2, Al_2O_3 and Fe_2O_3 with water, and the systems composed of water and the individual compounds present in cements. The practical applications to Portland cement have so far related mainly to the testing of the stability of cements and to steam-curing of precast concrete in order to improve its physical properties and to increase its resistance to the action of corrosive waters.

Very little systematic work has been done on the phase equilibria at high temperatures in systems containing water as one component. The investigations in this field have been confined mainly to the preparation and qualitative identification of the products formed under a given set of conditions. Reproduction of results is often not easy, as small variations in conditions may greatly influence the attainment of equilibrium.

In this report only the investigations relating to the compounds which may be present in Portland cement clinker or in hydrated cement will be considered. Attention will also be confined to reactions taking place at 100°, or at higher temperatures.

Descriptions of the various forms of apparatus used in hydrothermal investigations will not be given here. Suitable bombs for use at high pressures are described by BAUR (3) and by MOREY (28). For a more general account, reference should be made to the papers of EITEL (7), KÖNIGSBERGER (17), and EITEL and SKALIKS (8).

Hydrothermal Synthesis of Hydrated Silicates of Calcium.

In the early literature which is concerned mainly with reactions of interest to mineralogists and geologists such as changes in the crystalline form of the oxides and the synthesis of complex minerals, mention is occasionally made of the formation of Wollastonite or monocalcium silicate. DAUBRÉE (5) reports the formation of Wollastonite when glass was heated with a little water in a glass tube enclosed in a steel tube at 400°. GORGEU (12) reports the formation of $CaO \cdot SiO_2$ when moist air was passed over a mixture containing equivalent quantities of $CaCl_2$ and SiO_2 at red heat in an open vessel and the formation of $2CaO \cdot SiO_2$ when two equivalents of $CaCl_2$ were used. He also reports the formation of a chloro-silicate when 7 equivalents of $CaCl_2$ were used with one equivalent of SiO_2 under the same conditions. The identification of the dicalcium silicate is doubtful. A second paper (13) adds some further data on the composition of the chloro-silicates obtained. DOELTER (6) reports the formation of Wollastonite from a solution of calcium bicarbonate and silica gel at 400°—425°.

The very extensive investigations of SCHLÄPFER and NIGGLI (34) published in 1914, include the synthesis of hydrosilicates. The materials were heated with water in a silver crucible in a steel bomb of 20 cc capacity for 1 to 2 days at 470°. The formation of Hillebrandite ($2CaO \cdot SiO_2 \cdot H_2O$) is reported in mixes containing equivalent molar quantities of lime and amorphous silica together with calcium chloride. The crystals were orthorhombic positively elongated needles with parallel extinction, highest index between 1.609 and 1.623, birefringence slight. A sample containing a lime: silica ratio of 2:1 together with some calcium chloride gave, after treatment, a mixture of weakly birefringent orthorhombic crystals (index about 1.64) thought possibly to be a hydrated dicalcium silicate, and small rod-like monoclinic crystals (highest index = 1.657 +) with slight birefringence, showing penetration twinning. The last were supposed to be a monocalcium silicate. The monoclinic crystals also appeared in one case mixed with Hillebrandite.

THORVALDSON and SHELTON (38) described a crystalline phase formed in Portland cement-sand mortars when exposed to saturated steam at from 100° to 200°. On progressive steam-curing of the sand mortar they observed first the growth of hexagonal plates of $Ca(OH)_2$ and later the gradual disappearance of these with the appearance of the new phase. The crystals were thin elongated plates with square ends or bevelled edges showing parallel extinction; orthorhombic; refractive indices (with sodium light) $\alpha = 1.614$, $\beta = 1.620$, $\gamma = 1.633$ (all $\pm$ 0.002); positive; $2V = 68^\circ$; positive elongation; penetration twins common. The crystals were attacked slowly by dilute hydrochloric acid and by solutions of magnesium sulphate but not appreciably by solutions of sodium sulphate or calcium sulphate. The formation of the crystals was favored by raising the temperature between 100° and 175° but they were, as a rule, not as abundant in mortar treated at 200°. The formation of the crystals appeared to parallel the increase in the tensile strength and the increase in the stability of the mortar in sulphate solutions. In 1932 THORVALDSON (35) stated that VIGFUSSON and he had shown that this crystalline product was a hydrated calcium silicate formed mainly by the interaction of the lime, liberated during hydration of tricalcium silicate, on the silica sand. In his opinion the increase in strength produced by the curing of Portland cement mortars and concrete in steam under pressure was mainly due to this reaction, although other reactions also contributed materially.

NAGAI (29, 30) has published a number of reports[1] covering an extended investigation on the hydrothermal synthesis of calcium silicates. Mixtures of calcium oxide and powdered quartz in the molar ratios 5:1, 3:1, 2:1, 1:1, 1:2, 1:3, and 1:5, contained in nickel crucibles, were heated in the presence of water in an autoclave at 133°, 153°, 181°, 201°, and 212° (±1°) for 1, 2, 3, 6, and in some cases, 10 days. The products were dried over quick-lime and the loss on ignition, free lime, free silica (as the insoluble residue on warming in succession with a 10 %-solution of sodium carbonate and a 5 %-solution of hydrogen chloride), soluble lime and silica were determined. From these results the combined lime, silica and water, and the ratio of the combined lime to combined silica in the product were calculated. It was found that the mixtures with a lime : silica ratio of 5 : 1 and 3 : 1 gave, at the lower temperatures and for short periods of heating at the higher temperatures (2 days), a hydrosilicate with a lime : silica ratio of 3 : 2, but long treatments (6 days) at the higher temperatures produced a hydrated dicalcium silicate. The mixtures with a ratio of 2:1 and 3:2, treated at the lower temperatures and pressures, produced a hydrosilicate with a lime : silica ratio of 3:2 but this changed to a product with a 1:1-ratio at higher temperatures. On the other hand, with still lower initial lime : silica ratios a hydrate with a lime : silica ratio of 1:1 was formed at low temperatures, which was transformed into a product having a 3:2-ratio at higher temperatures. The water of hydration of the 3:2-

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[1] The results of these investigations were first published in the Journal of the Society of Chemical Industry, Japan. Volumes *34* and *35* (1931 and 1932).

silicate varied with the temperature at which it was formed. The hydrothermal products contained varying amounts of free lime and uncombined silica and this introduced difficulties in deciding the exact formula of the hydrosilicate formed. In many cases mixtures of silicates were apparently produced by the treatment.

Taking the experiments in which these impurities were at a minimum (hydrosilicate content 73.6 to 95.4 %, except in one case 50.2 %) and considering the chemical analyses, microscopic examinations and in some cases X-ray powder patterns, NAGAI arrives at the following conclusions:

1. The most basic mixtures at high temperatures give a product of the formula $2CaO \cdot SiO_2 \cdot H_2O$, the properties of which agree very nearly with those of the natural mineral Hillebrandite.
2. The less basic mixtures at low temperatures give compounds of which $3CaO \cdot 2SiO_2 \cdot 8H_2O$ with the crystal structure of Afwillite is the most typical.
3. The less basic mixtures at higher temperatures give among others the compounds $3CaO \cdot 2SiO_2 \cdot H_2O$ and $CaO \cdot SiO_2 \cdot 0.25H_2O$ corresponding to Xonotlite.

The optical and X-ray data are not recorded.

NAGAI (29, 30) also reports the results of a long series of experiments in which superheated steam mixed with air was passed over heated mixtures containing lime and silica in various proportions. The results are compared with those obtained in the dry synthesis of silicates from mixtures of calcium carbonate and silica. The presence of the steam appears to lower the temperature of reaction by about 300°. Below 600° the lime and silica did not react even in the presence of steam under the conditions of the experiments, while above 1 200° there was no difference between the synthesis with and without steam. The analyses were made in the way already described, but in addition attempts were made at separation of the silicate mixtures by means of 10 % Na_2CO_3 and 3 % HCl.

Mixtures containing $CaO : SiO_2$-ratios of 3:1, 2:1, 3:2, and 1:1 behaved in the same manner on hydrothermal treatment at atmospheric pressure. The products gave $CaO : SiO_2$-ratios of approximately 3:2 at low temperatures (600°—700°) and 2:1 at higher temperatures (900°—1 100°). Low initial ratios (1:1 and 1: 2) tended to give lower ratios for the final product after lengthy treatment or treatment at high temperatures. The results with the dry synthesis were similar except that a temperature about 300° higher was required for the corresponding reactions. Both dry and hydrothermal syntheses at the corresponding temperatures (1 420°—1 450° and 1 100°—1 200°, respectively) produce mixtures of the 1:1-, 3:2-, and 2:1-calcium silicates.

The products of the hydrothermal synthesis, however, are much richer in the 3:2-silicate.

Substitution of $CaCO_3$ for CaO in the hydrothermal synthesis using mixtures having CaO : SiO_2-ratios of 2:1 and 1:1 and temperatures of 700° to 1 200° did not lead to materially different results.

VIGFUSSON, BATES and THORVALDSON (45) prepared the crystalline phase described by THORVALDSON and SHELTON (38) in steam-cured Portland cement mortar by heating a thick slurry of calcium oxide and pure silica sand contained in a platinum crucible in an autoclave at 170°. They also prepared it by treating a mixture of pure tricalcium silicate and β-dicalcium silicate and silica sand under the same conditions. Presence of $CaCl_2$ or NaCl seemed to favor the formation of the crystals. A fairly homogeneous sample of the crystals was obtained from the lime-sand preparation by removing the sand grains by sieving and the free lime by repeated extraction of the sample with a glycerol-water solution (sp. gr. 1.142) until no more lime could be removed. The purified sample gave the analysis $1.94CaO \cdot SiO_2 \cdot 1.14H_2O$.

A sample of the crystals which appeared completely homogeneous on microscopic examination was also prepared by heating quartz crystals and silica plates in saturated lime-water (with a large excess of $Ca(OH)_2$ present) in silver containers in the autoclave at 170°.[1] The analysis of the sample gave the composition $2.07CaO \cdot SiO_2 \cdot 1.24H_2O$. This product will be referred to as (I). The X-ray powder patterns of the two samples of (I) were identical and were essentially identical with the X-ray pattern of a less pure sample of the crystals obtained by mechanical separation of the crystals from the hydrated cement of steam-cured Portland cement-sand mortar. Repeated determination of the optical properties of all these samples gave identical values. The X-ray pattern showed no similarity to that for natural Hillebrandite or Afwillite.[2] (See FIG. 1.)

Several similar treatments of a mixture of lime and silica gel, in the molar ratio of 4:1, in the autoclave at 170° with several intermediate grindings of the mixture, produced radiating clusters or masses of weakly birefringent prisms usually having needle-like or incomplete terminations. These prisms showed positive elongation, parallel extinction, and some twinning and parallel growths. The mean index of refraction was found to be 1.597 ± 0.003. The refractive index is decidedly lower than that of Hillebrandite and the X-ray powder patterns showed only very slight similarity. The refractive

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[1] Attempts to reproduce this preparation always gave samples with some admixture of other crystalline forms, *i. e.* the orthorhombic crystals mixed with fine needle-like crystals.

[2] The refractive indices of crystals (I) are very close to those of the natural mineral, Afwillite. The X-ray powder patterns are, however, entirely different as is the chemical composition.

index is close to that of Foshagite. The X-ray pattern was quite different from that of the orthorhombic crystals (I). (See FIG. 1.) Analysis of the material after removal of the uncombined lime by means of glycerol solutions gave $2.14CaO \cdot SiO_2 \cdot 1.42H_2O$. The crystals will be referred to as crystals (II).

In some of the experiments with silica plates and lime-water at 170° the plates were covered with a hard scum instead of being studded with individual crystals of Phase (I). This scum, which peeled off the silica plates easily, was weakly birefringent and gave on analysis the composition $0.86CaO \cdot SiO_2 \cdot 0.56H_2O$. The X-ray powder pattern differed entirely from those of crystals (I) and (II) described above although a few crystals of the hydrated orthosilicate (I) were observed imbedded in the scum. It seems possible that a thin rather impervious film of very fine crystals formed at first on the silica plate and that further growth of the film occurred between this and the plate at a very low concentration of lime, the film preventing free access of calcium from the solution.

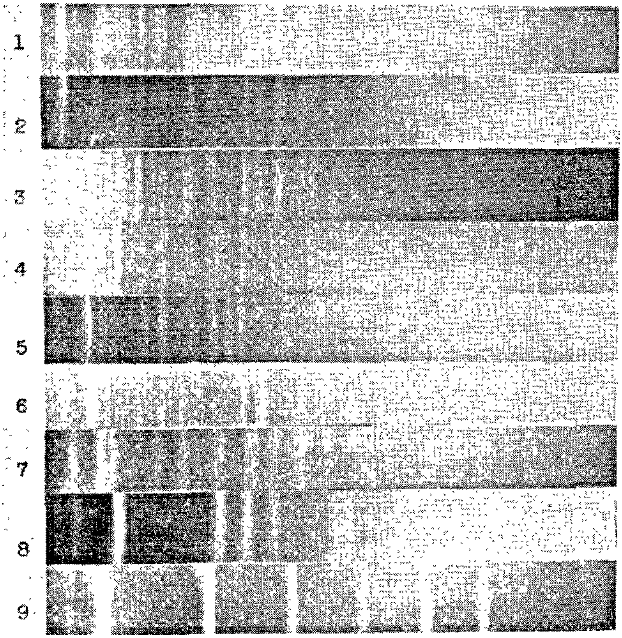

FIG. 1. X-ray Patterns of Calcium Hydrosilicates.

1. Phase I from steam-cured Portland cement mortar.
2. Phase I from steam-cured lime and silica sand.
3. Phase I from fused silica in saturated lime-water at 170°.
4. Phase II from lime and silica gel in saturated steam at 170°.
5. Phase II from lime and silica gel in saturated steam at 220°.
6. Natural Hillebrandite.
7. Natural Afwillite.
8. Calcium hydroxide.
9. Sodium chloride.

JEANNE FORET has published two reports (10) on the synthesis of hydrated calcium silicates from pure CaO and powdered quartz, using temperatures between 100° and 300°. Variation in pressure by means of nitrogen was found to have very little effect on the synthesis but increased temperatures greatly increased the rate of reaction. Mixtures with a 1:1 lime: silica ratio heated with water under pressure gave two different forms of $CaO \cdot SiO_2 \cdot H_2O$, one below 140°, the other above that temperature. When the lime : silica ratio equalled 2, the low temperature form of hydrated monocalcium silicate was formed up to 130°, but at higher temperatures all the free lime disappeared while the water of hydration decreased. With higher ratios and higher temperatures it appeared that 3 or 4 molecules of lime were absorbed but all the samples formed above 130° gave X-ray diagrams of the high temperature form of hydrated monocalcium silicate only. The assumption is made that this substance absorbs more or less lime without a change in the pattern. Partial dehydration of the hydrated monocalcium silicate did not change the X-ray pattern. There was no evidence of the formation of a silicate with a ratio of $CaO : SiO_2$ lower than 1.

Hydrothermal Reactions of the Anhydrous Calcium Silicates.

The hydrothermal and pneumatolytic alterations of the anhydrous silicates of calcium with the formation of hydrated products have also been studied. The hydrated dicalcium silicate described by THORVALDSON and SHELTON (38) in steam-cured mortar may have been formed by the hydrolysis of tricalcium silicate, by direct hydration of β-dicalcium silicate, by the reaction between free lime and the silica sand, or by a combination of these. In 1932 THORVALDSON (35) stated that one of his co-workers, Mr. N. B. KEEVIL, had succeeded in obtaining crystalline hydrates of both tricalcium silicate and β-dicalcium silicate in steam under pressure without any liberation of calcium hydroxide or free lime. In 1934 FLINT and WELLS (9), in the report of their extensive study of the system $CaO\text{-}SiO_2\text{-}H_2O$, stated that well defined crystalline dicalcium silicate is formed by the reaction between tricalcium silicate and water at 150°.

KÖHLER (16) reported in 1935 the results of a series of experiments in which $3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$ and $CaO \cdot SiO_2$ were heated with water at 150° to 290° in bombs with the liquid phase always present. At temperatures up to 220° the bombs were rotated in an oil bath. The silicate was therefore in contact with the liquid phase during the heating. The products were then washed with water-free methyl alcohol, dried, analyzed and the optical properties and X-ray powder patterns studied.

After 3 days at 150° the $3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$ gave only amorphous products, while at 200° minute needle-like crystals were produced and 6 days' heating at 200° gave a sample thoroughly permeated with the needles. The $CaO \cdot SiO_2$ was unchanged up to a temperature of 290°.

The $2CaO \cdot SiO_2$ heated at 212° for 10—14 days or at 290° for 8 days changed completely to birefringent material having the composition $2.2CaO \cdot SiO_2 \cdot \cdot H_2O$. The refractive index of the product was 1.600 to 1.614 as compared to $\alpha = 1.605$, $\beta = 1.610$, $\gamma = 1.613$ for Hillebrandite. The X-ray diagram was very similar to that given by VIGFUSSON (44) for Hillebrandite although according to the line diagrams a few lines were missing and there were some differences in intensities, assumed to be due to variation in visual estimation.

The water of hydration was very firmly held, being lost between 300° and dull red heat, anhydrous dicalcium silicate being formed.

When $3CaO \cdot SiO_2$ was treated in the autoclave in the same manner as $2CaO \cdot SiO_2$, the same needle crystals (Hillebrandite) were produced together with crystals of $Ca(OH)_2$. On dehydration of this product anhydrous dicalcium silicate and calcium oxide were formed.

Attempts at reproducing NAGAI's hydrothermal preparation of Afwillite were not successful. In some experiments using excess of lime with quartz or silica gel Xonotlite was obtained, in others Hillebrandite and in still others an unidentified crystalline phase of index 1.600.

KEEVIL and THORVALDSON (14) studied the action of saturated steam on $3CaO \cdot SiO_2$, β-$2CaO \cdot SiO_2$, γ-$2CaO \cdot SiO_2$, Hillebrandite and dehydrated Hillebrandite at temperatures between 50° and the critical temperature for water (374°). The silicates were contained in platinum crucibles exposed only to the vapor phase. This was perhaps the chief difference in conditions as compared to the experiments of KÖHLER (16) where the silicates were in contact with the liquid phase in the body of the steel autoclave. The free lime, the water held after drying over quick-lime and the optical properties of the products were determined and X-ray patterns were made.

Both the β- and γ-forms of dicalcium silicate gave the same crystalline products. At 110° and 170° the maximum hydration was usually attained in 2 weeks, the product having the composition $2CaO \cdot SiO_2 \cdot H_2O$ with no free lime present. At temperatures of 220° to 350° the absorption of water was not so reproducible, less water being usually absorbed at the higher temperatures. Microscopic examinations and X-ray patterns indicated that three different crystalline phases were formed, two of them being usually present in any one sample, although some samples were nearly homogeneous. Two of the crystalline phases were definitely identified as the phases (I) and (II) described above[1] (38, 45). The third crystalline phase, (III), which was also a hydrated dicalcium silicate, was the one most commonly observed especially at the higher temperatures. Five samples prepared at temperatures between 170° and 350° contained from 1.0 to 0.3 moles of water of hydration and gave a refractive index from 1.62 to 1.64 but showed no material variation in the X-ray pattern[3] which differed from those for (I) and (II) and Hillebrandite. (See FIG. 2.)

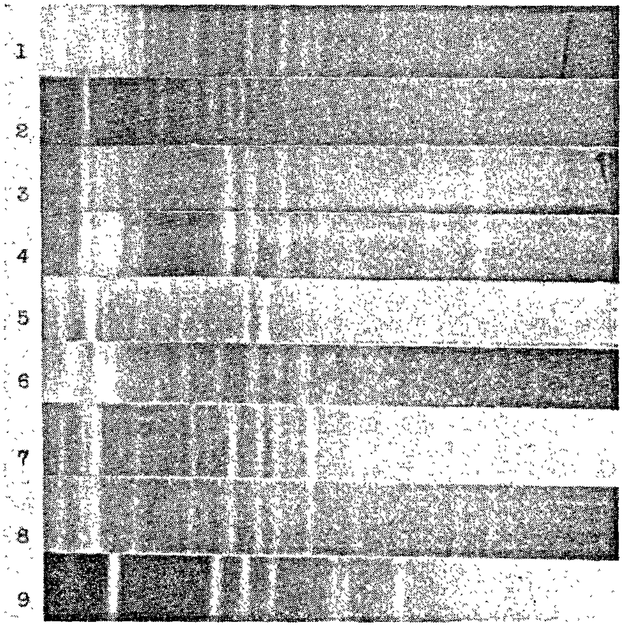

FIG. 2. X-ray Patterns of Calcium Hydrosilicates.

1. Phase I from silica plates in saturated lime-water at 170°.
2. Phase II from lime and silica gel in steam at 220°.
3. Phase III from β-C_2S in steam at 350° ($0.4H_2O$).
4. Phase III from γ-C_2S in steam at 350° ($0.4H_2O$).
5. Natural Hillebrandite.
6. Natural Afwillite.[2]
7. $3CaO \cdot SiO_2 \cdot 1.6H_2O$ from direct hydration in steam at 185°.
8. $3CaO \cdot SiO_2 \cdot 1.6H_2O$ from direct hydration in steam at 350°.
9. Calcium hydroxide.

Ignition of the hydrated dicalcium silicate (II) and (III) to constant weight at 900° produced no free lime; the products gave $N = 1.69$, but the X-ray pattern was that for β-$2CaO \cdot SiO_2$ ($\alpha = 1.717$; $\gamma = 1.735$).

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[1] Phase (I) was obtained as a homogeneous sample. Phase (II) was never so obtained by hydration of dicalcium silicate in steam. A nearly homogeneous sample of (II) was prepared by treating a 2 : 1-mixture of lime and silica gel in saturated steam at 160° and 220°.

[2] There appears to be a similar series of lines in the patterns for Afwillite and hydrated tricalcium silicate, except that the spacing of the lines is greater for Afwillite. Apart from this other lines of the two patterns show no correspondence.

[3] This was probably due to the formation of a dense surface layer of the monohydrate, the interior of the particles being only partially hydrated.

Eleven days treatment of natural Hillebrandite in the autoclave at 160° did not alter its weight or X-ray pattern. Ignition to constant weight at 900° and rehydration at 160° gave the original weight but the X-ray pattern of the product differed from that of Hillebrandite.

At temperatures of 110° or below, $3CaO \cdot SiO_2$ appeared to be partly hydrolyzed, giving $Ca(OH)_2$ and $2CaO \cdot SiO_2 \cdot H_2O$ (Phase I), and partly hydrated without liberation of $Ca(OH)_2$. At higher temperatures liberation of lime was almost prevented and direct hydration took place giving a finely grained crystalline material of low birefringence index $n = 1.59$. Sometimes there were observed intergrown sheaves of very small prismatic crystals with parallel extinction and refractive indices, $\alpha = 1.589$, $\gamma = 1.597$ ($\pm$ 0.003). Hydration products containing no free lime, or only a trace, and 1.3 to 1.9 moles of water per mole of the silicate gave the same X-ray pattern. (See FIG. 2.) On dehydration of the hydrated tricalcium silicate at 900° one mole of lime was always liberated, the X-ray pattern showing only the lines of calcium oxide and β-$2CaO \cdot SiO_2$.

Summary on Calcium Hydrosilicates.

The chief difficulties in interpreting the results of the work on the hydrothermal synthesis of the hydrosilicates of calcium are apparent multiplicity of crystalline forms obtained, and the inability to obtain pure forms in a reproducible manner. The most favorable conditions for obtaining a stable reproducible crystalline product are present when the solid phase separates slowly from a slightly supersaturated solution. In the hydrothermal synthesis of calcium hydrosilicates, where the crystalline phase forms very reluctantly and slowly, the condition of extreme supersaturation may be readily produced thus favoring the formation or even persistence of metastable forms. For similar reasons it is likely that the production of metastable forms is favored when the hydrosilicate is formed by the action of steam on the anhydrous silicate as compared with when it forms in contact with the liquid phase.

Hydrated dicalcium silicate has been prepared by hydrothermal methods from: 1. CaO and SiO_2, 2. anhydrous β- and γ-dicalcium silicate, 3. tricalcium silicate, and 4. Portland cement-sand mortar. Three different crystalline forms have been obtained by both the synthetic and direct hydration or hydrolytic methods, namely, Hillebrandite by SCHLÄPFER and NIGGLI (34), by NAGAI (30) and by KÖHLER (16), and the crystalline phases (I) and (II) (see above) by THORVALDSON and SHELTON (38), VIGFUSSON, BATES and THORVALDSON (45), and KEEVIL and THORVALDSON (14). The conditions under which each crystalline phase is formed are somewhat indefinite, but the formation of Hillebrandite appears to be favored by high temperatures and by contact between the solid and liquid phases, although it remains unchanged in steam at lower temperatures. Phase (I) appears to form at lower temperatures in the presence of the liquid or vapor phase and phase (II) at somewhat higher temperatures in contact with the vapor phase. All these crystalline phases appear to have the composition $2CaO \cdot SiO_2 \cdot H_2O$ although there seems to be a tendency for slightly higher proportions of CaO and of water of hydration. KEEVIL and THORVALDSON (14) also obtained by direct hydration another crystalline form (III) of hydrated dicalcium silicate which varied in water content from 1.0 to 0.3 moles and in refractive index from 1.62 to 1.64 with the temperature of preparation.

NAGAI (29, 30) reports also hydrothermal products from the interaction of CaO, SiO_2, and H_2O of the composition $3CaO \cdot 2SiO_2 \cdot 8H_2O$ at low temperatures and $3CaO \cdot 2SiO_2 \cdot H_2O$ at higher temperatures.

Among those reporting the hydrothermal formation of crystalline hydrated monocalcium silicate from the oxides are SCHLÄPFER and NIGGLI (34), NAGAI (29, 30), KÖHLER (16), and FORET (10), who records a low temperature and a high temperature form. There is no record of the direct hydration of anhydrous monocalcium silicate.

VIGFUSSON, BATES and THORVALDSON (45) report the formation of an apparently homogeneous sample of crystals of the composition $0.86CaO \cdot \cdot SiO_2 \cdot 0.56H_2O$ by the action of lime-water on quartz glass.

KEEVIL and THORVALDSON (14) report the direct hydration of tricalcium silicate in saturated steam above 110° to give a crystalline product of the composition $3CaO \cdot SiO_2 \cdot 2H_2O$.

The chief difference between the action of water and saturated steam on the calcium silicates at high temperatures and the hydration of these at ordinary temperatures, apart from the time required for the reactions, appears to be the formation of crystalline as against gelatinous calcium hydrosilicates. In addition, the hydrothermal treatment favors direct hydration of the silicates to form hydrated products with a lime: silica ratio not lower than 2, or possibly somewhat higher for $2CaO \cdot SiO_2$ in presence of $Ca(OH)_2$ and even approaching 3 for $3CaO \cdot SiO_2$ in contact with the vapor phase only at high temperatures. On the other hand, hydration at ordinary temperatures, especially in the presence of an excess of water, tends to give lower ratios of combined lime to combined silica, although in cement pastes the equilibrium ratios for dicalcium silicate may almost reach 2 and even higher for tricalcium silicate (2, 4).

Hydrothermal Synthesis of Calcium Hydroaluminates.

According to RENGADE (33), FRIEDEL (11) reported that he obtained the composition $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$ by the hydrothermal action of lime on aluminium chloride at 500°.

SCHLÄPFER and NIGGLI (34) reported the formation of a calcium aluminate in charges containing lime, alumina and caustic potash heated with water in a silver crucible in a steel bomb at 470° for 1 or 2 days. The identity of the product is uncertain. Anorthite was formed in a large number of mixtures containing lime, silica and alumina treated under the same conditions.

KLEIN and PHILLIPS (15) treated samples of monocalcium aluminate, 5:3-calcium aluminate and tricalcium aluminate with steam both at atmospheric pressure and mixed with excess of water, in an autoclave at 300 lbs. pressure. They report that the heat treatments in steam at atmospheric pressure at temperatures of 105° or higher gave incomplete hydration, amorphous material and fine anisotropic needles, identified as hydrated tricalcium aluminate, being formed in each case. The treatments in the autoclave gave complete hydration in two hours with no free lime liberated. The 1:1- and 5:3-aluminates gave amorphous matter and needles and hexagonal plates identified as hydrated tricalcium aluminate while the autoclaved 3:1-aluminate "was chiefly amorphous but contained a few hexagonal plates, as well as needles". Neither the refractive index nor the composition of the tricalcium aluminate hydrated in the autoclave is given.

THORVALDSON and GRACE (36) and THORVALDSON, GRACE and VIGFUSSON (37) found that an isotropic hydrate, trapezohedrons (icositetrahedrons) and cubes, of the composition $3CaO \cdot Al_2O_3 \cdot 6H_2O$ ($N = 1.604 \pm 0.002$) was formed both when anhydrous tricalcium aluminate and when a 3:1-mixture of calcium oxide and alumina were exposed to saturated steam in an autoclave at 150°. MATHER and THORVALDSON (18) found that this hydrate is stable in saturated steam up to at least 300°. ALLEN and ROGERS (1) had previously prepared this product ($3.24CaO \cdot Al_2O_3 \cdot 6.65H_2O$) by precipitation of hot lime-water by potassium aluminate, stating that the crystals resembled the corresponding hydrated strontium aluminate (dodecahedrons) obtained in a similar manner. The refractive index was not given. WELLS (46) reported the precipitation of small amounts of an isotropic crystalline phase having an index of 1.60 to 1.605 (icositetrahedrons and rhombic dodecahedrons) mixed with other solid phases from metastable solutions of 5:3-calcium aluminate and from solutions of a high alumina cement. The composition of the phase was not determined.

NAGAI (31) reported hydrothermal synthesis of calcium hydroaluminate by heating lime and anhydrous or hydrated alumina in saturated steam in an autoclave at 153°, 181°, and 212° (± 1°) for 1 day. The ratios of lime: alumina used were 4:1, 3:1, 2:1, and 1:1. Analysis of the products indicated that mixtures of hydrated tricalcium aluminate and hydrated dicalcium aluminate were usually formed. With the higher ratios of lime to alumina the ratio of combined lime to combined alumina after treatment approached 3, while with the lower original ratios it approached the value 2. The formulas of the products given by NAGAI are $3CaO \cdot Al_2O_3 \cdot 6H_2O$, $2CaO \cdot Al_2O_3 \cdot 7H_2O$ or $2CaO \cdot Al_2O_3 \cdot 6H_2O$ and $2CaO \cdot Al_2O_3 \cdot 3H_2O$, the last being formed when low lime: alumina ratios were used at the higher temperatures.

Experiments by NORMAN S. GRACE and WILLIAM G. SCHNEIDER in my laboratory indicate that when any one of the aluminates of calcium is placed in saturated steam in an autoclave at 150° the amount of water taken up and held after drying over lime agrees closely with that calculated for the formation of the hexahydrate of tricalcium aluminate and the monohydrate of alumina. Much higher absorption of water would be expected if hydrated dicalcium aluminate were formed. LAFUMA (17 a) also reports that hydrated dicalcium aluminate is transformed into the hexahydrate of tricalcium aluminate when heated in contact with its mother liquor at 80°. At ordinary temperatures the hexahydrate of tricalcium aluminate may be formed by the action of water on the anhydrous aluminate (36) and it appears to be the only hydrate formed in cement pastes at room temperature (4). Further studies on the hydrothermal reactions of the aluminates would be desirable.

Hydrothermal Changes of Tetracalcium Aluminoferrite and Dicalcium Ferrite.

MATHER and THORVALDSON (18, 35) studied the effect of exposing tetracalcium aluminoferrite and dicalcium ferrite to saturated steam between 100° and 300°. X-ray patterns of the resulting products were studied and the free $Ca(OH)_2$ and combined water were determined. Presence of the liquid phase in contact with the solid phase speeded up the hydrolytic reactions but gave the same final results as contact with the saturated vapor phase alone. Tetracalcium aluminoferrite was found to absorb 7 moles of water very rapidly. Possibly a heptahydrate is formed with subsequent rapid decomposition to the hexahydrate of tricalcium aluminate and the monohydrate of monocalcium ferrite. The latter then slowly decomposes with the production of calcium hydroxide and Hematite. The final products are $3CaO \cdot Al_2O_3 \cdot 6H_2O$, $Ca(OH)_2$ and Fe_2O_3 (Hematite).

Dicalcium ferrite under the same conditions absorbs 2 moles of water very rapidly, apparently forming the dihydrate which in turn decomposes to give $Ca(OH)_2$ and $CaO \cdot Fe_2O_3 \cdot H_2O$. The latter then decomposes slowly as stated above to give further $Ca(OH)_2$ and Hematite, the final product being $Ca(OH)_2$ and Hematite only.

Hydrothermal Treatment of Portland Cement and Concrete.[1]

The Effect on Strength and other Physical Properties.

The exposure of pats of cement paste to steam at 100° or to boiling water is a common accelerated test for determining the "soundness" of Portland cement. High pressure steam as a means of determining soundness was suggested more than fifty years ago but the test has not come into general use. Lately Young (50) has presented experimental evidence in favor of adopting an autoclave test for detecting the possibility of structural failure through delayed expansion. The test is necessary in the case of cements to be used for making concrete which is to be cured in steam under pressure.

Steam at atmospheric pressure was early used by manufacturers of cement products to accelerate the hardening of concrete building blocks, drain tile, fence posts, etc. Wig (47) investigated the effect of curing Portland cement mortars in steam under pressure. Among his conclusions were:

1. Steam at 80 lbs. per sq. in. gauge pressure has an accelerating action on the hardening of Portland cement mortar and concrete.
2. The effect on the compressive strength increases with the steam pressure and with the time of exposure to steam.
3. The strength obtained in two days with steam-curing sometimes was double that obtained after normal ageing for 6 months and the steam-cured mortar continued to gain strength with age after removal from the steam.
4. Steam-curing for short periods (3 hours) apparently had an injurious effect on the hardening of the mortar..

Wig and Davis (48) found that as the temperature of steam-curing is increased the tensile strength reaches a maximum and then decreases. The maximum varies with the cement and with the duration of steam-curing, being usually attained at a pressure not exceeding 150 lbs. per sq. in. (185°). Some cements begin to fail at pressures as low as 25 lbs. per sq. in.

Miller (22, 23) has reported on a very extensive investigation on the effect of steam-curing on the strength of concrete cylinders in connection with his

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[1] No attempt will be made to give a complete account of the literature on this subject. Attention will be confined mainly to the effect of hydrothermal treatment on the strength and on the resistance of the concrete to sulphate waters.

studies on the action of sulphates on cement and concrete. Basing his conclusion on the results of some 12 000 steam-cured cylinders made from cements from 14 different mills between 1921 and 1929, Miller found no great increases in ultimate strength as a result of 12 to 24 hours curing in water vapor between 100° and 350° F. (39° and 177° C.) as compared to those obtained in 28 days by damp-curing at room temperature. On the other hand, Woodworth (49) found that units cured in high pressure steam 4, 8, or 24 hours after molding developed strength at two days greatly in excess of the strength obtained in 28-day moist curing, air curing or low pressure steam-curing. He found also that high pressure steam-curing greatly reduced the shrinkage of concrete masonry panels laid up with wet units and practically eliminated the shrinkage when air dry units were used.

Thorvaldson and Vigfusson (40) and Thorvaldson and Shelton (38) confirmed the observation of Wig (47) that the first effect on steam-curing of mortars at 100° and above is a decrease in strength followed by an increase in strength. The initial loss increases with the age of the specimen at the time of steam-curing and with the temperature. The subsequent increase in strength also accelerates with increasing temperature of curing. These authors suggest that the loss in strength is due to hydrothermal changes in the tricalcium aluminate (this substance is rapidly stabilized against sulphate action by steam-curing) while the subsequent increase in strength is due to hydrothermal reactions of the silicates. Further work by Thorvaldson, Vigfusson and Wolochow (41) indicated that the loss of tensile strength during the initial period of steam-curing is proportionally much greater than the loss of compressive strength. Also that for short periods of steam-curing (up to 12 hours) the optimum temperature is about 175°.

Pearson and Brickett (32) exposed 3×6 in. cylinders of concrete made from seven different Portland cements to saturated steam in an autoclave at temperatures of 157° to 197° for from 12 to 66 hours. The following are some of the results:

1. There was gain in strength with temperatures up to 185° for any period of curing. Specimens exposed 18 hours or more at 170° or above usually attained 28-day strengths (damp-cured) or higher.
2. There was no marked gain in steaming longer than 42 hours (except at low temperatures) or at temperatures higher than 185°.
3. There was considerable variation in the efficiency of steam-curing with different cements with the high early strength cements tending to give lower strengths.
4. The cementing efficiency (strength per pound of cement per cubic foot of concrete) decreased with the richness of mix, and tended to a maximum

value for the leaner mixes. Neat cement specimens gave a very low cementing efficiency. A space-cement ratio theory was proposed to explain this.

5. The concrete specimens so far discussed were made with Delaware River sand. Concrete specimens made with a "dolomitic" marble and a "calcite marble" as aggregates gave very low strengths on steam-curing. It is suggested that this may be due to chemical reaction between the water and the marble.

In discussing these results Thorvaldson (35) proposed a theory of steam-curing of Portland cement mortars and concrete made with a siliceous aggregate. He considered that the initial loss in strength on steam-curing was due to changes in crystalline form of the hydrated tricalcium aluminate and to physical stresses during the expansion of the specimen. The increase in the strength was, on the other hand, due to the reaction between the free lime, liberated by hydrolysis, and the siliceous aggregate and to the direct hydration of dicalcium silicate and unhydrated tricalcium silicate to form crystalline hydrates. Later losses in strength on prolonged steam-curing at higher temperatures he attributed to the slow hydrolysis of the compound $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ and possibly to secondary changes in the calcium hydrosilicates.[1]

It was considered that this theory explained satisfactorily the observations of Pearson and Brickett (32). The low strength for steam-cured neat cement and for specimens made with a calcareous instead of siliceous aggregate would be due to the absence of the strength-conferring reaction between the free lime and aggregate. The increased cementing efficiency of the cement in the leaner mixes would be due to the increased area, per unit weight of cement, of the interface at which this reaction takes place. For the richer mixes the limiting factor for a moderately long steam treatment would be the amount of surface of the aggregate, while for the leaner mixes the limiting factor would be the quantity of cement, so that the strength developed per unit weight of cement per cubic foot of concrete, for a given exposure, tends to reach a maximum as the mix becomes leaner, at least at the higher temperatures of steam-curing where the reaction in lean mixes would be fairly complete.

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[1] The writer has very little further to add to this theory which was based on unpublished data on steam-cured mortars made with various aggregates, on studies on the action of sulphates on steam-cured mortars made with the pure cement substances and more particularly on the work of the writer and Shelton (38), Vigfusson and Bates (45), Keevil (14), and Mather (18). The last three pieces of work had been completed in 1932 but had not been published. The initial loss in strength may be due partly to the conversion of a gelatinous hydrated tricalcium aluminate, or the hexagonal form of this hydrate, to the crystalline hexahydrate and partly to the rapid hydration of hydrolysis of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ to give $3CaO \cdot Al_2O_3 \cdot 6H_2O$ and $CaO \cdot Fe_2O_3 \cdot H_2O$ (18) while the slow hydrolysis of the $CaO \cdot Fe_2O_3 \cdot H_2O$ may be one of the chief factors in causing the loss of strength on prolonged hydrothermal treatment of mortars and concrete at the higher temperatures.

MENZEL (19, 20, 21) has published a series of reports which give the results of a thorough study, made at the Research Laboratory of the American Portland Cement Association in Chicago, on the effect of high pressure steam-curing of Portland cement mortar and concrete. The purpose was to determine definitely suitable conditions for the manufacture of steam-cured cement products. A systematic study was made of the effect on the strength, volume changes and other properties of the temperature and duration of steam-curing, type of aggregate, size of silica particles, character of cement, amount of mixing water, age of concrete when steamed and other factors. The original papers must be consulted for the details. MENZEL showed conclusively that the presence of finely divided silica was a major factor in obtaining the best results in steam-curing. When the cement contained 30 to 50 % of silica (passing 200 mesh sieve), steaming at 177° produced strengths 20 to 50 % greater than the strength of neat cement alone cured 28 days in the damp closet and 2 to 3 times the strength attained by the steam-cured neat specimens. In the absence of finely divided silica the strengths obtained by steam-curing never reached that of 28-day damp-cured concrete.

The contraction of volume between the saturated and air-dried conditions was found to be much lower for steam-cured than for damp-cured specimens. Leaching of calcium hydroxide was reduced for steam-cured specimens containing finely divided silica and MENZEL expresses the opinion that in high pressure steam the silica combines with most of the soluble calcium hydroxide to form a fairly insoluble compound which contributes to the permanent strength and denseness of the hardened cementing paste. Tests at 10 months and 1 year indicated that the high flexural and compressive strength developed by proper steam-curing is permanent. The bond resistance in steam-cured concrete with both plain and deformed bars was much lower than with damp-cured concrete. Steam-curing of specimens, 4 to 48 hours after molding, for 8 hours upwards depending on the size of the specimen, was suggested for commercial purposes.

It is evident that in order to obtain uniform results on steam-curing, the nature, surface characteristics and grading of the aggregate, especially the fines, must be identical. This, together with variables due to the cement, suggests reasons for the inconsistencies between the results of different experimenters.

The Effect on the Resistance to Sulphate Action.

MILLER (24) was the first to study the effect of steam-curing on the resistance of mortars and concrete to the disintegrating action of sulphate waters. Two by four inch concrete cylinders of mix 1:3 by volume were cured in the damp-closet for 1 day, in steam at 100° for 2 and 6 days and in air for 18 and 14 days, with blanks cured in distilled water instead of steam. They were then exposed to a one-per-cent solution of sodium sulphate in the laboratory. Changes in length and compressive strength were determined from time to time. In one year's time the compressive strength of the untreated cylinders stored in the sulphate solution had dropped from 29 to 72 per cent of that of the blanks stored in water, while the steam-cured cylinders stored in sulphate solutions gave approximately the same or higher strengths than the steam-cured blanks stored in water. The expansion of the untreated cylinders stored in the sulphate solutions was also considerably greater than that of the steam-cured specimens stored under the same conditions. Cylinders made with 1 part cement and 3 parts standard sand and immersed in a one-per-cent solution of magnesium sulphate gave similar results (25). Steam-curing thus increases the stability of the test pieces as indicated both by strength and constancy of volume. Since the 28-day strength of the steam-cured specimens was somewhat lower than that of the corresponding untreated cylinders cured in water the increased resistance could not be due to a strength factor.

THORVALDSON, VIGFUSSON and LARMOUR (39) published expansion curves for very lean standard sand mortar prisms (1 : 7$^1/_2$) made with a Portland cement and with a mixture of tricalcium silicate, dicalcium silicate and tricalcium aluminate, exposed to solutions of sodium sulphate and magnesium sulphate after curing 10 days in steam at 98°. The steam-cured specimens of both the Portland and the composite cement gave very low expansions in the sulphate solutions as compared to the untreated specimens. While the untreated specimens expanded at nearly the same rate in solutions of Na_2SO_4 and $MgSO_4$ of equivalent molar concentrations, the steam-cured specimens had a much lower rate of expansion in the solution of Na_2SO_4. Steam-curing is thus a much better protection against the action of Na_2SO_4 than $MgSO_4$.

A large series of 2×4 in. concrete cylinders cured in steam at temperatures of 88° to 140° were immersed by MILLER (26) in Medicine Lake, S. D., which has a salt content varying from 2.34 to 4.72 per cent, the salts being mainly Na_2SO_4 and $MgSO_4$, the latter predominating. After 3 years' exposure in the lake the specimens steam-cured at 100° were in excellent condition while those cured in steam at lower temperatures or in water at room temperature had disintegrated. No deterioration was evident at the end of 1 $^1/_2$ years' exposure in the case of specimens cured in steam above 100°. All brands of Portland cement showed greatly increased resistance by steam-curing at 100° or above.

Two reports by THORVALDSON and VIGFUSSON (40) in 1928 and by THORVALDSON, VIGFUSSON and WOLOCHOW (41) in 1929, gave the results of a 4-year laboratory study on the effect of steam-curing of standard sand mortar prisms on the sulphate resistance as shown by measurement of linear expansion. Curing temperatures of 50° to 175° were used, the time of curing being varied up to 10 days. Several cements were used and the prisms were exposed in sealed vessels in a constant temperature room to various concentrations of sodium and magnesium sulphate and to a saturated solution of calcium sulphate. It was found that even with a 1:10 cement : standard sand mortar where the sulphate solutions must have very free access to the cementing particles steam-curing reduced the rate of expansion enormously. The treatment was most effective in preventing the action of solutions of sodium sulphate and least effective in preventing the action of magnesium sulphate. The beneficial effect increased with increasing temperature and duration of the steam-curing.

Reports by MILLER (22) and by MILLER and MANSON (27) giving results of $7^1/_2$ years' exposure in Medicine Lake show that curing in water vapor at temperatures of 100° to 177° increases the resistance of the concrete, as measured by maintenance of strength and volume constancy, to a remarkable degree, almost amounting to immunity under the best conditions of curing, the effect increasing with the temperature and duration of steam-curing.

In order to investigate the nature of the reactions which take place during disintegration of cements in sulphate solutions and the effect of hydrothermal treatment of mortars and concrete in modifying these reactions, THORVALDSON began in 1928 a series of experiments using mortars made with the pure cement substances and with composite cements made up of mixtures of these. The specimens used were 1:10 standard sand mortar prisms, the progress of the action being followed by measurement of expansion of the prisms in 0.15 molar solutions of Na_2SO_4 (2.1 %), $MgSO_4$ (1.8 %) and saturated $CaSO_4$ (0.2 %) at 21° and by occasional measurements of tensile strength. The object was to determine the relative stability of the cementing compounds or mixtures under the conditions of the experiments. The temperature chosen for steam-curing was 150° for 24 and 48 hours. Two reports (43, 42) of these experiments have been published, the latter giving the results of 9 years' exposures to the solutions. Only brief general statements as to the results and interpretations can be given.

1. Solutions of magnesium sulphate are (in the case of lean mortars) much more aggressive than solutions of sodium sulphate of equivalent concentration. A saturated solution of calcium sulphate (0.20 %) is, as a rule, slightly more aggressive than 0.15 molar sodium sulphate (2.1 %). This applies more particularly to steam-cured mortars.

2. The damp-cured mortars made with the aluminates of calcium alone were very unstable in all the solutions, the stability being of the same order or less than that of similar Portland cement mortars. Steam-curing, as a

rule, reduced the stability of the aluminate mortars somewhat while it increases the stability of the Portland cement mortars enormously.

3. Both damp-cured and steam-cured mortars made with the calcium silicates alone were extremely resistant to the action of sodium sulphate and calcium sulphate and, compared with the aluminate mortars, very resistant to the action of magnesium sulphate. Steam-curing increased the stability of the β-$2CaO \cdot SiO_2$-mortar only slightly but increased markedly the stability of the $3CaO \cdot SiO_2$-mortar particularly in solutions of $MgSO_4$. This indicates that the most significant result of steam-curing in these cases was the removal of free $Ca(OH)_2$ by combination with the silica of the aggregate and that the hydrosilicates are acted on by $MgSO_4$ but hardly at all by Na_2SO_4 (38). The mortar prisms made with γ-$2CaO \cdot SiO_2$ were very weak before steam-curing and give rather discordant results, but on steam-curing they attained approximately the same strength as the β-$2CaO \cdot SiO_2$ prisms and behaved very similarly (14). Mortars made with mixtures of $3CaO \cdot SiO_2$ and β-$2CaO \cdot SiO_2$ were more resistant than those made with either alone both before and after steam-curing. This may be due to differences in permeability but another possible explanation is that $2CaO \cdot SiO_2 \cdot H_2O$ may be able to take up some free lime (16, 45).

4. Mixtures in which 20 % of the silicate is replaced with the aluminates of calcium give mortars which in sulphate solutions behave like the mortars made with the aluminates alone. The same admixtures of tetracalcium aluminoferrite and dicalcium ferrite produce much more stable mortars. On steam-curing the stability of all these mortars is so greatly increased that they tend to behave after steam-curing more like mortars made with the pure silicates. For a given admixture to different silicate bases the stability of the mortars both before and after steam-curing arranged in ascending order is: 1. $3CaO \cdot SiO_2$, 2. $3CaO \cdot SiO_2 + \beta$-$2CaO \cdot SiO_2$, 3. β-$2CaO \cdot SiO_2$. The controlling factor thus appears to be the amount of free calcium hydroxide which may be liberated by the silicate base and its removal by steam-curing. On the other hand, for a given silicate, or silicate mixture, as the base the effect of the admixtures on the stability of the mortars in sulphate solutions both before and after steam-curing arranged in ascending order is: 1. $3CaO \cdot Al_2O_3$, 2. $5CaO \cdot 3Al_2O_3$, 3. $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, 4. $2CaO \cdot Fe_2O_3$. The most unstable mortar is the one where we have the combination of a high-limed silicate base with a large amount of tricalcium aluminate. This suggests that the instability in sulphate solutions may be connected with the formation of a very reactive hydrated tetracalcium aluminate in the mortar.

5. Considering these experiments together with the work on hydrothermal synthesis the stabilization of the mortars by steam-curing might be due mainly to the following factors:

a. The conversion of the aluminates present to the stable crystalline hexahydrate of tricalcium aluminate (36, 37, 18), or perhaps in the case of low-limed compositions to a hydrated dicalcium aluminate (31).

b. The removal of the free calcium hydroxide by combination with silica to form the less reactive crystalline calcium hydrosilicates (45).

c. The complete hydration of the silicates and the conversion of the gelatinous calcium hydrosilicate to the crystalline form (14).

d. The stabilization of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ as $3CaO \cdot Al_2O_3 \cdot 6H_2O$ and $CaO \cdot Fe_2O_3 \cdot H_2O$.

e. If dicalcium ferrite is present it is probably hydrolyzed to $CaO \cdot Fe_2O_3 \cdot H_2O$ with removal of the free lime as above.

6. From the standpoint of the high alumina type of cement it may be interesting to note that while mixtures of $3CaO \cdot SiO_2$ and $CaO \cdot Al_2O_3$ gave a very unstable mortar in all the solutions, mixtures of β-$2CaO \cdot SiO_2$ and $CaO \cdot Al_2O_3$ gave mortar prisms which were more stable in $MgSO_4$ than prisms made with β-$2CaO \cdot SiO_2$ alone. Steam-curing did not increase the stability in $MgSO_4$ materially, thus indicating that the determining factor was the action of the sulphate on the silicate (see paragraph 3 above). On the other hand, the stability of the damp-cured β-$2CaO \cdot SiO_2 + CaO \cdot Al_2O_3$-prisms in Na_2SO_4, although greater than in $MgSO_4$, was considerably less than that of the prisms made with β-$2CaO \cdot SiO_2$ alone, but on steam-curing the stability increased almost to the same order. This indicates that here the determining factor was the action of the sulphate on the aluminate and that this was stabilized by steam-curing possibly by crystallization as a very slightly soluble hydrate.

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Discussion.

MR. L. FORSÉN:[1]

By a steam-curing process developed in our laboratory a new type of light weight concrete, called Siporex, is manufactured from Portland cement and finely ground quartz.

During the steam treatment previously unknown reactions take place, *viz.* the complete conversion of C_3S to $CS \cdot Aq.$ in the presence of finely ground quartz. Furthermore the calcium aluminate double salt, ordinarily formed when cement reacts with water, is decomposed to tricalcium aluminate hexahydrate and gypsum. The product obtained consequently differs materially from ordinary concrete in that no free lime is present, the silicates are transformed to monocalcium silicate hydrate and finally to the stable tricalcium aluminate hexahydrate. Such concrete has a lower shrinkage and a greater resistance than ordinary concrete. Further, the change in properties on storage is less dependent on the chemical reactions being completed during the steam curing.

Some analytical data are presented in the following table. When calculating the molar ratio $CaO : SiO_2$, amounts of lime corresponding to free CaO, C_3A, CF, $CaSO_4$ and $CaCO_3$ have been deducted from the total amount of CaO.

Steam Curing Tests — Temperature 170°.

Materials	Time in Hours	Sol. SiO_2	Total CaO	Free CaO	Al_2O_3	Fe_2O_3	CO_2	SO_3	Molar Ratio $CaO : SiO_2$
C_3S alone	8	21.9	64.8	3.4	0.8	0	3.2	0	2.74
C_3S »	48	21.4	64.7	5.2	1.1	0	0.7	0	2.84
C_2S »	15	31.2	62.3	0.2	0.4	0	0.4	0	2.09
P. C. »	8	16.5	56.0	6.7	6.1	2.8	2.7	1.9	2.17[3]
P. C. »	7	15.9	53.9	7.3	5.5	2.9	2.2	1.6	2.20[3]
1 part C_3S + 2 parts SiO_2[2]	15	21.8	22.6	0.3	0.8	0	0.9	0	0.98
1 » C_2S + 2 » »	15	15.2	21.7	0.1	0.4	0	—	0	1.48
1 » C_2S + 2 » »	120	17.2	20.2	0.1	0.3	0	0.7	0	1.18
1 » P.C. + 2 » »	8	13.5	20.7	0.1	2.5	1.1	1.8	0.9	1.05
1 » P.C. + 2 » »	48	15.8	19.6	0.2	2.5	1.8	0.3	0.7	0.94

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[1] Dr.-Ing., Chief Chemist, Skånska Cementaktiebolaget, Limhamn, Sweden.

[2] In all cases added as finely ground quartz.

[3] If the Fe_2O_3 is calculated as C_4F, which compound according to preliminary experiments appears to be stable in the presence of excess lime, the ratio assumes the values of 1.98 and 2.00 respectively.

MR. T. THORVALDSON (*author's closure*):

Dr. FORSÉN's experimental work is of special interest as the conditions under which he worked differed materially from those of our experiments. In case of our original experiments (38), a Portland cement high in lime and containing a small amount of free CaO was mixed with standard silica sand, 20—30 mesh. No silica particles of less than 0.589 millimetres diameter were therefore present. The microscopic examination indicated that on steam-curing crystals of calcium hydroxide first formed and then gradually disappeared during the formation of crystals of the hydrosilicate. This shows that although excess of silica was present, the area of the surface, at which the lime liberated during the hydration of the C_3S could react with the silica, was so small that the hydrosilicate was formed in the presence of an excess of calcium hydroxide. The steam curing was not carried beyond the time necessary to cause the disappearance of the crystals of calcium hydroxide.

Under the above conditions the hydrosilicate formed is mainly the orthosilicate. In all our experiments where mixtures of silica gel or finely divided silica with calcium hydroxide were used, the object was to prepare the hydrosilicate in the pure state. Excess of lime was, therefore, used, as this could be more easily removed than excess of silica.

In Dr. FORSÉN's hydrothermal experiments with C_3S, C_2S, and Portland cement mixed with finely ground quartz, it seems probable that on account of the large area of interface the reaction with the sand occurred so rapidly that the concentration of free lime was always extremely low. Under these conditions monocalcium silicate appears to be the main product. If one assumes, as appears probable, that the mechanism of the hydration of C_3S and C_2S in water involves the complete hydrolysis of these substances to calcium hydroxide and hydrated silica with the subsequent building-up of the hydrosilicate, then one would expect that the lime content of the hydrosilicate formed is determined by the concentration of lime in the solution. When porous test pieces are cured in saturated steam, it seems unlikely that one ever obtains conditions where the liquid phase is not present in the pores of the material.

These experiments, however, do not answer the question whether the crystalline hydrated orthosilicate when once formed is decomposed to the hydrated monosilicate when treated hydrothermally in the presence of silica. Our experiments indicate that if such is the case, then the process takes place very slowly.

EFFECT OF WATER ON PORTLAND CEMENT

BY

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Introduction.

The standards for inorganic binders as a rule contain no definite specifications on their mineralogic and petrographic composition, where they represent compounded systems, as the chief purpose of the tests to which they are submitted is to obtain a picture of their properties and merits as building materials. Usually, a certain fineness of grain is demanded, and, furthermore, the time of setting, the minimum strength attainable, the permissible shrinkage and perhaps the rise of temperature during the setting are specified. In order to avoid undue presence of foreign materials, which might have a deleterious effect, the maximum percentage of inert materials, of sulphuric acid anhydride, and magnesia is sometimes also specified.

There are no clear data in the physico-chemical literature on inorganic binding materials, which might enable an unambiguous definition of the term "Portland cement".

For some years, various statements have been made as to which mineral components should be contained in Portland cement. From certain statements regarding the various moduli of mineral compounds called Portland cement, certain conclusions as to their quantitative composition are possible. It is, however, evident from the data referring to the gross chemical composition of Portland cement, that the name is applied to mineral compounds whose composition may vary within wide limits. The present paper refers to those cements which contain as chief clinker-components:

Tricalcium silicate (abbr. C_3S)
Dicalcium silicate (abbr. C_2S)
Tetracalcium aluminate ferrite (abbr. C_4AF)
Tricalcium and also pentatricalcium aluminate (abbr. C_3A and C_5A_3).

The microscopic and X-ray examinations have clearly shown that the three first-named chemical compounds are represented in crystalline form in the clinker minerals. It may also be assumed that the tricalcium aluminate is present in the clinkers in a free form. It is, moreover, established that it is also contained in the glassy main compound of the clinker and may form mixed crystals with the C_3S.

Those accessory components which are contained in all Portland cements, such as free lime and compounds of magnesium and alkalies, are of secondary importance and will not be considered in our detailed investigation; it should merely be stated that in contact with water, such components increase the alkalinity of the latter.

The cement clinkers, in course of the manufacture of the usual technical Portland cement, are ground with addition of gypsum. But the disintegration does not go far enough to produce a powder of thoroughly homogeneous granular composition; the technical cements rather represent a mineral powder which only yields a more or less uniform granulation or sedimentation analysis. The mechanical disintegration of the clinker is not sufficiently thorough to break up all the components of the clinker evenly enough to give a total surface corresponding to the percentage of all the chemical components. Microscopic and chemico-physical examinations have also shown that the various minerals in the various grain-sizes are not evenly distributed.

Inasmuch as only the free surface of the solid clinker components reacts with water, and owing to the low solubility of the products of such reaction, these agglomerate with the reacting surface, thus hampering the diffusion of the reacting water to the solid phase—it is evident that the course of this reaction, especially in such concentrations, as obtain in mortar consistency, will be substantially influenced by the granular structure or by the free surface. The reactions will thus be considerably slowed down, so that a great deal of time is required for the quantitative process, which is often not completed at all.

As all technical Portland cements carry certain amounts of gypsum to regulate the time of setting in accordance with prevailing specifications, gypsum must be considered as a normal component of technical Portland cement. Accordingly, when the effect of water on Portland cement is investigated, the chemical effect of gypsum must also be considered, although it is not to be regarded as a component of clinker. Such investigations may be carried out from two points of view, as follows:

1. The tests are performed with great excess of water and for longer periods, in order to examine the conditions of equilibrium between the basic body and the aqueous solution under certain external conditions. In this connection, allowance must be made for the fact that the newly formed bodies, owing to the low solubility, may envelop the basic material, and even if so-called shaking tests are carried out, it may take a long time before the basic material is wholly transformed. Only from this moment on, it is possible to obtain

reliable data on the equilibrium between the solid phase of the new formations and the aqueous solution. Such investigations are made chiefly for the purpose of studying the mechanism of the reaction and it is therefore necessary to be certain whether the primary reaction between water and the reacting solid base material is actually finished. If this is not carefully observed, mistakes may occur. Nacken (11) has also emphasized this point.

2. Water is made to react with Portland cement in such a concentration that a mortar-slurry is formed which is just workable. These conditions obtain in the practical application of Portland cement as building material and it is therefore important to study the various reactions processed under such conditions.

As Portland cement represents a mixture of various minerals which react with water differently, investigations of the process of hydration on the Portland cement itself cannot lead to unequivocal results, because the various processes run parallel and overlap and are, moreover, capable of mutually influencing one another; and there are as yet no methods available, analytical or physical, for their separation and single identification. Of recent years, therefore, attempts have been made to study the hydration and hydrolytic processes in the single components of the clinker, in order, from knowledge thus obtained to draw conclusions with greatest certainty regarding the reactions obtaining between water and Portland cement. Studies on equilibriums which occur under certain conditions show us which reactions are possible at all, and especially does it become clear, whether and in what degree, hydrates may be decomposed under certain experimental conditions. In judging, however, the reaction processes in the system Portland cement-water of mortar consistency, it must be remembered that the concentration conditions are absolutely different. It may, for example, be expected that the hydration and hydrolysis of the cement components of mortar consistency will not be so thorough as in great dilution with water.

I will first give a brief summary of the results of investigations carried out on hydration and hydrolysis of single components of Portland cement clinker, and I shall use these results for the discussions on the processes of hydration and hydrolyses of Portland cement proper.

Effect of Water on Single Clinker Components.

Calcium Silicates.

A great many experiments have been carried out on the effect of water on tri- and dicalcium silicate in comparatively high dilution without, however, fully explaining the temporal course of their hydrolytic decomposition as a function of the concentration and temperature. The solubility in water of the resulting products of hydration and the completion of equilibrium between base body and liquid phase have also not been determined as yet; but the results of the investigations tally in this, that the products of reaction represent hydrates of calcium silicate which are highly insoluble and which show very little inclination to crystallization and are segregated as gels. Furthermore, it is universally acknowledged that the speed of reaction decreases from C_3S to CS. KÜHL (9) has made a compilation of the relevant literature up to the year 1934, to which we may here refer.

NACKEN (11), on the basis of shaking tests, arrives at the conclusion that, when water reacts with C_3S, a certain equilibrium is obtained between base body and aqueous phase, provided that the hydration of the base material is complete. In the following TABLE 1 the results are presented in a somewhat different way from that adopted by this author. From the point of view of cement technique the fact is particularly important that, beginning with a concentration of 1.24 g $C_3S + 1\,000$ g H_2O, the decomposition at 20° proceeds only to $C_2S \cdot xH_2O$ and, with concentrations from over 4.92 g C_3S in 1 000 g H_2O, the base body consists of $C_2S \cdot xH_2O + Ca(OH)_2$.

Only at lower concentrations, according to NACKEN, do the base bodies $C_3S_2 \cdot xH_2O$ and $CS \cdot xH_2O$ begin to form. There was no decomposition down to silicic acid in his experiments; he arrives at the conclusion that $CS \cdot xH_2O$ is dissolved in water congruently, whereas the other hydrates are dissolved incongruently. These results are not to be compared directly with those of

Table 1. Equilibrium of $3CaO \cdot SiO_2$ with Water, from NACKEN.

g $3CaO \cdot SiO_2$ in 1 000 ml Pure Water	Solution g CaO in 1 000 ml	Basic Body
0 to 0.397	0.0 to 0.195 + SiO_2 in solution	$CaO \cdot SiO_2 \cdot xH_2O$
0.397 to 0.529	0.195[1]	$CaO \cdot SiO_2 \cdot xH_2O +$ $+ 3CaO \cdot 2SiO_2 \cdot xH_2O$
0.529 to 0.827	0.195 to 0.302[1]	$3CaO \cdot 2SiO_2 \cdot xH_2O$
0.827 to 1.241	0.302[1]	$3CaO \cdot 2SiO_2 \cdot xH_2O +$ $+ 2CaO \cdot SiO_2 \cdot xH_2O$
1.241 to 4.925	0.302 to 1.210[1]	$2CaO \cdot SiO_2 \cdot xH_2O$
over 4.925	1.210[1]	$2CaO \cdot SiO_2 \cdot xH_2O +$ $+ Ca(OH)_2$

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[1] SiO_2 in solution negligibly small.

KÜHL and MANN (10), because these work with constant dilutions and changing molecular proportions $CaO : SiO_2$ to maximal 2 : 1. The data found by these authors do not correspond with the actual equilibriums, when entered in NACKEN's diagram. This incongruency, according to NACKEN, is due to the fact that no equilibrium states have been attained.

In a later publication (12), NACKEN reports, after very long periods of shaking (278 days), a further decomposition than would correspond to the communicated state of equilibrium, finding at an initial concentration of 1.62 g C_3S + 1 000 g H_2O, 0.58 g CaO + 1 000 g H_2O in solution. According to this composition, a base body of $C_3S_2 \cdot xH_2O$ was calculated in lieu of $C_2S \cdot xH_2O$, as taken from the diagram. NACKEN ascribes this to the influence of the glass.

The slight solubility of the silicious hydrates thus established is in accordance with investigations by FLINT and WELLS (5). These investigators found that silicic acid dissolved in the aqueous phase, even with a content of 0.3 g CaO per litre, is below 0.005 g SiO_2 per litre. It may be concluded from these examinations that with such concentration conditions as obtain in the mortar consistency of the mixture C_3S + water, the products of decomposition will be, besides $Ca(OH)_2$, $C_2S \cdot xH_2O$; this because the required concentration of CaO of 0.2 g/l is reached almost instantaneously and the product of reaction, owing to its hard solubility, is segregated at once even if no aluminates are present.

Our previous investigations on the hydrolysis of C_3S in great dilution (15) do not contradict NACKEN's results, as it could be shown that, with concentrations of lime in the aqueous solution of below 0.4 g CaO/l, a decomposition of C_3S beyond $C_2S \cdot xH_2O$ takes place.

NACKEN has attempted the hydrolysis of C_2S; it was impossible, however, to make his results tally with his system, but, as a certain hydrolysis has been proved besides hydration, the apparent discrepancy was explained by the slow and incomplete reaction and the non-equilibrium between solution and base body.

We also found non-equilibriums during our shaking tests, on varying the concentration of C_2S in water or solutions of $Ca(OH)_2$. It was shown that on shaking in lime-water of 0.4 g CaO/l, from the base body, no lime will go into solution and with greater concentrations of lime (0.6 g CaO/l) lime is even absorbed from the solution by the base body. That a hydrolysis of C_2S had nevertheless taken place could be proved by the formation of gel-like bodies. It is highly probable that this is a matter of adsorptive binding, which may also occur in the hydrolysis of C_3S. NACKEN has not made any observations on this. We leave the question open as to whether and in what degree his investigations, which determine the base body by quantitative analysis of the solution, have been interfered with by adsorption phenomena.

During the years 1932—1934 I carried on experiments with BERCHEM (2) on the effect of water on C_3S of mortar consistency, by making test bodies of 10 × 10 × 30 mm in size and under varying conditions, trying as far as possible to eliminate CO_2, storing these during certain defined periods after which they were examined.

By preliminary experiments, the amount of water required to obtain mortar consistency, and the time of setting were determined. Stability tests were taken, on the test bodies, the volume shrinkage of the system (hydraulite + water) was measured, the chemical analysis of the set material was carried out and the vapour-pressure isotherms were taken, as well as microscopic and X-ray pictures.

In these experiments, as mentioned above, the granular structure and also the properties of the grain have a considerable influence on the development of the reaction, for which reason comparative examinations should always be carried out with bodies of equal shape; for only then has one to deal with defined and comparable surfaces which are subject to the effect of water. The material which was at our disposal for the investigation was not of fully homogeneous grain, but all grains remained below 60 μ.

During the hydration and hydrolysis of C_3S of mortar consistency (about 36 % addition of water), there is no evidence of primary substance which goes into solution. There is formation of $Ca(OH)_2$, part of which remains dissolved, and also of a coat of gel which envelopes the grain which has not as yet been changed in zones. The reaction proceeds to a certain depth, after which it slows down greatly, since the access of further water is greatly delayed by the more difficult diffusion within the coat of gel. In any case, careful experimentation shows clearly that this coat of gel increases in the course of time. The liberated $Ca(OH)_2$ is, as a rule, of very fine grain, embedded in the gel and easily to be shown by X-rays. Under favourable conditions, large crystals of $Ca(OH)_2$ may form in the capillaries of the gel mass or on the surface. The glycolate-method (16) presents a way for the quantitative determination of the split-off free $Ca(OH)_2$ (17). Inasmuch, however, as the determination of the free $Ca(OH)_2$ alone does not lead to definite results on the number of mols. of lime which become free on hydration, owing to the great difficulties in determining the percentage of hydrated $C_3S \cdot xH_2O$, we attempted to produce a completely hydrated tricalcium silicate.

It is possible to influence the reaction tricalcium silicate + water by changing the water ratio, by raising the temperature, or by increasing the surface of the tricalcium silicate by applying it in finer granulation. Several series of experiments were therefore carried out.

In the hardened tricalcium silicate mortar, the content of free calcium hydroxide, of water and of carbonic acid was determined. In the test bodies which had been stored in water for a long time, the dissolved lime was calculated by analysis. By the addition of the free calcium hydroxide (deducting the constitutional water), of the lime bound to carbonic acid, and of the dissolved lime, one can estimate the total lime released. If this figure is expressed in per cents of the total lime, present in the primary material and bound to silicic acid, a measure is obtained for the degree of the splitting-off of lime during the hydration and hydrolysis of the tricalcium silicate. Theoretically, in the splitting-off of one mol. Ca, the amount of the split-off lime would be maximum 33.3 % given complete hydrolysis into dicalcium silicate hydrate. The results of the experiments may be briefly summarized as follows:

Influence of the Amount of Water and Time of Storing.

The depth of reaction ultimately reached is dependent on the amount of water present in the mortar during the setting of the tricalcium silicate, since during the setting, the space in the mortar occupied by the water, owing to the swelling of the tricalcium silicate, is filled with gel. In the case of a densely packed mortar with low water content, this space is smaller than with a voluminous mortar rich in water. In order to arrive at a final state with equal products of hydration, namely to a dense, hardened calcium silicate hydrogel, more tricalcium silicate has to be hydrolysed in the second case than in the first. If the volume of the water exceeds a certain limit—about 45 %—there is formed, in water storing, a less dense product of hydration richer in water and with lower stability though the depth of reaction increases very little.

Influence of Temperature.

The rise of temperature does not produce any decisive increase in the depth of reaction, but only an acceleration of the process of hydration by increase in the speed of the reaction.

Influence of Grain-Size.

Experiments on grains of tricalcium silicate between 1 and 7 μ which, according to their fineness, required water from 45 % to 49 %, have shown that already after three days storing at 100° in a closed glasstube, more than 26 % lime has been split off. The examination under the microscope confirmed the results obtained by analysis. In polarized light, a slight clarification was already recognizable. Thus, the ageing of the gel is accelerated by increase of temperature and pressure.

The X-ray examination of a preparation in which the splitting-off of the lime reached the value of 0.875 mol., and the free lime of which had been extracted by glycol, showed the presence of dicalcium silicate hydrate. Vapour-pressure isotherms which were taken, led to the conclusion that the gel at 20° and a water—vapour-pressure equivalent to 3 mm Hg contained 4 mols. of bound water.

The investigations thus lead to the conclusion that in mortars of pure tricalcium silicate, formation of a gel of dicalcium silicate hydrate, and crystalline $Ca(OH)_2$ takes place. The gel, at a water—vapour-pressure of 3 mm Hg and 20°, contains about 4 mols. of bound water. The tendency to crystallization of the gel is very low; it is favoured by increase of temperature and pressure. BOGUE and LERCH (3) likewise state that C_3S of mortar consistency is decomposed to C_2S-hydrate.

The examinations of the system C_2S-H_2O of mortar consistency confirm the known fact that the setting of the C_2S proceeds very slowly; no free lime is split off.

Calcium Aluminates.

Amongst the aluminates of lime, the C_3A in Portland cement is by far the most predominant. We shall, therefore, specially refer here to its behaviour with water. According to ASSARSSON (1), in a mixture of one part C_3A to 20 parts of water, the following equilibriums are arrived at:

At 5°, there are present as base bodies crystalline, hexagonal $C_3A \cdot 12H_2O$, besides crystallized $C_2A \cdot 7H_2O$ and a small amount of gel. Accordingly, the solution contains an excess of lime.

At 20°, the decomposition goes on at first as at 5°. But after some time, the tabloid-shaped aluminates are transformed into regular $C_3A \cdot 6H_2O$; the content of calcium in the solution decreases in such a manner that Al_2O_3 and CaO are contained in it in equal proportions of weight.

At 40° and 90°, the C_3A reacts with water very quickly and a coat of regular $C_3A \cdot 6H_2O$ is formed on the anhydro-bodies; nevertheless, the thorough hydration into $C_3A \cdot 6H_2O$ takes place and CaO and Al_2O_3 are present in the solution in equal amounts.

According to experiments by NACKEN (12, 13), at 23°, the solubility of the C_3A, within 0.48—5.96 g in 1 000 g H_2O is constantly congruent and amounts to 0.68 g/l. The compound $C_2A \cdot 7H_2O$ exists in the base body in traces. The hexagonal hydrate of tricalcium aluminate is not stable against lime solutions below 20° and it is transformed under their influence into the stable hydrate of tetracalcium aluminate (up to 0.33 g CaO/l the α-form, with more CaO the β-form), whilst the regular hydrate of tricalcium aluminate suffers no transformation. In systems rich in lime, the hydrate $C_4A \cdot x H_2O$ does not occur at 23°.

The statement of FORSÉN (6) that the reaction of the non-aqueous trialuminate with water takes place under a constant hydrolytic decomposition into the corresponding hydroxides, whereupon the aqueous compounds appear as new formations, cannot be supported in this general form. Genuine solutions occur according to ASSARSSON, in contacting layers, which can then react further. The formation of the hydrolytic base bodies is dependent on the concentration. Within the range of temperature between 20° and 40° regular $C_3A \cdot 6H_2O$ is always formed.

As applied to Portland cement, it is shown that at lower temperatures than 20° and in the absence of gypsum, $C_4A \cdot x H_2O$ is formed, while above 20°, the regular $C_3A \cdot 6H_2O$ occurs, being formed in very small crystals; if gypsum is present, calcium sulpho-aluminates are formed from the dissolved hydrate of tricalcium aluminate.

If C_3A of mortar consistency reacts with water, the temperature rises, owing to the high speed of reaction, to such a degree that the regular $C_3A \cdot 6H_2O$ may be formed.

Brownmillerite.

It is stated in the literature (8, 14) that C_4AF is decomposed with water into tricalcium aluminate hexahydrate and ferro calcium hydrates. Our investigations (2) carried out in mortar consistency, have shown that free lime is present in the set Brownmillerite. Thus, in a hardened sample, 3—3.2% CaO was determined as free calcium hydroxide, from which it may be concluded that in a set Brownmillerite, hydrated oxide of iron must occur. The Brownmillerite of mortar consistency sets comparatively slowly, very little heat being discharged.

The microscopic examination of the hardened Brownmillerite mortar shows that the hydration proceeds comparatively slowly. After short water storage, a hardened sample of Brownmillerite consisted of three substances, *viz.* of a nucleus of non-hydrated, dark-brown material, of a light-yellow coloured substance surrounding this nucleus, and finally of a colourless substance filling the rest of the space and consisting of small grains of hydrate of tricalcium aluminate. After long storing in water, the nucleus of non-hydrated Brownmillerite which becomes luminous in polarized light and is thus recognizable, had disappeared. Besides the dark-brown mass of gel, small hexagonal laminæ were visible which became luminous in polarized light and were coloured blue by α-naphthol-phthalein, and which must be taken for calcium hydroxide or also for hydrate of tetracalcium aluminate.

The hydration of the Brownmillerite, then, leads to the appearance of the hydrates of calcium aluminate, according to the conditions of the reaction, in the form of tri- or tetracalcium aluminates. It is, however, to be assumed that the formation of C_4A recedes behind the formation of C_3A.

In long water-storage, the stability of the Brownmillerite mortar decreased, and the material became friable. It seems that there is a certain relation between the formation of hydrate of tetracalcium aluminate and the weakening of the structure of the mortar. The investigations along these lines are being continued.

Portland Cement.

Proceeding from the reactions and conditions of equilibrium already discussed, we wish now to deal with the effect of water on Portland cement.

From the technical point of view, it is especially the processes which go on during the setting and hardening of Portland cement of mortar consistency which are interesting, because the kind, quantity and quality of the various reaction products in the mortar after setting influence the mechanical stability and chemical power of resistance of the mortar.

If the various Portland cements, during the setting and hardening, show very different behaviour, this is above all caused by their composition and their granular structure, which may vary within wide limits. As it is a matter of contacting surface reactions, the nature of the surface, besides the chemical mechanism, determines the course of the reaction.

From the investigations discussed above, it follows that it is the development of temperature in the reacting mass and the presence of free lime in the aqueous solution which control the course of the reaction. These factors cause various Portland cements in setting and hardening under various conditions to behave differently. The logical conclusion to be drawn from these discussions is that, in studying the processes which take place in Portland cement on contact with water, it is absolutely necessary to form as precise an idea as possible of its mineralogic composition, on the basis of chemical, microscopic, and X-ray examinations (4); the granular composition and shape of grain has also to be determined. It is also necessary to keep a temperature chart of the setting and the subsequent storing.

During such experiments, it should also be established, whether and in what way the single mineral components have an influence on the hydration and hydrolysis. It is, for example, of interest to know whether the hydration and hydrolysis of the C_2S are affected by the presence of tricalcium aluminate. Our investigations of the splitting-off of free lime in mixtures of tricalcium silicate with tricalcium aluminate of mortar consistency have shown that in the presence of C_3A, actually more free lime is produced than when water acts upon tricalcium silicate alone. Furthermore, it could be shown that in water-storage at low temperatures, a part of the liberated lime may become bound again, under formation of hydrate of tetracalcium aluminate. The amount of the split-off free lime increases with the rising content of C_3A in the mixture. Thus, in the examination of a certain Portland cement clinker, we found that the hydrate of calcium silicate gel contained less than 2 mols. CaO to 1 mol. of silicic acid. The solution of tricalcium aluminate and lime has a lower P_H-value than pure saturated lime solution, or than the supersaturated solution forming on hydration. Under such conditions, the hydrate of dicalcium silicate becomes further hydrolysed and there is thus a possibility of the decompositions going further than on the addition of water to pure tricalcium silicate of mortar consistency. On termination of the hydration of C_3A, a P_H-value corresponding to the hydroxide of calcium may again be attained, so that the remaining tricalcium silicate would become further decomposed under formation of hydrate of dicalcium silicate.

These considerations show further how important it is clearly to realize what bearing the addition of gypsum has on the setting of Portland cement of mortar consistency. The delaying effect of gypsum on the setting process is generally accounted for by the formation of sulpho-aluminates of calcium. According to FORSÉN (6), this is supposed to prevent the precipitation of silicic acid by the aluminates, which in its turn is supposed to retard the setting process. We were able to confirm by our experiments that silicic acid and alumina precipitate each other floccularly, but, on the other hand, we also established in accordance with the investigations on equilibrium mentioned above that the quantities of silicic acid in solution are very slight; the question, therefore, arises whether the quick setting of a mixture of C_3S and aluminate is caused chiefly by this deflocculation. The delaying effect of the added gypsum may also be accounted for by the formation of sulpho-aluminates of calcium taking place in the immediate vicinity of the contacting surfaces tricalcium aluminate/water, and by the fact that the diffusion of further quantities of water to the unchanged tricalcium aluminate is hampered by the increased formation on the contacting surfaces of salts difficult of solution. Experiments with models show the formation of double-salts on the contacting surfaces (TABLE 2). The reaction, after their formation, continued only very slowly. This does not mean that the double-salts can not also form in other parts of the mortar, but a necessary condition for this is that hydrate of tricalcium aluminate should be present in the aqueous phase.

If the reaction takes place in the manner described along the outer surface of the tricalcium aluminate, it appears plausible that after the setting and hardening from the unchanged tricalcium aluminate at comparatively low

Table 2. Reaction Tests on Mixtures of $3CaO \cdot Al_2O_3 + CaSO_4 \cdot 2H_2O$ *+ Water.*

Data of Proportions of Mixtures refer to Parts of Weight.

Mixture	I	II	III	IV	V
$3CaO \cdot Al_2O_3$ $CaSO_4 \cdot 2H_2O$ Water	100 — 60	100 5 60	100 10 60	100 20 60	100 40 60
Characteristic of setting	Strong increase of temperature about 80°	Increase of temperature hardly noticeable		Increase of temperature hardly noticeable	
Microscopic description of product of setting after one hour	Quantitative transformation into regular $3CaO \cdot Al_2O_3 \cdot 6H_2O$	Very light circumferential zones of $C_3A \cdot CaSO_4 \cdot 12H_2O$; C_3A very little attacked		Small circumferential zones of Ettringite surrounding grains of C_3A which are scarcely attacked	
Microscopic description of product of setting after 24 hours	Unchanged, as above	Distinct circumferential zones of $C_3A \cdot CaSO_4 \cdot 12H_2O$ surrounding grains of C_3A, most of which are unattacked		Strong circumferential zones of Ettringite surrounding grains of $3CaO \cdot Al_2O_3$, most of which not yet hydrated	

temperature and in the presence of calcareous water and absence of gypsum, hydrate of tetracalcium aluminate may form. In this way it is also possible to explain the subsequent appearance of gypsum expansion in the set cement under the action of water containing gypsum.

That the delaying effect is less if instead of gypsum equal amounts of anhydrite are added to the cement is easily understandable if one bears in mind the speed of solution of the two substances.

In studying the setting and hardening of a Portland cement of the following mineralogic composition in mortar consistency,

$3CaO \cdot SiO_2$	63.3 %
$2CaO \cdot SiO_2$	11.4 %
$3CaO \cdot Al_2O_3$	3.9 %
$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	16.4 %
MgO	1.8 %
CaO free	0.59 %
Addition of gypsum	4.7 g

we found that the speed and depth of the reaction were substantially higher than with pure tricalcium silicate of practically the same granular structure. The amount of CaO split off from tricalcium silicate is calculated at about 1.5 mol. The influence of the aluminates in the clinker was distinctly noticeable.

When Portland cement of mortar consistency sets the picture of the reaction is as follows:

From the silicates are formed crystalline calcium hydroxide and a hydrate-gel of calcium silicate which contains 2 mols. SiO_2 to about 3 mols. CaO; though it is not yet clear whether this gel represents a hydrate of calcium silicate of the composition $3CaO \cdot 2SiO_2 \cdot xH_2O$, or whether it is a mixture of hydrate of dicalcium silicate and monocalcium silicate.

The effect of the gypsum is caused by the formation of sulpho-aluminates; it may be assumed that these agglomerate in a finely dispersed form along the outer surfaces of the aluminate. The Brownmillerite is decomposed to tricalcium aluminate hydrate in the finest dispersion, while at the same time, free calcium hydroxide can be shown, so that it must be assumed that also hydrate of ferric oxide appears.

Owing to the hard solubility and the gel-character of the main products, and also to the extremely fine distribution of the crystalline products of transformation, the base material is not totally transformed. The depth of reaction on the grains is chiefly dependent on the fineness of grain and the composition of the cement. Increase of temperature accelerates the reaction considerably, while the amount of water over and above a certain percentage appears at first to remain without influence.

Upon the practically completed hardening, further reactions may develop in the mass, as, for instance, formation of tetracalcium aluminate, or subsequent formation of sulpho-aluminates of calcium in the presence of gypsum-water. Decompository reactions take place if the hydration, owing to access of water, continues. If the new formation is removed by solution processes, the well known chemical lixiviation of the cement (7) takes place.

We shall not here discuss the effect on the set cement of such aqueous solutions as contain acids or salts.

Summary.

1. Reactions in Portland cement clinker which occur on contact with water are discussed.

2. With respect paid also to the reactions under 1., processes which develop upon the addition of water to technical Portland cement of mortar consistency are described.

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Discussion.

Mr. G. E. Bessey:[1]

Professor Schläpfer indicates in his report that in the setting of Portland cement the silicates yield a gel approximating to the composition $3CaO \cdot 2SiO_2 \cdot \underline{x}\, H_2O$. This conclusion is based upon free lime determinations. Some tests which have recently been carried out by the present writer on samples of completely hydrated cement lead to similar conclusions although different metods of free lime determination were used.

These tests were carried out with the dual object of checking the validity of different methods of free lime determination on hydrated cements, and of comparing the determined values of free lime content with values calculated by application of the results of work on phase equilibria.

A number of different cements of widely varying composition, and including a white Portland cement, a high lime cement and low heat Portland cements were chosen. They were hydrated by mixing to a thin paste with water, curing for 28 days at 17°, drying *in vacuo* at ordinary temperature, crushing and grinding, and repeating this procedure until hydration was complete as judged by microscopic examination of the fine powder and by a constancy in the loss on ignition after consecutive periods of hydration. The analyses of the cements used are given in Table 1.

Free lime, carbonate, and loss on ignition determinations were carried out on the completely hydrated samples after grinding to pass a 100-mesh British Standard sieve. The methods of free lime determination used were the calori-

Table 1. Analysis of Cements.

Substance	I Low Heat Portland	II Low Heat Portland	III Rapid Hardening Portland	IV White Portland	V Rapid Hardening Portland	VI Normal Portland
CaO	63.40 %	59.65 %	66.69 %	65.10 %	64.50 %	64.60 %
SiO_2	26.28 »	22.88 »	21.14 »	21.56 »	20.25 »	19.09 »
Al_2O_3	2.89 »	5.12 »	3.91 »	5.96 »	6.13 »	7.64 »
Fe_2O_3	2.18 »	4.44 »	3.54 »	0.52 »	2.59 »	3.30 »
SO_3	1.65 »	1.42 »	1.39 »	2.23 »	2.20 »	2.19 »
Na_2O	0.37 »	0.92 »	0.42 »	0.28 »	0.35 »	0.25 »
K_2O	0.46 »	0.68 »	0.52 »	0.31 »	0.74 »	0.57 »
TiO_2	0.23 »	0.15 »	0.25 »	0.07 »	0.38 »	0.34 »
MgO	1.61 »	3.73 »	1.27 »	0.54 »	0.36 »	0.56 »
Loss	1.20 »	1.45 »	0.94 »	3.70 »	2.57 »	1.60 »

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Table 2. Loss on Ignition and Carbonate Contents of Completely Hydrated Cements.

Cement	Loss in Weight on Ignition at 1 000° Per Cent	CO_2 Per Cent
I Low Heat Portland	30.0	2.1
II Low Heat Portland	23.0	3.1
III Rapid Hardening Portland	30.4	4.0
IV White Portland	31.0	3.5
V Rapid Hardening Portland	27.3	2.3
VI Normal Portland	33.1	2.5

metric and lime-solution extraction methods described by the present author, the glycerol-alcohol method according to LERCH and BOGUE, and the ethylene-glycol method as described by SCHLÄPFER and BUKOWSKI. On two of the cements free lime was only determined by the calorimetric method. The free lime results are shown at the bottom of TABLE 3, and the carbonate and loss on ignition values in TABLE 2. The calorimetric and lime-solution extraction methods show reasonable agreement, the glycerol-alcohol method in one case gives a result much higher than those obtained from the first two methods, and the ethylene-glycol method gives results which in two cases are somewhat lower, and in one case higher than the other methods.

The possible major errors and the significance of the results with the four methods of determination are as follows:

1. The calorimetric method might suffer from errors caused by decomposition of the hydrated compounds or by combination of free lime with other compounds during the ignition. Tests have not been carried out on all the possible compounds which may occur in a set cement, but the pure hydrated silicates and some hydrated aluminates have been tested by heating alone and with lime at 550° and no marked reactions of this nature have been observed. There do not appear to be any other major sources of error.

2. The lime-solution extraction method is carried out by shaking the sample with a half saturated lime solution in such proportion that the final lime concentration is between 0.8 and 1.0 g per litre. The lime extracted is determined from the difference in initial and final lime concentration of the solutions by direct titration or gravimetrically. A small correction is necessary for aluminate in solution. The result, according to existing knowledge of the phase equilibria in the hydrated systems involved, should give the free lime in equilibrium with the compounds $3CaO \cdot 2SiO_2 \cdot Aq.$; $3CaO \cdot Al_2O_3 \cdot Aq.$ *or* $4CaO \cdot Al_2O_3 \cdot Aq.$; $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot Aq.$; and possibly $3CaO \cdot Fe_2O_3 \cdot Aq.$ It is not necessarily the true free lime value in the solid hydrated cement, as compounds of higher basicity may exist in contact with saturated lime

Table 3. Calculated and Observed Free Calcium Hydroxide Content of Completely Hydrated Cements.

Compounds		I Low Heat Portland		II Low Heat Portland		III Rapid Hardening Portland		IV White Portland		V Rapid Hardening Portland		VI Normal Portland	
		Anhydrous Compound %	CaO %	Anhydrous Compound %	CaO %	Anhydrous Compound %	CaO %	Anhydrous Compound %	CaO %	Anhydrous Compound %	CaO %	Anhydrous Compound %	CaO %
Compound content calculated on unhydrated material	$3CaO \cdot 2SiO_2 \cdot$ Aq.	63.1	36.8	55.0	32.1	50.6	29.6	51.8	30.2	48.7	28.4	45.9	26.8
	$3CaO \cdot Al_2O_3 \cdot$ Aq.	5.8	3.6	11.9	7.4	8.8	5.4	13.3	8.3	13.8	8.6	17.8	11.0
	$3CaO \cdot Fe_2O_3 \cdot$ Aq.	4.5	2.3	9.1	4.7	7.3	3.7	1.1	0.5	5.3	2.7	6.8	3.5
	$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot$ Aq.	4.7	2.3	4.0	2.0	3.9	2.0	6.3	3.1	6.2	3.1	6.2	3.1
	$Ca(OH)_2$	18.4	18.4	13.5	13.5	26.0	26.0	23.0	23.0	21.7	21.7	20.2	20.2
Calculated on hydrated material	$Ca(OH)_2$ expressed as CaO		13.1		10.6		18.3		16.7		16.4		13.8
	CaO found present as carbonate		2.7		3.9		5.1		4.5		3.0		3.2
	Nett $Ca(OH)_2$ expressed as CaO		10.4		6.7		13.2		12.2		13.4		10.6
If $4CaO \cdot Al_2O_3 \cdot$ Aq. is assumed instead of $3CaO \cdot Al_2O_3 \cdot$ Aq. Nett CaO (calculated as above)			9.5		4.7		12.1		10.1		11.2		8.1
If $2CaO \cdot SiO_2 \cdot$ Aq. is assumed instead of $3CaO \cdot 2SiO_2 \cdot$ Aq. Nett CaO (calculated as above)			1.7		Nil		6.3		4.9		6.2		4.5
Free CaO found,	I Calorimetric		9.1		6.6		13.8		12.3		10.4		7.8
	II Extraction to 0.9 g CaO per litre final concentration		9.2		8.8		14.3		12.3		—		—
	III Glycerol-alcohol		11.5		6.8		13.7		18.4		—		—
	IV Ethylene-glycol		7.3		6.5		16.5		10.7		—		—

solution. If, however, the results of the calorimetric method (which does not decompose the more basic compounds) are in agreement with the results by this method, it may be inferred that both give the true free lime value.

The lime-solution method will be less accurate when applied to partly hydrated cements, since further hydration with liberation of free lime may occur during the test.

3. The glycerol-alcohol and glycol extraction methods are liable to both positive and negative errors, the former arising from attack of other compounds, and the latter from the difficulty of dissolving crystalline calcium hydroxide sufficiently rapidly in these reagents. The latter error is usually greater with the ethylene-glycol method.

The most probable compounds in hydrated cements, from existing phase equilibria data, would appear to be $2CaO \cdot SiO_2 \cdot$ Aq.; or $3CaO \cdot 2SiO_2 \cdot$ Aq.; $4CaO \cdot Al_2O_3 \cdot$ Aq. or $3CaO \cdot Al_2O_3 \cdot$ Aq.; $4CaO \cdot Fe_2O_3 \cdot$ Aq. or $3CaO \cdot Fe_2O_3 \cdot$ Aq.; $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot$ Aq., and free $Ca(OH)_2$. The proportion of these compounds was calculated from the cement analyses, ignoring minor components, and the theoretical free calcium hydroxide value recalculated to the hydrated material from the loss on ignition data. The lime present as carbonate, which was rather high owing to the method of preparing the samples, was assumed to have been derived entirely from carbonation of free lime and was therefore deducted from the gross theoretical free lime value. This assumption may not be strictly correct but is most probably substantially so.

The results given in TABLE 3 show that the assumption of the compounds $3CaO \cdot 2SiO_2 \cdot$ Aq.; $3CaO \cdot Al_2O_3 \cdot$ Aq. or $4CaO \cdot Al_2O_3 \cdot$ Aq.; $3CaO \cdot Fe_2O_3 \cdot$ Aq., and $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot$ Aq. agrees most closely with the determined free lime values by both the calorimetric and extraction methods. The difference in the calculated results for different iron compounds or aluminates is not sufficient to enable any positive differentiation to be made, but the difference in the case of the silicate is very considerable if any compound other than $3CaO \cdot 2SiO_2 \cdot$ Aq. be assumed and the results must be taken as strong evidence that the silica in completely hydrated Portland cement is present as this compound. It seems unlikely that the silicate can be present as a mixture of dicalcium and monocalcium silicate hydrates, as suggested alternatively by Prof. SCHLÄPFER, as the phase equilibria data do not indicate that these two compounds can exist in equilibrium. The possible causes of occurrence of the compound $3CaO \cdot 2SiO_2 \cdot xH_2O$ rather than dicalcium silicate hydrate are mentioned in the discussion on Dr. FORSÉN's report.

The agreement of results of the lime-solution extraction and calorimetric methods, and of the calculated values, provides some confirmation of the validity of these two methods, and of the value of the calorimetric method as applied to hydrated Portland cements.

Mr. G. HAEGERMANN:[1]

I wish to give a brief account of the tests which we have made on the hydration of tricalcium silicate. In order to ascertain the kind of silicate hydrate formed, we have used the following method. Pure tricalcium silicate was treated with water and was left to harden under hermetic conditions for 28 days. The test specimen was then crushed and treated with water again. This procedure was repeated about 20 times. We have arrived at the following result. If the percentage of free lime in the test specimen previously heated to 700° is determined according to EMLEY's method, dicalcium silicate is ultimately formed in addition to calcium hydroxide. Only when the test specimen is treated with water in excess, and when the solution is continually replaced by pure water, does further decomposition of dicalcium silicate hydrate take place.—*(Translated from German.)*

Mr. P. SCHLÄPFER[2] *(author's closure):*

I.

It is generally acknowledged to-day that the glycolate-method (3), which has been devised in our institution, represents a reliable and quick method for the determination of free lime in cement clinkers. We have attempted to demonstrate by long and systematic experiments what are the essentials in this determination in order to receive useful values. The instructions for carrying through the analysis have been drafted in accordance. Subsequently, several authors have proposed some changes, in order to adapt the method to their more special purposes, or in order to simplify it. I mention here only the proposition made by S. RORDAM (2), because so far as I know, it has been rather adopted in America and England.

The glycolate-method, as well as the glycerate-method, which has been modified by us, has been more disputed when the determination of the free calcium hydroxide in such mortars is concerned, which are wholly or partially set. We ourselves have pointed out that the quantitative determination of the free $Ca(OH)_2$ is in this case rendered somewhat more difficult and also less accurate, because, on one hand, some calcium-aluminium-hydrates and their double salts might be attacked by glycol and also by glycerine-alcohol

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[2] Dr. ESENWEIN and Mr. BINGGELY assisted me in the experimental part of this report, and I herewith pronounce my thanks to them.

mixtures, and, on the other hand, the formation of glycolate, *viz.* glycerate proceeds more slowly than with CaO (3). The contents of certain hydrates of calcium aluminates in the substance investigated, its granulation, the time of shaking and the temperature may all exert certain influences on analytical results. Notwithstanding this, by our investigation we came to the conclusion that both methods for the determination of free $Ca(OH)_2$ in set mortars are applicable, provided the necessary precautions are taken. The accuracy actually attainable has to be judged in each particular case. We have applied the glycolate-method in connection with other measurements also for the observation of the development of reaction between C_3S and water in mortar-consistency.

Dr. BESSEY doubts the usefulness of the method in pointing out that he has found no conformity between the values for free $Ca(OH)_2$, as determined by his calorimetric- and also extraction-method with solution of lime and the glycolate-method. I will deal with his statements somewhat more closely by also submitting some new results of experiments, which might be considered a contribution for the elucidation of this question. As our experiments are not fully terminated we shall publish the completed material later.

II.

S. RORDAM proposes to simplify the glycolate-method by heating the specimen powder with 30 ml glycol and 15 ml ethyl-alcohol absolute to boiling for 30 min. under the reflux-condensor (at ab. 82°—84°), as against our original prescription: shaking of the finely powdered specimen with 50 ml pure glycol in the water bath at 75°—80° during at least 30 min., adding a trifle quartz sand.

Checking analyses which we carried through with calcium hydroxide, cement powder and specimens of set concrete, showed clearly that with the modified procedure by RORDAM the formation of Ca-glycolate is not completed within the prescribed time of reaction of 30 min. As is shown by the results compiled in TABLE 3, of the pure $Ca(OH)_2$, *e. g.* only 80 % of the free lime was converted after 30 min. Even after an action of 2 hours, the formation of calcium glycolate was not accomplished quantitatively.

These results are thoroughly in accordance with our previous experiences. It was shown already in our first treatise on the glycolate-method that the formation of Ca-glycolate at 70°—80° in presence of ethyl-alcohol in considerable quantity evolves more slowly than with pure glycol. Besides, the agitation

Table 3. Determination of Free Lime by the Glycolate-Method by SCHLÄPFER *and* BUKOWSKI *and the Modified Method by* S. RORDAM.

Description of the Analyse-Substance	Weight in	Time of Reaction in	Contents of Free Lime found					
			Method by SCHLÄPFER and BUKOWSKI: Shaking with 50 ml glycol at 75°—80° during at least 30 min.			Modified Method by S. RORDAM: With 30 ml glycol + 15 ml Alcohol under the Reflux-Condensor, boiling during 30 min.		
	g	Min.	ml $\frac{N}{10}$ HCl	% CaO	% $Ca(OH)_2$	ml $\frac{N}{10}$ HCl	% CaO	% $Ca(OH)_2$
Hydrate of lime	0.050	30	12.9	72.3	95.5	10.6	59.4	78.5
»	0.050	60	13.0	72.7	96.1	11.4	63.8	84.4
»	0.050	120	12.9	72.3	95.5	11.7	65.5	86.6
Portland cement	1.0	30	3.9	1.09	—	2.6	0.73	—
»	1.0	60	4.0	1.12	—	3.1	0.87	—
Set Portland cement mortar	2.0	30	13.6	1.90	2.51	8.3	1.16	1.53
	2.0	60	13.5	1.89	2.50	8.8	1.23	1.62
	2.0	120	13.6	1.90	2.51	9.7	1.36	1.80

of the reacting mixture in the shaking-machine and in presence of an abrasive agent (quartz sand) is much more thorough than with the mere boiling of the compound. During our comparative analyses we have repeatedly observed formation of lumps in the weighed specimens in the boiling glycol-alcohol mixture. We like to emphasize again, therefore, that the glycolate-method leads to incontestable results, when our direction of procedure is accurately followed. The modification proposed by RORDAM yields values which are too low; we cannot, therefore, recommend it.

III.

G. E. BESSEY (1), in some of his studies has dealt with the determination of the free calcium hydroxide in set cement-mortars. With the application of the glycolate-method he finds values too low, whereas the glycerate-method, following LERCH and BOGUE's modification yields too high values, according to BESSEY.

He has obtained relatively well consistent values by the calorimetric-method proposed by him—(determination of the difference of the heat reaction between the specimen heated to 350° and that to 550° and re-calculation of it for CaO based on the known heat of reaction)—and his recently favoured extraction-method with lime-water. Therefore, he concludes that these two methods should be preferred for the determination of free lime in set mortars.

We have at other occasions called attention to the fact that by the calorimetric method usually too high values are obtained for the free lime, as, besides the free hydrate of lime, other hydrates contained in the mortar, such as hydrates of calcium silicates and calcium aluminates, undergo noticeable conversions within the temperature-interval of 350°—550° under dehydration, and that results may be influenced thereby.

Dr. BESSEY very kindly called my attention to his calculation of the free calcium hydroxide from the difference of the losses of weight at 550° and 350° by the formula:

$$Ca(OH)_2 = \frac{74}{18} \cdot (\text{loss of weight at } 550° - 1.09 \cdot \text{loss of weight at } 350°)$$

whilst we used the formula:

$$Ca(OH)_2 = 1.09 \cdot \frac{74}{18} \cdot (\text{loss of weight at } 550° - \text{loss of weight at } 350°).$$

The loss of weight, according to BESSEY's formula, is somewhat smaller, so that the calculated content of $Ca(OH)_2$ will be accordingly lower. Yet, the basic sources of errors established by us (dehydration from silicates of lime and hydrates of calcium aluminate above 350°) remain unquestioned, so that by the method suggested no absolute values can be obtained. Dr. BESSEY has written me that he employs the method of loss in weight only for fresh cements, in which the loss at 350° reaches seldom more than 1 %. He also states that the loss-of-weight method is not applicable with sufficient accuracy, whenever the presence of hydrates others than $Ca(OH)_2$ is considerable. In his communications he cites cases where the content of $Ca(OH)_2$, as determined by the loss-of-weight method, amounts to 10 % and more. Dr. BESSEY, so far as I know, is engaged at present to further compare the various methods with each other, as he does not consider the results communicated so far as final ones.

Table 4. Results of the Lime-Water-Extracting Method with Pure Portland Cement.

Substance applied in g	Time of Reaction in Min.	Concentration of the Lime-Water applied in mg CaO : 100 ml	Contents of Lime of the Solution after the Reaction in mg CaO : 100 ml	Found Contents of Free Lime	
				in mg CaO	in % CaO
0.5	30	79.0	86.8	7.8	1.56
0.5	120	79.0	89.0	10.0	2.00
0.5	30	69.0	79.2	10.2	2.04
0.5	120	69.0	81.0	12.0	2.40
0.5	240	55.2	77.8	22.6	4.52
2.0	30	79.0	104.0	25.0	1.25
2.0	120	79.0	116.8	37.8	1.89
2.0	240	55.2	103.5	48.3	2.42
1.0	30	determined by the glycolate-method		10.9	1.09

Results of the Lime-Water-Extracting Method with Set Concrete.

Substance applied in g	Time of Reaction of the Lime Solution in Min.	Initial Concentration of the Lime-Water in mg CaO:100 ml	Contents of Lime of the Solution after the Reaction in mg CaO : 100 ml	Found Contents of Free Lime	
				in mg CaO	in % CaO
0.5	120	79.0	85.2	6.2	1.22
0.5	120	69.0	78.4	9.4	1.88
2.0	120	69.0	91.7	22.7	1.13
2.0	120	55.2	79.6	24.4	1.22
2.0	30	determined by the glycolate-method		38.1	1.90
2.0	60	determined by the glycolate-method		37.8	1.89

The extraction-method by lime-water, according to BESSEY, *consists in the following*. The set mortar to be examined is being pulverized and shaken with half-saturated lime-water in such proportions, that, after extraction of the calcium hydroxide contained in the mortar, the lime-solution is nearly saturated, *i. e.* that it contains 0.85 to 1 g CaO/l. BESSEY states that by this method, in presence of not yet hydrated cement components, less accurate results will be obtained. Now it is an established fact that in cement-mortars, after normal setting, there are non-hydrated components left, as such mortars will set again after pulverization and addition of water. Therefore, a basic error must necessarily be attached to that method.

We have carried through some parallel tests with fresh Portland cement and a set, rapid-hardening cement. As was to be expected for theoretical reasons, they showed, especially in the case of the fresh cement that the CaO-values obtained by the extraction-method are dependent on the time of action of the lime-water upon the cement. We extended the extraction until the lime-solution originally applied was nearly saturated. In the attached TABLE 4 some of these results are compiled.

Table 5. Results of the Lime-Water-Extraction Method (BESSEY) *with Set Pure Portland Cement "G", passed through a 900-Mesh Sieve.*

Weight in g	0.50		0.25		0.25		0.25		Glycolate-Method	Glycerate-Method
Initial concentration of the lime-water in mg CaO:100 ml	23.5		43.5		56.0		68.2		Weight 1 g	
Time of reaction (shaken)	Final conc. CaO mg/l	CaO %	Final conc. CaO mg/l	CaO %	Final conc. CaO mg/l	CaO %	Final conc. CaO mg/l	CaO %	CaO %	CaO %
30 min.	87.6	10.80	70.0	10.60	77.0	8.82	84.3	6.40	8.14	2.80
60 »	92.0	11.48	73.0	11.09	80.0	9.61	84.9	6.72	9.28	7.00
120 »	102.2	14.28	76.0	12.70	84.0	11.70	90.7	8.96	10.02	7.16
240 »	107.2	14.56	77.2	13.21	84.5	11.98	91.5	9.29	10.78	8.26
Results of the Lime-Water-Extraction Method (BESSEY) *with Set Portland Cement "J", passed through a 900-Mesh Sieve.*										
30 min.	61.6	3.80	46.7	1.36	62.2	1.25	68.6	1.20	2.10	0.80
60 »	67.2	3.92	50.9	3.02	62.7	2.73	73.5	1.51	3.64	1.40
120 »	75.0	4.70	51.9	3.02	63.0	2.80	73.6	2.13	3.92	3.08
240 »	78.0	4.76	53.0	3.14	63.3	2.82	73.9	2.24	4.04	3.11

It may be seen from the results that those figures for free $Ca(OH)_2$, which are obtained by the lime-extraction method, may vary, according to the initial concentration of lime and the time of reaction. This fact caused us to carry on comparative series of tests on various set mortars, by which we established which relations existed between the ascertained contents of free lime and the initial concentration of the solution at varying times of reaction. Likewise, comparative tests were made by the glycolate- and the glycerate-method. We cite, from the figures obtained, first two series of tests, which

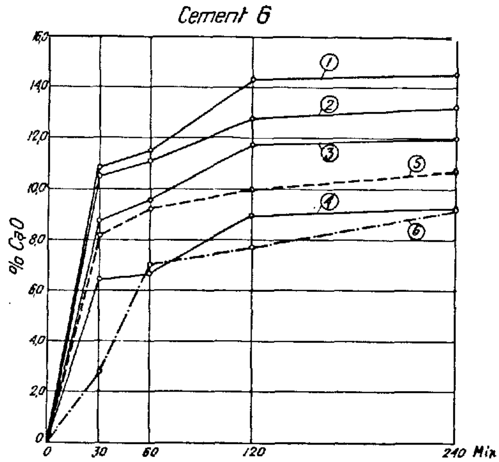

FIG. 1. Determination of Free $Ca(OH)_2$ in Set Cement "G".
(Influence of the time of reaction.)

Concentration of the Lime Solutions 1, 2, 3, 4.

1. 28.5 mg CaO:100 ml
2. 43.5 mg CaO:100 ml
3. 56.0 mg CaO:100 ml
4. 68.2 mg CaO:100 ml
5. Glycolate-method.
6. Glycerate-method.

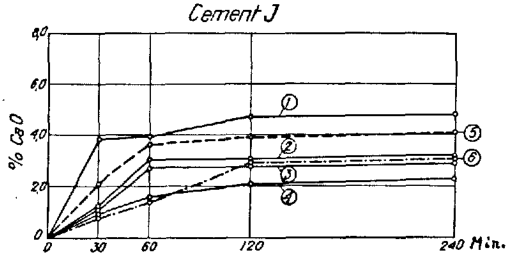

FIG. 2. Determination of Free $Ca(OH)_2$ in Set Cement "J".
(Influence of the time of reaction.)

Concentration of the Lime Solutions 1, 2, 3, 4.

1. 28.5 mg CaO:100 ml
2. 43.5 mg CaO:100 ml
3. 56.0 mg CaO:100 ml
4. 68.2 mg CaO:100 ml
5. Glycolate-method.
6. Glycerate-method.

were taken on a rapid-hardening cement *"G"* and a normal cement *"J"*. The two cements, when delivered, showed different finenesses; the lime content of the cement *"G"* was higher. The cements were treated with an excess of water under exclusion of CO_2. The specimens, after hydration, were pulverized and passed through a 900-mesh sieve, rinsed with absolute alcohol and then carefully preserved for analysis. The tests proper were then executed in rapid succession. The results are compiled in TABLE 5 and FIGS. 1 and 2.

The investigation has clearly proved that the results, by all three methods which were compared, are dependent on the *time of action of the reagent*, and, with the lime-extraction-method, on the initial concentration of the lime-solution as well. It is characteristic that, with all three methods, a state of equilibrium is attainable, after which, notwithstanding extension of time for reaction, the contents of free lime found do not increase any more substantially.

With the glycolate-method and the lime-extraction-method, (with a half-saturated solution of lime), this equilibrium is comparatively soon arrived; but when the initial concentration of the lime-solution is raised beyond the half saturation, the final equilibrium is delayed and it remained, for the materials tested, below that obtained by the glycolate-method. With the glycerate-method, the equilibrium is reached much later—which is in accordance with our previous statements that mixtures of glycerine and alcohol react more slowly than glycol. We have also carried through tests according to LERCH and BOGUE and have established for cement *"G"* that the final equilibrium, owing to the high viscosity of glycerine, is reached still later.

On the basis of our investigations, we cannot agree with BESSEY, that the glycolate-method should yield too low values. We also could demonstrate that by proper method of operation, the various methods lead to final equilibria, which give values for the contents of free lime in a product, which are not as far divergent as BESSEY states. For the lime-extraction-method, it is important to keep the initial concentration not too low, but also not substantially higher than at half the saturation point.

The glycolate-method proposed by us, for the determination of free lime in set hydraulic products, furnishes useful values. If the time of reaction should not exceed 60 min., it is, however, necessary to apply the original product for analysis in finely pulverized form; the same, however, holds good for the other methods as well, as our systematic experiments have clearly shown. In case the behaviour of a set product is not known at all, yet it is always advisable to make preliminary tests with varying time of reaction, in order to establish when a practically constant equilibrium is reached. Finally, we should emphasize again that in judging the results one should always be aware of the possible sources of error. The determination of free lime in set hydraulic binders cannot be pronounced to be "an absolute method" in the sense of analytical chemistry, nor should that be, except in rarest cases, the purpose of the method, which primarily should furnish us a view on the degree of the hydration of hydraulites. The result obtained is chiefly interpreted in connection with other pertinent investigations.

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THE CHEMISTRY OF RETARDERS AND ACCELERATORS

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Abstract.

A report is submitted here—preceded by a short review of the literature on the subject—of some new results gained from experimental work on accelerators and retarders for Portland cement, carried out during recent years at the research laboratory of the Skånska Cement AB. in Limhamn. In this work I have been assisted by Mr. P. S. HÅKANSON, Mr. R. HEDIN, Mr. H. WENNERSTRÖM and Mr. O. KALLAUNER, and to these gentlemen I beg to express my gratitude for their valuable help.

From earlier work and from our own experiments the following conclusions can be drawn:

When Portland cement reacts with water the components enter into solution in the same stoichiometric proportions as the water-free components have, forming solutions which are supersaturated with respect to hydrates as solids.

From the principal component of the cement—C_3S—a solution is formed which at first contains $3CaO : 1SiO_2$ and which on account of the precipitation of $Ca_2SiO_4 \cdot 4H_2O$ gradually changes into a supersaturated lime solution. The hardening of cement is the result of a continuous dissolving of the silicate compounds and a following precipitation of the hydrate mentioned, which acts as a gluing agent. The formation of a voluminous mass—the "Swelling" —when cement or calcium silicate is shaken with water or with various solutions is effected by the dissolving of the silicates and precipitation of calcium silicate hydrates.

The normal hardening of cement, which is the result of a continuous dissolving of calcium silicates and precipitation of the gluing agent—dicalcium silicate hydrate, can be influenced in different ways by substances dissolved in the solution in which the cement reacts. Dissolved calcium salts accelerate the hardening. The P_H-value of the solution is decreased, and as a consequence the calcium silicates are more speedily dissolved. Finally, the calcium ion concentration is increased, causing a rapid precipitation of the hydrate. Dissolved aluminates hinder or disturb the formation of the $Ca_2SiO_4 \cdot 4H_2O$ normally formed by precipitating gels containing aluminium hydroxide and silicic acid with a small amount of lime.

At normal setting a solution is instantaneously formed in which the solubility of the aluminates is considerably reduced. Any dissolved aluminates are immediately deposited as films around the cement grains, thus protecting them and retarding the velocity of their dissolution. These films consist of lime-rich aluminate compounds that are instantaneously precipitated as a semipermeable membrane when a saturated or a supersaturated calcium aluminate solution is combined with a lime solution or with a lime-containing calcium salt solution. The precipitates consist of tetracalcium aluminate, or, as the case may be, of tricalcium aluminate double salt with a calcium salt.

Retarders are compounds that give rise to such precipitates. The most prominent ones are calcium salts in moderate concentrations in the presence of dissolved lime (from C_3S, the dissolution of which is considerably accelerated by calcium salts) or dissolved lime alone from such a lime compound (alkali-free clinker with a high content of C_3S, or active lime) as is able to introduce lime into solution with such a velocity and in such a quantity as is required for an instantaneous precipitation of aluminates. If certain calcium salts such as $CaCl_2$ and others are present in high concentrations, the P_H-value of the solution—even if the latter is saturated with lime—is decreased to such a degree that the aluminates enter into solution without being precipitated. Consequently, no retardation occurs. When calcium hydroxide and gypsum are both present, a tricalcium aluminate double salt—probably the monosulphate $3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$—is formed. This is insoluble in lime-water. When cement reacts normally with water, the speed at which the aluminates react with the gypsum can be experimentally followed by determining SO_4'' soluble in lime-water. The quantity in question corresponds to free gypsum.

Retarders are also Mg-salts which cause normal set by instantaneously forming a precipitate of $Mg(OH)_2$ on the surfaces of the cement grains, thus protecting them from rapid reactions. The slaking of burnt lime is in like manner, by precipitation of a surface film of $Mg(OH)_2$, considerably retarded by a 10 %-solution of magnesium sulphate. Barium hydroxide and barium salts also act as retarders by precipitating aluminates. Another retarder is a 5 %-solution of alkali hydroxide. The retarding effect of alkali hydroxide and barium hydroxide is much less than that of the calcium salts, because the solubility of the aluminates is decreased only to a certain degree, leaving some aluminate in solution to react with silicate. The normal setting conditions are to some extent disturbed and the mechanical strength is correspondingly lowered.

In quick setting cement which without gypsum has become slow setting through the influence of moist air, the cement grains are covered with a protecting film of set cement. If such cement is reground, or the film is dissolved, the cement becomes quick setting again.

Quick setting occurs when no retarding solution is present or immediately formed. In such a case aluminates and silicates are speedily dissolved. The high amount of heat evolved is a result of the rapid reactions. The instantaneous water consumption is due to the rapid formation of hydrates and the coagulation of aluminium silicates. The low strength, finally, is caused by the coagulation of aluminium silicate, which prevents the formation of the cement glue—Ca_2SiO_4, $4H_2O$.

Most technical cements containing alkali are quick setting without gypsum. Alkali aluminate and silicates enter instantaneously into solution and coagulation between silicate and aluminate occurs. The quick set of such cement cannot be prevented by the addition of lime, because the solubility of the lime is low in the instantaneously formed alkali hydroxide solution and because the lime is dissolved much slower than the alkali aluminate and the alkali silicate. The addition of readily soluble gypsum or other soluble calcium salts neutralizes the alkali hydroxide because calcium hydroxide is less soluble than alkali hydroxide. A saturated or supersaturated solution of calcium hydroxide in a calcium and alkali salt solution is formed and the aluminates are immediately precipitated. A protecting film is formed around the cement grains, which retards the dissolution of the components including the alkali compounds.

Alkali-free cements that are quick setting without retarders can be retarded with gypsum or other calcium salts, but, in contrast to alkali-containing cements, their setting can be controlled by lime alone. Such cements are normal setting without retarders if they are high in C_3S, even if they contain comparatively much aluminate, because C_3S instantaneously gives a saturated or a supersaturated lime solution that precipitates tetracalcium aluminate.

Alkali-free cements that, owing to high C_3S-content, are slow setting without retarders show a normal final set if they are free from iron, whereas such cements show an abnormally slow final set if they do contain iron compounds. If such ferrite-containing cements are given an addition of gypsum or other calcium salts, their final set becomes normal. This phenomenon probably depends on a gelatinous iron compound being formed when no calcium salt is present. This gel is precipitated on the cement grains and retards the reaction. Calcium salts, however, produce a precipitate of another structure —most likely crystalline.

In mechanical strength the cements without alkali are far superior to those containing alkali. The lower strength of the alkali-containing cements is attributable to the fact that as soon as the gypsum or any other calcium salt is consumed by the aluminates the alkali appears as free hydroxide. As previously mentioned, some aluminate will then enter into solution and coagulate with silicate, which impairs the strength.

Alkali-containing cements may sometimes become quick setting after having been stored. Through the action of moisture and carbonic acid, alkali carbonate is formed. When the cement is mixed with water, the carbonate dissolves quickly and precipitates calcium carbonate. The lime content of the solution is decreased, calcium aluminate is not precipitated, and quick set results.

Sugar and humic acid act injuriously on the setting of cement because solutions of these substances dissolve the aluminates even in the presence of lime, and quick setting results. Boric acid and borax also dissolve calcium aluminate and cause quick set with low strength.

Reactions similar to those which have here been discussed for Portland cement also take place when granulated basic blast-furnace slag reacts with water. Without retarders silicate and aluminate cause coagulation on the surface of the grains and the reaction is stopped. Retarders such as lime or Portland cement (C_3S), or alkali hydroxide, which forms a lime solution from the sulphides of the slag, decrease the solubility of the aluminates, the silicates enter into solution and are precipitated as lime-rich silicate hydrates, similar to the cement glue.

Earlier Works.[1]

Scott (46) published in 1857 a paper on the beneficial influence of sulphurated fuels on the strength of burnt lime. Such lime did not slake, but after being ground and mixed with water it hardened like cement. This observation led in 1870 to Scott's patent for "Selenite mortar" (47), which was produced by burning lime and gypsum together. As a result of Scott's publications Schott (43) investigated the influence of gypsum mixed with various kinds of lime. He found that the strength of hydraulic lime was much increased when gypsum was mixed in, but that ordinary lime was not

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[1] A general discussion of much of the earlier work is given by Bogue, Rock Products, May—September 1928, and by Watson & Craddock, Cement and Cement Manuf., 1935, *8*, 50, 63.

improved. Berger (8) claims that Scott was the first to suggest control of the setting time of Portland cement with gypsum, whereas this for Portland cement so important discovery is attributed by Goslich (21) to Michaëlis. According to Candlot (12) the addition of gypsum to Portland cement in industrial use emanates from Germany, where this procedure had been in use since the early seventies as a secret process for improvement of the soundness and for control of the setting time.

Quick setting cement was earlier controlled by storing the ground cement. According to Schott (44) the moisture and the carbonic acid of the air cause the cement grains to be covered by a thin film of hydrates and carbonates, which is thought to retard the setting by preventing the water from penetrating. The addition of gypsum substitutes the seasoning—according to Schott—by covering the cement grains with a gypsum film formed by the adsorption of gypsum from the solution in which the cement reacts.

Candlot (12, 13) was the first to undertake a systematic, chemical investigation on the cause of the retarding effect exercised by gypsum. Candlot showed that cements with low content of aluminate are not influenced, whereas the influence on aluminate-rich cements is remarkable. Candlot found that the dissolving of aluminates is checked in the presence of lime and that gypsum increases the retarding influence of lime on the dissolving of aluminates, but that gypsum alone is not able to precipitate the aluminates. Candlot also found that the gypsum is precipitated from the solution when cement reacts with water and that a double salt is formed which is insoluble in lime-water. Candlot gave the formula $3CaO \cdot Al_2O_3 \cdot 2{,}5CaSO_4 \cdot Aq.$ to this salt. Candlot considered that the setting of cement begins with the dissolution and hydration of the aluminates and that the retardation of the set by means of lime or lime and gypsum was caused by the decreased solubility of the aluminates. Quick set in spite of the presence of gypsum was found to be due to lack of lime in the solution, and Candlot assumed that the quick set depended on the copious formation of a crystallized calcium aluminate sulphate. Candlot also investigated the influence of calcium chloride, and found that this salt in low concentration reduces the solubility of the aluminates and also controls the setting time, but that calcium chloride in high concentration dissolves the aluminates and renders the cement quick setting. Candlot further showed that alkali carbonates render the cement quick setting, which was explained as depending on precipitation of the retarding lime.

The old method of controlling the setting time with moisture was again taken up by Bamber (5), who in 1903 was granted a patent for controlling the setting time by introducing steam, if desired in a mixture with air and carbonic acid, in the cement mill. The advances made by colloid chemistry induced ROHLAND (38, 39) to explain the influence of various additions as catalytic, and ROHLAND classified the alkali hydroxides as positive catalysts —accelerating the coagulation—and considered the action of the gypsum to depend on neutralization of the alkalies. REIBLING (37) considered that gypsum decreases the solubility of the calcium compounds solely by increasing the calcium ion concentration. KLEIN and PHILLIPS (28) pointed out that neither the formation of the insoluble double salt nor the calcium ion action can explain the retarding influence of gypsum, since also other substances such as calcium chloride, borax and sugar are retarders. The problem was still open to discussion, but it was suggested that the explanation was to be found in the different influence exercised by various electrolytes on the coagulation of the aluminates.

In a comprehensive investigation on the cement components BATES and KLEIN (6) showed that C_3S sets and hardens like Portland cement, and that C_3A reacts violently with generation of much heat and has no hydraulic qualities whether alone or in the presence of gypsum, but that added to C_3S in small quantities it raises the strength of this compound. GADD (20) found that the ability of the gypsum to control the setting time was in some cases uncertain, whereas the control by means of steam or water was more dependable. According to GADD, the control of the set is effected through the formation of a protecting film of hydrated cement. This film prevents the water from penetrating. The quantity of water required can be introduced in the form of water, of steam or of water-containing salts such as gypsum dihydrate. KÜHL (30) explained the action of the gypsum to consist in precipitating the insoluble double salt which CANDLOT had discovered and which MICHAËLIS (34) had found to have the composition $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 30H_2O$. This salt is precipitated until the supply of gypsum is exhausted, then the aluminates enter into solution and the trivalent aluminate ion coagulates the dissolved silicates, causing the cement paste to harden.

The injurious influence of sugar, which had been reported earlier by NEWHALL (36), HUNDESHAGEN (24) and others (29), was also investigated by BURCHARTZ (11), who by microscopical observations found that the presence of sugar caused gel-formation, while crystalline products appeared when cement normally reacted with water. According to a later investigation by HUNDESHAGEN (25), an abundant precipitate of aluminium silicate gel is formed when cement is treated with a sugar solution. TIPPMANN (50), who examined the ability of cement to swell when shaken with water, found that gypsum promotes this swelling or gel-formation. He accordingly considered that quick set is caused by crystallization from a supersaturated solution, while at normal set in the presence of gypsum gels are slowly formed.

The property of certain cements to become quick setting on seasoning was investigated by GRIMM (22), who found that this change depended on the formation of alkali carbonates when alkali-rich cements took up moisture and carbonic acid from the air. These carbonates consume gypsum through the formation of calcium carbonate, and hence a large excess of gypsum is advantageous for alkali-rich cements. The tendency of light-burned cements to be quick setting was attributed by KILLIG (27) to a higher alkali content of these cements, alkali not being vapourized to the same extent as when cement is burned at higher temperatures. BERGER (8) showed that quick setting cements without gypsum give solutions with higher hydroxyl ion concentration than cements with gypsum do. The retarding ability of different modifications of gypsum has been much investigated, and has also been dealt with by BERGER in the cited as well as earlier works (7). Readily soluble gypsum semihydrate, which, as is known, forms strongly supersaturated solutions, is the most effective regulator, when added in small amounts.

The retarding property of gypsum dihydrate grows with increased grinding fineness because the dissolving velocity is thereby accelerated (18). Natural anhydrite has, on account of its low solubility, a very small retarding effect. Gypsum semihydrate, especially in large quantities, causes false quick set, a phenomenon which is dealt with in a number of publications (51, 53) and which is considered to be due to a certain stiffening owing to the hardening of the gypsum semihydrate. An experiment by SCHACHTSCHABEL (41) showing that false quick set is overcome by the addition of some dihydrate supports this interpretation. Quick set caused by gypsum semihydrate is not injurious to the mechanical strength of the mortar.

HAEGERMANN (23) showed that the strength of C_3S was much increased by the addition of C_3A or $CaCl_2$.

FORSÉN (19) has demonstrated that solutions of inorganic calcium salts are able to control the setting time and that these precipitate hexagonal crystals of a double salt—insoluble in lime-water—of the type $3CaO \cdot Al_2O_3 \cdot CaX \cdot 10H_2O$. These double salts are probably isomeric with $3CaO \cdot Al_2O_3 \cdot (CaSO_4 \cdot 2H_2O) \cdot 10H_2O$ and tetracalcium aluminate. At normal set in the presence of calcium salts in small amounts no aluminate could be detected in the solution, whereas certain quantities of aluminate were found in rapidly prepared solutions from quick-setting cements—even when the quick set was caused by large amounts of soluble calcium salts. FORSÉN considered quick set to depend on coagulation of aluminate-silicate solutions in the same manner as occurs when an alkali-silicate solution is poured into an alkali-aluminate solution. At normal set, on the other hand, the calcium salts precipitate the aluminates. C_3S sets normally in a solution of 3 % KOH, whereas quick set occurs if aluminium powder is first dissolved in the KOH-solution.

Spohn (48) showed that the set of C_4AF is accelerated by gypsum. Assarsson (2) has found that anhydrous calcium aluminates at first enter into solution in unchanged stoichiometric proportions and that the transformation into hydrates proceeds very slowly in lime-water because a protecting film is formed around the grains. This film is microscopically visible as a border. Assarsson (3) found that the alkalis from alkali-containing cements speedily pass into solution. Sundius (49) examined solutions obtained from mortar with humus-containing sand and found that the gypsum instantaneously disappears. Sundius, as also earlier Forsén, considered that quick set was the reason for the injurious effect of the humus-containing sand.

Roller (40) has analysed solutions squeezed out from cement mortar and found that the alkalies speedily enter into solution. Roller considers the gypsum to act by forming calcium hydroxide from gypsum and alkali hydroxide. Tetracalcium aluminate is precipitated as a protecting film and the reactions are retarded. Roller also showed that the lime content of the solution was considerably lower when the cement was quick setting than when it was normal setting.

Nacken (35) and Schwiete (45) determined the water fixation and evolution of heat in gypsum-free cements and cements admixed with gypsum and certain other chemicals. The amount of heat initially generated as well as of the water bound was found to be much higher in the quick-setting, gypsum-free cements than in the normal setting ones. Schwiete also found that a supersaturated solution of lime was formed when cement reacts with water. This very important fact at first stated by Le Chatelier is by Le Chatelier explained through the formation of supersaturated silicate solutions from which silicates poor in lime separate out. Fill (16) investigated the influence of beryllium, barium and calcium chloride on gypsum-free cement with respect to setting time, strength, water fixation and heat generation, and found that calcium and barium chloride in low concentrations could replace gypsum and that beryllium chloride acted similarly to sugar. Eitel (15) applied Donnan's theories for membrane hydrolysis to the system cement-water, and assumed that the cement grains became surrounded with a semipermeable membrane of calcium silicate hydrates and that the gypsum acted by increasing the calcium ion concentration and thus retarded the hydrolysis and the transformation of the silicates. Bogue and Lerch (10), in a recently published fundamental work on the reactions between the cement components and water, have demonstrated that the final set of C_3S is delayed to about 24 hours by an addition of C_4AF or C_2F, but that a normal final set is attained by the addition of 5 % gypsum. Bogue and Lerch thought that the explanation of this phenomenon might be that—in the absence of gypsum—a colloidal calcium ferrite hydrate was precipitated as a protecting film around the C_3S-grains, whereas in the presence of gypsum a more crystalline double salt of calcium ferrite and gypsum is formed. Bogue and Lerch also found that the reaction of pure C_3A, though not of C_5A_3, is considerably retarded by the addition of gypsum. Pure C_3A forms with gypsum the double salt $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot Aq.$, preventing the formation of tricalcium aluminate hydrate and thus retarding the hardening. An addition of C_3A increases the strength of C_3S reached after rather short periods but decreases that reached after rather long periods. C_3S forms an orthocalcium silicate hydrate, and the beneficial influence of C_3A is attributed by Bogue and Lerch to the fact that it binds water and, consequently, lowers the water : : cement ratio for the C_3S. After later periods C_3A has an injurious influence on the structure.

With reference to the many theories which have been advanced to explain the influence of various additions on the setting time of cement, Lea (31) says in his excellent work—*The Chemistry of Cement and Concrete:* "It cannot be said that at the present time any definite decision as to the correctness of these various theories can be made, as it seems not unlikely that certain elements of the whole truth may reside in many of them."

New Investigations.

Components.

Methods.

When normal setting cement is mixed with water, there is instantaneously formed a solution which is saturated or supersaturated with lime and gypsum. As these substances are consumed for the various reactions, new amounts are constantly supplied from the C_3S and from the available excess of gypsum. The composition of the solution consequently remains practically unchanged for a considerable time. Similar conditions to these are obtained if small amounts of the finely ground components are treated with a large excess of a solution saturated with lime or with lime and gypsum. If 0.2 gram of a cement component—for instance "C_2A"-melt—is shaken with one litre of a solution saturated with—for instance—lime, the resultant reactions change the concentration of the solution so little that the change can be disregarded. By analysing the composition of the solution and of the solid after various lengths of time, from 1 minute to 3 months, the speed of reaction and the composition of the compounds formed have been determined for the different cement components.

The substances under investigation have been C_3S, C_3A, "C_2A"-melt, "CAS"-melt corresponding to RANKIN's point 17 (that is, the glass residue in cement produced from CaO, SiO_2 and Al_2O_3), alkali-containing "C_2A"-melt, and to some extent β-C_2S (stabilized with 0.5 % of boric acid) and C_4AF. The pure crystalline compounds have been obtained from the Kaiser-Wilhelm-Institut as well as from the Bureau of Standards and Building Research Station, and I take this opportunity to express my sincere gratitude to Professor W. EITEL, Dr. R. H. BOGUE and Dr. F. M. LEA for their kindness in putting these preparations at my disposal. The various aluminate melts have been prepared by us according to a method by DYCKERHOFF (14), involving melting and rapid cooling in mercury and a following purification by means of centrifuging the pulverized melts in heavy liquids.

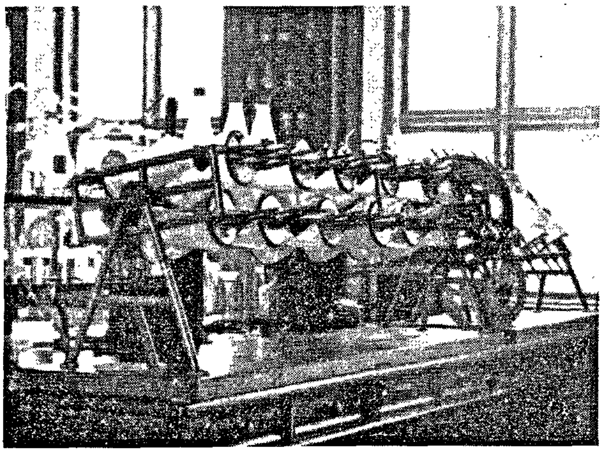


FIG. 1. Shaking Machine.

The reactions of the components have been examined (in the proportions 0.2 g substance to 1 litre solution) in: H_2O, saturated $Ca(OH)_2$-solution, saturated $CaSO_4 \cdot 2H_2O$-solution, supersaturated gypsum solution from $CaSO_4 \cdot {}^1/_2H_2O$, solution saturated with $Ca(OH)_2$ and $CaSO_4$, 5 % $CaCl_2$-solution, respectively 5 % and 30 % $CaCl_2$-solution saturated with $Ca(OH)_2$, 1 % sugar solution, 1 % sugar solution saturated with $Ca(OH)_2$, alkali humate solution and boric acid solution. C_3S has also been treated with calcium aluminate solution and a number of other solutions.

Shaking machines of a type shown in FIG. 1 have been used. To prevent carbonic acid from diffusing in through the rubber stoppers it has proved necessary to treat these with molten paraffin and to cover them and the neck of the flasks with rubber caps.

After each time-period the whole content of a flask was filtered. The residue was washed with alcohol and ether. After the ether had been drawn off in a vacuum desiccator, the loss on drying was determined in vacuum at 105° and the amount of firmly fixed water by heating the dried sample at 1 000°. If sulphates were present in the residue, SO_3 was determined before and after the ignition and a correction for volatilized SO_3 made, if necessary. The calculation of the degree of conversion has been based on the known fact that all calcium aluminates, after drying in vacuum at 105°, have the composition $x\mathrm{Ca(OH)_2} \cdot y\mathrm{Al(OH)_3}$. Sulphates and calcium chloride have been calculated as water-free and the calcium silicate hydrate as $Ca_2SiO_4 \cdot 4H_2O$ or $CaSiO_3 \cdot$ $\cdot H_2O$ in the experiments in pure water—the latter in consequence of results obtained in this work.

The results of the investigations are shown in diagrams. The experimental material, details and the results of some long time tests are given in the Appendix.

The new-formed end products have been isolated in a few cases and examined analytically and microscopically. Finally, some precipitates formed from clear solutions have also been isolated and examined.

The Behaviour of the Components in Water.

Assarsson (2) has shown that the various calcium aluminates dissolve in water in such manner that first of all solutions are formed which have the same oxide proportions as the water-free components. This we have also been able to confirm for the aluminate components "C_2A"-melt and C_3A-crystals examined by us. Flint and Wells (17) have earlier examined the behaviour of C_2S and C_3S in water (20 g per 1 litre) and found that after even short periods of shaking the proportion of lime to silicic acid was higher in the solution than in the water-free components. Working with 0.2 gram per litre, however, we found the same molar proportions in the solutions as in the water-free components. (See Diagram 1 and Tables 3, 15, 36 and 46.)

When using large quantities of substances—as did Flint and Wells—the lime content of the solution is increased because, after even short periods, calcium silicate hydrates with a low content of lime are precipitated.

The solutions formed are supersaturated when in contact with the new-formed hydrates as solids. This fact was already assumed by Le Chatelier (32) and later verified by Wells (52) and by Assarsson for the aluminates and by Flint and Wells for the silicates.

From an extract of tricalcium silicate (containing 0.198 g/l CaO and 0.052 g/l SiO_2) a cotton-like precipitate settled out after 24 hours. This was, carefully protected against the carbonic acid of the air, filtered off, washed with alcohol and ether, dried for 2—3 hours at 105°, ignited at 1 000°, and analysed. The composition after drying at 105° was $CaSiO_3 \cdot 1H_2O$. The results of analyses from two different preparations are given in TABLE 1.

When cement reacts with water, the dissolution occurs in a saturated or supersaturated lime solution. Hence it was of great interest to examine the product obtained when a tricalcium silicate solution was poured into a large excess of a saturated lime solution (0.5 litre C_3S-solution to 2 litres of lime-water). Very soon a precipitate was formed which was similar to the one previously obtained. The composition, however, was now in this case $Ca_2SiO_4 \cdot 4H_2O$, as is evident from TABLE 1, where the results from some experiments are recorded. Preliminary X-ray tests carried out by Dr. W. BÜSSEM at the Kaiser-Wilhelm-Institut show that the $Ca_2SiO_4 \cdot 4H_2O$ is crystalline.

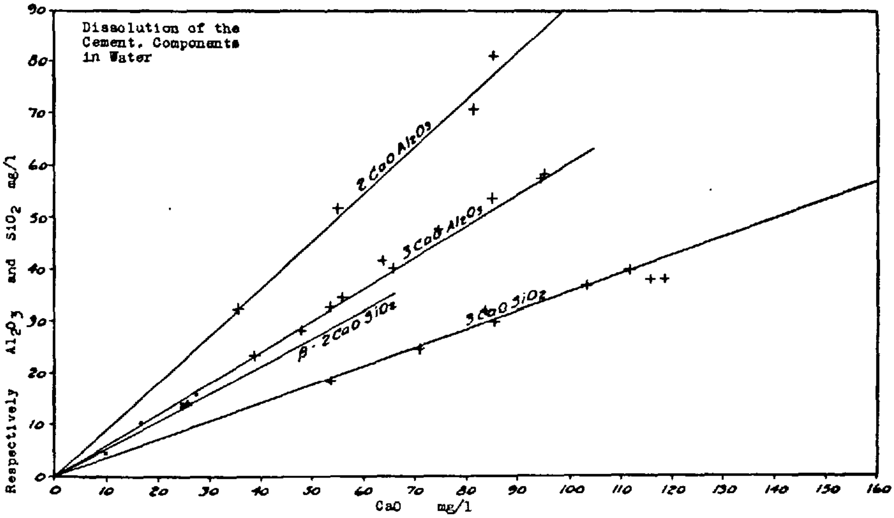


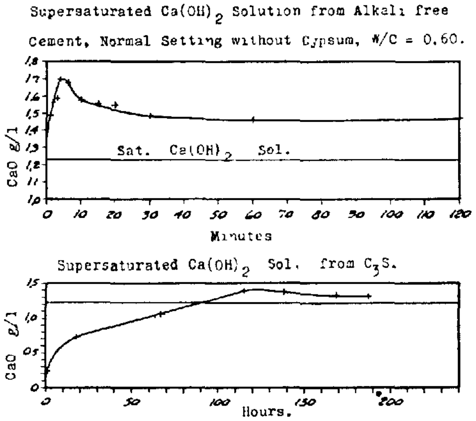
DIAGRAM I.

FLINT and WELLS have earlier found that amorphous precipitates containing from 1.1 to 1.8 mols. CaO on 1 mol. SiO_2 are formed from supersaturated calcium silicate solutions. The formation of $Ca_2SiO_4 \cdot 4H_2O$ from C_3S, when this is mixed with and stored under water, has recently been demonstrated by SCHLÄPFER (42) by means of determinations of free lime and combined water. Accordingly, it is evident from the investigations above mentioned and from our own that calcium orthosilicate—$Ca_2SiO_4 \cdot 4H_2O$—is formed when cement normally reacts with water. This fact has earlier been reported as probable by ASSARSSON (4).

As seen in DIAGRAM 2, a supersaturated solution of $Ca(OH)_2$ is generated from C_3S or from alkali-free, lime-rich clinker powder through a continuous dissolution of tricalcium silicate and precipitation of orthocalcium silicate hydrate.

The experiments with cement were carried out by forcing the solution out of a cement mortar with the water : cement ratio 0.6. The lime content of the solution was then found to be as high as 1.7 grams per litre, whereas a lower degree of supersaturation was obtained with pure C_3S owing to only 10 grams per litre being available for this purpose. From these experiments it is evident that a supersaturated lime solution is formed when C_3S or alkali-free cement reacts with water as already stated by LE CHATELIER.

As it was established that cement reacts with water in such a manner that, first of all, the components enter into solution, it was of interest to combine a C_3S-solution with a solution of "C_2A"-melt. Within a few minutes an aluminium silicate gel was formed. This gel had a low lime content and a variable composition (see TABLE 1).



Supersaturated $Ca(OH)_2$ Solution from Alkali free Cement, Normal Setting without Gypsum, W/C = 0.60.

Supersaturated $Ca(OH)_2$ Sol. from C_3S.

DIAGRAM 2.

If immediately after being combined, the solutions of C_3S and "C_2A"-melt are poured into a saturated lime solution or into a saturated lime-gypsum solution, lime-rich compounds precipitate consisting of crystallized lime-rich aluminate hydrates or, as the case may be, of their double salts with gypsum and also a lime-rich silicate hydrate (TABLE 1).

The reactions above described have been carried out in solutions which as to composition closely agree with the solutions formed at quick set or at normal set, later to be discussed.

Experiments with Aluminate Components.

In addition to the crystalline components C_3A and C_4AF the following components have been investigated: "C_2A"-melt (51.7 % CaO, 48.1 % Al_2O_3), "CAS"-melt corresponding to RANKIN's point 17 (55.8 % CaO, 7.4 % SiO_2, 36.8 % Al_2O_3), "KCA"-melt (39.3 % CaO, 56.1 % Al_2O_3, 4.6 % K_2O) and

"C_4AF"-melt, because the behaviour of these vitreous melts throws good light on the reactions of clinker glass.

The results of the shaking tests are reproduced in DIAGRAMS 3—9 and TABLES 3—35.

It will be seen that for all the aluminate components the speed of transformation shows the same progress as the solubility and that these are considerably checked in a saturated lime solution or a saturated lime-gypsum solution.

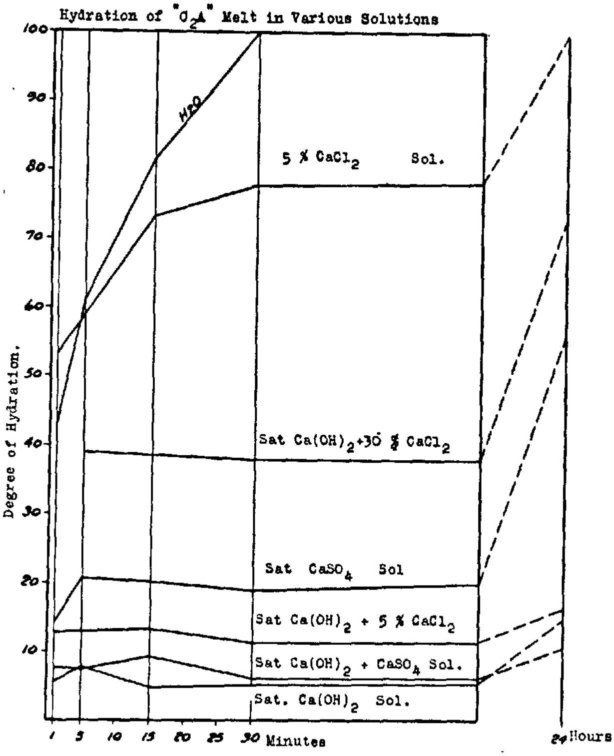


DIAGRAM 3.

High speed of reaction and high solubility prevail in those solutions in which quick set occurs, whereas the reactions are slow and the solubility is low in solutions where the set is normal.

When the solubility of the aluminates is low, the reaction is checked owing to the grains being coated with insoluble precipitates that prevent the water from penetrating.

As to the individual components, the following facts have also been demonstrated:

"C_2A"-*melt:* (DIAGRAMS 3 and 4, TABLES 3—12.) The reaction velocity is much diminished in a saturated lime-gypsum solution, a saturated lime solution and a saturated lime solution containing 5 % calcium chloride. A saturated gypsum solution alone retards less—owing to the double salt being soluble in the absence of lime. In a saturated lime solution containing 30 % calcium chloride no retardation or diminution of the solubility occurs. The P_H-values of the various solutions are recorded in TABLE 50, and it seems likely that the different speed of reaction in a saturated lime solution with 5 % and with 30 % calcium chloride depends on an increased solubility at lower P_H-values.

Solubility of "C_2A" Melt in Various Solutions.

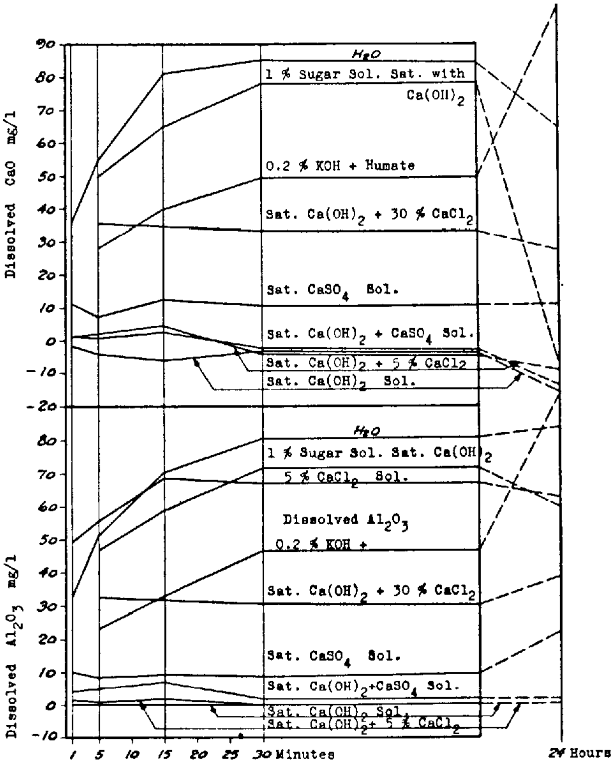


DIAGRAM 4.

Of special interest is the solubility of the "C_2A"-melt in saturated lime-water with 30 % calcium chloride, in a sugar solution saturated with lime, in boric acid and in humate solutions (DIAGRAM 4). In these, quick set occurs and lower strengths result, as will be seen from the chapter on cement.

"*C_3A"-crystals* (DIAGRAMS 5 and 6, TABLES 15—19) behave like "C_2A"-melt but with the difference that the retarding influence of the gypsum is smaller and the solubility is higher.

The retarding influence of gypsum on "*KCA"-melt* (DIAGRAMS 7 and 8, TABLES 27—30) is very great and the solubility is greatly diminished. As

Roller (40) assumed, this probably depends on the formation of an alkali hydroxide solution around the KCA-grains and a following supersaturation with lime when this alkaline solution reacts with the gypsum.

"CAS"-glass (Diagram 9, Tables 31—35) contains lime-rich silicates, and a solution with a high lime concentration is rapidly formed, which in the presence of gypsum causes precipitation of a protective film of aluminates. Consequently, the retarding influence of gypsum is great.

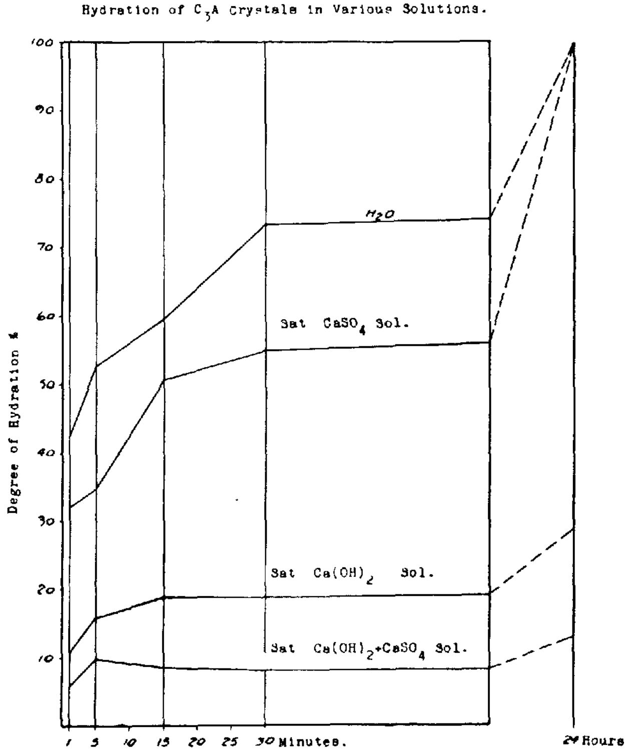


Diagram 5.

C_4AF (Tables 20—26) seems to react slower in the form of crystals than it does in the form of a rapidly cooled melt. Further investigation of the influence of the iron components is required. Their retarding influence on the set of cement, however, is to some extent dealt with in the chapter on cement.

The results of a comparative investigation on the retarding influence of KOH and $Ca(OH)_2$ on "C_2A"-melt are reproduced in Diagram 10 and Tables 13 and 14, from which it is evident that the retardation is much more effective in $Ca(OH)_2$ than in KOH. It is also seen that the solubility in KOH is diminished, although it is still considerable.

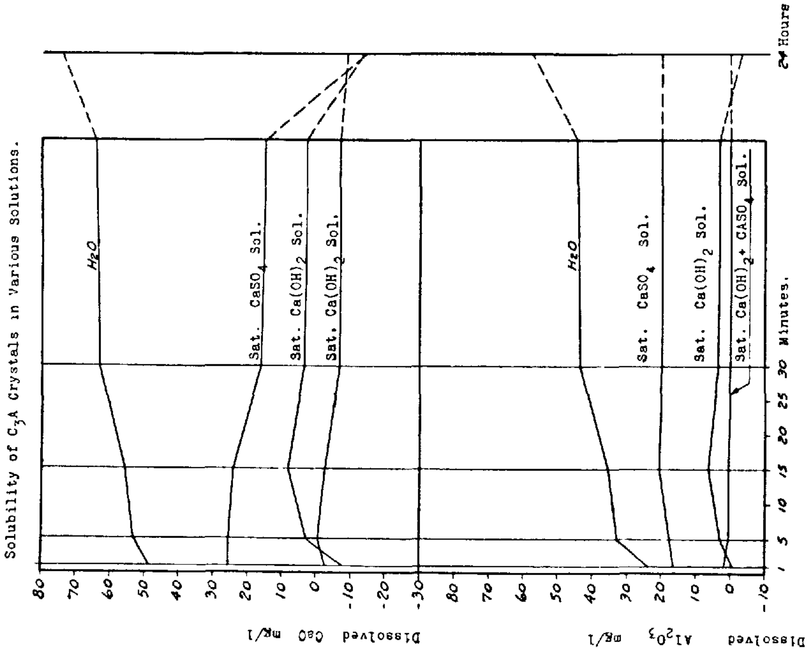


DIAGRAM 6.

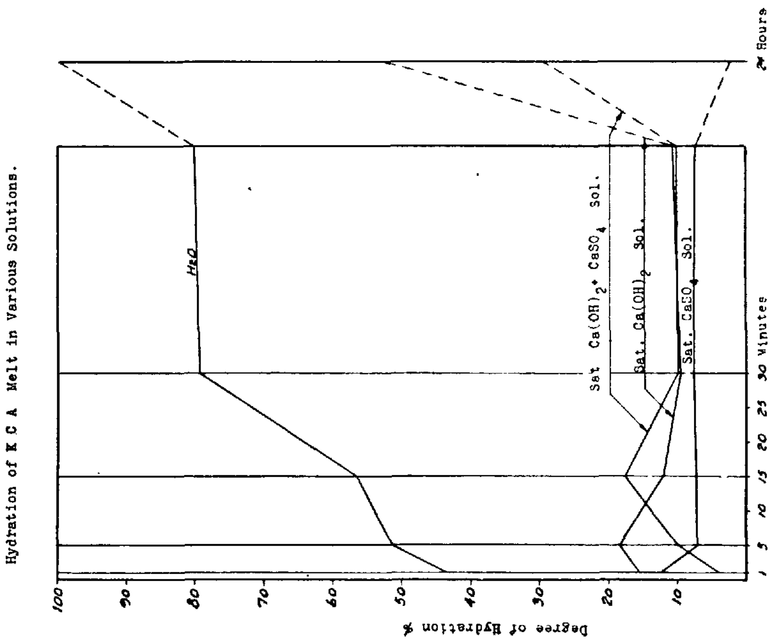


DIAGRAM 7.

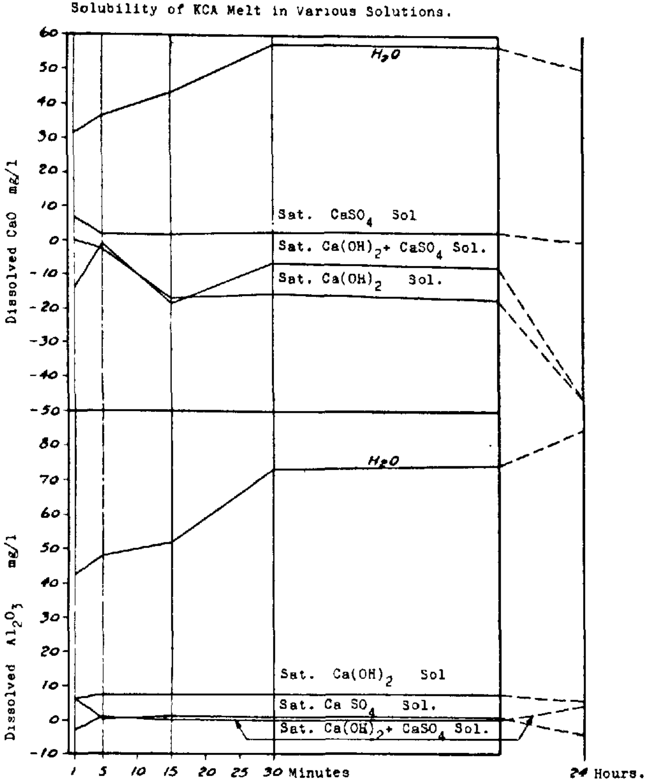


DIAGRAM 8.

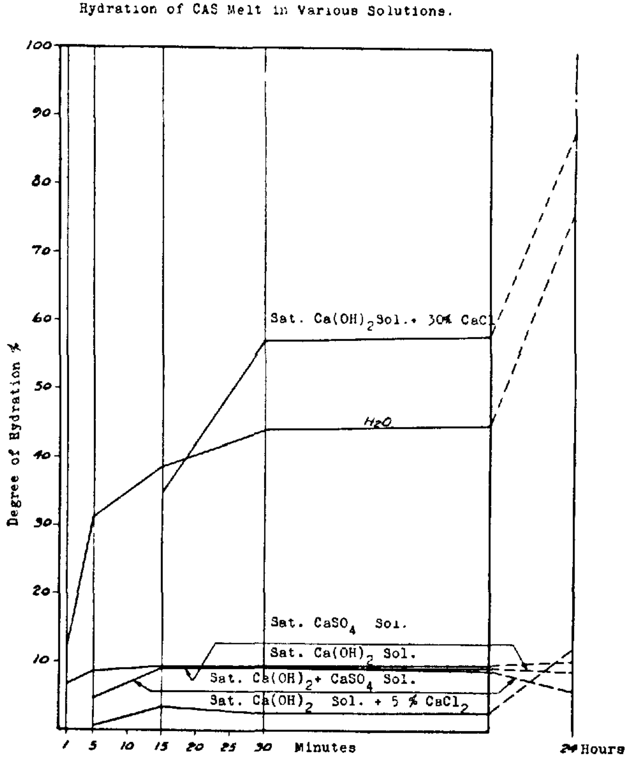
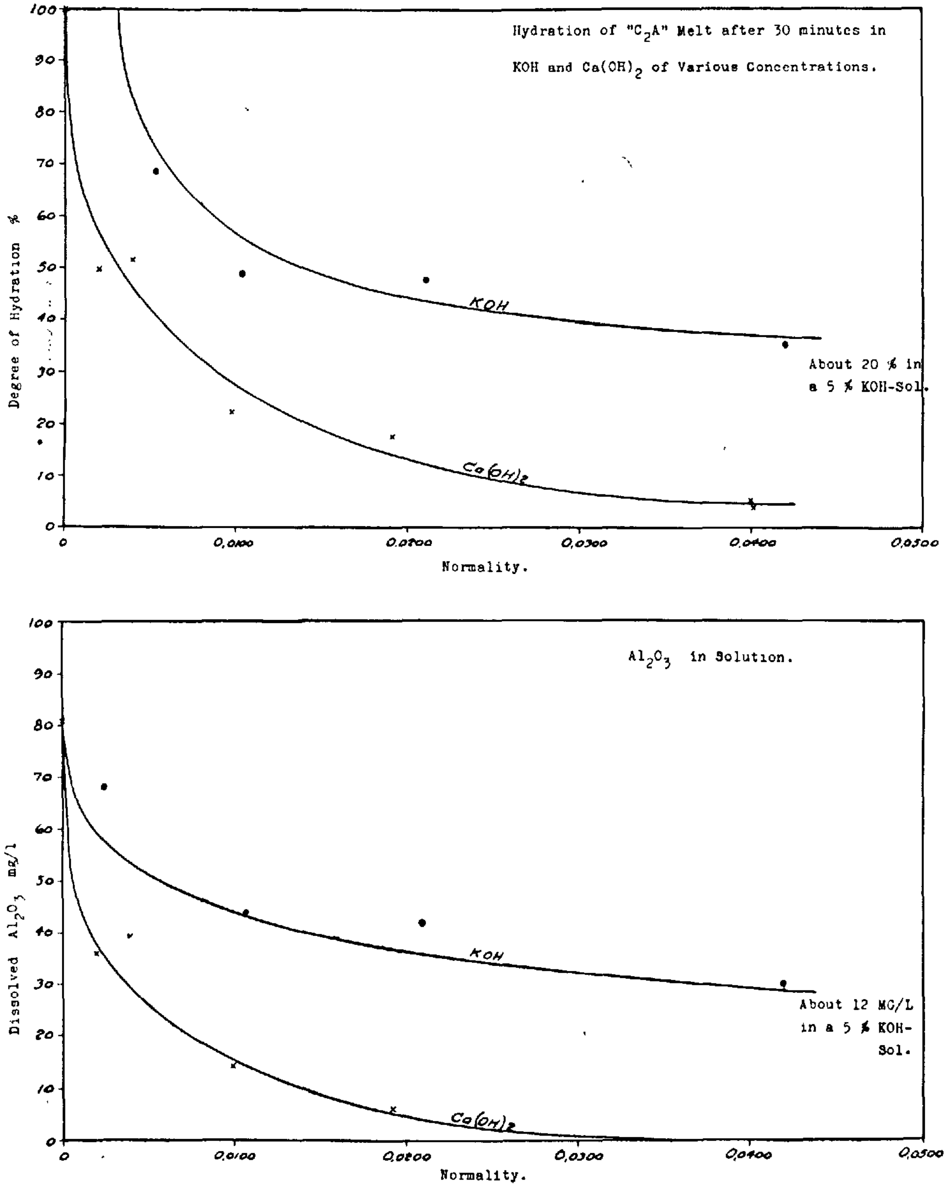


DIAGRAM 9.



Diagrams 10 A and 10 B.

The composition of the solids obtained when "C_2A"-melt and C_3A-crystals are shaken with saturated lime-water or with a saturated lime-gypsum solution for 3 months is seen in Table 2. From the "C_2A"-melt we obtained tetracalcium aluminate hydrate (optical properties: hexagonal crystals, $\beta = 1.535$, $\alpha =$

slightly more than 1.516) or, in the case of gypsum being present, tricalcium aluminate monosulphate. The analytical composition of the solids in the experiments with C_3A suggests that tricalcium aluminate hexahydrate and monosulphate is respectively formed. However, as the precipitates still contained embedded C_3A-grains, the reaction was not yet completed. Microscopically, no new-formed crystals could be identified in the preparations from C_3A.

Hydration of C_3S in Various Solutions.

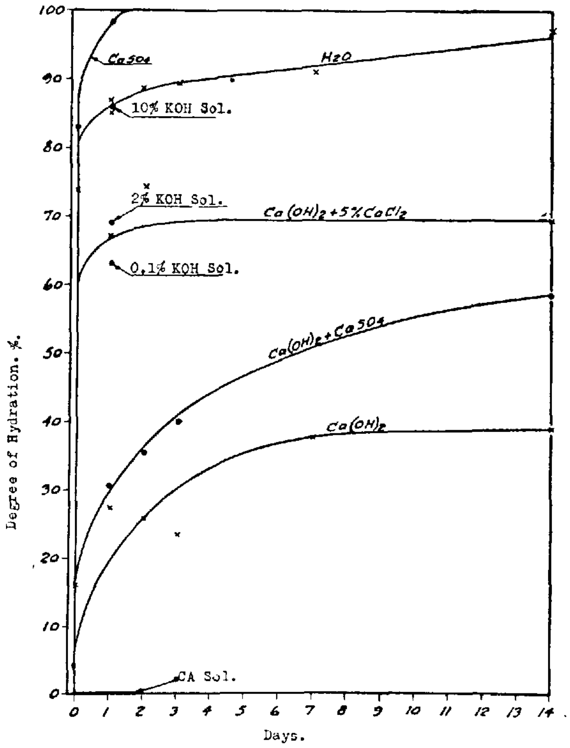


DIAGRAM 11.

Experiments with Silicate Components.

A number of experiments have been carried out with C_3S, and the results obtained are recorded in TABLES 36—45 and DIAGRAMS 11 and 12.

The otherwise greatly retarding influence of lime-water is diminished as the P_H-value of the solution is decreased. The acceleration caused by calcium chloride may partly depend on the decreased P_H-value of the lime solution, partly on the more rapid precipitation of the calcium silicates owing to the increased concentration of calcium ions (see DIAGRAM 12). Gypsum acts in the same way as calcium chloride does, although on account of its lower solubility the action is weaker.

The results of experiments in diluted calcium aluminate solutions (see TABLE 43) show that the transformation of C_3S is practically completely stopped in this solution. This is owing to the film of aluminium hydroxide-silicic acid gel that forms around the C_3S-grains.

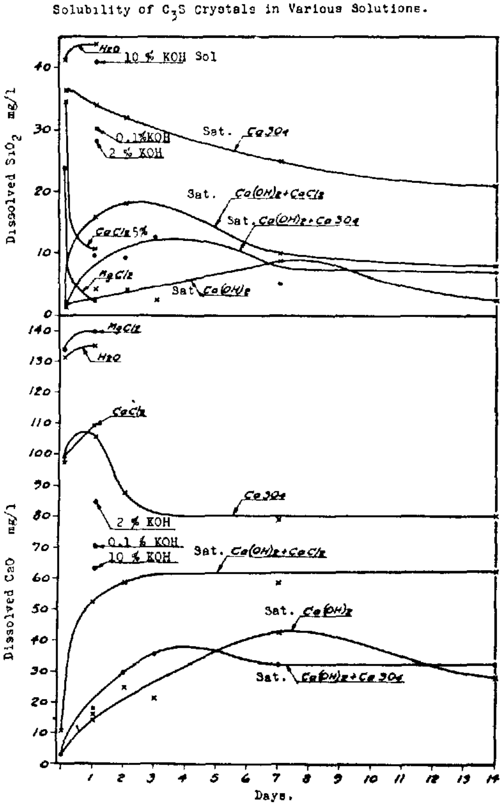


DIAGRAM 12.

In another experiment the aluminate solution was drawn off after two days and substituted by a saturated lime solution (TABLE 44). A very strong reaction ensued, showing a degree of transformation as high as 64 % after only three days.

A saturated lime solution consequently extinguishes the retarding effect of the surface film—probably owing to a dissolution of the gel and a precipitation of lime-rich compounds.

WELLS (52) has earlier demonstrated that C_3S "swells" in water but not in an aluminate solution. The swelling, which is a result of a dissolution of the silicates and a precipitation of amorphous hydrate, is prevented in aluminate solutions through the action of the film.

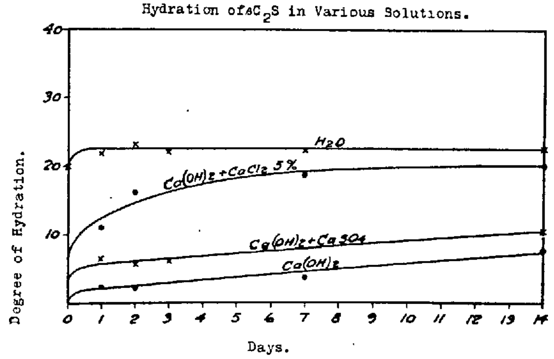


Diagram 13.

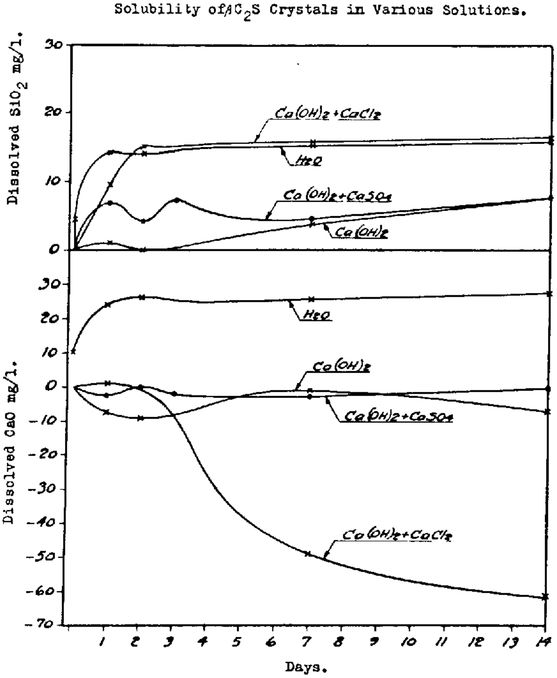


Diagram 14.

Experiments in KOH-solutions of different concentrations (Table 45) were carried out in order to establish whether the transformation of the C_3S was retarded only on account of the increased P_H-value. The conversion of C_3S, however, seems to progress rapidly even in KOH-solutions of considerable concentration. The speed of reaction, therefore, depends on the P_H as well as on the lime content of the solution.

β-C_2S, stabilized with 0.5 % boric acid, has been examined with respect to hydration velocity in various solutions. From the results, which are reproduced in DIAGRAMS 13 and 14 and TABLES 46—49, it is seen that β-C_2S reacts much slower than C_3S does and that lime solutions have a similar influence on β-C_2S as it has on C_3S.

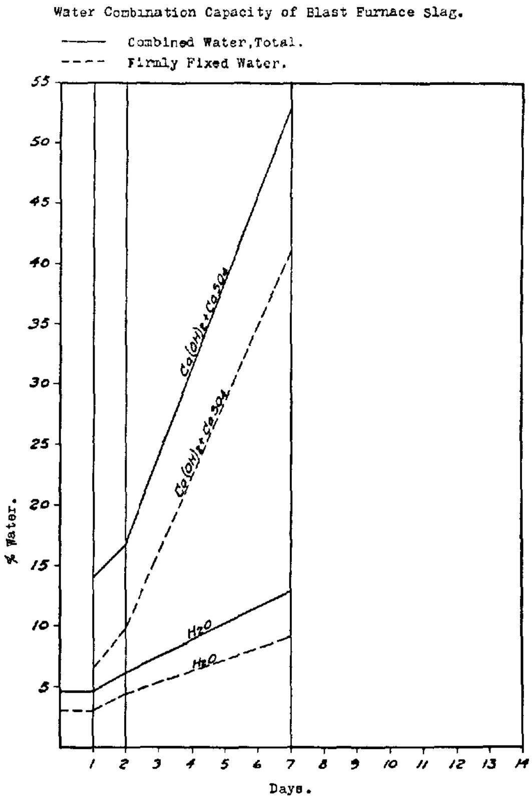


DIAGRAM 15.

The water combination of basic blast-furnace slag, when shaken in water and in saturated lime-gypsum solution, was investigated. As seen in DIAGRAM 15, the reaction proceeds very slowly in water but rapidly in the latter solution. This is owing to a checking surface precipitate of silicic acid-aluminium hydroxide being formed in water, whereas the aluminates are transformed to lime-rich compounds in the lime-gypsum solution. Hence, slag reacts in water in the same manner as C_3S does in a diluted aluminate solution (quick set), whereas the reactions in a saturated lime-gypsum solution correspond to those of C_3S in the same solution (normal set).

Cements.

Setting Time of Various Cements.

A number of alkali-free cements (Table 51) have been prepared and investigated with respect to their relation to regulators. Some results from setting tests are recorded in Table 52. This table contains two series of alkali-free cements—Nos. *1—4* low in C_3S [about 40 % when calculated according to Bogue's formula (9) for equilibrium] and Nos. *5—8* high in C_3S (about 60 %). The table also contains two iron- and alkali-free cements—No. *9* with a normal and No. *10* with an unusually high amount of C_3A. Both these cements are low in C_3S. Finally, one ordinary technical cement (No. *11*) is also included.

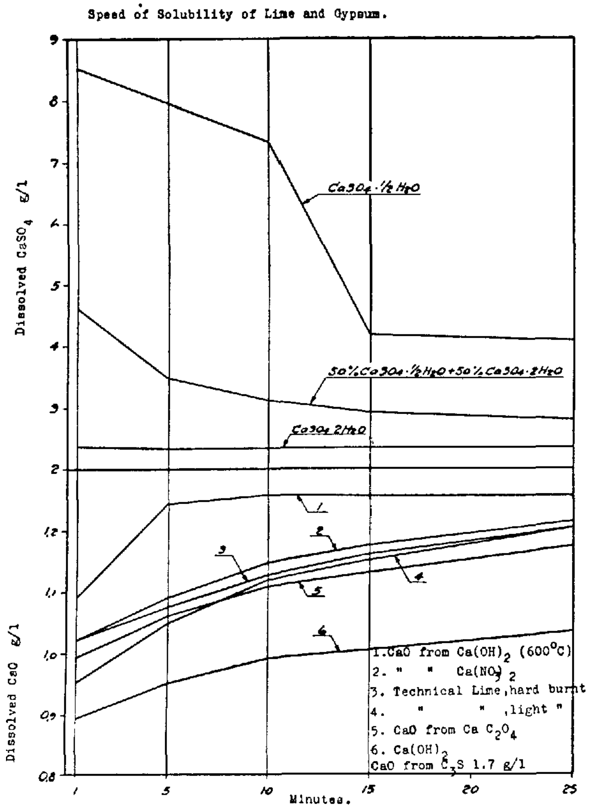


Diagram 16.

For all the setting tests with gypsum a mixture of 75 % dihydrate and 25 % semihydrate has been used, as the effect of dihydrate is somewhat uncertain owing to its low rate of dissolution. The lime used has been prepared by igniting calcium hydroxide at 600°. Such lime has been found to be the most effective of all the kinds tried and in this paper is called active lime.

The speed of dissolution and the solubility of gypsum and of lime prepared in different ways are indicated in Diagram 16 and Tables 53 and 54.

The initial and the final setting times are, as is known, measured by the time that elapses until the mortar has reached a certain stiffness and a certain strength, respectively. As this method is very uncertain, the results must be judged with some degree of caution. With this reservation I will draw the following conclusions from the results.

Alkali-free cements with a high content of C_3S (*5—8*) are normal setting without additions, whereas the cements with lower C_3S-content (*1—4*) are quick setting. After a short period of storage, however, these cements become slow setting and then again quick setting after having been reground. For this reason all the setting tests have been carried out with freshly ground clinker. When ground with gypsum the quick setting cements (*1—4*) become normal setting, whereas the addition of gypsum shortens the setting time of the slow setting cements (*5—8*). An addition of 1 % calcium chloride, dissolved in the water, renders all these cements normal setting.

Of special interest are the experiments with 3 % active lime, which addition effectively regulates the setting time of the quick setting cements in the series *1—8*.

At normal set without additions, or with active lime as a retarder, all the alkali-free, iron-containing cements require as much as 24 hours to reach their final set, and as Bogue and Lerch (10) have demonstrated, mixtures of C_3S with C_4AF or C_2F behave in the same manner. The addition of gypsum or calcium chloride to the cements, or of 5 % gypsum to the components, however, reduces the final setting time to normal length. As Bogue and Lerch have pointed out, a colloidal ferrite is probably precipitated from lime solutions when no calcium salts are present. This precipitate retards the dissolution and the transformation of the grains. In the presence of calcium salts, on the other hand, a more crystalline precipitate is formed. A further proof of the retarding influence of the iron compounds is that alkali-free cements have a normal final setting time when their iron content is low.

The No. *10* cement, being low in C_3S and high in C_3A, is quick setting with most retarders. It could be regulated only with the most efficient retarder investigated, *viz.* 1 % $KOH + 3$ % $CaCl_2$ (of the cement weight) dissolved in the gauging water. This mixture gives rise to a supersaturated lime solution in KCl and $CaCl_2$ as well as a finely divided freshly precipitated $Ca(OH)_2$.

The technical cement (No. *11*), which contained 1.2 % K_2O and 0.1 % Na_2O, could not be retarded with any kind of CaO. With gypsum and with 1 % calcium chloride, however, an efficient retardation was obtained.

Composition of the Liquid Phase of the Mortar.

A technical Portland cement clinker (No. *II* in TABLE 51) was ground to cement fineness, firstly without gypsum and secondly with the addition of 4 % gypsum mixture. The gypsum-free cement was quick setting, whereas the one containing gypsum had a normal setting time. The two cement samples were gauged with water (w:c ratio 0.6) and the liquid phase filtered off after periods varying from 1 to 120 minutes. From the chemical analyses (see TABLE 55) it is evident that the liquid phase at quick set consists of a potassium hydroxide solution containing but small amounts of lime, and that the liquid phase from cements with gypsum contains considerable quantities of Ca-ions, whilst the potassium hydroxide is appreciably neutralized to sulphate.

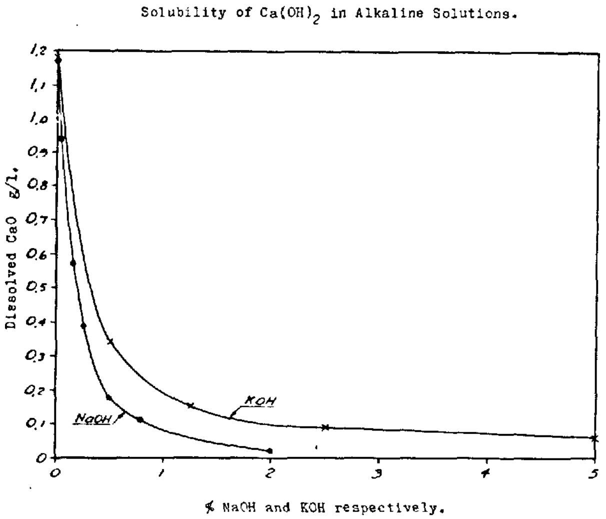


DIAGRAM 17.

Similar experiments with alkali-free cements indicated that the lime content after one minute was lower in the quick setting than in the normal setting (gypsum-free) cements. In all cases a saturated or a supersaturated lime solution was obtained very rapidly.

In order to study more closely the chemical composition of the liquid phase during the very first moments of reaction the experiments recorded in TABLE 56 were carried out. 100 grams of cement were placed on a filter paper in a BUCHNER-funnel and covered with a filter paper and cotton. 125 mls of water were then rapidly sucked through the cement layer. The results obtained show a high concentration of Ca-ions at normal set and considerably lower concentrations of these ions at quick set.

The experiments with active lime and alkali-free cement show normal set and a high lime concentration in the solution, whereas the extract from the technical cement (*11*) ground with 3 % active lime contains only a small amount of CaO, although in this case a saturated lime solution was used instead of water. The velocity of dissolution of the alkali compounds is greater than that of the active lime, and the solubility of lime is greatly decreased in the alkali hydroxide solution formed (see Diagram 17). Therefore, alkali-containing cements cannot be retarded with lime. The solutions from the alkali-free cements contained larger amounts of aluminates at quick set than at normal set.

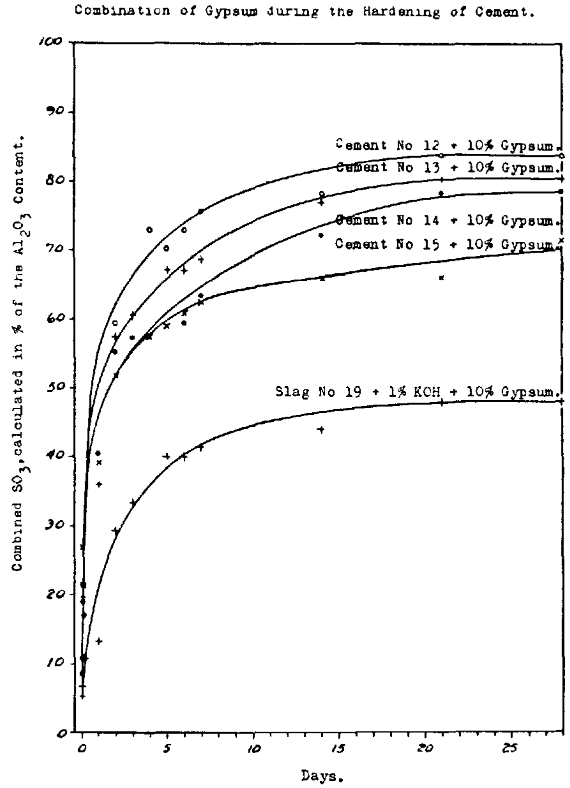


Diagram 18.

Combination of Gypsum during the Hardening of Cement.

Gypsum is soluble in lime-water to approximately the same degree as in water, whereas the calcium aluminate sulphates are almost insoluble in lime-water. This difference in solubility has been utilized in an investigation on the combination of the gypsum when cement reacts with water.

Set cement was stored in moist air free from carbonic acid, and after varying lengths of time samples were taken out and pulverized. The total quantities of SO_3 and of SO_3 soluble in lime-water were determined, and it was found that technical cement with normal gypsum content already contained after one day practically no soluble SO_3. In order to study the possibilities of further gypsum combination four different cements (Nos. *12—15* in TABLE 51) were mixed with 10 % additional gypsum, and the soluble SO_3 was determined after periods of up to 28 days. The results of the tests, which also include a basic blast-furnace slag (No. *19* + 1 % NaOH + 10 % gypsum) are recorded in DIAGRAM 18, where the amount of combined SO_3 is expressed in per cent of the alumina content.

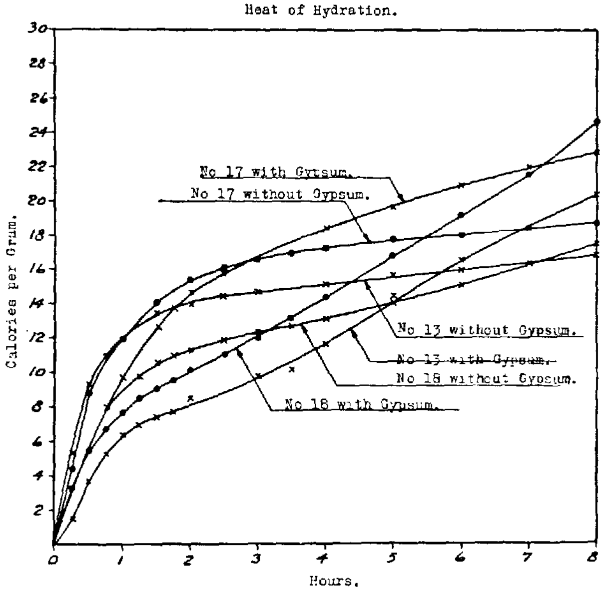


DIAGRAM 19.

The experiments show that considerable amounts of gypsum are combined in insoluble double salts. For the present, results are available only up to 28 days. These indicate that in the Portland cements 80 % SO_3 by weight of the Al_2O_3 is combined, which corresponds to tricalcium aluminate monosulphate. The monosulphate was also the end product obtained in the experiments earlier described with aluminate components in lime-gypsum solution.

Heat of Hydration and Water Combination.

The evolution of heat was determined by means of an adiabatic calorimeter, HÅKANSON's method (26). In some cases the tests were carried on for four days, in others for eight hours only. Three different brands of cement have been investigated, *viz.* one technical cement (*13*), one alkali-free quick setting (*17*), and finally one alkali-free normal setting cement (*18*). These have been examined, firstly, without gypsum admixture and, secondly, after having been carefully mixed with 4 % gypsum. The results are reproduced in Diagrams 19 and 20, from which it will be seen that, in the initial stage, the gypsum-free cements generate more heat than the gypsum-containing ones. The largest difference is shown by the alkali-containing cement. Very soon, however, the generation of heat is more rapid in the case of the cements that contain gypsum.

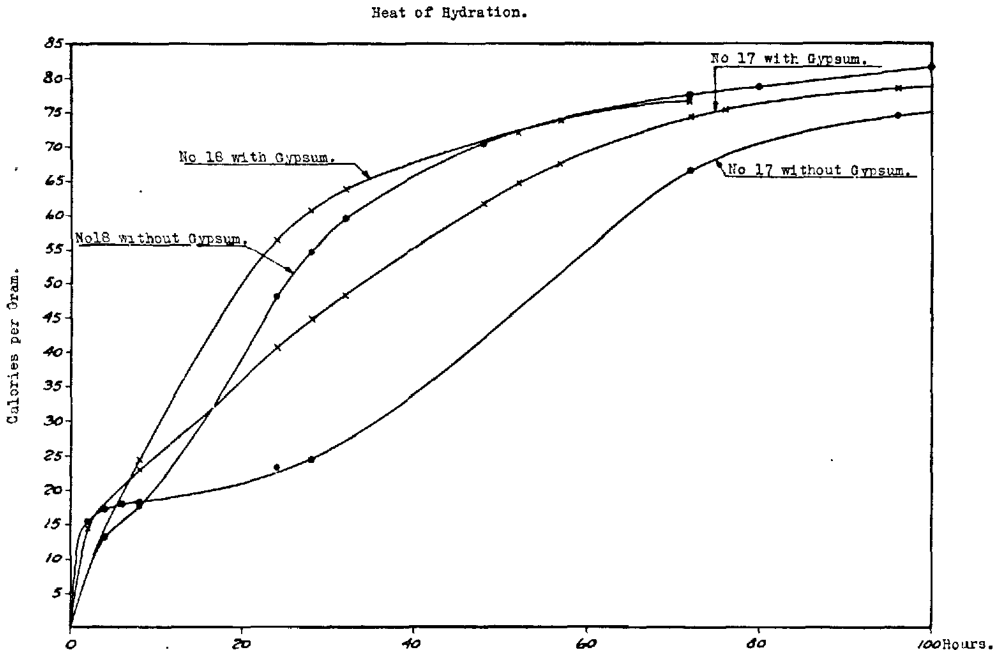


Diagram 20.

The heat of hydration after 3, 7 and 28 days has been determined by Lerch's method (33). This investigation has been carried out in the laboratory of Mr. S. Giertz-Hedström. From the results, recorded in Table 57, it is seen that the amount of heat evolved is considerably increased by the addition of gypsum. Calcium chloride acts in the same way, whereas potassium hydroxide and, above all, sugar greatly decrease the evolution of heat.

The amount of firmly combined water (see Table 58) has been determined in the following way. The cement has been gauged with 40 % of water and then stored in moist air free from carbon dioxide. After varying periods, samples have been taken out and pulverized. Firmly combined water has been recorded as the amount of water retained on heating in vacuum to 105°, but lost at 1 000°. The water combination and the heat evolution proceed alike in so far that at the outset both of them are greater in the gypsum-free cements than in the ones containing gypsum.

Influence on Setting Time and Strength of Portland Cements and Blast-Furnace Slags.

The influence of Ca, Sr, Ba and Mg-salts on the setting time of various cements has been investigated. The salts have been dissolved in the gauging water, except the gypsum, which has been ground in with the cement. In addition to the experiments with salt solutions, studies have also been made with active lime ground with the cement, solutions of alkali hydroxides and potassium aluminate and, finally, with a mixture of calcium chloride and alkali hydroxide solutions. The results are indicated in TABLE 59.

All the calcium salts act in the same way on the alkali-free cements as on the alkali-containing ones. Magnesium salts seem to have a greater influence on cements with alkali than on those without. This is probably owing to the protective magnesium hydroxide film being formed very rapidly in the alkaline solution.

To give a better understanding of the influence of the additions on retardation and acceleration, the results of some strength tests are reproduced in TABLES 60—63. The strengths have in some cases been determined according to the Swedish Standard Specifications (like the German ones) and in some cases on concrete cubes.

From the investigations on setting time and strength the following conclusions can be drawn:

The addition of gypsum or other calcium salts controls the setting time of quick setting cements and raises to an appreciable degree the strength of all the cements examined. The addition of large amounts of certain calcium salts such as chloride, bromide, nitrate, and nitrite renders the cement quick setting.

Alkali hydroxides in amounts of about 5 % possess the property of preventing quick set, but they lower the strength considerably, which may be attributed to the fact that the aluminates are somewhat soluble in alkali hydroxide solutions.

Large amounts of gypsum—up to 11 % has been tried—have a very beneficial influence on the strength of alkali-containing cements, as they keep the alkalies combined as sulphates for a longer time. This effect is not to be seen in alkali-free cements.

Barium salts are able to control the setting time but have an injurious influence on the strength. Extracts from cements mixed with barium hydroxide or barium salts contain more dissolved aluminate than similar extracts from cements controlled with calcium salts.

Magnesium salts in small amounts control the setting time of alkali-containing cements and give strengths equal to those obtained with calcium salts as regulators. The best results are obtained with magnesium sulphate. In large amounts magnesium salts lower the strength very much.

High-basic, granulated blast-furnace slag sets like Portland cement if it is admixed with substances that precipitate aluminates. Such substances are active lime alone or together with calcium salts, alkali hydroxides, and mixtures of alkali hydroxide with calcium salts. The action of alkali hydroxide alone depends on the formation of a saturated lime solution from the calcium sulphide of the slag.

With a good basic slag a strength equal to that obtained with Portland cement can be reached if the reactions of the aluminates are retarded with a calcium hydroxide solution simultaneously as the reactions of the silicates are accelerated with a calcium salt solution of a suitable concentration (see Table 64).

Influence of Humus.

The amount of harmful humus in sand is, as is known, determined according to Abrams and Harder (1) by shaking the sand with caustic soda lye and comparing the coloration of the liquid with a colour scale. The humus substance is dissolved as alkali humate.

Alkali-containing cements are sensitive to humus because the alkali hydroxide liberated forms an alkali humate solution that dissolves the aluminates and causes quick set. Alkali-free cements are less sensitive to humus, as is evident from Table 65. For preparing the test specimens—prisms 4×4×16 cm—a plastic mortar of cement and sand containing large amounts of humus was used. In the presence of magnesium salts, good strengths are obtained even with alkali-containing cements. This is owing to the rapid neutralization of the alkalies to alkali salts, which cannot dissolve the humus substance.

Sugar and humus, which is oxidized carbohydrate or a similar product, dissolve the aluminates (see Tables 11 and 12) and cause quick set. If humus is present, this is gradually precipitated as insoluble calcium humate, whereupon the normal reactions of the cement can proceed. Sugar, on the other hand, remains in solution, with the result that the aluminates are soluble and cause the precipitation of aluminium silicate gels. As a consequence of this continuous perturbation of the normal reactions no appreciable strength is obtained.

Surface Precipitates.

The formation of surface precipitates as films is of the greatest importance for the reactions between cement and water. Some experiments which throw light on these phenomena will be described below.

Soluble magnesium salts control the setting time of cement and have also a greatly retarding influence on the slaking of pure lime. Pure lime was introduced into a 10 %-magnesium sulphate solution. Even after 24 hours the solids consisted to a great extent of unslaked lime. A coating of magnesium hydroxide, which renders the passage of the water difficult, appears to be instantaneously formed. When aluminous cement reacts with water, the grains become covered with a protective film of hydrated cement, which retards the reaction. This is evident from the microscopical examinations of ASSARSSON (2) and also from the fact that aluminous cement concrete cannot be transported in a revolving mixer. The film is worn off by the action of sand and stone, the progress of the reactions is not checked and the concrete hardens in the mixer.

The effectively retarding film that is formed when C_3S is shaken in a diluted calcium aluminate solution can be redissolved and transformed into compounds of another structure if the aluminate solution is drawn off after a suitable time and replaced by a saturated lime solution. A similar phenomenon occurs in concrete with humus-containing sand. As is known, such concrete may remain soft for a long time and yet finally become fairly good if it is kept moist, especially if it can be pounded after the pouring. Owing to the ability of the alkali humate solution to dissolve aluminates, a gel of aluminium silicate is formed on the cement grains. In spite of this the reaction goes on to some extent if the concrete is kept moist. A saturated lime solution is finally formed, which precipitates the humates and also redissolves the film previously formed. The influence of the mechanical treatment may also be explained as a result of the film being destroyed.

The importance of the film formation when slag reacts with water is evident from the following experiment. Slag was mixed with sand and water. One part of the mixture was left untouched for 7 days, while another part of the same mixture was mixed during 10 hours per day for 7 days. At the end of the test period, the amount of combined water was determined and found to be 3 % in the first case and 31 % in the latter. The film of coagulated aluminium silicate was apparently worn off continuously, in the same way as when aluminous cement concrete is exposed to prolonged mixing.

Quick setting alkali-free cements become rapidly slow setting when exposed to moist air, and again quick setting when reground. The retardation is a result of a film of hydrated cement being formed on the surfaces of the cement grains. On regrinding the hydrated layer is worn off simultaneously as unattacked surfaces are exposed.

When gypsum-containing Portland cement reacts with water a saturated lime-gypsum solution is immediately formed, and when this comes in contact with a calcium aluminate solution, lime-rich aluminates are precipitated which at normal set form a semipermeable membrane around the cement grains. The formation and behaviour of such a film have been studied in the following experiment. Two vessels with bottoms of porous glass plates were filled with a saturated calcium aluminate solution. One was immersed in a saturated lime-gypsum solution and the other one in a saturated lime solution. After two days the surrounding solutions were replaced with distilled water. A proof of the formation of a semipermeable membrane was obtained in that the liquid column in the vessels rose owing to the osmotic pressure of the colloidal aluminate solution. The film formed in the lime solution had the composition $3.9CaO : 1 Al_2O_3$, whereas the one formed in the lime-gypsum solution had the composition $3.7CaO : 1 Al_2O_3 : 0.3CaSO_4$ — corresponding to a mixture of $7CA \cdot Aq. + 3C_3A \cdot CaSO_4 \cdot Aq.$

In another experiment the vessel with the porous glass bottom was filled with a saturated calcium aluminate solution and then immersed in a C_3S-solution. A practically impermeable film of a lime-poor aluminium hydroxide-silicic acid gel was formed. The low permeability of this film explains why the reaction of slag with water stops when no retarders are present. It also explains the low strength obtained with Portland cement in the presence of sugar or humus.

When a saturated calcium aluminate solution (containing 0.654 g Al_2O_3 and 0.445 g CaO per litre) was introduced drop-wise into a saturated lime-gypsum solution, a precipitate was formed which had the composition $2.83CaO : 1.85CaSO_4 : 1Al_2O_3 : 7.14H_2O$. This indicates that a calcium aluminate double salt is precipitated. The known phenomenon that in some cases quick setting gypsum-containing cement can be rendered normal setting after the addition of slaked lime depends on the gelatinous film being most easily formed in a saturated lime solution in which the aluminates are rapidly precipitated.

Another phenomenon which on several occasions has been observed by us is that gypsum-free cement, rendered normal setting through seasoning, becomes quick setting in very diluted calcium salt solutions. A redissolution or conversion apparently occurs in such a lime-poor calcium salt solution.

Readily soluble calcium salts such as chloride and nitrate retard the set more effectively than gypsum does, because the gelatinous film is rapidly formed in solutions with comparatively high calcium ion concentration.

Summary.

1. The cement components enter into solution in the same stoichiometric proportions as the water-free components have.

2. The hardening of the cement is effected through the formation of supersaturated solutions from which the cement glue—$Ca_2SiO_4 \cdot 4H_2O$—is precipitated.

3. At normal set the solution contains large amounts of calcium hydroxide and the solubility of the aluminates is greatly decreased. The reactions are retarded by a protective film containing tricalcium aluminate double salts with calcium salts or tetracalcium aluminate.

4. At quick set the solution contains but small amounts of calcium hydroxide and the aluminates and the silicates enter rapidly into solution. A gelatinous precipitate containing chiefly silicic acid and aluminium hydroxide is formed. The low strength at quick set is due to the mechanical qualities of this gel.

5. Retarders are compounds that decrease the solubility of the aluminates and that form a semipermeable membrane around the cement grains.

6. Accelerators, *e. g.* calcium chloride, hasten the dissolution of the silicates by decreasing the P_H and increasing the calcium ion concentration—without dissolving the aluminates.

7. Destroyers are such compounds as sugar, borax, and humus, which dissolve the aluminates and cause quick set, or such compounds as phosphates and fluorids, which form an insoluble and impermeable film around the cement grains or cause quick set through the precipitation of lime compounds.

8. The alkalies, which are present in cement as readily soluble compounds, cause quick set and lowered strength. The action of the alkalies can be greatly reduced by calcium and magnesium salts through neutralization to alkali salts.

9. Basic blast-furnace slag reacts like Portland cement if the solubility of the aluminates is reduced by the action of retarders. Simultaneously the reaction of the silicates can be quickened by accelerators.

10. The influence of gypsum on quick setting, alkali-containing Portland cement must be considered to be the resultant of three different actions. Gypsum in the form of dihydrate gives off some of its water of crystallization in the mills and forms to some extent a protective film of hydrated cement. The saturated or supersaturated gypsum solution, instantaneously formed when cement is mixed with water, neutralizes the alkali hydroxides liberated and forms a saturated solution of calcium hydroxide. Calcium hydroxide and gypsum are, accordingly, abundantly present in the solution, and the protective film of aluminate compounds is rapidly precipitated.

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Appendix.

The experimental material on which my paper "The Chemistry of Retarders and Accelerators" is based is recorded in the following 66 tables. Of these the TABLE 66—results from 3 months' shaking tests—was not in the preprint.

The calculation of "% conversion" is for the aluminates based on the known fact that all calcium aluminate hydrates and their double salts after being dried at 105° retain water corresponding to the formulae

$$x\mathrm{Ca(OH)_2} + y\mathrm{Al(OH)_3} \text{ or } x\mathrm{Ca(OH)_2} + y\mathrm{Al(OH)_2} + z\mathrm{Ca\,X_2}$$

respectively.

Example: TABLE 3, "C_2A"-melt in water. The composition of the "C_2A"-melt used was 48.1 % Al_2O_3 and 51.7 % CaO (p. 310). If the unhydrated residue is x mg, the amount of unhydrated $Al_2O_3 = 0.481 \cdot x$ mg and of unhydrated $CaO = 0.517 \cdot x$ mg. If the solid phase contains C mg CaO and A mg Al_2O_3 the composition of its hydrated part is

$$\underset{\text{mg CaO}}{(C - 0.517 \cdot x)} + \underset{\text{mg Al}_2\text{O}_3}{(A - 0.481 \cdot x)} + \underset{\text{mg H}_2\text{O.}}{q}$$

In this formula q denotes firmly bound water. As 1CaO binds $1H_2O$ and $1Al_2O_3$ binds $3H_2O$, we obtain the following equation

$$q = \frac{(C - 0.517 \cdot x)\ 18.02}{56.07} + \frac{(A - 0.481 \cdot x)\ 3 \cdot 18.02}{102.2}$$

$$x = 0.764\ C + 1.258\ A - 2.376\ q$$

From TABLE 3, column 1 (shaking time 1 minute) the following values are taken:

$$C = 68.0 \qquad A = 64.0 \qquad q = 7.8$$

$$x = 0.764 \cdot 68.0 + 1.258 \cdot 64.0 - 2.376 \cdot 7.8 = 114.0 \text{ mg.}$$

In the experiment 200 mg of substance were used. 114.0 mg or 57 % remained unhydrated and consequently 43 % were hydrated. These are recorded as "% conversion".

In all experiments given in TABLES 3—49 and in TABLE 66 200 mg of substance pro litre of liquid have been used. The figures given in these tables are in milligrams. The amounts of dissolved CaO, Al_2O_3, etc. are calculated by difference between substance used and solid phase obtained.

Corresponding calculation of "% conversion" has been carried out for the silicates under assumption that the composition of the hydrated products, after drying to 105° is $C_2S \cdot 4Aq.$ in TABLES 37—45 and 47—49 and $CS \cdot 1Aq.$ in TABLES 31—36, 45 and 46.

Table 1. Reactions of Solutions of C_3S and of "C_2A"-Melt.

Composition of the solution													
C_3S-extract ml	2 000	2 000	500	500	500	100	500	500	500	750	500	500	500
containing CaO g/l	0.198	0.198	0.201	0.201	0.201	0.124	0.224	0.124	0.124	0.168	0.224	0.207	—
and SiO_2 g/l	0.052	0.052	—	—	—	0.044	0.079	0.044	0.044	—	—	—	—
Aluminous cement extract ml	—	—	—	—	—	100	500	500	250	500	500	500	500
containing CaO g/l	—	—	—	—	—	0.124	0.224	0.124	0.124	0.168	0.224	0.207	—
and Al_2O_3 g/l	—	—	—	—	—	0.112	0.312	0.112	0.112	—	—	—	—
Additional solution ml	—	—	2 000	2 000	2 000	—	—	—	250	10 000	10 000	2 000	10 000
saturated with	—	—	$Ca(OH)_2$	$Ca(OH)_2$	$Ca(OH)_2$	—	—	—	H_2O	H_2O	$Ca(OH)_2$ $CaSO_4$	$Ca(OH)_2$	$Ca(OH)_2$
Composition of the precipitate after drying at 105°													
Loss on ign. mg	22.7	25.5	37.7	44.9	27.1	5.8	—	19.2	9.5	8.9	—	94.6	28.2
CaO »	64.1	84.0	56.5	73.8	45.1	9.9	21.9	26.9	11.2	1.0	55.2	142.8	47.9
SiO_2 »	65.1	80.0	29.6	39.8	23.7	12.0	21.2	19.5	9.0	22.4	2.5	22.2	3.6
Al_2O_3 »	—	—	—	—	—	6.5	28.9	25.4	13.5	1.1	21.6	68.7	22.5
SO_3 »	—	—	—	—	—	—	—	—	—	—	33.1	—	—
Molecular ratio													
CaO	1.06	1.13	2.06	1.99	2.05	2.78	1.38	1.93	1.52	0.05	2.70	3.80	3.89
SiO_2	1	1	1	1	1	3.13	1.24	1.35	1.13	1	0.2	0.55	0.27
Al_2O_3	—	—	—	—	—	1	1	1	1	0.03	1	1	1
$CaSO_4$	—	—	—	—	—	—	—	—	—	—	1.96	—	—
H_2O	1.17	1.07	4.27	3.79	3.84	5.07	—	4.28	3.99	1.33	—	7.82	7.13

Table 2. Composition of the Solid Phase obtained by Shaking "C_2A"-Melt and C_3A resp. in Various Solutions. The analyses were carried out on substances dried in vacuum at 105°.

0.1 g C_2A-melt in 1 500 ml $Ca(OH)_2$ sol.	3.7 CaO :	1 Al_2O_3 :	7.7 H_2O	—
0.2 g » » 1 000 » » »	3.99 CaO :	1 Al_2O_3 :	7.02 H_2O	—
0.2 g » » 1 000 » » »	3.74 CaO :	1 Al_2O_3 :	6.75 H_2O	—
0.1 g » » 1 500 ml $Ca(OH)_2$-$CaSO_4$-sol.	2.54 CaO :	1 Al_2O_3 :	6.37 H_2O :	0.97 $CaSO_4$
0.2 g » » 1 000 » »	2.99 CaO :	1 Al_2O_3 :	6.49 H_2O :	1.0 $CaSO_4$
0.2 g C_3A-cryst. in 1 000 ml $Ca(OH)_2$ sol	3.04 CaO :	1 Al_2O_3 :	6.04 H_2O	—
0.2 g » » » 1 000 ml $Ca(OH)_2$-$CaSO_4$ . .	3.42 CaO :	1 Al_2O_3 :	6.42 H_2O :	0.95 $CaSO_4$

Table 3. "C_2A"-Melt in Water.

Shaking time	1 min.	5 min.	15 min.	30 min.
Solid phase	145.1	104.8	57.0	52.8
Loss on drying	5.3	5.6	5.5	4.4
Loss on ignition	7.8	6.6	5.0	14.3
CaO	68.0	48.6	21.9	18.1
Al_2O_3	64.0	44.4	25.5	15.4
Total	145.1	105.2	57.9	52.2
% Conversion	43.0	61.4	81.5	100.0
Dissolved CaO	35.4	54.8	81.5	85.3
Dissolved Al_2O_3	32.2	51.8	70.7	80.8

Table 4. "C_2A"-Melt in Saturated Lime Solution.

Shaking time . . .	1 min.	5 min.	15 min.	30 min.	1 d.	2 d.	3 d.	7 d.	14 d.
Solid phase	212.1	224.4	220.7	218.7	265.5	297.4	295.6	318.7	364.4
Loss on drying .	4.0	8.7	6.0	7.3	22.8	17.0	13.7	14.9	33.9
Loss on ignition .	4.6	6.5	4.2	4.8	16.6	33.8	43.1	56.1	69.4
CaO	104.7	107.1	108.9	106.3	120.0	146.6	142.3	150.0	161.0
Al_2O_3	98.2	100.3	101.1	97.6	101.5	98.2	96.4	97.2	98.0
Total	211.5	222.6	220.2	216.0	260.9	295.6	295.5	318.2	362.3
% Conversion . .	5.6	7.8	4.8	5.1	14.9	22.3	36.2	48.1	59.3
Dissolved CaO . .	—1.3	—3.7	—5.5	—2.9	—16.6	—43.2	—38.9	—46.6	—57.6
Dissolved Al_2O_3 .	—	—	—	—	—	—	—	—	—

Table 5. "C_2A"*-Melt in Saturated Lime-Gypsum Solution.*

Shaking time...	1 min.	5 min.	15 min.	30 min.	1 d.	2 d.	7 d.	14 d.	1 mo.
Solid phase.....	208.8	207.2	208.0	216.6	257.8	249.6	324.0	304.2	316.2
Loss on drying .	3.8	3.7	5.7	5.7	19.8	15.0	33.6	36.3	30.5
Loss on ignition .	5.2	5.5	5.9	6.3	15.0	14.8	28.1	36.7	21.7
CaO...........	102.3	102.6	100.7	105.6	117.5	114.7	153.5	134.5	145.5
Al_2O_3..........	94.4	95.2	94.2	97.2	98.1	95.2	97.0	97.0	98.0
SO_3 bef. ign....	—	—	—	—	10.7	8.0	14.4	18.1	18.2
SO_3 after ign...	—	—	—	—	6.7	8.1	14.4	0.0	18.2
Total	205.7	207.0	206.5	214.8	257.1	247.8	326.6	304.5	313.9
% Conversion ..	7.8	7.5	9.4	6.0	10.7	16.6	17.5	14.9	13.9
Dissolved CaO..	1.1	0.8	2.7	— 2.2	—14.1	—11.3	—50.1	—31.1	—42.1
Dissolved Al_2O_3.	1.8	1.0	2.0	—	—	1.0	—	—	—

Table 6. "C_2A"*-Melt in Saturated Gypsum Solution.*

Shaking time...............	1 min.	5 min.	15 min.	30 min.	1 d.
Solid phase.................	190.2	206.5	196.6	196.6	237.3
Loss on drying.............	5.0	10.7	7.5	6.1	27.5
Loss on ignition	2.3	10.3	7.3	6.8	31.4
CaO.......................	91.8	96.0	91.2	92.8	93.2
Al_2O_3....................	86.1	87.4	86.7	87.2	74.2
SO_3 bef. ign...............	1.9	2.5	1.9	2.8	14.1
SO_3 after ign..............	—	—	—	—	—
Total	187.1	206.9	194.6	195.7	240.4
% Conversion..............	14.1	20.8	20.1	18.9	56.3
Dissolved CaO..............	11.6	7.4	12.2	10.6	10.2
Dissolved Al_2O_3.............	10.1	8.8	9.5	9.0	22.0

Table 7. "C_2A"*-Melt in Supersaturated Solution of Gypsum (from Semihydrate).*

Shaking time.............	1 min.	5 min.	15 min.	24 h.
Solid phase...............	171.7	143.8	174.6	4 743.3
Loss on drying...........	6.2	8.6	10.8	907.1
Loss on ignition..........	3.6	4.5	5.3	59.3
Al_2O_3....................	75.2	60.3	72.2	88.4
CaO......................	81.4	67.3	81.3	1 569.5
SO_3 bef. ign..............	4.1	4.2	6.4	2 125.0
SO_3 after ign.............	3.6	4.0	6.0	2 123.0
Total	170.0	144.7	175.6	4 747.3
% Conversion............	25.8	42.0	30.2	—
Dissolved CaO............	22.0	36.1	22.1	—
Dissolved Al_2O_3...........	21.0	35.9	24.0	—

Table 8. "C_2A"-Melt in 5 % Calcium Chloride Solution.

Shaking time	1 min.	5 min.	15 min.	30 min.	24 h.
Solid phase	113.0	100.4	71.1	86.8	98.3
Loss on drying	2.2	2.4	1.6	4.8	3.9
Loss on ignition	4.3	4.5	4.3	9.2	40.3
CaO	54.2	47.7	34.7	36.2	40.9
Al_2O_3	50.6	45.2	30.4	33.2	7.8
Cl	2.2	1.6	1.7	2.7	4.6
Total	113.5	101.4	72.7	86.1	97.5
% Conversion	53.2	59.2	73.2	77.0	(128.8)
Dissolved CaO	49.2	55.7	68.7	67.2	62.5
Dissolved Al_2O_3	45.6	51.0	65.8	63.0	88.4

Table 9. "C_2A"-Melt in Saturated Lime Solution + Calcium Chloride.

Conc. of $CaCl_2$	5 %				30 %		
Shaking time	1 min.	15 min.	30 min.	24 h.	5 min.	30 min.	24 h.
Solid phase	208.4	196.8	215.5	228.5	138.0	144.5	179.8
Loss on drying	3.1	2.7	3.7	4.5	0.4	1.7	7.9
Loss on ignition	8.4	6.1	9.9	15.9	3.5	4.4	30.3
CaO	102.5	99.0	107.4	112.7	67.7	70.2	76.1
Al_2O_3	92.2	89.3	94.5	94.8	64.0	66.0	57.6
Cl	—	—	—	—	3.4	3.5	5.8
Total	206.2	197.1	215.5	227.9	139.0	145.8	177.7
% Conversion	12.8	13.3	11.3	16.2	39.0	37.9	72.7
Dissolved CaO	0.9	4.4	—4.0	—9.3	35.7	33.2	27.3
Dissolved Al_2O_3	4.0	6.9	1.7	1.4	32.2	30.2	38.6

Table 10. "C_2A"-Melt in Various Solutions.

Solution of	1 % Boric Acid	5 % Ca-Acetate $Ca(OH)_2$	10 % $MgCl_2$			2 % Sugar
Shaking time	5 min.	5 min.	1 min.	5 min.	15 min.	5 min.
Solid phase	187.5	217.2	185.9	186.4	196.5	77.1
Loss on drying	2.1	9.3	—	0.9	1.6	0.6
Loss on ignition	5.4	11.5	3.2	3.7	3.1	3.7
CaO	90.6	101.9	93.5	93.4	98.0	37.3
Al_2O_3	84.3	94.6	89.8	89.0	94.8	34.7
Total	182.4	217.3	186.5	187.0	197.5	76.3
% Conversion	—	—	11.6	12.8	6.6	68.3
Dissolved CaO	12.8	1.5	9.9	10.0	5.4	66.1
Dissolved Al_2O_3	11.9	1.6	6.4	7.2	1.4	61.5

Table 11. "C_2A"-Melt in 1 % Sugar Solution Saturated with Lime.

Shaking time	5 min.	15 min.	30 min.	24 h.
Solid phase	107.9	78.0	52.5	332.6
Loss on drying	1.6	1.4	1.6	79.9
Loss on ignition	3.4	1.2	1.9	104.5
CaO	53.4	38.3	25.3	110.9
Al_2O_3	49.3	37.3	24.3	36.3
Total	107.7	78.2	53.1	331.6
Dissolved CaO	50.0	65.1	78.1	— 7.5
Dissolved Al_2O_3	46.9	58.9	71.9	59.9

Table 12. "C_2A"-Melt in KOH + Humus.

% KOH	0.2 % Solution				2 % Solution
Shaking time	5 min.	15 min.	30 min.	24 h.	30 min.
Solid phase	155.9	139.6	117.5	8.1	172.8
Loss on drying	3.6	6.7	6.7	0.5	13.8
Loss on ignition	4.2	6.0	8.1	2.3	20.8
CaO	75.4	63.6	52.0	2.4	74.3
Al_2O_3	73.1	63.2	49.6	3.1	63.4
Total	156.3	139.5	116.4	8.3	172.3
Dissolved CaO	28.0	39.8	49.4	101.0	29.1
Dissolved Al_2O_3	23.1	33.0	46.6	93.1	32.8

Table 13. "C_2A"-Melt in KOH-Solution. Shaking time 30 minutes.

Normality	0.0026	0.0053	0.0105	0.021	0.042	0.089	0.193	0.378	0.535	0.705	0.874	1.756
% KOH	0.015	0.029	0.059	0.118	0.235	0.50	1.08	2.12	3.00	3.95	4.90	9.85
Solid phase	152.0	171.4	120.0	123.8	148.2	178.1	174.8	184.6	179.2	189.3	188.6	188.6
Loss on drying	3.1	2.6	2.2	2.1	1.9	7.9	4.7	5.2	3.9	6.2	5.2	6.4
Loss on ignition	44.6	29.8	3.6	4.7	4.3	9.4	7.4	7.4	6.5	6.4	7.7	8.4
Al_2O_3	28.1	55.3	52.8	54.8	66.7	74.4	78.0	81.2	78.6	84.7	83.5	83.6
CaO	74.2	83.7	58.8	60.9	73.9	86.6	85.5	89.9	88.3	92.8	91.4	90.5
K_2O	—	—	1.5	1.0	1.3	—	—	—	—	—	—	—
Total	150.0	171.4	118.9	123.5	148.1	178.3	175.6	183.7	177.3	190.1	187.8	188.9
% Conversion	(106.9)	68.7	48.3	47.7	34.7	31.3	27.1	12.4	24.5	18.9	21.7	22.8
Dissolved CaO	29.2	19.7	44.6	42.5	29.5	16.8	17.9	13.5	15.1	10.6	12.0	12.9
Dissolved Al_2O_3	68.1	40.9	43.4	41.4	29.5	21.8	18.2	15.0	17.6	11.5	12.7	12.6

Table 14. "C_2A"-Melt in Lime Solution. Shaking time 30 minutes.

Normality	0.0019	0.0040	0.0098	0.0192	0.0404
Solid phase	146.1	128.9	191.2	218.8	220.7
Loss on drying	5.1	4.6	5.6	13.5	5.6
Loss on ignition	12.5	6.9	7.9	11.6	6.5
Al_2O_3	60.0	56.8	82.2	90.4	98.8
CaO	69.7	62.1	93.3	102.6	109.0
Total	147.3	130.4	189.0	218.1	219.9
% Conversion	50.5	51.3	21.6	17.7	4.0
Dissolved CaO	33.7	41.3	10.1	0.8	— 5.6
Dissolved Al_2O_3	36.2	39.4	14.0	5.8	0

Table 15. C_3A-Crystals in Water.

Shaking time	1 min.	5 min.	15 min.	30 min.	24 h.
Solid phase	149.7	125.1	124.6	104.3	72.3
Loss on drying	3.7	4.6	4.6	5.0	4.4
Loss on ignition	8.4	7.2	10.8	15.2	19.2
Al_2O_3	51.9	42.5	40.3	32.2	18.1
CaO	85.2	70.3	67.8	50.3	29.7
Total	149.2	124.6	123.5	102.7	71.4
% Conversion	41.9	52.6	59.5	77.5	100.0
Dissolved Al_2O_3	23.7	33.1	35.3	43.4	57.5
Dissolved CaO	38.6	53.5	55.9	73.5	94.1

Table 16. C_3A-Crystals in Saturated Lime Solution.

Shaking time	1 min.	5 min.	15 min.	30 min.	24 h.
Solid phase	225.4	208.4	200.0	212.0	265.0
Loss on drying	4.7	6.5	6.8	6.5	18.5
Loss on ignition	10.9	9.8	8.9	11.8	28.5
Al_2O_3	76.1	72.3	69.1	71.8	78.6
CaO	131.5	120.6	115.5	120.3	137.0
Total	223.2	209.2	200.3	210.4	262.6
% Conversion	10.3	15.8	18.8	18.7	28.5
Dissolved Al_2O_3	0	3.3	6.5	3.8	0
Dissolved CaO	— 7.7	3.2	8.3	3.5	— 13.2

Table 17. C_3A-Crystals in Saturated Lime-Gypsum Solution.

Shaking time	1 min.	5 min.	15 min.	30 min.	24 h.
Solid phase	213.2	214.3	215.4	222.9	241.1
Loss on drying	3.4	5.6	6.2	5.5	11.7
Loss on ignition	7.7	7.5	7.0	8.6	13.8
Al_2O_3	73.7	75.0	75.1	76.2	76.8
CaO	126.1	124.3	126.0	130.5	132.2
SO_3 before ign.	1.7	0.9	1.1	1.2	6.4
SO_3 after ign.	1.7	0.9	1.2	1.3	5.5
Total	212.6	213.3	215.5	222.1	240.0
% Conversion	10.3	9.8	8.5	8.0	12.9
Dissolved Al_2O_3	1.9	0.6	0.5	0	0
Dissolved CaO	— 2.3	— 0.5	— 2.2	— 6.7	— 8.4

Table 18. C_3A-Crystals in Saturated Gypsum Solution.

Shaking time	1 min.	5 min.	15 min.	30 min.	24 h.
Solid phase	179.6	181.8	193.6	216.1	392.4
Loss on drying	10.3	9.8	12.2	20.1	69.5
Loss on ignition	8.9	10.7	21.8	28.4	131.5
Al_2O_3	58.9	57.7	55.3	55.7	55.4
CaO	98.3	98.4	99.4	107.7	137.9
SO_3 before ign.	3.5	4.0	5.7	6.7	64.7
SO_3 after ign.	2.7	2.9	5.1	5.5	—
Total	179.1	169.5	193.8	217.4	394.3
% Conversion	32.0	34.8	50.8	54.9	(104.6)
Dissolved Al_2O_3	16.7	17.9	20.3	19.9	20.2
Dissolved CaO	25.5	25.4	24.4	16.1	— 14.1

Table 19. C_3A-Crystals in 5 % Magnesium Chloride Solution.

Shaking time	15 min.
Solid phase	205.4
Loss on drying	1.3
Loss on ignition	5.8
Al_2O_3	75.1
CaO	121.5
MgO	2.3
Cl	—
Total	206.0
% Conversion	7.3
Dissolved Al_2O_3	0.4
Dissolved CaO	2.3

Table 20. C_4AF-Melt in Water.

Shaking time	1 min.	5 min.	15 min.	30 min.	24 h.
Solid phase	198.3	174.2	194.6	191.7	168.1
Loss on drying	4.3	1.4	1.9	2.7	9.0
Loss on ignition	1.5	0.7	4.8	5.1	10.3
Al_2O_3	40.5	38.1	40.0	39.6	27.0
Fe_2O_3	64.2	57.6	63.2	61.3	62.7
CaO	86.4	76.8	84.4	83.0	58.6
Total	196.9	174.6	194.3	191.7	167.6
% Conversion	6.9	13.8	13.0	15.2	41.0
Dissolved Al_2O_3	3.7	6.1	1.8	4.6	2.3
Dissolved Fe_2O_3	0.8	7.4	4.2	3.7	17.2
Dissolved CaO	4.4	14.0	6.4	7.8	32.2

Table 21. C_4AF-Melt in Saturated Lime Solution.

Shaking time	1 min.	5 min.	15 min.	30 min.	24 h.
Solid phase	200.1	197.2	197.8	202.2	204.0
Loss on drying	2.1	4.2	2.3	2.9	3.6
Loss on ignition	1.6	1.6	3.3	2.5	2.9
Al_2O_3	44.1	41.2	41.3	44.2	41.7
Fe_2O_3	63.9	61.5	62.7	64.7	64.4
CaO	87.7	87.0	87.5	87.7	90.1
Total	199.4	195.5	197.1	202.0	202.7
% Conversion	4.1	7.5	9.0	4.9	6.3
Dissolved Al_2O_3	0.1	3.0	2.9	—	2.5
Dissolved Fe_2O_3	1.1	3.5	2.3	0.3	0.6
Dissolved CaO	3.1	3.8	3.3	3.1	0.7

Table 22. C_4AF-Melt in Saturated Lime-Gypsum Solution.

Shaking time	1 min.	5 min.	15 min.	30 min.	24 h.
Solid phase	200.8	203.9	199.2	204.4	205.3
Loss on drying	4.3	4.1	4.0	3.8	3.7
Loss on ignition	1.1	3.3	2.1	4.1	3.8
Al_2O_3	41.4	44.9	42.0	42.3	43.7
Fe_2O_3	64.2	65.0	63.3	63.9	65.0
CaO	88.6	87.4	88.2	88.5	87.3
SO_3	—	—	—	—	—
Total	199.6	204.7	199.6	202.6	203.5
% Conversion	4.9	5.5	6.3	8.4	7.0
Dissolved Al_2O_3	2.8	—	2.2	1.9	0.5
Dissolved Fe_2O_3	0.8	—	1.7	1.1	—
Dissolved CaO	2.2	3.4	2.6	2.3	3.5

Table 23. C_4AF*-Melt in Saturated Gypsum Solution.*

Shaking time.....	1 min.	5 min.	15 min.	30 min.	1 d.	2 d.	3 d.
Solid phase......	199.5	190.1	198.8	203.3	205.7	197.8	201.9
Loss on drying...	2.0	2.8	2.3	2.0	4.8	3.1	4.0
Loss on ignition..	1.4	—	0.6	4.1	1.3	1.1	—
Al_2O_3...........	43.9	40.8	44.1	43.8	42.8	43.3	45.2
Fe_2O_3...........	63.7	60.0	61.9	62.1	65.9	64.9	66.1
CaO.............	87.2	83.9	88.7	88.9	88.3	86.0	86.6
SO_3 before ign....	—	—	—	4.0	—	—	—
SO_3 after ign	—	—	—	4.0	—	—	—
Total	198.2	187.5	197.6	204.9	203.1	198.4	201.9
% Conversion....	4.3	7.7	3.3	8.6	3.4	4.3	0.7
Dissolved Al_2O_3 ..	0.3	3.4	0.1	0.4	1.4	0.9	—
Dissolved Fe_2O_3 .	1.3	5.0	3.1	2.9	—	0.1	—
Dissolved CaO ...	3.6	6.9	2.1	1.9	2.5	4.8	4.2

Table 24. C_4AF*-Crystals in Water.*

Shaking time ...	1 min.	5 min.	15 min.	30 min.	1 d.	2 d.	3 d.	7 d.	1 mo.
Solid phase.....	185.7	203.8	199.1	190.0	204.2	194.8	198.8	189.8	196.6
Loss on drying..	—	—	0.5	0.4	1.1	0.1	0.2	0.4	0.7
Loss on ignition	1.5	1.7	2.1	1.8	1.0	1.7	1.6	2.1	1.5
Al_2O_3..........	39.0	42.4	42.1	36.4	42.2	41.0	39.4	40.2	41.2
Fe_2O_3..........	61.4	67.0	66.4	66.2	66.5	65.2	63.0	63.2	65.2
CaO...........	83.8	91.4	89.5	85.6	93.0	87.4	85.4	84.6	87.2
Total	185.7	202.5	200.6	190.4	203.8	195.4	189.6	190.5	195.8
% Conversion...	11.3	3.3	5.2	10.6	2.1	6.8	9.7	10.2	6.6
Dissolved Al_2O_3 .	2.4	—	—	5.0	—	0.4	2.0	1.2	0.2
Dissolved Fe_2O_3	5.8	0.2	0.8	1.0	0.7	2.0	4.2	4.0	2.0
Dissolved CaO ..	7.4	—	1.7	5.6	—	3.8	5.8	6.6	4.0

Table 25. C_4AF*-Crystals in Saturated Lime Solution.*

Shaking time	30 min.	1 d.	2 d.	3 d.	7 d.	14 d.	1 mo.
Solid phase......	205.4	236.3	205.5	216.8	210.0	193.8	224.8
Loss on drying...	0.7	3.2	1.0	1.0	1.3	1.7	2.8
Loss on ignition..	1.9	9.6	3.3	4.3	4.2	3.9	8.7
Al_2O_3...........	40.8	38.9	42.4	40.7	41.8	37.7	41.0
Fe_2O_3...........	67.2	68.2	67.2	66.8	64.8	64.6	64.6
CaO.............	93.0	116.0	92.3	104.5	95.6	86.8	107.2
Total	203.6	235.9	206.2	217.3	207.7	194.7	224.3
% Conversion....	4.0	5.3	4.5	2.5	6.3	12.8	8.0
Dissolved Al_2O_3 ..	0.6	2.5	—	0.7	—	3.7	0.2
Dissolved Fe_2O_3 .	—	—	—	0.4	2.4	2.6	2.6
Dissolved CaO ...	— 1.8	— 24.2	— 1.1	— 13.3	— 4.4	4.4	— 20.0

Table 26. C_4AF-Crystals in Saturated Lime-Gypsum Solution.

Shaking time.....	30 min.	1 d.	2 d.	3 d.	7 d.	14 d.	1 mo.
Solid phase......	203.5	223.5	222.8	214.6	240.3	236.6	280.6
Loss on drying...	0.7	4.5	3.8	1.5	3.5	5.9	17.7
Loss on ignition..	1.4	3.3	4.7	3.3	5.0	8.1	17.9
Al_2O_3...........	43.5	39.7	44.0	42.1	42.1	41.8	41.6
Fe_2O_3...........	66.2	68.0	67.4	67.8	66.7	67.0	67.5
CaO.............	91.6	104.0	98.0	96.8	121.0	114.0	135.1
SO_3 before ign....	—	1.7	1.9	3.4	2.0	—	—
SO_3 after ign.....	—	1.5	1.8	3.2	1.9	—	—
Total	203.4	221.0	219.7	214.7	240.2	236.8	279.8
% Conversion....	2.5	1.9	2.6	2.2	(— 4.0)	2.6	4.1
Dissolved Al_2O_3 ..	—	1.7	—	—	—	—	—
Dissolved Fe_2O_3 .	1.0	—	—	—	0.5	0.2	—
Dissolved CaO ...	— 0.4	— 12.8	— 6.8	— 5.6	— 29.8	— 22.8	— 43.9

Table 27. "KCA"-Melt in Water.

Shaking time.................	1 min.	5 min.	15 min.	30 min.	24 h.
Solid phase..................	127.4	119.2	114.0	80.1	110.1
Loss on drying..............	2.6	4.5	8.8	8.2	17.0
Loss on ignition.............	3.9	6.2	6.5	10.2	33.2
Al_2O_3.......................	69.8	63.9	60.2	38.8	27.8
CaO........................	47.8	42.3	35.4	21.1	28.3
K_2O........................	3.5	4.1	4.7	3.8	3.3
Total	127.6	121.0	115.6	82.1	109.6
% Conversion[1]..............	(43.2)	(51.4)	(56.5)	(79.4)	(110.2)
Dissolved Al_2O_3	42.4	48.3	52.0	73.4	84.4
Dissolved CaO...............	31.2	36.3	43.2	57.5	50.3
Dissolved K_2O...............	5.7	5.1	4.5	5.4	5.9

[1] The calculation of "% conversion" is somewhat uncertain owing to the fact that alkali aluminates or, as the case may be, alkali hydroxide passes more speedily into solution than the "C_2A" does.

Table 28. "KCA"-Melt in Saturated Lime Solution.

Shaking time	1 min.	5 min.	15 min.	30 min.	24 h.
Solid phase	204.7	221.2	254.8	249.2	333.4
Loss on drying	4.3	18.0	14.5	13.1	28.6
Loss on ignition	9.3	12.1	18.9	16.2	61.0
Al_2O_3	105.6	104.7	118.4	118.0	106.6
CaO	78.6	81.0	95.7	94.3	124.7
K_2O	5.9	5.9	7.5	8.6	7.4
Total	203.7	221.7	255.0	250.2	328.3
% Conversion[1]	(15.5)	(18.5)	(12.1)	(9.5)	(57.4)
Dissolved Al_2O_3	6.6	7.5	—	—	5.6
Dissolved CaO	—	— 2.4	— 17.1	— 15.7	— 46.1
Dissolved K_2O	3.3	3.3	1.7	0.6	1.8

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[1] The calculation of "% Conversion" is somewhat uncertain owing to the fact that alkali aluminates or, as the case may be, alkali hydroxide passes more speedily into solution than the "C_3A" does.

Table 29. "KCA"-Melt in Saturated Lime-Gypsum Solution.

Shaking time	1 min.	5 min.	15 min.	30 min.	24 h.
Solid phase	235.1	212.0	270.5	221.3	367.7
Loss on drying	5.1	5.7	14.5	7.9	54.0
Loss on ignition	9.0	7.2	22.6	8.8	37.5
Al_2O_3	115.0	110.5	117.5	112.0	116.2
CaO	92.3	79.4	97.0	84.2	125.2
K_2O	6.8	6.4	6.4	4.2	1.8
SO_3 before ign.	4.9	1.9	10.6	3.2	33.2
SO_3 after ign.	4.0	1.9	10.1	3.5	32.9
Total	232.2	211.1	268.1	220.6	367.6
% Conversion[1]	(3.7)	(10.0)	(17.4)	(9.7)	(29.3)
Dissolved Al_2O_3	—	1.7	—	—	4.0
Dissolved CaO	— 13.7	— 0.8	— 18.4	— 5.6	— 46.6
Dissolved K_2O	2.4	2.8	2.8	5.0	7.4

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[1] The calculation of "% Conversion" is somewhat uncertain owing to the fact that alkali aluminates or, as the case may be, alkali hydroxide passes more speedily into solution than the "C_3A" does.

Table 30. "KCA"-Melt in Saturated Gypsum Solution.

Shaking time	1 min.	5 min.	15 min.	30 min.	24 h.
Solid phase	187.5	197.2	197.1	197.2	203.3
Loss on drying	1.4	1.6	1.6	1.6	0.7
Loss on ignition	4.2	4.0	4.0	4.0	2.9
Al_2O_3	105.5	111.6	111.2	111.1	116.5
CaO	72.2	76.8	76.7	76.2	78.6
K_2O	4.6	3.5	3.6	3.4	3.8
SO_3	—	—	—	—	—
Total	187.9	197.5	197.1	196.3	202.5
% Conversion[1]	(12.4)	(7.1)	(7.3)	(7.6)	(2.0)
Dissolved Al_2O_3	6.7	0.6	1.0	1.1	—
Dissolved CaO	6.4	1.8	1.9	2.4	—
Dissolved K_2O	4.6	5.7	5.6	5.8	5.4

[1] The calculation of "% Conversion" is somewhat uncertain owing to the fact that alkali aluminates or, as the case may be, alkali hydroxide passes more speedily into solution than the "C_2A" does.

Table 31. "CAS"-Melt in Water.

Shaking time	1 min.	5 min.	15 min.	30 min.	24 h.
Solid phase	176.3	171.4	157.9	155.2	143.5
Loss on drying	0.8	17.2	10.7	12.3	12.1
Loss on ignition	—	3.8	6.2	8.1	20.6
SiO_2	14.0	14.8	13.8	14.3	14.0
Al_2O_3	64.7	54.3	51.2	49.8	35.0
CaO	98.2	82.0	77.6	73.1	62.8
Total	177.7	172.1	159.5	157.6	144.5
% Conversion	12.1	31.5	38.7	44.1	75.9
Dissolved SiO_2	0.7	—	0.9	0.4	0.7
Dissolved Al_2O_3	8.9	19.3	22.4	23.8	38.6
Dissolved CaO	13.4	29.6	34.0	38.5	48.8

Table 32. "CAS"-Melt in Saturated Lime Solution

Shaking time	1 min.	5 min.	15 min.	30 min.	24 h.
Solid phase	200.0	200.3	199.7	199.1	204.0
Loss on drying	0.8	1.0	0.9	1.3	4.3
Loss on ignition	4.0	4.9	5.1	5.1	6.0
SiO_2	14.8	14.4	14.0	14.0	14.0
Al_2O_3	73.3	72.1	71.6	71.4	72.1
CaO	109.1	109.2	108.9	108.8	109.0
Total	202.0	201.6	200.5	200.6	205.4
% Conversion	6.8	8.7	9.4	9.6	10.2
Dissolved SiO_2	—	0.4	0.8	0.8	0.8
Dissolved Al_2O_3	0.3	1.5	2.0	2.2	1.5
Dissolved CaO	2.5	2.4	2.7	2.8	2.6

Table 33. "CAS"-Melt in Saturated Lime-Gypsum Solution.

Shaking time	5 min.	15 min.	30 min.	24 h.
Solid phase	194.0	198.9	188.0	200.6
Loss on drying	3.2	20.0	1.2	3.6
Loss on ignition	1.0	0.6	1.3	2.2
SiO_2	14.6	13.1	13.7	14.4
Al_2O_3	70.6	67.3	67.9	69.5
CaO	107.2	100.8	102.1	107.6
SO_3 before ignition	—	—	0.1	0.9
SO_3 after ignition	—	—	0.1	0.9
Total	196.6	201.8	186.3	198.2
% Conversion	4.6	9.2	9.5	5.6
Dissolved SiO_2	0.1	1.6	1.0	0.3
Dissolved Al_2O_3	2.3	5.6	5.0	3.4
Dissolved CaO	3.4	9.8	8.5	3.0

Table 34. "CAS"-Melt in Gypsum Solution.

Shaking time	15 min.	30 min.	1 d.	7 d.	7 d.[1]
Solid phase	184.4	189.6	197.4	209.2	183.7
Loss on drying	0.7	1.1	3.0	5.0	3.1
Loss on ignition	1.5	1.7	4.7	8.3	7.0
SiO_2	14.2	14.1	13.4	14.2	11.9
Al_2O_3	69.0	68.3	71.9	72.8	65.5
CaO	100.8	101.8	107.2	110.7	100.8
SO_3 before ignition	—	—	—	0.7	0.8
SO_3 after ignition	—	—	—	0.7	0.8
Total	186.2	187.0	200.2	211.7	189.1
% Conversion	9.2	9.5	8.8	11.5	19.8
Dissolved SiO_2	0.5	0.6	1.3	0.5	2.8
Dissolved Al_2O_3	3.9	4.6	1.0	0.8	7.4
Dissolved CaO	9.8	8.8	3.4	1.1	9.8

[1] The melt was mixed with 0.5 % $CaSO_4 \cdot 2$ Aq. cryst.

Table 35. "CAS"-Melt in Saturated Lime Solution with Calcium Chloride.

Conc. of $CaCl_2$	5 %					30 %		
Shaking time	1 min.	5 min.	15 min.	30 min.	24 h.	15 min.	30 min.	24 h.
Solid phase	201.8	201.4	200.0	208.1	215.0	176.1	113.5	140.4
Loss on drying	0.9	1.2	0.9	1.4	4.9	0.5	1.0	12.4
Loss on ignition	0.2	1.1	2.1	3.0	8.8	9.8	6.6	25.0
SiO_2	14.8	14.7	14.3	14.8	12.7	12.9	6.9	14.3
Al_2O_3	73.7	72.9	72.6	76.2	75.0	59.9	37.3	27.8
CaO	112.6	112.4	111.6	113.4	113.1	95.3	60.7	62.2
Cl	—	—	—	—	1.2	1.2	1.7	1.7
Total	202.2	202.3	201.5	208.8	215.7	179.6	114.2	143.4
% Conversion	—	0.6	3.5	2.6	12.1	34.8	57.1	87.7
Dissolved SiO_2	—	—	0.4	—	2.0	1.8	7.8	0.4
Dissolved Al_2O_3	—	0.7	1.0	—	—	13.7	36.3	45.8
Dissolved CaO	— 1.0	— 0.8	—	— 2.8	— 2.5	16.6	51.3	49.8

Table 36. C_3S-Crystals in Water.

Shaking time ...	1 min.[1]	1 min.	5 min.	15 min.	1 d.	2 d.	3 d.	7 d.	14 d.
Solid phase.....	487.5	127.4	100.7	54.3	77.1	118.3	106.8	59.8	57.7
Loss on drying .	2.3	0.5	0.8	—	11.3	13.4	4.8	6.1	5.6
Loss on ignition.	2.5	1.3	2.0	1.3	6.8	15.8	15.5	5.8	7.7
SiO_2............	127.0	34.6	25.3	12.5	15.3	21.3	23.0	16.7	15.6
CaO............	352.0	91.8	73.1	35.0	43.1	65.8	63.8	31.0	28.3
Total	483.8	128.2	101.2	48.8	76.5	116.3	107.1	59.6	57.2
% Conversion...	6.4	40.2	54.4	78.9	85.1	88.7	89.5	91.2	97.1
Dissolved SiO_2 ..	4.0	18.4	27.7	40.5	37.7	31.7	30.0	36.3	37.4
Dissolved CaO ..	14.5	55.2	73.9	112.0	103.9	81.2	83.2	116.0	118.7

[1] 0.5 g C_3S in 100 ml H_2O.

Table 37. C_3S-Crystals in Saturated Lime Solution.

Shaking time...	30 min.	1 d.	2 d.	3 d.	7 d.	14 d.	1 mo.
Solid phase.....	197.5	203.5	185.4	212.9	172.0	216.4	212.4
Loss on drying.	0.2	7.1	4.8	22.7	11.7	26.7	14.3
Loss on ignition	6.9	14.7	9.9	10.3	11.0	20.3	17.4
SiO_2...........	44.2	48.8	48.9	50.6	44.2	50.5	53.4
CaO...........	144.5	132.6	122.1	125.9	104.4	118.9	124.5
Total	195.8	203.2	185.7	209.5	171.3	216.4	209.6
% Conversion ..	2.1	27.6	25.7	23.4	37.9	38.9	30.9
Dissolved SiO_2..	8.8	4.2	4.1	2.4	8.8	2.5	—
Dissolved CaO..	2.5	14.4	24.9	21.1	42.6	28.1	22.5

Table 38. C_3S-Crystals in Saturated Lime-Gypsum Solution.

Shaking time.............	30 min.	1 d.	2 d.	3 d.	14 d.	1 mo.
Solid phase...............	197.2	189.4	184.7	172.4	210.5	205.0
Loss on drying...........	0.2	2.2	8.5	6.5	18.7	17.1
Loss on ignition..........	6.6	12.7	13.1	12.6	30.7	24.6
SiO_2.....................	44.5	43.5	43.9	40.2	44.9	46.3
CaO.....................	144.5	129.1	117.1	111.6	114.7	116.4
SO_3 before ignition	0.3	0.3	—	—	0.9	0.3
SO_3 after ignition.........	0.3	0.3	—	—	0.9	0.3
Total	196.1	197.8	182.6	170.9	209.9	204.7
% Conversion............	2.0	30.5	35.5	40.0	58.4	48.7
Dissolved SiO_2............	8.5	9.5	9.1	12.8	8.1	6.7
Dissolved CaO............	2.5	17.9	29.9	35.4	32.3	30.6

Table 39. C_3S-Crystals in Saturated Gypsum Solution.

Shaking time	30 min.	1 d.	2 d.	3 d.	7 d.	14 d.
Solid phase	79.9	90.0	123.8	106.2	155.0	158.2
Loss on drying	0.7	4.5	7.6	6.2	11.0	12.8
Loss on ignition	11.6	23.2	34.6	30.5	45.5	45.2
SiO_2	15.5	19.0	20.9	18.3	28.5	31.9
CaO	49.9	41.7	59.1	48.7	67.9	67.0
SO_3 before ign.	0.9	0.8	1.0	1.3	0.8	0.8
SO_3 after ign.	0.9	0.8	1.0	1.3	0.8	0.8
Total	78.6	89.2	123.2	105.5	153.7	157.7
% Conversion	82.9	98.3	(104.2)	(105.3)	(108.7)	(106.1)
Dissolved SiO_2	37.5	34.0	32.1	34.7	24.5	21.1
Dissolved CaO	97.1	105.3	87.9	98.3	79.1	80.0

Table 40. C_3S-Crystals in Saturated Lime Solution containing 5 % Calcium Chloride.

Shaking time	1 min.	5 min.	15 min.	30 min.	1 d.	2 d.	3 d.	7 d.	14 d.	1 m.
Solid phase	215.3	204.9	208.4	192.0	193.8	201.1	182.4	201.0	196.6	194.2
Loss on drying	1.3	0.4	0.7	0.4	24.4	38.8	20.8	37.8	37.0	29.9
Loss on ignition	3.6	2.7	1.3	1.2	22.8	25.8	22.1	24.4	28.8	32.9
SiO_2	54.8	53.5	53.5	46.9	37.1	35.0	38.3	43.1	45.0	40.9
CaO	156.6	148.2	150.7	136.4	94.6	88.3	96.0	88.2	85.2	80.0
Cl	—	—	—	5.2	14.9	13.2	4.6	6.4	4.8	9.5
Total	216.3	204.8	206.2	190.1	193.8	201.1	181.8	199.9	200.8	193.2
% Conversion	—	2.4	—	12.1	67.1	74.4	60.8	64.4	69.2	80.1
Dissolved SiO_2	—	—	—	6.1	15.9	18.0	14.7	9.9	8.0	12.1
Dissolved CaO	—9.6	—1.2	—3.7	10.6	52.4	58.7	51.0	58.8	61.8	67.0

Table 41. C_3S-Crystals in 5 % Calcium Chloride Solution.

Shaking time	1 min.	5 min.	15 min.	30 min.	24 h.
Solid phase	132.7	111.4	73.0	74.8	118.9
Loss on drying	0.7	0.3	—	0.3	25.6
Loss on ignition	2.2	2.3	5.2	6.3	12.9
SiO_2	35.7	27.8	18.4	18.2	42.4
CaO	92.5	79.6	48.9	48.1	37.5
Total	131.1	110.0	72.5	72.9	118.4
% Conversion	38.1	49.4	72.7	74.6	69.0
Dissolved SiO_2	17.3	25.2	34.6	34.8	10.6
Dissolved CaO	54.5	67.4	98.1	98.9	109.5

Table 42. C_3S-Crystals in 5 % Magnesium Chloride Solution.

Shaking time	1 min.	5 min.	15 min.	30 min.	24 h.
Solid phase	148.6	106.6	115.8	118.3	197.4
Loss on drying	7.9	11.0	16.7	19.6	39.2
Loss on ignition	12.1	15.6	17.2	21.6	39.8
SiO_2	34.0	25.8	26.6	29.1	50.6
CaO	78.8	37.0	31.9	19.5	7.5
MgO	9.6	16.3	20.9	25.3	52.4
Cl	5.1	3.2	3.1	3.4	5.4
Total	147.5	108.9	116.4	118.5	194.9
% Conversion	53.7	76.9	77.8	83.8	77.1
Dissolved SiO_2	19.0	27.2	26.4	23.9	2.4
Dissolved CaO	68.2	110.0	115.1	133.5	139.5

Table 43. C_3S-Crystals in CA-Solution (0.434 g/l CaO + 0.550 g/l Al_2O_3; $P_H = 12.05$ at 20°).

Shaking time	2 d.	3 d.	14 d.
Solid phase	230.2	228.6	213.4
Loss on drying	4.5	3.7	8.7
Loss on ignition	6.7	8.3	9.8
SiO_2	51.3	52.4	49.3
Al_2O_3	10.0	7.8	14.4
CaO	155.7	155.4	131.1
Total	228.2	227.6	213.3
% Conversion	—	2.4	12.1
Dissolved SiO_2	1.7	0.6	3.7
Dissolved CaO	—8.7	—8.4	15.9

Table 44. C_3S-Crystals — 2 Days in CA-Solution, then 3 Days in Saturated Lime Solution.

Solid phase	215.7
Loss on drying	26.0
Loss on ignition	35.1
SiO_2	42.2
Al_2O_3	10.9
CaO	101.6
Total	215.8
% Conversion	64.4
Dissolved SiO_2	10.8
Dissolved CaO	45.4

Table 45. C_3S-Crystals in KOH-Solutions of Various Concentrations. Shaking time 24 hours.

Conc. of KOH	10 %	2 %	0.125 %	0.06 %	0.03 %	0.0 %
Solid phase	138.0	117.6	128.1	80.6	88.2	77.1
Loss on drying	12.9	11.8	10.4	14.4	16.4	11.3
Loss on ignition	24.0	11.7	10.6	3.4	3.9	6.8
SiO_2	12.1	24.7	22.7	15.5	15.9	15.3
CaO	83.4	62.3	76.6	44.5	47.4	43.1
K_2O	5.0	6.0	6.4	3.0	4.0	—
Total	137.4	116.5	126.7	80.8	87.6	76.5
% Conversion[1]	86.4	69.3	63.5	73.7	72.6	79.5
» [2]	92.0	80.1	67.8	75.7	74.3	85.1
Dissolved SiO_2	40.9	28.3	20.3	37.5	37.1	37.7
Dissolved CaO	59.6	80.7	66.4	98.5	95.6	99.9

[1] The hydrated part of the solid phase assumed to consist of $2CaO \cdot SiO_2 \cdot 4H_2O$.

[2] The hydrated part of the solid phase assumed to consist of $CaO \cdot SiO_2 \cdot H_2O$.

Table 46. β-C_2S in Water.

Shaking time	5 min.	15 min.	30 min.	1 d.	2 d.	3 d.	7 d.	14 d.
Solid phase	187.2	170.7	165.5	164.0	161.5	162.6	163.2	159.2
Loss on drying	—	0.2	—	—	—	—	—	—
Loss on ignition	0.7	0.5	0.6	1.2	1.3	1.1	1.0	0.6
SiO_2	65.5	58.7	55.9	55.4	55.7	55.2	54.6	53.9
CaO	120.0	113.4	105.8	105.6	103.9	105.0	104.6	102.8
Total	186.2	172.8	162.3	162.2	160.9	161.3	160.2	157.3
% Conversion	9.5	14.1	20.0	21.8	23.3	22.1	22.1	22.5
Dissolved SiO_2	4.4	11.1	13.9	14.4	14.1	14.6	15.2	15.9
Dissolved CaO	10.1	16.8	24.4	24.6	26.3	25.2	25.6	27.4

Table 47. β-C_2S in Saturated Lime Solution.

Shaking time	1 d.	2 d.	7 d.	14 d.
Solid phase	210.5	215.7	198.8	205.4
Loss on drying	—	0.4	—	0.3
Loss on ignition	3.5	4.9	1.5	5.3
SiO_2	68.8	70.0	66.0	62.0
CaO	137.4	139.6	131.2	137.2
Total	209.7	214.9	198.7	204.8
% Conversion	2.3	2.2	4.2	8.8
Dissolved SiO_2	1.0	—	3.8	7.8
Dissolved CaO	—7.2	—9.4	—1.0	—7.0

Table 48. β-C_2S in Saturated Lime-Gypsum Solution.

Shaking time	1 d.	2 d.	3 d.	7 d.	14 d.
Solid phase	199.2	199.2	196.8	202.0	198.0
Loss on drying	—	—	0.2	0.8	1.2
Loss on ignition	1.8	1.8	1.2	0.6	3.5
SiO_2	63.0	65.7	62.5	65.2	62.0
CaO	132.6	130.2	132.4	133.0	129.8
SO_3 before ign.	1.2	0.9	1.1	1.7	1.5
SO_3 after ign.	1.2	0.9	1.1	1.6	1.3
Total	198.6	198.6	197.4	201.2	197.8
% Conversion	6.5	5.4	6.2	3.4	10.5
Dissolved SiO_2	6.8	4.1	7.3	4.6	7.8
Dissolved CaO	—2.4	—	—2.2	—2.8	0.4

Table 49. β-C_2S in Saturated Lime Solution containing 5 % Calcium Chloride.

Shaking time	1 d.	2 d.	7 d.	14 d.
Solid phase	196.6	198.2	263.6	279.3
Loss on drying	—	0.5	—	0.3
Loss on ignition	2.0	3.4	19.9	23.8
SiO_2	60.4	54.7	54.1	53.6
CaO	129.1	131.0	179.8	191.8
Cl	4.8	8.5	9.1	9.2
Total	196.3	198.1	262.9	278.7
% Conversion	11.0	17.1	18.8	20.1
Dissolved SiO_2	9.4	15.1	15.7	16.2
Dissolved CaO	1.1	—0.8	—49.3	—61.6

Table 50. P_H-Value of Various Solutions at 22°.

$^1/_1$ saturated lime solution	12.65
$^1/_2$ » » »	12.45
$^1/_5$ » » »	12.05
$^1/_{10}$ » » »	11.70
Active CaO in water	12.70
Saturated lime solution containing 5 % $CaCl_2$	12.10
» » » » 30 % $CaCl_2$	11.30
Active CaO + $CaSO_4 \cdot 2H_2O$ in water	12.70
$CaSO_4 \cdot 2H_2O$ in water	9.25
Active CaO + $CaSO_4 \cdot \frac{1}{2}H_2O$ in water—after 2 min.	12.60
» » » » » » » 15 min.	12.60

Table 51. Chemical Composition of Cements Investigated.

Cement No.	CaO %	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	MgO %	K_2O %	Na_2O %	SO_3 %	Loss on ign. %	C_3S %	C_2S %	C_3A %	C_4AF %	Free CaO %
1.	63.3	24.1	4.3	6.7	1.5	0.0	0.0	0.0	0.0	37	42	0	20	0.1
2.	64.0	23.6	4.8	5.6	1.9	0.0	0.0	0.0	0.0	42	36	3	17	0.1
3.	63.8	23.6	5.5	4.3	1.9	0.0	0.0	0.0	0.0	37	40	7	13	0.2
4.	64.6	23.2	6.4	3.1	2.0	0.0	0.0	0.0	0.0	41	36	11	9	0.2
5.	64.5	20.6	4.3	7.1	2.2	0.0	0.0	0.0	0.0	63	11	1	22	0.2
6.	65.0	20.9	5.7	5.6	2.2	0.0	0.0	0.0	0.0	60	15	6	17	0.3
7.	65.6	20.8	6.2	4.7	2.2	0.0	0.0	0.0	0.0	61	14	9	14	0.3
8.	65.5	21.4	7.1	3.5	2.2	0.0	0.0	0.0	0.0	51	23	13	11	1.0
9.	66.7	24.6	6.2	0.8	1.6	0.0	0.0	0.0	0.0	35	44	15	2	1.8
10.	66.5	23.1	8.9	0.3	1.4	0.0	0.0	0.0	0.0	35	40	23	1	0.1
11.	65.2	21.1	6.7	3.7	1.7	1.2	0.1	0.2	0.4	55	19	11	11	—
12.	62.4	24.6	3.6	2.8	2.2	0.4	0.2	2.2	1.0	33	45	5	9	—
13.	63.9	20.3	6.4	3.6	1.6	1.2	0.1	2.0	1.2	53	18	11	11	—
14.	65.1	21.9	5.1	2.8	1.9	0.3	0.2	2.0	0.8	55	22	9	9	—
15.	64.3	19.8	6.7	4.3	0.8	0.6	0.1	1.2	2.2	57	14	11	13	—
16.	65.7	19.8	4.6	2.7	2.1	—	—	3.0	1.5	74	1	8	8	—
17.	65.5	21.3	8.4	4.2	—	0.0	0.0	0.0	0.0	37	33	15	13	1.3
18.	65.0	23.4	6.4	3.8	1.5	0.0	0.0	0.0	0.0	38	38	11	12	0.2
19.[1]	47.4	35.0	9.0	0.3	3.8	—	—	[2]	2.0	—	—	—	—	—
20.	66.1	20.9	6.9	4.3	—	0.0	0.0	0.0	0.0	55	18	11	13	1.0
21.	67.9	22.4	6.0	3.2	0.5	0.0	0.0	0.0	0.0	58	21	11	10	1.2

[1] Blast-furnace slag.
[2] S = 1.8 %.

All cements were ground to such a fineness that 4 % were retained on a sieve with 4 900 meshes per cm².

Table 52. Setting Tests.

No.	Without Additions		4.5 % $CaSO_4 \cdot 2H_2O$ 1.5 % $CaSO_4 \cdot \frac{1}{2}H_2O$		3 % Active CaO		1 % $CaCl_2$	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
1.	2′	20 h.	6 h.	14 h.	1 h.	23 h.	2½ h.	8 h.
2.	15′	18 h.	½ h.	11 h.	1 h.	22 h.	4 h.	12 h.
3.	15′		2 h.	11½ h.	2 h.	22½ h.	3 h.	8 h.
4.	quick		2 h.	11 h.	2 h.	19 h.	3 h.	8¼ h.
5.	30′	24 h.	4½ h.	15 h.	1 h.	23½ h.	1½ h.	6 h
6.	1½ h.	19 h.	½ h.	9 h.	3 h.	23½ h.	1¼ h.	5¾ h.
7.	3½ h.		1½ h.	10 h.	4 h.	23 h.	2½ h.	6¼ h.
8.	4 h.	20 h.	3 h.	10 h.	2¾ h.	22 h.	2 h.	6 h.
9.	½ h.	8 h.	3¾ h.	8 h.	¾ h.	12 h.	2 h.	6 h.
10.	quick		Slow only with 1 % KOH + 3 % $CaCl_2$:				(20′)	(2 h.)
11.	quick		2½ h.	7 h.	quick		1½ h.	6 h.

Table 53. Dissolving Velocity of Gypsum. Gypsum shaken with 100 ml H_2O at 21°.

Shaking time	100 % $CaSO_4 \cdot 2H_2O$	50 % $CaSO_4 \cdot 2H_2O$ 50 % $CaSO_4 \cdot \frac{1}{2}H_2O$	100 % $CaSO_4 \cdot \frac{1}{2}H_2O$
1 min.	2.365 g/l $CaSO_4$	4.600 g/l $CaSO_4$	8.518 g/l $CaSO_4$
5 »	2.351 »	3.475 »	7.973 »
10 »	2.361 »	3.099 »	7.325 »
15 »	2.358 »	2.896 »	4.157 »
60 »	2.358 »	2.555 »	3.067 »

Table 54. Dissolving Velocity of Lime. 0.6 g Lime shaken with 200 ml H_2O at 21°.

Shaking time	CaO from CaC_2O_4	$Ca(OH)_2$	Technical light burnt lime	Technical hard burnt lime	CaO from $Ca(NO_3)_2$	CaO from $Ca(OH)_2$
1 min.	0.994 g/l CaO	0.895 g/l CaO	0.952 g/l CaO	1.022 g/l CaO	1.022 g/l CaO	1.091 g/l CaO
5 »	1.063 »	0.952 »	1.049 »	1.078 »	1.092 »	1.245 »
10 »	1.109 »	0.993 »	1.119 »	1.129 »	1.148 »	1.258 »
15 »	1.133 »	1.006 »	1.152 »	1.162 »	1.175 »	1.256 »
25 »	1.175 »	1.035 »	1.203 »	1.203 »	1.216 »	1.256 »

Table 55. Composition of the Liquid Phase of Cement Mortar.

Shaking time	Technical, Gypsum-free Cement No. 11. Quick setting				Technical Cement No. 11 + 4 % Gypsum. Normal setting			
	mg ekv/litre				mg ekv/litre			
	CaO	K_2O	OH	SO_3	CaO	K_2O	OH	SO_3
1 min.	5.7	152	152	0	40.5	—	82	72
2 »	5.9	—	162	»	41.7	121	87	73
3 »	5.5	—	163	»	42.9	—	88	73
5 »	5.2	—	167	»	42.8	—	91	81
10 »	6.1	156	163	»	42.9	—	92	73
15 »	8.3	—	170	»	42.2	—	83	71
60 »	9.4	—	186	»	51.1	—	95	89
120 »	8.2	187	191	»	38.4	—	84	75

Table 56. Chemical Composition of the Liquid Phase of Cement Mortar—rapidly extracted.

Cement No.	Addition	Set	mg ekv per litre					mg/l
			CaO	K_2O	OH	SO_3	Cl	Al_2O_3
20	None	Quick	17	—	17	—	—	33
»	3 % active CaO	Slow	54	—	54	—	—	9
»	4 % gypsum	Slow	66	—	32	(34)	—	6
10	None	Quick	14	—	13	—	—	70
»	1 % KOH + 3 % $CaCl_2$	Slow	—	—	42	—	—	13
11	None	Quick	6	152	152	0	—	—
»	4 % gypsum	Slow	37	108	68	74	—	—
»	3 % $CaCl_2$ sol.	Slow	460	25	47	—	427	—
»	3 % active CaO	Quick	13	—	127	—	—	—

Table 57. Heat of Hydration.

Cement No.	Admixture	Calories per Gram after		
		3 d.	7 d.	28 d.
11	None	79	85	94
»	1 % $CaCl_2$	92	92	103
»	3 % $CaSO_4 \cdot 2$ Aq. + 1 % $CaSO_4 \cdot \frac{1}{2}$ Aq.	83	94	98
4	None	64	83	94
»	1 % $CaCl_2$	76	89	107
»	3 % $CaSO_4 \cdot 2$ Aq. + 1 % $CaSO_4 \cdot \frac{1}{2}$ Aq.	74	91	104
»	1 % cane sugar	23	27	32
6	None	67	90	97
»	1 % $CaCl_2$	89	99	111
»	3 % $CaSO_4 \cdot 2$ Aq .+ 1 % $CaSO_4 \cdot \frac{1}{2}$ Aq.	81	95	108
»	2 % KOH	72	76	86
»	1 % cane sugar	20	21	31

The soluble substances were dissolved in the gauging water, whereas the gypsum was ground in with the cement.

Table 58. Water Combination.—Firmly Fixed Water.

	Cement No. 10		Cement No. 11	
Addition	None	1 % KOH + 3 % $CaCl_2$	None	1% $CaSO_4 \cdot \frac{1}{2}$ Aq. +3% $CaSO_4 \cdot 2$ Aq.
Setting time	Quick	Slow	Quick	Slow
Time	%	%	%	%
10 min.	7.3	4.0	3.4	2.5
30 »	7.3	4.1	3.8	3.3
60 »	7.3	4.5	3.8	3.3
1 d.	13.4	15.0	8.3	9.2
2 »	16.4	15.5	11.9	13.9
3 »	18.6	17.0	13.9	—
4 »	—	—	—	15.9
5 »	19.6	18.3	16.2	16.6
6 »	18.6	19.2	16.2	17.3
7 »	17.7	—	16.7	16.4
28 »	22.6	23.0	—	—
44 »	—	—	19.7	18.4

Table 59 a. Setting Tests.

Addition	Cement No.	Initial	Final	Cement No.	Initial	Final
None	14[1]	Quick	—	1	2 min.	20 h.
1 % $CaSO_4 \cdot \frac{1}{2}$ Aq. + 3 % $CaSO_4 \cdot 2$ Aq.	»	3½ h.	7 h.	»	4½ h.	15 h.
1 % $CaCl_2$	»	2¾ h.	7 h.	»	1 h.	8¾ h.
9 % »	»	Quick, hot	—	»	Quick, hot	—
2 % $Ca(NO_3)_2$	»	3¾ h.	—	»	1 h.	15½ h.
9 % »	»	Quick, hot	—	»	5 min.	3¾ h.
2 % $Ca(NO_2)_2$	»	3¾ h.	9¾ h.	»	1½ h.	12 h.
2 % $CaBr_2$	»	2 h.	6½ h.	»	1¾ h.	6¼ h.
9 % »	»	45 min.	2¾ h.	»	7 min.	2¾ h.
3 % CaI_2	»	3½ h.	9 h.	»	6½ h.	9 h.
9 % »	»	1¾ h.	3¾ h.	»	2½ h.	7 h.
3 % CaO, active	»	Quick	—	»	1 h.	23 h.

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[1] Without gypsum.

Table 59 b. Setting Tests.

Addition	Cement No.	Initial	Final	Cement No.	Initial	Final
None	11	Quick	—	4	Quick	—
1 % $Ba(OH)_2$	»	2 ½ h.	9 ¼ h.	»	—	—
2 % $BaCl_2$	»	2 ¼ h.	5 ½ h.	»	3 h.	11 h.
2 % $SrCl_2$	»	2 ½ h.	6 h.	»	5 h.	12 ½ h
2 % $Mg Cl_2$	»	1 ¼ h.	4 ¾ h.	»	5 min.	9 ½ h.
4 % »	»	—	—	»	6 h.	8 ½ h.
2 % $Mg SO_4$	»	4 ½ h.	11 h.	»	10 min.	18 ½ h.
4 % »	»	—	—	»	12 h.	20 h.
2 % NaOH	»	¼ h.	5 ¾ h.	—	—	—
2 % KOH	»	1 h.	5 h.	—	—	—
None	21	6 h.	23 h.	—	—	—
1 % KOH	»	4 ¼ h.	12 ¼ h.	—	—	—
1 % KOH saturated with Al	»	Quick, hot	—	—	—	—

Table 60. Alkali-free Cements.

Swedish Standard Specifications.

Cement No.	% Gypsum added.	Strength in kg/cm²					
		Compressive			Tensile		
		2 d.	7 d.	28 d.	2 d.	7 d.	28 d.
1	5	237	380	558	26	33	43
2	5	269	370	614	27	33	47
3	2	272	398	599	31	35	48
	5	262	352	588	25	32	47
	8	248	338	581	16	26	44
4	5	297	416	577	27	37	47
5	2	330	441	597	35	39	46
	5	334	514	646	35	39	51
	8	268	427	550	24	33	37
6	2	387	533	607	40	44	45
	5	346	410	592	35	37	43
	8	264	450	586	23	31	39
7	2	386	584	616	36	36	48
	5	398	584	644	36	42	48
	8	285	436	596	21	32	44
8	0	282	451	559	29	33	36
	5	427	616	721	41	40	49
9	5	368	382	570	28	28	42

Table 61. Influence of Various Retarders on Cement No. 11.
Swedish Standard Specifications.

Retarder	Amount %	Strength in kg/cm^2					
		Compressive			Tensile		
		2 d.	7 d.	28 d.	2 d.	7 d.	28 d.
$CaSO_4$	4	328	480	496	33	33	39
	12	244	430	554	18	26	46
$CaCl_2$	2	362	517	574	32	40	42
$Ca(NO_3)_2$	2	298	432	470	31	36	33
$MgCl_2$	4	260	366	414	25	28	35
	8	138	180	202	21	26	30
	12	24	58	74	5	14	15
$MgSO_4$	4	308	500	510	29	34	46
	8	76	174	188	15	26	42
	12	32	40	54	11	17	11
$Ba(OH)_2$	2	251	388	430	31	33	30
$BaCl_2$	2	264	384	390	33	31	35
$Ba(NO_3)_2$	2	201	282	356	27	31	27
$SrCl_2$	2	272	395	448	28	33	31
$Sr(NO_3)_2$	2	224	312	410	32	33	31
None		213	320	355	25	38	35
$CaCl_2$ + KOH	5 0.5	401	558	618	28	36	38

Table 62. Influence of Sodium Hydroxide.
Swedish Standard Specifications.

Cement No.	% NaOH added	Strength in kg/cm^2					
		Compressive			Tensile		
		2 d.	7 d.	28 d.	2 d.	7 d.	28 d.
8[1]	0	427	616	721	41	40	49
8[1]	2	250	310	341	27	28	36
8[2]	0	282	451	559	29	33	36
8[2]	2	146	200	256	31	31	30
12	0	103	182	342	13	23	28
12	2	91	136	181	19	21	33
12	5	55	98	142	12	20	25
13	0	319	474	553	33	35	43
13	2	142	188	215	35	30	29
13	5	91	116	176	14	15	17
14	0	214	428	454	26	28	34
14	2	160	226	275	27	26	30
14	5	80	106	136	13	14	21
16	0	369	569	617	36	39	39
16	2	208	276	298	38	34	36
16	5	96	128	192	16	15	22

[1] With 4 % gypsum.
[2] Without gypsum.

Table 63. Compressive Strength of Concrete.

Cement No. 11—250 kg/m³. W : c = 0.70.

Addition	After curing			
	3 d.	7 d.	28 d.	90 d.
None	126	230	353	372
1 % $CaSO_4 \cdot \frac{1}{2}$ Aq. + 3 % $CaSO_4 \cdot 2$ Aq	225	327	420	467
1 % $CaCl_2$	167	264	421	480
1 % $Ba(OH)_2$	130	195	279	321
2 % $Mg\,Cl_2$	211	173	409	478
1.5 % $Mg\,SO_4$	187	261	407	463

Table 64. Compressive and Tensile Strength of Blast-Furnace Slag No. 19.

Swedish Standard Specifications.

Retarder	Amount %	Strength kg/cm²					
		Compressive			Tensile		
		2 d.	7 d.	28 d.	2 d.	7 d.	28 d.
Active lime $CaCl_2$	3 % + 2 %	127	280	398	17	27	34
Active lime $CaSO_4 \cdot 2$Aq. $CaSO_4 \cdot \frac{1}{2}$Aq.	3 % + 3 % + 1 %	117	240	304	19	39	30
$CaCl_2$ NaOH	5 % + 0.8 %	170	340	468	21	36	44
NaOH	2 %	122	162	226	22	35	32

Soluble salts were dissolved in the gauging water.
Gypsum was ground in with the slag.

Table 65. Influence of Humus.

Cement No.	Sand	Admixture	Strength in kg/cm²					
			Compressive			Flexural		
			2 d.	7 d.	28 d.	2 d.	7 d.	28 d.
13	Pure	—	55	190	328	16	37	52
13	Humus-containing	—	0	88	204	0	18	33
13	» »	1 % $MgCl_2$	93	160	252	30	35	38
13	» »	1 % $MgSO_4$	63	172	298	12	31	44
7	Pure	3% $CaSO_4 \cdot 2H_2O$	81	203	353	19	37	58
7	Humus-containing	»	46	150	249	11	25	39

The pure sand was obtained by washing the humus-containing sand with caustic soda and water.

The specimens were prepared from plastic mortar.

Table 66.

Shaking time 3 months	"C_2A"-Melt in Lime Sol.	"C_2A"-Melt in Lime-Gypsum Sol.	C_4AF-Cryst. in Water	C_4AF-Cryst. in Lime Sol.	C_4AF-Cryst. in Lime-Gypsum Sol.	C_3S-Cryst. in Water	C_3S-Cryst. in Lime Sol.	β-C_2S in Lime Sol.	β-C_2S in Lime-Gypsum Sol.	β-C_2S in Lime —5% $CaCl_2$-Sol.
Solid phase............mg	284.0	593.3	122.1	252.2	346.0	86.6	227.5	236.4	256.7	274.2
Loss on drying........mg	15.6	132.0	13.5	5.4	42.1	26.8	30.7	5.5	8.6	10.2
» » ignition....... »	70.8	63.8	18.9	12.9	22.8	10.1	33.0	5.9	13.6	18.7
CaO................. »	117.3	222.0	11.2	124.6	152.0	31.6	110.5	151.5	164.8	163.2
SiO_2................. »	—	—	—	—	—	17.7	52.8	70.0	69.8	70.0
Al_2O_3................ »	79.4	96.4	11.6	41.4	40.7	—	—	—	—	Cl = 11.3
Fe_2O_3................ »	—	—	66.5	67.4	67.4	—	—	—	—	—
SO_3 before ignition .... »	—	77.5	—	—	19.5	—	—	—	0.0	—
SO_3 after » .... »	—	77.0	—	—	19.5	—	—	—	0.0	—
Total	283.1	591.4	121.7	251.7	344.5	86.2	227.0	232.9	256.8	273.4
% Conversion..........mg	89.4	50.4	83.8	4.8	12.7	100.0	56.7	0.0	6.0	12.6
Dissolved CaO......... »	—13.9	—118.6	80.0	—33.4	—60.8	115.4	36.5	—21.3	—34.6	—33.0
Dissolved SiO_2......... »	—	—	—	—	—	35.3	0.2	0.0	0.0	0.0
Dissolved Al_2O_3........ »	16.8	0.0	29.8	0.0	0.7	—	—	—	—	—
Dissolved Fe_2O_3 .... »	—	—	0.7	0.0	0.0	—	—	—	—	—

Discussion.

Mr. C. PONTOPPIDAN:[1]

When we turn to the achievements and experiments of colloidal chemistry, it is noticeable that a great deal of experimental work has been done on the organic colloids like the proteins but very little work has been done with the silicates. When we turn the pages of the latest text books, we find certain few references to silica gel and aluminum hydroxide, but we find no mention of cement or calcium silicates on a single page. Yet, everybody will admit that with hydrated cement we have to do with one of the most important colloids in the technical world.

It may perhaps not be out of the place here to refer to some of the more important experiences from the field of the proteins and see what evidence we can find that some of the rules governing the precipitation of these colloids can be applied to the setting and the hardening of Portland cement and aluminous cement.

The rules governing the coagulation or precipitation of the proteins from a disperse colloidal solution are by no means very clear; neither can they be applied generally; certain distinct tendencies stand out, however.

We see, for example, that coagulation can be brought about by the electrolytes in solution, so that if we have to do with a negative gel the coagulation is brought about by absorption to the gel of some of the positive ions in solution, and if we have to do with the positive gel by the negative ions.

We further see that the coagulating power of an ion sometimes, but not always, is governed by the valence of same, so that the divalent ions have a much stronger coagulating power than the monovalent.

We further see that it is not always that the coagulating power of an ion depends on the valence of same, but we often find that the order of coagulating potency of the various ions in question follows a certain sequence without regard to the valence. For precipitation of certain proteins we may find *e. g.* that lithium precipitates stronger than sodium, sodium stronger than potassium, and potassium stronger than magnesium ions, and for precipitation of a positive gel we may find that chlorine precipitates stronger than nitrate, and nitrate acts stronger than sulphate. In colloidal chemistry these series of precipitating ions are called the "HOFFMEISTER"-series.

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[1] Ing., F. L. Smidth & Co., A/S, Vestergade 33, København, Denmark.

It is not only the ions of opposite electric charge, which are of importance in connection with precipitation of the gel. Also the ions of the same electric sign as the gel play an important role; these ions act as contra-ions restraining the influence of the ions of opposite sign. If, for instance, we have to do with precipitation due to calcium ions, and we also have chlorine ions in solution, these will tend to restrain the action of the calcium ions. Also here the valence rules hold good to a certain extent, so that for instance sulphate ions in many cases would have a stronger restraining influence on the action of the calcium ions than would the chlorine ions because of the higher valence of the sulphate ion. It is not quite clear whether this restraining action exists in the adsorption of both kinds of ions by the diffuse double layer of the colloid, but, at any rate, it seems certain that the contra-ions exert an important impeding influence on the coagulation.

We further see when it comes to coagulation of a protein gel that the P_H-concentration of the solution is of importance; precipitation takes place when the P_H-concentration approaches the isoelectric point; in other words if we have a colloidal disperse solution with a high P_H-value we will have to lower the P_H-value to some point on the basic side, but near the isoelectric point before precipitation can occur, and *vice versa,* if we have a colloidal disperse solution with a low P_H-value we have to heighten the P_H-value to a point still on the acid side but near the isoelectric point before coagulation can take place.

We further see that some of the proteins are ampholytes, meaning that when we are on the basic side of the isoelectric point the gel is electro-negative and precipitated by the cations at a point near the isoelectric and if we are on the acid side of the isoelectric point the gel is electro-positive and coagulated by the anions when we increase the P_H-value to a point near the isoelectric.

We further see that it is possible to coagulate the gel by adding another gel, which is of opposite electric sign.

Finally, the concentration of the gel solution and of the electrolytes is of much importance in connection with coagulation as higher concentration begets quicker coagulation.

I would now like to raise the point how far some of these experiences from the organic colloids can be applied to the setting and hardening of Portland cement and aluminous cement.

I would like first to turn to the question of the P_H-concentration of the serum, which is obtained by filtering a paste of cement and water at normal consistency. The composition of this serum has been investigated by several investigators; we ourselves, meaningt hereby the laboratories of F. L. Smidth & Co., have through a number of years investigated many cements in this way. It may be recalled that the serum always contains considerable amounts of alkalies besides calcium sulphate and calcium hydroxide in solution. For alkali-free cement without gypsum we only find calcium hydroxide in solution. For cement of the Portland cement type the serum contains hardly any silica and alumina, but for aluminous cement the serum contains a certain small amount of calcium aluminates.

The P_H of this serum has been measured by several investigators. We have quite some years ago investigated the P_H of the serum of six different commercial cements and also the serum of an alkali-free cement made in the laboratory. The P_H was measured by special electrode giving very quick results, and it was measured directly after the paste was made up with water and then again of the serum filtered off, when the pat began to show initial set. In five cases out of six we found a raise in the P_H-value although with some of the cements only a slight one. This would seem to indicate that the P_H-value is of certain importance in connection with the setting of the cement and the well known fact that the set is quickened when we heighten the P_H-value by adding sodium or potassium hydroxide may perhaps be taken as a confirmation of the measurements during setting.

We are then entitled to say that there are certain indications that the coagulation of the gel of calcium silicates and calcium aluminates does not take place until we approach a definite P_H-concentration in the serum. We can also say that if this was a rule it would be in accordance with the precipitation of lyophile organic colloids by an electrolyte.

In the serum of commercial Portland cements we have in solution the three positive ions: calcium, potassium, and sodium, and the two negative ions: sulphate and hydroxyl. Let us for the time being think of the cement with no or a very slight amount of calcium aluminates, so that the hydrated product only consists of hydrated calcium silicates. If the disperse gel of these silicates is electro-negative we will expect precipitation from the three named positive ions and we would rather expect that the divalent calcium ions would have a much stronger coagulating power than the monovalent potassium and sodium ions. On the other hand, if the gel of calcium silicates is electro-positive we would expect coagulation from the two named negative ions and rather a much stronger coagulation by the divalent sulphate ions than by the monovalent hydroxyl ion. While it is generally assumed that the silica gel itself is electro-negative, I have found no reference to the electric charge of calcium silicates. It seems to me that there is a certain evidence in favour of both of these theories.

If we take it to be electro-negative we should find that an increase in the concentration of positive ions and particularly the divalent calcium ions would accelerate the setting due to coagulation. Certain of the facts about the setting of Portland cement seem to strengthen this believe. If we take an ordinary Portland cement without any gypsum it sets quickly due to the fact that alkalies go into solution; as already said the cause of the quick set may perhaps be the heightening of the P_H-value. When we add the gypsum, the alkalies are instantly transferred to sulphates and we get no heightening of the P_H-value. In this case the action of the gypsum on the setting time is largely to neutralize the action of the alkalies, and the ion effect of the gypsum is therefore obscured.

The true action of gypsum on Portland cement we see when we add gypsum to alkali-free cement. These cements have, as you already will know, a very long setting time, although we have with some of them found a slight stiffening of the pat, when it is made up; by adding gypsum the setting time is reduced to normal. This fact may perhaps be taken as evidence that the addition of gypsum brings about an increased concentration of divalent calcium ions and, therefore, coagulation and setting. In this case the sulphate ion will act as a contra-ion and because this ion also is divalent it will have a considerable restraining effect on the action of the calcium ion.

Our experiments with alkali-free cements have shown that if instead of calcium sulphate we add calcium chloride or calcium nitrate we get a stronger and quicker action and this may be interpreted as showing that because the chlorine and nitrate ions are monovalent their restraining action as contra-ions is less strong than the action of the sulphate ion, for which reason the calcium ions are able to act stronger in the form of calcium chloride or calcium nitrate than it is in the form of calcium sulphate.

If we have to do with an alkali-free cement without any addition of electrolytes, such as calcium sulphate, the coagulation of the gel should then be brought about slowly by an increase in P_H-concentration and in the calcium ion concentration, if we assume that the gel is electro-negative and the hydroxyl ions would then be the contra-ions.

What I have said here is about all the evidence I can find for the theory that the calcium silicate is an electro-negative colloidal gel, and I think perhaps that there is as much evidence or more pointing to the believe that the gel is electro-positive and not electro-negative.

Let us return to the action of gypsum on an alkali-free cement. As stated the setting time is shortened very much by the addition of gypsum, but it is quite possible to say that the coagulation is brought about not by the increase in calcium ion concentration but by the presence of negative divalent sulphate ions acting on a positive gel. As the divalent sulphate ion often has a much stronger coagulating action than a monovalent hydroxyl ion we should expect a shortening of the setting time by the addition of sulphate ions, if we assume the gel to be electro-positive. Our tests show that an addition of sodium sulphate to alkali-free Portland cement acts stronger than gypsum, which also may be taken as evidence that the concentration and valence of the anions are important for the coagulation of the gel. As the contra-ion here is sodium, which is monovalent, we would expect the sulphate ion from sodium sulphate to act stronger than the sulphate ion from calcium sulphate. Again, if we add sodium chloride to an alkali-free cement we get quicker setting than by the addition of gypsum, but not so quick a set as by the addition of sodium sulphate and this would be in accordance with the valence rule and might further be taken as evidence that it is the anions, which are of importance in connection with coagulation of the gel from calcium silicates.

There is another observation rather pointing to the belief that the calcium silicate gel is electro-positive and that is the observation that coagulation takes place when the P_H-value is increasing, going from a more acid to a less acid value. That would rather point to coagulation by the anions and not to coagulation by the cation, if we take the examples from coagulation of proteins.

It seems to me that, whether we assume the hydrated calcium silicates to be electro-negative or we assume them to be electro-positive, we cannot get all the evidence to fit the theory and I am content to leave it at that. There seems to be a considerable amount of research work to do in this connection.

When we turn to the aluminous cement, the hydrated product is largely hydrated tricalcium aluminate or tetracalcium aluminate and aluminum hydroxide. The latter compound is an important part of the hydrated product, and of the aluminum hydroxide we know that it is amphoteric, meaning that it is sometimes electro-negative and sometimes electro-positive; however, prevailingly it is thought to be electro-positive. If nothing is added to the aluminous cement made into a paste we would then get a slow increase in P_H-value and at the same time a slow increase in the concentration of calcium, hydroxyl, and monoaluminate ions. We may then assume that, when a certain P_H-value is reached, we get coagulation by means of hydroxyl ion or if the gel is negative by the calcium ions.

If we now add gypsum to aluminous cement we get quicker setting due to the addition of divalent sulphate ions, if we assume that the aluminum hydroxide is electro-positive. If, however, we assume the aluminum hydroxide to be electro-negative the effect of the gypsum would be to give an increase in the concentration of calcium ions and thereby coagulation and setting.

About aluminous cement we further know that a small addition of calcium hydroxide or Portland cement also makes it quick-setting and this may be explained by the increase in P_H-value due to this addition and further to the concentration of calcium ions or hydroxyl ions according to what charge we assume the aluminum hydroxide to have. Our measurements show that P_H-concentration is going up in the serum from aluminous cement from the time the pat is made to initial setting occurs, and these measurements tend to confirm the experimental evidence that an increasing P_H-value from calcium hydroxides or alkali hydroxides to a point approaching the isoelectric brings about coagulation or setting. The fact that the coagulation occurs when the P_H-value is moving from a more acid to a less acid value strengthens the believe that the coagulation is brought about by the negative ions and that the hydrated aluminous cement therefore, as a whole, is electro-positive, even if it perhaps contains electro-negative silicates.

It is with the aluminous cement as with the Portland cement, I think the evidence, which we have, is not sufficient to decide what is the sign of the electric charge of the colloidal particles. I think, however, there is something which speaks for the idea that the electric sign of the hydrated aluminates as a whole is opposite of that of the hydrated calcium silicates. What I have in mind is the fact that a small addition of aluminous cement makes Portland cement quick-setting. I think that if we accept the evidence from other fields of the colloidal chemistry we may explain this phenomenon by the action of two gels, precipitating one another because they are of opposite electric sign. If the aluminum hydroxide is electro-positive it would instantly precipitate the gel of hydrated calcium silicates, if this was electro-negative, and *vice versa.* We would in that case to some extent get a similar reciprocating action with the hydration of Portland cement, which contains both silicates and aluminates

Mr R. H. BOGUE:[1]

Our laboratory has been interested in the reactions of cements with water and in retarders and some years ago we made a study of what we call "false set"—that condition where a surface hardening develops, but wherein the final set throughout the specimen is actually not obtained. We found two conditions that might appear in commercial operations for causing false set. One was the dehydration of the gypsum during the grinding process occurring when the temperatures became too high. Usually it was found that when water was run over the grinding mill the temperatures could be kept down to a point where the dehydration of gypsum did not occur, and consequently the false set, which was really a plaster set, did not take place.

Another condition that may give rise to false set is the presence of alkalies in the form of carbonate. When they are in the form of hydroxide or silicate, or other combinations—as perhaps the prismatic phase, the alkali does not

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[1] Dr., Research Director, Portland Cement Association Fellowship at the National Bureau of Standards, Washington, D. C., U. S. A.

give rise to a false or flash set. But the alkali carbonate which may be formed during storage in the presence of water vapour and carbon dioxide of the air appears to react with the lime and the calcium hydroxide of hydrolysis giving rise to a condition of false set.

It may be of interest to give you a résumé at this time of what we have found on the effects of glass on certain properties of the cement, as that is a proper consideration for the topic being discussed. I shall use data obtained on the 23 commercial clinkers to which I referred yesterday, each clinker of which had been so treated that we had 3 portions of each, one low glass, one high glass and one of intermediate glass which was the original clinker. Those clinkers were ground to cements of a uniform size distribution and a uniform gypsum content and test specimens prepared in the usual way. We have the compressive strength, the tensile strength, the length changes in water and air and perhaps some other tests, but these extend at the present time—or at the time I had this information—only through 28 days. However, it is interesting to note that the quickly cooled, high glass clinkers gave very generally the higher strengths at 7 and 28 days. At earlier ages there was no material difference. That was true of both the compressive and the tensile strengths. The expansions in water were not materially affected by this different heat treatment or by glass content. In some cases the free lime increased or was greater in one of these preparations than in another and the free lime content materially affects the expansions in water but, eliminating that effect, there was no apparent difference observed by the glass content. However, the quickly cooled clinker, high glass content, shows the lowest contraction in air, in comparable conditions.

In examining those data we observed that the differences in strength between the quickly cooled and the slowly cooled clinkers were inappreciable with the low $Al_2O_3 : Fe_2O_3$-ratio cements; with the high $Al_2O_3 : Fe_2O_3$-ratio cements the differences between the quickly cooled and the slowly cooled clinkers were relatively large, the quickly cooled having the higher strengths. And the third group that we have taken in this analysis, that is, of intermediate glass content, shows also intermediate differences between those two groups.

Mr A. EIGER:[1]

If you will permit me, Gentlemen, I will say a few words in connection with the remarkable reports presented by Dr. FORSÉN and Mr. BESSEY, from the point of view of the cement manufacturer and the cement user.

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[1] Dr.-Ing., Mazowiecka 7, Warszawa, Poland.

It is, I think, of extreme importance for us to know what is the nature of the gel, which we consider chiefly responsible for the cement properties in practical use, starting within a period of some days after the beginning of hydration. It seems most important to know whether the gel we get by hydration of C_3S and by hydration of C_2S is the same gel. It is somehow different from that what we are used to know about gels, what the German scientists call their "history" being considered as determining their properties. In this case the history is quite different, the hydrate of C_2S being obtained by a surface reaction while this of C_3S is a product of precipitation from solution. It is very difficult to have any direct evidence and so we can only judge by their physical properties—and I beg to apologize to you, Mr. President, when I make a little excursion into a further report—but all the tests we made attempting to find a figure for the hydration whether it was water retained or

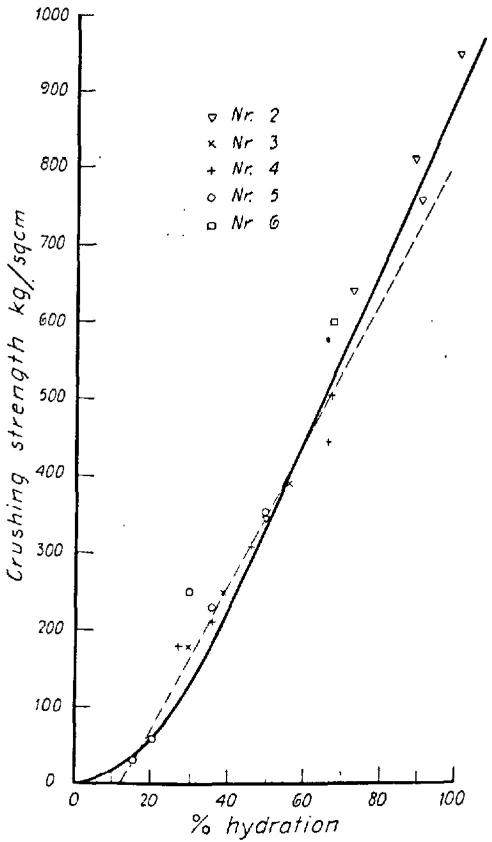

Fig. 1.

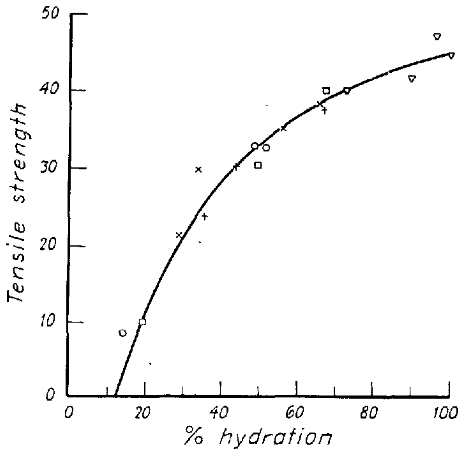

Fig. 2.

change of specific gravity plotted against tensile strength, elastic properties (not on synthetic mixes but on cement) varying from cements which had a potential crystallization of C_3S equal to zero up to a very high content of C_3S and very little C_2S we always found the same relation. (FIGS. 1 and 2.) From this we might say that in all cases we have to deal with the same gel. In order to check once more the author's method, a cement was tested and its strength plotted against hydration rate. Then it was reground most finely as to give the following granulometric composition:

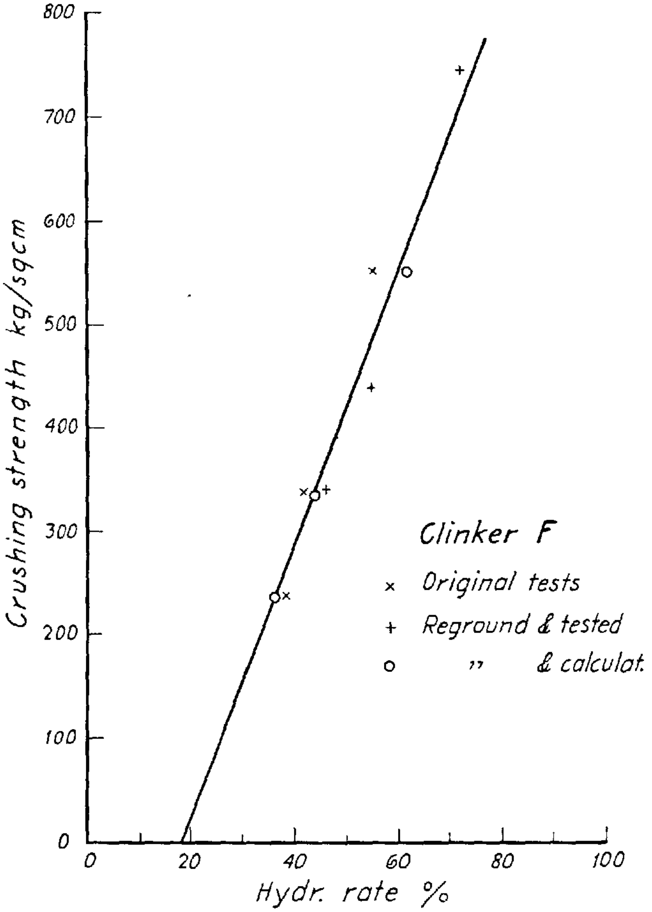

FIG. 3.

Grains smaller than microns	90	64	32	16	8	4	3
%	99.3	96.4	88	63.1	38.4	22.5	13.3

The strength obtained with this cement and the points calculated according to the author's method lay very closely on the straight line, which, for usually hydration rates (up to 70 %) is a good substitute for the curve (FIG. 3).

I think we will not be very far from truth if we say that the action of compounds of iron, alumina, and alkalies is of two kinds. In the first phase of hydration these compounds which, according to former experience, seem to hydrate quicker than the silicates can affect the strength of the cement paste by forming fluffy precipitation or gel layers on the silicate paste.—In the former period, when crystallized, they seem to act merely as a filler in the silicate gel.

I am not convinced that this gel has the proportion that Mr. Bessey stated, because, if we try to form a gel, starting with C_3S_2, we probably get no strength of any kind. This is another reason why I think that the composition given by Dr. Forsén is correct as to the proportion of C and S. It has been confirmed by some experiences on C_3S carried out by Mr. Rogoziński and myself.

Regarding the water content proposed by Dr. Forsén, I understand that it is practically impossible to talk of the water content of a gel because, roughly speaking it is depending on the hygrometric state of the air and so we can say that it has on Monday a different water content than on Saturday. But if it were so as Dr. Forsén stated, it would mean that for every per cent of silica present in cement we would need 1.2 per cent water merely to hydrate the silicates. That would mean, for an average cement, if we say that it is hydrated up to 80 %, which is the usual rate—it will come to 20—22 % only for the hydration of the silicates, leaving nothing for the hydration of compounds that take much more proportion of water than silicates do. For this reason, I think that the amount of water eliminated between 105° and 1 000° from hydrated C_2S, which we found to be (between 120° and 1 000°) 1.5 mols., lies about 2 molecules of water, and I hope we will be able to say something more definite about it as soon as we will know the exact composition and possible structure of the gel.

Mr F. M. Lea:[1]

Dr. Forsén's paper forms an outstanding contribution to our knowledge of the retardation of cements.

The theory that rapid setting is in all cases accompanied by the accumulation of alumina in solution, followed by the precipitation of an "alumina-silica gel" of relatively low lime content, affords a coherent explanation of a wide number of otherwise disconnected observations which are to be found in the literature.

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[1] D. Sc., F. I. C., Building Research Station, Garston, Herts, England.

The theory seems well established from the evidence put forward in Dr. FORSÉN's paper, but the mechanism of the action by which retarders precipitate the alumina merits some further discussion.

From the data of TABLE 56 it appears that quick set takes place when the concentration of alumina in solution rises to some value between 13 and 33 mg per litre. Similarly the results given in TABLES 3—35 show that the percentage hydration in 30 minutes of alumina-containing compounds is relatively high ($>$ 20 per cent) when the concentration of alumina in solution exceeds some 10—15 mg per litre, and that in the cases where retardation is most effective the value is only a few milligrams per litre.

When calcium hydroxide is the only retarder present, a lime-solution concentration above 0.5 g CaO per litre is required for effective retardation (TABLES 55 and 56). It is of interest to compare these values with the curve for the solubility of $3CaO \cdot Al_2O_3 \cdot 6H_2O$ given in FIG. 2 of Mr. BESSEY's paper to the Symposium. With this compound the solubility of alumina remains low—only a few milligrams per litre—down to a lime concentration of about 0.4 g CaO per litre, but at lower lime concentrations it rises rapidly. Since in the setting cement some degree of supersaturation with respect to alumina may occur, the critical lime concentration for alumina solubility—in the absence of other calcium salts—found by Dr. FORSÉN is in general agreement with Mr. BESSEY's solubility data.

In the presence of KOH the solubility of lime drops below 0.5 g CaO per litre when the KOH-concentration rises above about 0.3 per cent, and, as such a concentration is rapidly established in alkali-containing cements, retardation by lime alone becomes impossible. It will be noticed, however, (TABLE 13) that the hydration of the "C_2A-melt" is retarded considerably in higher concentrations of KOH, *e. g.* 2 per cent, and this may be linked with the observation (TABLE 59 b) that a 2 per cent KOH-solution effectively retarded the commercial cement No. 11. The mechanism of this effect of KOH at higher concentrations is not clear. In the case of the cement it is possible that the "alumina-silica gel" becomes more soluble and is not precipitated preferentially to the calcium aluminate and silicate hydrates.

The mechanism of the action of calcium salts—and particularly calcium sulphate—in producing retardation may be discussed, as it appears to the writer that the retardation is to be ascribed primarily to the precipitation of the complex salts of the type of the calcium sulpho-aluminates. Though Dr. FORSÉN seems in part to accept this explanation, in one or two cases (*e. g.* p. 312 for "KCA"-melt) he suggests that the effect of gypsum may be ascribed to the formation of supersaturated calcium hydroxide solutions, by reaction of the gypsum with the alkali hydroxide liberated from the cement, and that this favours the precipitation of hydrated calcium aluminates. The theory that the prime effect of gypsum is to cause precipitation of $4CaO \cdot Al_2O_3 \cdot Aq.$ has been advanced by Mr. ROLLER. Measuring the concentration of calcium hydroxide in the mixed electrolyte as the mean molality of the $Ca^{\cdot\cdot}$- and OH'-ions, there is however no indication that the solutions obtained, even at the earliest period, are supersaturated. Thus, if the data of TABLE 55 are examined by calculating the mean molality of the calcium hydroxide and the ionic strength of the solution, and the result compared with Mr. ROLLER's curve (Bibl. No. 40) for mean molality plotted against ionic strength for calcium hydroxide, it is found that for cement No. 11, with or without gypsum, the points[1] obtained fall only slightly above Mr. ROLLER's curve. It is evident that no appreciable supersaturation with calcium hydroxide occurs, and that when the $CaSO_4$- and KOH-solutions interact there is immediate precipitation of calcium hydroxide leaving only its saturated solution.

When no gypsum is present and the solution contains only KOH and saturated calcium hydroxide, both derived from the cement, Dr. FORSÉN finds, with cement No. 11 for example, that alumina accumulates in solution and rapid set occurs. The addition of gypsum raises the concentration of $Ca^{\cdot\cdot}$-ions in solution, reduces the OH' in concentration and sets up an SO''_4-ion concentration which, by calculation of the mean molality, can be shown to correspond to a saturated solution of $CaSO_4$ in the mixed electrolyte. At the same time alumina is precipitated from the solution and slow setting occurs. From knowledge of the conditions necessary for precipitation of $4CaO \cdot Al_2O_3 \cdot Aq.$ it seems doubtful if such a change would favour precipitation of this compound. Thus with KOH the amount of alumina obtained in solution from "C_2A-melt" (TABLE 13) increases as the OH'-ion concentration decreases. The precipitation of alumina, when gypsum is added to alkali-containing cements, must, it seems, be ascribed primarily to the formation of calcium sulpho-aluminate. There is however one other point. The formation of the "alumina-silica gel" will depend on the amount of silica, as well as of alumina, in solution, and FORSÉN has shown (TABLES 36—39) that lime is much more effective than gypsum in keeping the silica in solution low. The presence of lime, as well as gypsum, may be essential therefore on this account.

In the past it has generally been thought that the high sulphate form of calcium sulpho-aluminate, and not the monosulphate compound, is formed in the setting of cement. The evidence now put forward by Dr. FORSÉN, and also by Professor SCHLÄPFER, indicates that the monosulphate compound is

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[1] For cement No. 11 with 4 per cent gypsum the mean molality of $Ca(OH)_2$ at 2 minutes is 0.054 mols. per litre and the ionic strength of the solution 0.22. For the same cement without gypsum the corresponding values at 10 minutes are 0.043 and 0.165. Both values fall slightly above ROLLER's curve, but the calculated ionic strengths will be a little low since they are calculated from the analyses given in TABLE 55 which do not cover all the ions in solution.

formed. Investigations at the Building Research Station have shown that only $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot Aq.$ exists at 25° as a stable phase in the aqueous system $CaO\text{-}Al_2O_3\text{-}CaSO_4\text{-}Al_2(SO_4)_3$ and that the monosulphate compound does not occur. LERCH, ASHTON and BOGUE, in agreement with this, found that the monosulphate compound, when placed in water, saturated $CaSO_4$, or saturated $Ca(OH)_2$, tended to change to the high sulphate form. In 3 per cent NaOH-solution, however, the monosulphate compound remained stable, and it is to the effect of the increased hydroxyl ion concentration that the formation of the monosulphate compound with alkali-containing cements can be attributed. With the evidence at present available it is not safe to assume that the monosulphate compound is always formed in the setting of cements for the conditions necessary to render it stable may not exist in all cement solutions; variations in OH'-ion concentration, for example, may result in some cases in precipitation of the high sulphate compound. The present findings open an interesting field for further research on this point.

The influence of high concentrations of calcium chloride and other calcium salts in causing rapid setting may be attributed to an increase in the alumina solubility, after passing through a minimum in the regions where slow setting occurs, but data on this are at present lacking. Alternatively the formation of calcium oxychloride and similar compounds at these high salt concentrations may be the cause of quick set.

The observation that the addition, in large amounts, of magnesium salts, causes a decrease in strength may perhaps be attributed to the formation of hydrated magnesium silicates of lesser cementing power than the calcium compounds. It is known that the combination of magnesia and hydrated silica to form a hydrated magnesium silicate produces little cementing action.

Although in quick setting the initial rapid reaction of the alumina compounds causes a retardation of the hydration of the silicate compounds, owing, as Dr. FORSÉN shows, to formation of coatings of the "alumina-silica gel", the effect of this disappears after some days. This may be seen from the values for combined water given in TABLE 58, and suggests that the film is dissolved as slow hydration of the C_3S gradually builds up a saturated lime solution. This would be anticipated from the results in TABLE 44.

The experiments showing the effect of humus and sugar solutions (TABLES 11 and 12) in increasing the amount of alumina in solution relate to "C_2A-melt" without gypsum. It would be of interest to know if the effects were similar when gypsum was present and if quick setting was observed, and also whether commercial cements show a corresponding behaviour.

Mr. G. E. BESSEY:[1]

Dr. FORSÉN has, in the course of the work discussed in his report, shown that various hydrated compounds are precipitated from the unstable solutions initially formed on hydration of the cement compounds and he has applied these results to the complex system, Portland cement. Whilst in many cases the assumption that the same compounds are formed may be correct, it requires experimental proof, for the other components may have a profound influence upon the equilibria and upon the stability of individual compounds.

The silicates may be mentioned here specifically. The dicalcium silicate hydrate gel, prepared by Dr. FORSÉN, has been found by the present writer to be stable only in saturated lime solution at normal temperatures. It seems that depression of the solubility of lime by other components in the solution in contact with the setting cement may render this compound unstable, and lead to formation of the less basic compound $3CaO \cdot 2SiO_2 \cdot xH_2O$. Dr. FORSÉN has shown (DIAGRAM 17) that the solubility of lime is rapidly depressed by alkalies in solution; the proportion of alkali in cement is sufficient to give a high concentration in the water mixed with cement, and the lime solubility is depressed very considerably.

Results have been reported by the present writer (Professor SCHLÄPFER'S Report. Discussion p. 285) of tests on completely hydrated cements of widely differing composition which indicate that the silicate is present as the compound $3CaO \cdot 2SiO_2 \cdot xH_2O$ in these samples. This, and some similar results mentioned by Professor SCHLÄPFER, are in accord with the foregoing argument, and suggest that the dicalcium compound does not normally exist in set Portland cement.

Mr. P. S. ROLLER:[2]

A correct mechanism of setting is important for controlling the property of setting, particularly in view of the recent introduction of finely ground high-strength Portland cement that is prone to quick set. Succinctly, FORSÉN'S theory of setting is predicated on the solubility of the calcium aluminates. The retarding action of added calcium salts is attributed to the formation either of insoluble tetracalcium aluminate or of an insoluble double salt of calcium aluminate and the added calcium salt.

When the aluminates are soluble, they coagulate with the soluble silicates

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and quick setting ensues. The effect of water vapor is to form a protective film of hydrated cement; its retarding action is apparently considered different from that of the added calcium salts.

FORSÉN's conclusion that retardation is due to the formation of protective tetracalcium aluminate is in agreement with deductions arrived at by the writer.[1] In other respects, however, our deductions differ radically.

Let us consider three general facts of setting. The first of these is that, when cement is quick-setting, calcium sulphate is not to be found in the liquid phase even though calcium sulphate may have been added to the cement. Conversely, when cement is slow-setting, calcium sulphate is present in the liquid phase even though no calcium sulphate may have been added to the cement. This general observation shows that formation of the double salt, calcium sulphate aluminate, is not associated with slow-setting, but rather with quick-setting.

A second fact is that an excess of calcium chloride or sulphate (the latter in much less amount than is required for rapid stiffening by the plaster of Paris reaction) causes the setting to change from slow to quick. FORSÉN explains this by assuming that the excess calcium salt lowers the P_H to such an extent that the aluminates are dissolved. Examination of the liquid phase shows, however, that the P_H is actually higher than that corresponding to slow-setting. Furthermore, in spite of the excess calcium salt, little or none is to be found in solution. Here, again, is evidence that the formation of double salt is associated with quick-setting.

Finally, reference is made to the general fact that while about 1 per cent water vapor slows the setting, a greater amount progressively speeds it (at constant addition of mixing water). This phenomenon is not explicable in the simple hypothesis that water vapor acts by forming a protective film of hydrated cement.

These facts and many others may be explained by a theory developed by the writer on the basis of the known properties of the compounds in cement and experiments with commercial cements. As this theory has been set forth in the publications mentioned, no description will be given here; suffice it merely to state that the theory is a unitary one inasmuch as the action of added calcium salts and of water vapor is traced to the same cause.

Experiment has shown that the concentration of calcium aluminate is actually higher during quick-setting than during slow-setting. However, at best, the solubility is very low (as would be expected from the approximately lime-saturated state of cement liquor); neither the aluminate nor silicate solubility is great enough to give rise to a significant mass coagulation. The

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[1] Ind. and Eng. Chem., 1934, *26*, 669, 1077; 1936, *28*, 362. U. S. Bureau of Mines Technical Paper 578 (1938).

changes in calcium aluminate solubility conform to the changes in calcium hydroxide concentration. They are considered by the writer to be merely a reflection of the latter and therefore, in accordance with the theory, a reflection of changes in setting time.

MR. A. TRAVERS:[1]

Mechanism of the Setting of Metallurgical Cements.

I would like to draw the attention to the following work carried out at the Faculté des Sciences de Nancy.

1. To study the mechanism of metallurgical cements we attempted first of all to define the rôle of the slag *alone.*

It is known that this sets very slowly (several months are required) in ordinary temperature; if one utilizes the reaction of *water-vapour* in the autoclave (15 kg) for about 10 hours, one obtains very important compressive-strengths (of the order of 230 kg). The X-ray analysis shows a very clear crystallization; no lime is shown, which is confirmed still more precisely by the chemical analysis (glycol test, SCHLÄPFER's method).

The same slag re-heated to 800° does not set.

The pure β-dicalcium silicate, hydrated in the same conditions in the autoclave, also sets; the product obtained, when examined by X-rays, appears very well crystallized, as in the previous case, and it, too, shows no free lime.

We were unable to identify the two products.

We are, however, of the opinion that the setting of the slag in the autoclave is due to the hydration pure and simple of the β-dicalcium silicate, since this slag, when *re-heated* or slowly re-cooled, does not set (change to γ-silicate).

These facts force us to admit that despite the solidity, the constituents of *equilibrium* of the slag are formed, at least in part, after the solidification. The region of basic slags in the SiO_2-Al_2O_3-CaO-diagram, indicates in fact, of the number of constituents in equilibrium, the dicalcium silicate.

The poor conductibility of the slag would explain that the cooling had only been superficial. This would only serve to maintain in the β-state, that is to say in the hydraulic state, the dicalcium silicate.

2. We then attempted to understand the rôle:

   a) of the clinker—or of the lime,
   b) of the calcium sulphate.

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The above experiments having led us to think that the constituent foreseen in the diagram of *equilibrium* might be admitted, *at least in part,* one may predict as the second constituent of equilibrium of the slag the Gehlenite, $2CaO \cdot SiO_2 \cdot Al_2O_3$.

We investigated the question as to whether the influence of the lime and of the calcium sulphate, which act as "excitants", could not be traced to the reaction of the two bodies on this third product.

The curves of fixation of $CaSO_4$ by the slag and by the Gehlenite have the same course.

The presence of lime, which acts as a source of OH-ions—or of clinker, which liberates lime during the setting—accelerates the fixation of $CaSO_4$.

What is the mechanism of this fixation? We have not been able to explain it clearly.

The *concomitant* diminution of the $Ca(OH)_2$- *and* the $CaSO_4$-content leads one naturally to think of the formation of the sulpho-aluminate of CANDLOT, derived from the *tri*calcium aluminate. This hypothesis has frequently been put forward.

As a matter of fact we have not been able to show *free* aluminate in the slags from the region of Lorraine (see contribution to the discussion on Dr. SUNDIUS' paper) which is still in accordance with the diagram of equilibrium. If this salt already exists in a slag this would only be on account of a *false* equilibrium, something that is, moreover, not impossible.

An interesting remark has been made by several authors: at the moment of its setting, metallurgical cement *darkens* in consequence of the formation of FeS. The sulphur contained in the slag—CaS—appears to be in a "complex" state, that is to say "concealed" from its reagents, in particular from the property of dissolving in water. Dr. KAEMPFE had supposed that it is a matter of a compound of addition, "aluminate-sulphide". It is possible that under the action of the P_{II} (liberation of lime by the clinker) and of $CaSO_4$, this complex dissociates and liberates the aluminate, which would enable its reaction on $CaSO_4$.

This hypothesis explains nothing, for it would be necessary to show why the combination dissociates. One may assume equally that there is dissociation of the Gehlenite, as follows:

$$2CaO \cdot SiO_2 \cdot Al_2O_3 = CaO \cdot SiO_2 + CaO \cdot Al_2O_3,$$

but this hypothesis is equally gratuitous.

It is, however, in any case, impossible, in cement that has set, to recognize *under the microscope* the sulpho-aluminate, although the latter is very characteristic. It is true that one might find a double salt differing from that of CANDLOT (salt at $30H_2O$), showing for example a different hydration.

It is, however, necessary to add that in favour of the hypothesis of the formation of the double salt the following fact may be adduced: when metallurgical cement, finely ground (0 g 5) and *having set* is treated with boiling water (boiling for 5 to 10 minutes), there passes into solution a certain quantity of aluminate.—*(Translated from French.)*

Mr. L. FORSÉN *(author's closure):*

Mr. P. S. ROLLER considers that the retarding influence of gypsum is effected through reaction with the readily soluble alkaline compounds contained in the cement. The dissolved gypsum reacts with alkali hydroxide and forms calcium hydroxide and alkali sulphate. The former precipitates a protective film of tetracalcium aluminate, which retards the following reactions.

The neutralizing influence of gypsum on solutions from alkali-containing cements, experimentally demonstrated by ROLLER, has been verified by me (TABLE 55). I have also verified—analytically and synthetically—the formation of a protective film of tetracalcium aluminate when anhydrous calcium aluminates react with lime-water. This fact was first established—microscopically—by ASSARSSON. In my paper I have also shown that quick setting alkali-free cements can be controlled with lime (see TABLE 52). In this case the retardation is evidently brought about through the precipitation of a protective film of tetracalcium aluminate.

With regard to the action of gypsum I cannot agree with Mr. ROLLER. To me it appears to be clearly established by experiments that the double salt $3CaO \cdot Al_2O_3 \cdot 1CaSO_4 \cdot 12H_2O$, and not the tetracalcium aluminate, is precipitated. Among others the following reasons support this opinion:

1. Quick setting *alkali-free* cements can be rendered normal setting with interground gypsum or with diluted calcium salt solutions (TABLE 52). In this case a formation of calcium hydroxide is out of the question.

2. When cement sets normally the gypsum, which is soluble in lime-water, is combined to a double salt, insoluble and resistant in lime-water. Ordinarily, all the gypsum is rapidly consumed. If an excess of gypsum is present, the amount of combined SO_3 approaches the molecular proportions $1Al_2O_3 : 1SO_3$ (see DIAGRAM 18).

3. When a solution of calcium aluminate is combined with a solution of lime and gypsum calcium aluminate sulphate is precipitated.

4. According to Prof. P. SCHLÄPFER's paper the hydration of pure tricalcium aluminate is effectively retarded by gypsum dihydrate. Microscopically a protective layer of $3CaO \cdot Al_2O_3 \cdot 1CaSO_4 \cdot 12H_2O$ can be seen surrounding the C_3A-grains.

5. Alkali-free, quick setting cements, retarded with lime, require an abnormally long time to reach their final set, whereas the same cements, retarded with gypsum, behave normally.

From experiments with burnt gypsum (plaster of Paris) Mr. ROLLER has drawn general conclusions as to the action of gypsum. It is necessary, however, to take into consideration that the dihydrate and the semihydrate, which latter is four to five times more soluble, behave quite differently. In technical cements a mixture of the two hydrates is generally present. The solubility of such a mixture rapidly approaches that of the dihydrate (see TABLE 53).

Solutions of gypsum dihydrate and of gypsum semihydrate show a considerable difference with respect to their ability to dissolve aluminates. In a dihydrate solution (TABLE 6) the same solubility is obtained as in a 5 % calcium chloride solution saturated with lime (TABLE 9), whereas the solubility in a semihydrate solution (TABLE 7) is as great as in a 30 % calcium chloride solution saturated with lime (TABLE 9).

In the diluted $CaCl_2$-solution normal set occurs whereas the concentrated $CaCl_2$-solution renders the cement quick setting.

A technical quick setting cement (No. 11, TABLE 51) was rendered normal setting with dihydrate and with a mixture of dihydrate and semihydrate (3:1) but was quick setting with varying amount of semihydrate (1—15 %). In this case the gypsum apparently behaves quite differently if it is present as di- or as semihydrate. The dihydrate controls the set, but the semihydrate does not. The same phenomenon has been demonstrated by Mr. ROLLER. E. CANDLOT has shown that normal setting, gypsum-free cement can be rendered quick setting with semihydrate. CANDLOT, and later also ROLLER, has shown that gypsum rapidly disappears from the solution in the case of cement made quick setting with semihydrate.

As seen, the gypsum acts on cement quite differently if it is present as di- or as semihydrate. This is due to the fact that the difference in solubility gives rise to different reactions with the aluminates. Two different calcium aluminate sulphates are known—$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31^1/_2 H_2O$ and $3CaO \cdot Al_2O_3 \cdot$ $\cdot 1CaSO_4 \cdot 12H_2O$.

From preparative work it was earlier known that the trisulphate is readily formed—well crystallized—from aluminate solutions containing much gypsum and a fairly small amount of lime. The monosulphate, on the other hand, is precipitated in pure form only if the calcium aluminate solution is combined with a lime-rich gypsum solution.

Microscopical examinations, carried out with the kind aid of Dr. N. SUNDIUS of the Swedish Geological Survei, on C_3A-crystals and "C_2A"-melt show the influence of different gypsum solutions on the reactions of the aluminates. In water, pure C_3A was rapidly hydrated, forming gel of alumina and hexagonal crystals of tetracalcium aluminate and of aluminium hydroxide (FIG. 2). In a solution of gypsum dihydrate the C_3A-crystals were immediately surrounded by a border consisting of $3CaO \cdot Al_2O_3 \cdot 1CaSO_4 \cdot 12H_2O$ in finely crystalline form (FIG. 3). The transformation of the grains proceeded slowly. In a supersaturated solution from gypsum semihydrate, on the other hand,

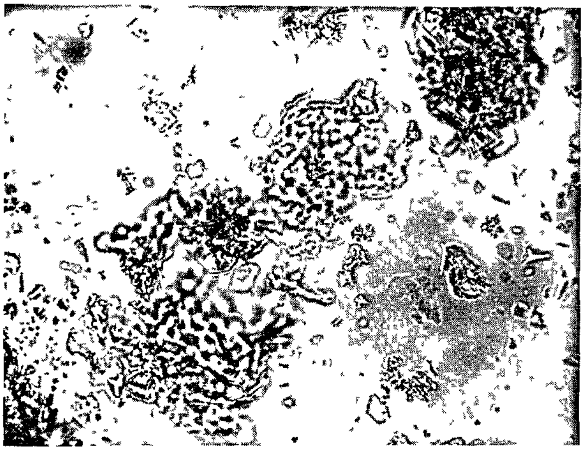

FIG. 2. C_3A in Water.

Observations:
$C_4A \cdot Aq.$ $\alpha = 1.510$, $\gamma = 1.531$ opt. neg. hex.
$Al(OH)_3$ cryst. $\alpha = 1.536$, $\gamma = 1.591$.
$Al(OH)_3$ gel $1.591 < n < 1.610$.

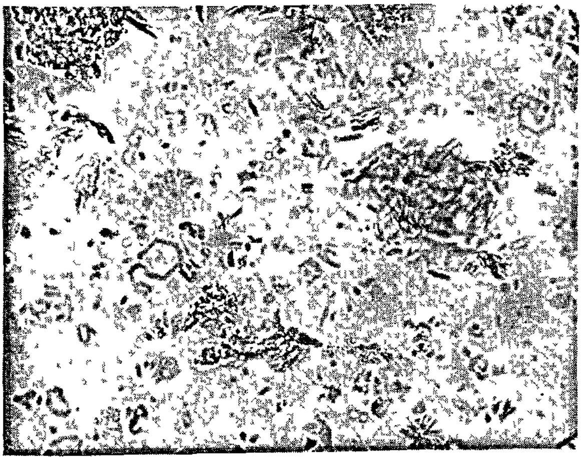

FIG. 3. $C_3A + CaSO_4 \cdot 2H_2O$ in Water.

Observations:
$C_3A \cdot CaSO_4 \cdot 12H_2O$ $\alpha = 1.499$, $\gamma = 1.517$ opt. neg. hex.

the C_3A-grains were rapidly dissolved and transformed into Ettringite, $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31^1/_2H_2O$, which crystallized out of the solution (FIG. 4).

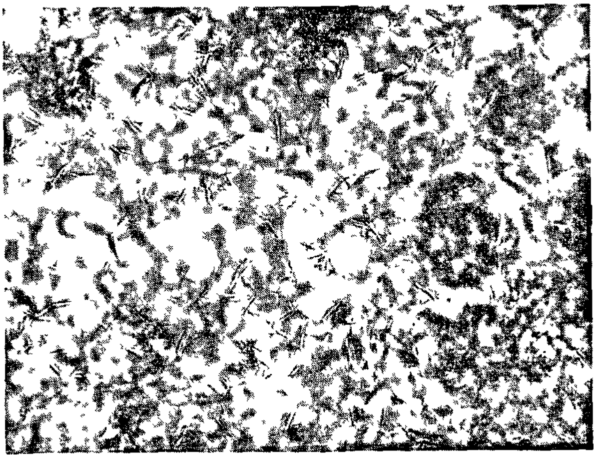

FIG. 4. $C_3A + CaSO_4 \cdot {}^1/_2H_2O$ in Water.
Observations:
$C_3A \cdot 3CaSO_4 \cdot 31^1/_2H_2O$ α and $\gamma \sim 1.469$.

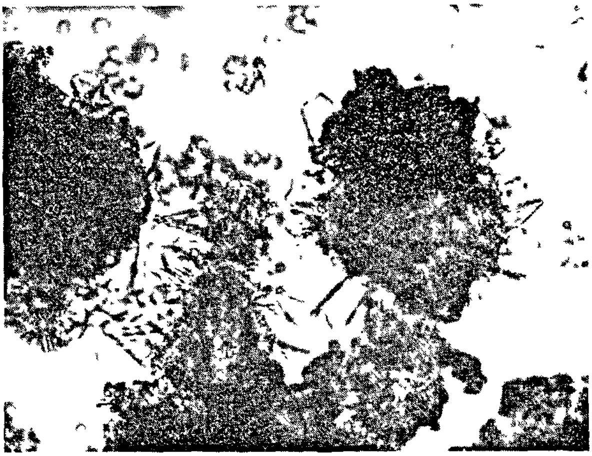

FIG. 5. $C_3A + Ca(OH)_2$ in Water.
Observations:
$C_4A \cdot Aq.$ $\alpha \sim 1.500$, $\gamma < 1.536$ opt. neg. hex.

Thus, at low gypsum concentration (dihydrate) a retarding film of monosulphate was formed, whilst at high concentration (semihydrate) the aluminate dissolved and the trisulphate crystallized—without forming a protective film.

In a saturated lime solution the C_3A-grains were rapidly surrounded by a border of tetracalcium aluminate (FIG. 5). In a saturated lime solution saturated with $CaSO_4 \cdot 2H_2O$ the transformation proceeded very slowly. The same was the case with a saturated lime solution supersaturated with $CaSO_4 \cdot \frac{1}{2}H_2O$, which solution contains 7.5 g $CaSO_4$ per litre. The formation of tetracalcium aluminate or Ettringite could not be established. Newly formed products observed, consisted of the monosulphate (FIG. 6). Thus, as the aluminates are dissolved, the monosulphate, being almost insoluble in lime-water, is precipitated as a retarding film around the aluminate grains. The lime content of the solution accordingly increased the retarding effect of gypsum dihydrate and rendered the semihydrate retarding.

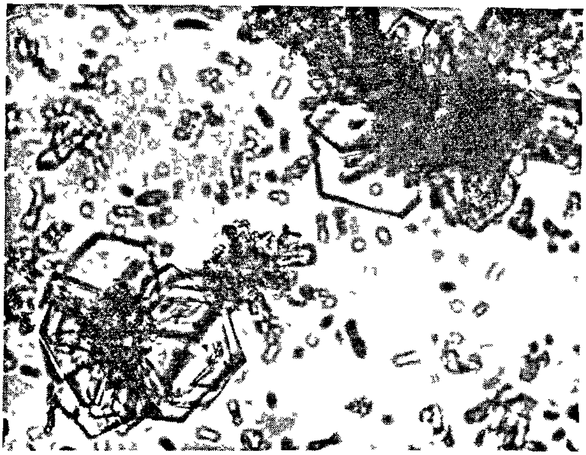

FIG. 6. $C_3A + CaSO_4 \cdot 2H_2O + Ca(OH)_2$ in Water.
Observations:
$C_3A \cdot CaSO_4 \cdot 12HO_2$ α and $\gamma \sim 1.505$ opt. neg. hex
$Ca(OH)_2$ $\alpha = 1.544$, $1.575 < \gamma < 1.580$ opt. pos.!! hex.

The ability of the lime to increase the retarding effect of gypsum on C_3A is also elucidated by the known phenomenon that certain quick setting cements can be controlled by means of a small addition of lime. Such cements are, for instance, some quick setting cements with too low a content of gypsum, some gypsum-containing cements with too low a lime content, and some cements which are quick setting with gypsum semihydrate.

Mr. ROLLER also discusses the question of the influence of calcium chloride, and he considers that an excess of this salt causes quick set because a double salt is formed. Against this opinion I would point out that small amounts of calcium chloride, even with alkali-free cements, precipitate a double salt and control the set, further, that large amounts of calcium chloride dissolve aluminates and cause quick set. [TABLES 9, 59 a, FORSÉN (19), FIGS. 7 and 8]. The ability of calcium chloride to lower the P_H-value of a saturated lime solution is evident from TABLE 50 (saturated lime solution 12.7, saturated lime solution with 5 % and 30 % $CaCl_2$ 12.1 and 11.3 respectively).

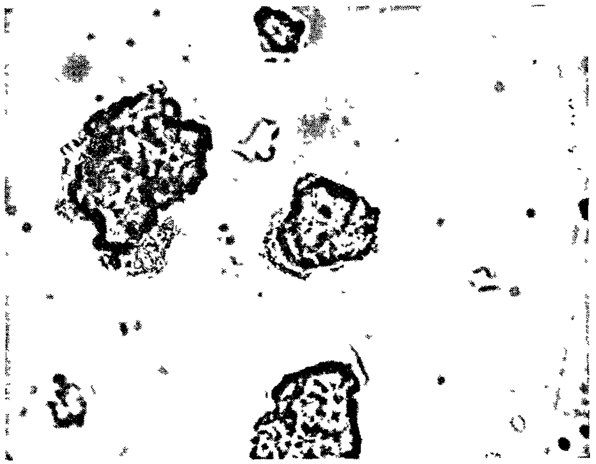

FIG. 7. C_3A in 5 % $CaCl_2$-Solution.
Observations:
$C_3A \cdot CaCl_2 \cdot 10H_2O$ as border α and $\gamma \sim 1.532$.

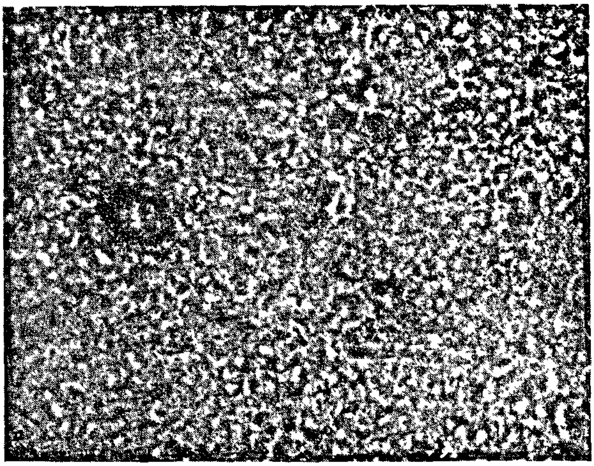

FIG. 8. C_3A in 30 % $CaCl_2$-Solution.
Observations:
$Al(OH)_3$ gel n high.

The retarding influence of aeration on cement is considered by Mr. ROLLER to depend on the liberation of a certain amount of lime, which later precipitates tetracalcium aluminate from the solution. Against this conception it may be pointed out that the set of alkali-containing cements cannot be controlled with lime owing to the solubility of lime being greatly reduced in the rapidly formed solution of alkali hydroxide. Nevertheless, such cements can be retarded through seasoning in moist air. When reground, however, they are again quick setting, which clearly indicates that on aeration a protective coating of hydrated cement is formed around the grains. On regrinding, the coatings are destroyed and new surfaces are exposed.

Mr. ROLLER has tried to explain the action of moisture and carbon dioxide as causing, sometimes an activation, sometimes a deactivation of the silicates and the aluminates. As the cements investigated by Mr. ROLLER contain much alkali, it is probable that the influence of moisture and carbon dioxide is connected with the formation of alkali carbonates. It appears to me that the results found by Mr. ROLLER could be explained as follows. When the cement is aerated for a short time a protective film of hydrated cement is formed, whilst after prolonged seasoning a considerable amount of readily soluble alkali carbonate is formed, which later precipitates calcium carbonate from the solution. Lack of lime in the solution then causes quick set.

When studying the reactions between cement and water and the influence of gypsum on these reactions, it is necessary to pay attention to the composition of the cement—not to forget the alkalies which are of dominating importance—and to distinguish between the different kinds of gypsum. As demonstrated, the solubility, the physical structure and the topo-chemical properties of the newly formed compounds play a fundamental part when the cement grains react with water.

Dr. R. H. BOGUE conceives the action of burnt gypsum as plaster set. This explanation, which would be the simplest, is one in which I have also believed. Some facts, however, demonstrated by E. CANDLOT and by P. S. ROLLER and also verified by me cannot be explained in the way Dr. BOGUE suggests. Gypsum-free cements rendered normal setting through aeration become quick setting on addition of burnt gypsum. The gypsum immediately disappears from the solution and in some cases the quick set is even accompanied by a considerable liberation of heat. As I have pointed out in my answer to Mr. ROLLER, the aluminates are dissolved in a supersaturated gypsum solution if its lime content is low. From the resulting solution Ettringite crystallizes without forming a protective film. In the presence of dihydrate or semihydrate and lime in solution, on the other hand, a film of almost insoluble monosulphate is formed.

The carbonic acid forms, as Dr. BOGUE remarks, alkali carbonate that precipitates calcium carbonate. The lime content of the solution is in that way lowered to such an extent that the aluminates can dissolve and cause quick set through coagulation with the silicates.

The different phenomena at the setting of cement, as I understand it, can be explained by the following chemical reactions:

False quick set.

$$\mathrm{3CaO\cdot Al_2O_3+3[CaSO_4\cdot \tfrac{1}{2}H_2O]+30H_2O \longrightarrow 3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 31\tfrac{1}{2}H_2O}$$

large crystals

Normal set.

$$\mathrm{3CaO\cdot Al_2O_3+CaSO_4\cdot 2H_2O+10H_2O \longrightarrow 3CaO\cdot Al_2O_3\cdot 1CaSO_4\cdot 12H_2O}$$

crystals as film

$$\mathrm{3CaO\cdot SiO_2+5H_2O \longrightarrow Ca_2SiO_4\cdot 4H_2O}$$

microcrystalline

Quick set.

$$\mathrm{3CaO\cdot Al_2O_3+Aq.} \longrightarrow \text{Calcium aluminate solution}$$

$$\mathrm{3CaO\cdot SiO_2+Aq.} \longrightarrow \text{Calcium silicate solution}$$

$$\text{Silicate solution} + \text{Aluminate solution} \longrightarrow x\mathrm{Si(OH)_4}\cdot y\mathrm{Al(OH)_3}\cdot z\mathrm{H_2O}.$$

coagulate

Dr. BOGUE refers to some strength tests on clinkers cooled in different ways. These results are in the best agreement with a fact which I have shown (19), *viz.* that more C_3S is formed at rapid cooling then at heating to final equilibrium. Of special interest is also that smaller differences were found when the A:F-ratio was low. This is in agreement with my observation that final equilibrium is rapidly reached at low A:F-ratio.

Dr. A. EIGER deals with question of the mechanism of reaction when C_3S and C_2S are hydrated, and shows that the amount of combined water in the set product is the same for cements with varying contents of these compounds, which indicates that the mechanism of reaction is similar for both. From my own investigations I find this quite probable, as C_3S as well as C_2S reacts in such a manner that firstly the components enter into solution. Obviously the same product $C_2S\cdot Aq.$ is precipitated from the lime-rich solutions formed.

Dr. EIGER also discusses the water content of the calcium orthosilicate. We have found the composition $C_2S\cdot 4H_2O$ after 2—3 hours of drying at 105°. DIAGRAM No. 21, which shows the loss of water at isobaric dehydration, indicates the existence of a tetrahydrate in the crystallites that form the gel. The examined preparations of $C_2S\cdot 4Aq.$, however, all contain traces of carbonic acid and this might cause some error in the results. Further experiments with preparations free from carbonic acid will be conducted.

R. H. BOGUE and WM. LERCH (10) have gauged C_3S with water and stored the specimens for 2 years. In a sample dried at 105° for 24 hours the amount of water combined with the silicate (12.4 %) was twice as great as that combined in the calcium hydroxide (6.2 %). This seems to indicate that a dihydrate of

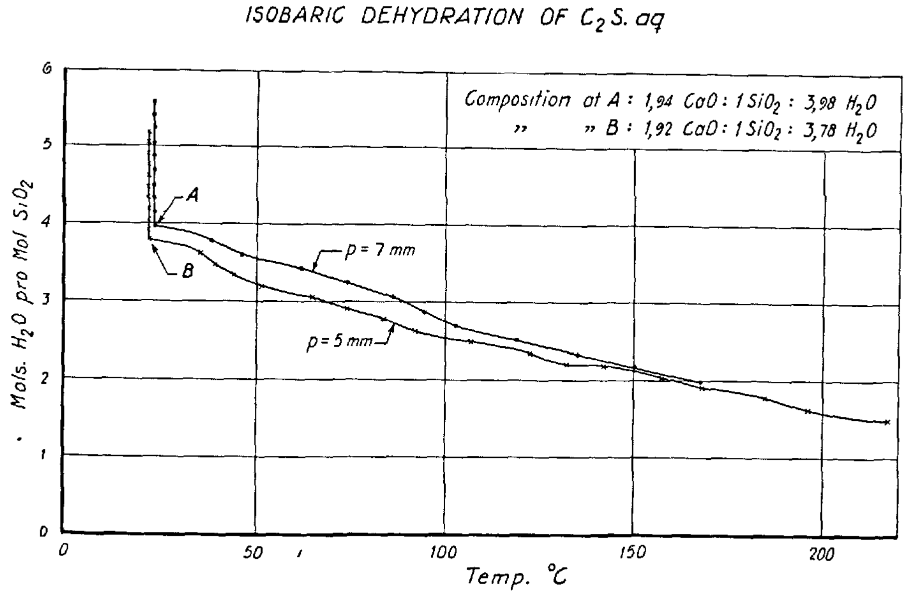

Diagram 21. Isobaric Dehydration of $C_2S \cdot Aq$.

the C_2S is stable at these drying conditions. In a C_3S-preparation, treated with water for 3 months and then dried for a long time in vacuum at 105°, we found a water content corresponding to the formula $CaSiO_4 \cdot 2H_2O$.

These investigations, which will be continued, indicate the existence of two calcium orthosilicates, *viz.* one with $4H_2O$ and one with $2H_2O$.

As it is shown that the cement glue has a definite stoichiometric composition, it is very likely that the compound is crystalline, although no crystals could be detected microscopically. An X-ray examination carried out by Dr. W. Büssem of the Kaiser-Wilhelm-Institut shows, however, a diffraction pattern (Diagram 22). In Table 67, which has been placed at my disposal by Dr. Büssem, X-ray data on various calcium silicate hydrates have been compiled from works by Chassevent, Foret, Strätling and Brandenberger. A marked similarity between the different preparations seems to exist.

Diagram 22. Diffraction Pattern of $C_2S \cdot Aq$.

The conception of Le Chatelier as to the cause of the hardening of cement has been strongly supported by our experimental work. Thus, we have found that tricalcium silicate dissolves in unchanged stoichiometrical proportions in water and forms a supersaturated solution from which submicroscopic crystals of calcium orthosilicate are precipitated. As LE CHATELIER assumes, the hardening of cement accordingly occurs in a like way as the hardening of burnt gypsum.

Table 67. X-Ray Investigation on Calcium Silicate Hydrates compiled by Dr. W. BÜSSEM.

No.	1. d.	1. Int.	2. d.	2. Int.	3. d.	3. Int.	4. d.	4. Int.	5. d.	5. Int.
1	—	—	3.9	WW	—	—	—	—	—	—
2	3.10	SS	3.0	SS	3.06	SS	3.03	SS	3.02	SS
3	2.78	S	2.8	M	2.8	M	2.76	W	2.77	W
4	2.47	—	2.5	M	2.48	W	2.49	W	2.46	W
5	2.26	—	2.3	M	—	—	—	—	2.29	W
6	2.07	—	2.1	M	2.14	W	2.09	W	2.09	M
7	2.03	—	1.95	M	2.01	W	—	—	—	—
8	1.90	—	1.90	M	—	—	—	—	1.92	W
9	1.85	—	1.85	W	—	—	—	—	1.87	W
10	1.82	—	—	—	1.82	S	1.82	M	1.82	W
11	1.66	M	1.64	M	1.66	M	1.69	W	1.65	W
12	1.58	—	—	—	—	—	—	—	1.58	W
13	1.52	—	1.54	M	1.52	W	—	—	1.52	W
14	1.39	—	—	—	1.40	M	—	—	—	—
15	1.19	—	—	—	1.18	WW	—	—	—	—
16	1.07	—	—	—	1.07	W	—	—	—	—

1. CHASSEVENT, L. — Compt. rend. 1934, *199*, 673.
2. FORET, JEANNE. — Compt. rend. 1936, *203*, 82; 1937, *204*, 977.
3. STRÄTLING, W. — Dissertation Braunschweig 1937. — Zement 1938.
4. BRANDENBERGER, E. — Schweiz. Arch. f. ang. Wiss. u. Techn. 1937, *3*, 239.
5. FORSÉN, L. — Symposium Stockholm 1938, $Ca_2SiO_4 \cdot 4H_2O$.

d. = planar spacing; Int. = relative intensity; SS = very strong; S = strong; M = medium; W = weak; WW = very weak.

Dr. F. M. LEA considers that an aluminate sulphate and not tetracalcium aluminate is formed when the set of cement is controlled with gypsum. As is evident from my paper and from my answer to Mr. ROLLER, I quite agree with Dr. LEA on this point.—The tetracalcium aluminate is precipitated when alkali-free cements are controlled with lime. This reaction is of interest for explaining the chemistry of the setting-time control, but when gypsum is present it does not occur until the gypsum is precipitated.

The alkali content of a cement undeniably plays an important part at the control of the setting time. Through reaction between liberated alkali hydroxide and added gypsum or other calcium salts the solution is immediately saturated with lime—initially it may even be supersaturated before equilibrium is reached through the precipitation of $Ca(OH)_2$. In such a lime solution the aluminates are slowly dissolved and then precipitated as $3CaO \cdot Al_2O_3 \cdot 1CaSO_4 \cdot 12H_2O$.

Dr. LEA also touches upon the question of the composition of the sulphate formed when alkali-free cements are controlled with gypsum.—In one experiment an excess of gypsum dihydrate was added to an alkali-free cement. After 14 days it was found that an amount of gypsum was combined that corresponds to the formation of the monosulphate ($0.95SO_3 : 1Al_2O_3$). This experiment as well as the microscopical investigations referred to in my answer to Mr. ROLLER indicates that the monosulphate is formed when cement sets normally.

Alkali hydroxide and also barium hydroxide are to some extent able to control the set, but the strength obtained is very poor. The solubility of the aluminates is that much lowered that quick set does not occur. Some alumina is dissolved, however, and this is probably precipitated as alumina-silica gel. Pure C_3A is very slowly hydrated in a 2 % KOH-solution—microscopically no newly formed products could be seen even after 2 days. From a calcium aluminate solution tetracalcium aluminate was precipitated when a baryta solution was added and, when a potassium hydroxide solution was added, a precipitate containing $Ca(OH)_2$, KOH and Al_2O_3 was formed. Thus, it seems as if the setting time was controlled by these basic solutions in about the same manner as when an alkali-free cement is controlled by lime.

The quick set obtained with calcium chloride in high concentrations depends on the solubility of the aluminates in such solutions [FORSÉN (19), TABLE 9].

Dr. SUNDIUS (49) has shown that the gypsum disappears from the solution when humus is present. Obviously this depends on the fact that large amounts of aluminates enter into solution, just as the case is when "C_2A" reacts in sugar or humus solutions. With technical cements to which large amounts of sugar have been added I have also noticed flash set.

Quick set, evidently, must be considered to be the resultant of two different actions, firstly, the rapid dissolution of the aluminates and, secondly, the reactions between the dissolved aluminates and other substances present in the solution. In the most common case of quick set of gypsum-free cement, dissolved aluminates and silicates coagulate forming a lime-poor alumina-silica gel. At quick set with gypsum semihydrate the dissolved aluminates are precipitated partly as Ettringite. In the presence of humus and possibly also sugar a part of the aluminates is precipitated as sulphate.

The most important factor of quick set is that the aluminates quickly enter into solution. At the dissolution and hydration heat is liberated. The amount of heat liberated depends on whether reaction-checking precipitates are formed or not.

Mr. G. E. BESSEY considers that the silicate formed when technical cement reacts with water has the composition $C_3S_2 \cdot Aq.$, and not $C_2S \cdot Aq.$ as I have stated.

Mr. BESSEY has shown that calcium orthosilicate is stable in saturated lime-water. Accordingly it is natural that this compound is formed from pure C_3S as P. SCHLÄPFER and I have found.

When a technical cement reacts, however, an alkali hydroxide solution is formed in which the solubility of lime is greatly reduced, and Mr. BESSEY justly remarks that no data are available as to the stability of silicates in such solutions.

To throw some light on this point the following experiment was carried out. A solution was prepared by shaking 2 grams of C_3S in a 2 % KOH-solution. After filtering, 0.5 g of $C_2S \cdot Aq.$ was introduced and the whole was shaken for 72 hours. The solid phase was then examined and found to consist of unchanged $C_2S \cdot Aq.$ containing no free lime. This experiment indicates that $C_2S \cdot Aq.$ is also stable in such alkali-containing solutions as may be formed from cement.

Mr. BESSEY makes an attempt to deduce the composition of the silicates by calculations based on the determination of free lime in set cement. This procedure, however, seems to me to be rather uncertain, more especially because the quantitative estimation of free lime is of doubtful accuracy. In the extraction method the $C_2S \cdot Aq.$, if formed, is decomposed to $C_3S_2 \cdot Aq.$, and with respect to the calorimetric method it is probably necessary to investigate whether $C_2S \cdot Aq.$ and the other hydrates are stable at 550°.— Furthermore, it is difficult to ascertain whether the reactions are fully completed. C_4AF, C_2F and the ferrite-containing glass react extremely slowly in saturated lime-water, and therefore I believe it is rather uncertain that these compounds—as Mr. BESSEY assumes—should be quantitatively transformed into respectively $C_4A \cdot Aq.$, $C_3A \cdot Aq.$ and $C_3F \cdot Aq.$ The gypsum is probably combined as monosulphate and not as trisulphate. Finally it is assumed by Mr. BESSEY that the calcium carbonate emanates from the free lime. This is rather doubtful. Owing to their structure it is likely that the calcium silicates are just as rapidly—or probably more rapidly—attacked than the crystals of calcium hydroxide.

Mr. BESSEY also refers to an experiment by Prof. SCHLÄPFER. In a set mixture of C_3S and C_3A more free lime is present than there would be if $C_2S \cdot Aq.$ had been formed. In this case, however, quick set has probably occurred and a quantity of a lime-poor gel of aluminium hydroxide and silicic acid has been formed.

As the estimation of the degree of hydration and the amount of free lime is extremely uncertain, and as we do not know which compounds are attacked by the carbonic acid, it appears to me that, for the present at any rate, an investigation of the formation and stability of the pure hydrates offers the best prospect of explaining the reaction products of cement. The fact that

C_3S with water forms strongly supersaturated lime solutions in which the calcium orthosilicate is stable indicates, it seems to me, that this compound is formed when cement sets normally.

Prof. A. Travers takes up the question of the reactions of slags. On the strength of earlier work and of results from my own experiments I believe that the reactions occurring between slag and water can be explained in the following way.

Rapidly cooled slag contains calcium silicates and calcium aluminates in a non-crystallized glass. When the finely pulverized slag is mixed with water the silicates and the aluminates rapidly enter into solution. A gel of aluminium hydroxide and silicic acid is instantaneously precipitated around every grain, and the reaction is effectively checked. In the presence of lime, or lime and gypsum, or lime and calcium chloride in a low concentration the solubility of the aluminates is greatly reduced and the small amount of dissolved aluminate is immediately precipitated around the grains as a film, which moderately retards the reactions. The film consists of tetracalcium aluminate or double salts with $CaSO_4$ or $CaCl_2$. The deleterious quick-set reaction does not occur and the silicates are not prevented from gradually entering into the solution, from which a lime-rich silicate is precipitated forming the cementing glue. Probably the same compound is formed as when Portland cement reacts with water.

It appears to me that the different phenomena met with in the chemistry of slags can be explained on the basis of this theory. For instance, Professor Travers asks why slag mixed with lime or Portland cement combines with gypsum so much more rapidly than slag without this addition does. The reason for this is that the aluminates are soluble in lime-free gypsum solution. Consequently, aluminates and silicates are abundantly present in the solution and a precipitation of an almost impermeable film occurs. The reactions, including the combination of the gypsum, are almost completely checked. If, on the other hand, the solution contains lime, the solubility of the aluminates is greatly reduced and the reactions proceed normally.

To verify my theory I have carried out the experiments described in my paper. It was especially interesting to test the most effective retarder—a mixture of NaOH and $CaCl_2$, the latter in a small excess. With this mixture a basic solution is obtained in which the aluminates have a low solubility and a low rate of hydration whilst the conversion of the silicates is rapid. Normal set and very good strength was obtained, which, I believe, confirms my conception of the mechanism of the setting of slags.

Mr. PONTOPPIDAN, in an interesting contribution, brings forth colloidal-chemical views on the reactions between cement and water. The reaction which occurs at quick set is, in my opinion, a typical colloidal reaction consisting in a coagulation of silicate and aluminate solutions. This coagulation can easily be demonstrated by dropwise introducing a solution of alkali aluminate into an alkali silicate solution. I have also shown that coagulation occurs between calcium aluminate and calcium silicate solutions. The gel formed contains a small amount of lime, but consists chiefly of aluminium hydroxide and silicic acid in varying proportions. It is also known that colloidal silicic acid (negative colloid) and aluminium hydroxide (positive colloid) coagulate each other.

Although the reactions at quick set are accordingly of typical colloidal character, the normal set seems to be effected through the formation of supersaturated solutions with subsequent precipitation of hydrates in crystalline or subcrystalline form. It appears to me that the colloidal theory, firstly advanced by MICHAËLIS, applies to quick set conditions only, whereas LE CHATELIER's theory of crystallization from supersaturated solutions is of general validity at normal set.

Without entering into particulars concerning the colloidal-chemical problems discussed by Mr. PONTOPPIDAN, I must say that it does not seem possible to me to explain most phenomena of retarders and accelerators with the aid of colloidal chemistry. Many of the laws and rules of the colloidal chemistry are not valid for colloidal silica solutions, as for instance the dependence of the valence on the coagulation power of ions. For that reason I believe it is more appropriate to try to solve the problems of retarders and accelerators by studying the solubility relations than with the aid of colloidal chemistry.

THE MINERAL CONTENT OF ALUMINOUS CEMENT

BY

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Chemical Composition of Aluminous Cement.

Early investigations—Sefström (30), Fremy (16), Michaëlis (26)—disclosed that the oxides of calcium and aluminium combine in different proportions and form compounds with hydraulic properties. Le Chatelier (25) distinguished and gave the physical properties of three aluminates, designated as $3CaO \cdot Al_2O_3$, $3CaO \cdot 2Al_2O_3$ and $CaO \cdot Al_2O_3$, formulae which in the main have proved valid. Later workers—Schott (29) and Killig (19)—made further studies of the hydraulic properties of the aluminates and different mixtures of lime and alumina, and the approximate boundaries of the lime content for practically useful mixtures—already suggested by the previous authors—were fixed. At about the same time (the years before 1908) Bied carried out his experiments leading to the introduction of the French Ciment Fondu.

Since the work of Rankin on the equilibrium relations in the system $CaO \cdot Al_2O_3\text{-}SiO_2$ had appeared in 1915, a basis was supplied for more systematic tests concerning the range of hydraulic mixtures in this system. On account of the experiences from a series of melts, Endell (14) bounded off a stripe from the Al_2O_3-CaO-line in the system to the vicinity of the area of Portland cement, though only the melts in the monoaluminate-field and its environs were supposed to possess real cement qualities. At about the same time Bates studied a number of melts from these latter parts of the system and found them to harden in a short time and to give products of high strength. Endell's results were corroborated and further developed by Agde—Klemm (1) and Berl—Löblein (4). The latter gave as the boundaries of aluminous cement the following values: $SiO_2 = 0—12\ \%$, $Al_2O_2 = 45—70\ \%$, $CaO = 28—47\ \%$. Richter (28) recommends for good cements a maximum content of 6 per cent of SiO_2, calculated on the melted product. From the relations in technical cements BIEHL (5) concluded that SiO_2 = 5—10 %, Al_2O_3 = 35—55 %, CaO = =35—45 %, Fe_2O_3 = 5—15 %, TiO_2 = 1—3 %.

An interesting paper was published in 1933 by SOLACOLU (32). According to him, aluminous cements were in reality divided into two groups, the highest strength of the investigated melts being distributed along two lines, one running in the component triangle 5 : 3-aluminate-2CaO · SiO_2-CaO · Al_2O_3 close to the conjugation line of the two latter ("cements of the first kind"), the other lying in the field of 3 : 5-aluminate ("cements of the second kind"). This, in a certain sense, would be a parallel to the two kinds of Portland cement, *viz.* that rich in CaO and the "silicate-cement". As in the case of Portland cement, the two groups of aluminous cement also behave in different manners, the CaO-rich members rapidly attaining high strength, whereas the members of the second kind set more slowly but continually gain increased and high values of strength. Yet the maxima of strength recorded by SOLACOLU are not very prominent and as a whole the total area of mixtures with good cement qualities as given by him (FIG. 1) does not materially differ from that of former authors.

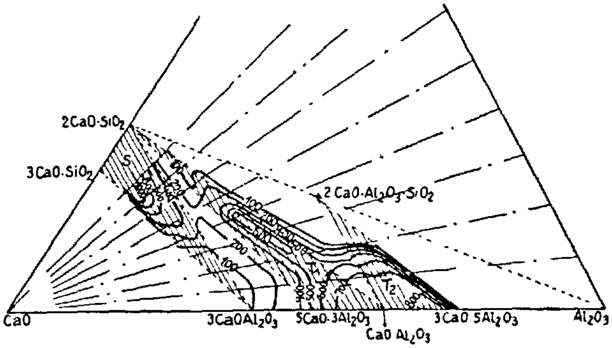

FIG. 1. Curves of Equal Strength in the Ternary Diagram, according to S. SOLACOLU.

For the position of the cement area a moderate content of iron does not seem to play any greater part. In the mixtures used by some of the beforementioned authors this oxide was present and its influence studied both under reducing and oxidizing conditions. Thus, the figure reproduced here from SOLACOLU in reality refers not to the pure CaO-Al_2O_3-SiO_2-system but to a section in the tetrahedron of these oxides and Fe_2O_3, though the position of the section is quite close to the pure system. The influence and the manner of combination of the iron were object of a special study by RICHTER. According to him the iron oxide compounds lower the strength and retard the setting. It is believed that the content of iron oxide must not exceed 15 per cent. AKIYAMA (2), when testing a series of melts, corroborated RICHTER's experience as to the retarding influence of Fe_2O_3 on the set, but found that moderate quantities of iron have a favourable influence on the properties of the cement.

In FIG. 2, the position of 23 technical cements have been plotted in the triangle of CaO-Al_2O_3-SiO_2. The collection includes both oxidized and reduced products. For the calculation, the values of CaO, Al_2O_3 and SiO_2 have been used unchanged without deductions for compounds of TiO_2 and Fe_2O_3 present. If regard should be taken to these, the points would move somewhat in the direction from the CaO-corner.[1] The FIGURE 2 is of interest as it shows that the area of commercial cements in reality is rather small. All the calculated cements belong to SOLACOLU's first kind. Evident representatives of his second kind are missing though the points to the far right in the figure are situated in the vicinity of its area. Another point of interest is that nearly all the cements are grouped around the broken line shown in the diagram and regarded by SOLACOLU (*loc. cit.* p. 252) as the site of CaO-contents of cements of highest strength [conjugation line of $CaO \cdot SiO_2$—quintuplepoint ($CaO \cdot Al_2O_3$—$2CaO \cdot \cdot SiO_2$— $5CaO \cdot 3Al_2O_3$)—$2CaO \cdot SiO_2$].

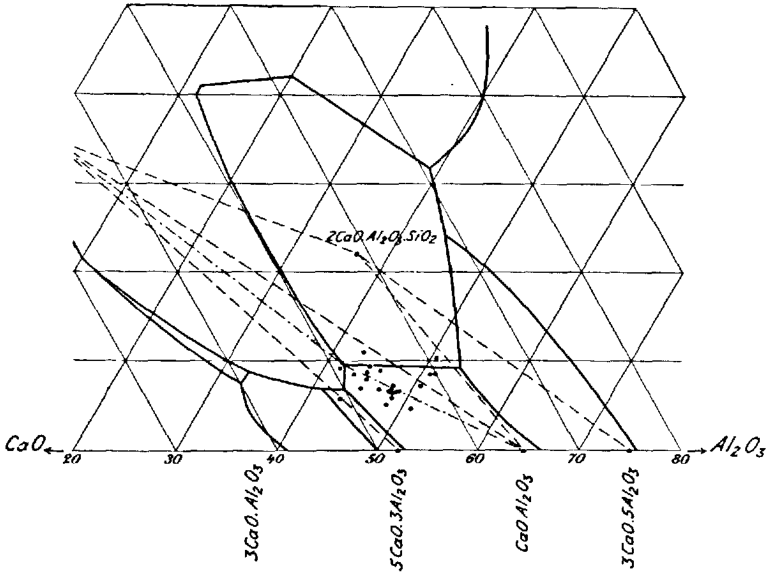

FIG. 2. Position of 23 Technical Cements in the CaO-Al_2O_3-SiO_2-Diagram.

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[1] Sixteen of the analyses originate from TABLE LXVI in the work of LEA and DESCH (p. 297), three analyses refer to an earlier paper by the author (1933), and three to cements described in the following (Sweden and France). One analysis represents a cement from Finland.

Minerals in the Aluminous Cement.

Notices about minerals observed in laboratory melts, more rarely also in technical cements, are found in the works of several authors (ENDELL, BATES, DYCKERHOFF, AGDE—KLEMM, BERL—LÖBLEIN, CARSTENS, KÜHL—IDETA, RICHTER, SOLACOLU, SUNDIUS a. o.). According to the informations gained from them, the chief carriers of the cement properties are monocalcium aluminate, dicalcium silicate, and in certain cases also 3 : 5-calcium aluminate. By some authors Gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$) has been recorded, but the presence of this compound in the products examined is generally denied. The stable modification of the 5 : 3-aluminate is reported from CaO-rich melts. On the other hand, DYCKERHOFF examined laboratory melts and reached the conclusion that the unstable modification may be of importance in cements corresponding chemically to the Ciment Fondu, this being confirmed by SUNDIUS through observations in technical cement.

According to BATES, the mineral reaction process in the melts may closely agree with the relations found by RANKIN in the CaO-Al_2O_3-SiO_2-system. The results of SOLACOLU from an X-ray examination of several samples point in the same direction but according to SOLACOLU it is doubtful whether a state of complete equilibrium is reached.

The minerals found by SHEPHERD, RANKIN and WRIGHT in the binary system CaO-Al_2O_3 have been reinvestigated and checked, and the formulae of two of the compounds given by them, 5 : 3-aluminate and 3 : 5-aluminate, have been disputed. Thus KOYANAGI (21) instead of $5CaO \cdot 3Al_2O_3$ suggested a proportion of $3CaO \cdot 2Al_2O_3$ as being more correct. The determinations of KOYANAGI refer to a laboratory product, which seems to be comparable with the unstable modification of the compound in question. According to BÜSSEM and EITEL (10), the composition of the corresponding stable modification must be richer in CaO than according to RANKIN and on account of structural-geometrical considerations they suggest the formula $12CaO \cdot 7Al_2O_3$. A similar result has been arrived at by LAGERQVIST, WALLMARK and WESTGREN (23) though by them the proportion $9CaO : 5Al_2O_3$ is admitted as an alternative possibility. TAVASCI (36) failed to obtain 3 : 5-aluminate and instead of it he states the formula $CaO \cdot 2Al_2O_3$ to be the right one. This result was corroborated by LAGERQVIST, WALLMARK and WESTGREN, who made a complete study of the binary system and obtained a new compound $3CaO \cdot 16Al_2O_3$, which of course is situated beyond the area of the aluminous cement.

The proposed new formulae would somewhat alter the site of the respective compounds, the greatest change being found in the 3 : 5-aluminate. However, in this paper, the old formulae have been kept as the discussion cannot as yet be considered concluded. Furthermore, with the exception of one single case, they do not enter the calculations.

The authors who have dealt with iron-bearing melts generally consider the oxides of this metal to enter Fe_3O_4 (Magnetite), $2CaO \cdot Fe_2O_3$, and in CaO-rich melts also $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. In his experiments RICHTER, using the method of NAGAI and ASAOKA, did not succeed in proving the existence of monoferrite in the melts and so concluded that diferrite and Magnetite are the only iron-bearing compounds in normal cements, except Brownmillerite which can develop in CaO-rich mixtures. SOLACOLU, on the other hand, found that monoferrite was present in the second kind of cements, those poorer in CaO, but was absent in the others.

Rather little is known from the experimental works referred to about the behaviour of TiO_2. In nearly all cases the melts were performed from mixtures of pure oxides and without the inclusion of TiO_2. In technical cements, the latter amounts to about 1.7—2.4 % and thus it may have a noticeable influence on the formation of minerals. In technical cements, petrographically investigated by SUNDIUS, this author found the only perceptible Ti-bearing mineral to be a compound which, according to an X-ray diagram by AMINOFF, could be identified as Perovskite ($CaO \cdot TiO_2$). KÜHL and OMAR (22) found that a moderate quantity of TiO_2 (up to 4.5 %) has a favourable influence on the cement properties. In an experimental study of the possible ratios of combination of CaO and TiO_2, PARGA-PONDAL and BERGT (27) found that by raising the temperature the quantity of CaO combined with TiO_2 is increased, up to $3CaO \cdot 2TiO_2$ above 1 250°. Below this temperature only monotitanate is formed. If the mixture is poor in CaO, the latter compound is stable also at higher temperature. In the experiments with SiO_2 added, no probability of the presence of the compound $CaO \cdot TiO_2 \cdot SiO_2$ (Titanite) could be established.

The following is a survey of the cement minerals and their properties, chiefly summarized from the various authors who have dealt with the subject but with the introduction of recent experiences from related iron-bearing mineral series.

Stable 5 : 3- (12 : 7- or 9 : 5- ?) calcium aluminate (CaO = 47.8, 48.5, or 49.7 %, resp., Al_2O_3 = 52.2, 51.5, or 50.3 %, resp.), reg., n = 1.608, no cleavage, spec. grav. = 2.69—2.71.[1]

Unstable 5 : 3-(3 : 2- ?) calcium aluminate (CaO = 47.8, 45.2 %, resp., Al_2O_3 = 52.2, 54.8 %, resp.). According to DYCKERHOFF, this modification is obtained only with difficulty from pure binary melts but it is easily formed from ternary mixtures. Observations made by the author on various cements

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[1] According to newer determinations, cf. BÜSSEM—EITEL. The older value given by RANKIN was 2.828.

indicate that it is a common constituent in CaO-rich cements, and here it seems to substitute the stable modification, not as yet recognized in technical products. The mineral appears as needles or laths, often grouped in a spherical arrangement. The properties are given somewhat differently by different authors. According to RANKIN—WRIGHT: colour weakly green with pleochroism, α = blue-green, γ = olive-green, $n_\alpha = 1.687$, $n_\gamma = 1.692$, double refraction weak, axial plan, and direction of the extinction parallel to the needles, opt. character probably negative, crystal system probably orthorhombic. DYCKERHOFF found: n about 1.69, double refraction = 0.004, longitudinal direction of the fibres = γ, small angle of extinction, crystal system probably monoclinic or triclinic. SUNDIUS in a sample of Ciment Fondu found: parallel to the prisms blue colour and the direction of γ, perpendicularly hereto weakly brownish-yellow. Double refraction about 0.004, anomalous interference colours common. Opt. character positive, the direction of the acute bisectrice parallel to the prisms and small axial angle, $n_\alpha = 1.695$.

The author studied the mineral in a melt placed at his disposal by Pargas Kalkbergs Aktiebolag, Finland, and further discussed in the following. In this case, the aluminate was the predominant component in the melt associated with a rather small amount of monoaluminate and a yet smaller quantity of disilicate. The 5 : 3-aluminate forms longer or shorter laths with distinct and straight boundary lines (FIG. 7). Besides these, there are other sections of broader dimensions and more indistinct contours against the adjoining interstitial matter. The properties of the aluminate are perhaps best illustrated by the drawing in FIG. 3. The axial angle seen on the more tabular sections is small but varies somewhat and the interference picture shows strong axial dispersion. Opt. character probably positive but not definitely determinable. The refraction of the direction perpendicular to the laths (weakly yellow) about 1.693, double refraction low but not determinable on account of the anomalous interference colours which in sections of 0.015 mm thickness are yellowish or brownish grey. The anomalous optical properties also prevent any statement regarding the crystal system. The direction of the extinction is always parallel to the elongation of the laths. The spec. grav. as found on an attempt to separate the mineral in a heavy fluid is about 3.10—3.15.

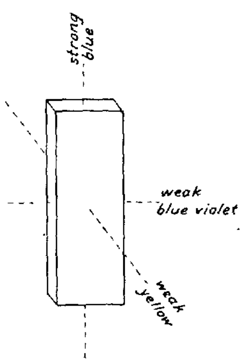

FIG. 3. Drawing, illustrating the Optical Relations in the Unstable 5 : 3-(3 : 2-?)-Aluminate.

There is little doubt as to the identity of the minerals described by the various authors. The differences found may partly depend on the inferior crystal development of the mineral but partly they may originate from the anomalous optical properties which render exact determinations difficult or even impossible. Furthermore—as will be discussed in greater detail in the following—it is conceivable that the aluminate is not pure but holds contaminations of dissolved oxides.

Monocalcium aluminate ($CaO \cdot Al_2O_3$, $CaO = 35.4\ \%$, $Al_2O_3 = 64.6\ \%$), orthorhombic or monoclinic, twinning frequent and best observable in sections perpendicular to the acute bisectrice, cleavage in one direction parallel to α, $n_\alpha = 1.641—1.643$, $n_\gamma = 1.661—1.663$, $\gamma—\alpha = 0.020$. Opt. character negative with an axial angle of $54^\circ—56^\circ$[1]. Spec. grav. = 2.981 according to WRIGHT. An older value, given by SCHOTT is 2.91.

Stable 3:5-(1:2-?) calcium aluminate ($CaO = 24.8$, $21.5\ \%$, resp., $Al_2O_3 = 75.2$, $78.5\ \%$, resp.), probably monoclinic, opt. character positive, $2V = 0^\circ—5^\circ$. If developed as prisms the aluminate shows an extinction angle of γ to the prismatic axis up to 39°, $n_\alpha = 1.617—1.618$, $n_\gamma = 1.652—1.654$, $\gamma—\alpha = 0.035—0.036$, twinning and cleavages are occasionally seen.

Dicalcium silicate[2] ($2CaO \cdot SiO_2$, $CaO = 65.1\ \%$, $SiO_2 = 34.9\ \%$), *α-modification:* probably triclinic, thin twinning lamellae in a cross-system often present, $n_\alpha = 1.719$, $n_\gamma = 1.733$, $\gamma—\alpha = 0.013—0.016$, opt. character positive, $2V = 36^\circ$. *β-modification:* probably triclinic, thin twinning lamellae sometimes seen in sections perpendicular to the acute bisectrice, $\gamma = 1.717$, $n_\gamma = 1.736$, $\gamma—\alpha = 0.020—0.021$, opt. character positive, $2V = 64^\circ—69^\circ$. When disilicate is present in cement clinkers it generally forms inconsiderable grains easily overlooked and recognizable chiefly through their high refraction and rather high double refraction. It is hardly possible to determine whether the modification present is the α- or β-form. The spec. grav. of both forms is 3.27—3.28.

It has been shown by BOWEN, SCHAIRER and POSNJAK (6) that dicalcium silicate can dissolve up to 10 per cent of Fe_2SiO_3. This may be of some importance in reduced cements where some greater part of the iron remains as FeO. According to the authors mentioned, the liability to dust is raised by increasing content of the iron compound.

Gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$, $CaO = 40.8\ \%$, $Al_2O_3 = 37.2\ \%$, $SiO_2 = 22\ \%$), tetragonal with one good cleavage according to (001), opt. character negative, $n_\omega = 1.667—1.669$, $n_\varepsilon = 1.658$, $\omega—\varepsilon = 0.011$. The mineral is developed as tables or as thick rectangular prisms. In the cement clinker an intimate intergrowth with monoaluminate is common. In such cases both compounds are distinguished through their different powers of refraction and double refraction. Spec. grav. = 3.038 (WRIGHT).

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[1] According to CARSTENS and SUNDIUS. WRIGHT found 36°. According to CARSTENS, the pure synthetic mineral will be nearly uniaxial.

[2] All data except that of the spec. grav. (WRIGHT) refer to the determinations by SUNDIUS.

Gehlenite belongs to a group of tetragonal minerals (the melilite group), long known from slags and certain basic, CaO-rich rocks. One of these minerals is *Åkermanite* ($2CaO \cdot MgO \cdot 2SiO_2$) with which Gehlenite forms a complete series of solid solutions. The properties of Åkermanite are: tetragonal, opt. positive, $n_\omega = 1.631$, $n_\varepsilon = 1.638$, $\omega - \varepsilon = 0.007$, spec. grav. = 2.944 (FERGUSON and BUDDINGTON, 15). A similar compound with FeO instead of MgO ($2CaO \cdot FeO \cdot 2SiO_2$) has recently been recorded by BOWEN, SCHAIRER and POSNJAK (6). The properties of it as given by them are: probably tetragonal, uniaxial and negative, $n_\omega = 1.690$, $n_\varepsilon = 1.673$, $\omega - \varepsilon = 0.017$. A mineral of this type ("Fe-Åkermanite"), containing about 80 per cent of the compound above, was described already in 1904 by HLAWATSCH, from a slag. Further compounds which belong here and whose behaviour have been studied by BUDDINGTON (9) are: $3CaO \cdot Al_2O_3 \cdot 3SiO_2$, $3CaO \cdot Fe_2O_3 \cdot 3SiO_2$[1], $3Na_2O \cdot Al_2O_3 \cdot 3SiO_2$, which all to a greater or lesser extent form isomorphic mixtures with Gehlenite and Åkermanite.

The oxides of all these compounds are present in most aluminous cements and, therefore, it is quite probable that the compound Gehlenite found in the clinker will not be pure but contaminated with other oxides dissolved in it. This is corroborated by its high values of refraction ($n_\omega = 1.680$ instead of 1.667—1.669 in the pure mineral), found by SUNDIUS. The same thing is indicated by the appearance of anomalous optical properties, observed on the mineral in clinkers and by the appearance of zonal buildings.

Dicalcium ferrite[2] ($2CaO \cdot Fe_2O_3$, CaO = 41.2 %, Fe_2O_3 = 58.8 %), biaxial, moderate axial angle, positive, n_α (Li) = 2.20, n_γ (Li) = 2.29, yellowish-brown colour by transmitted light in slides.

Monocalcium ferrite[2] ($CaO \cdot Fe_2O_3$, CaO = 25.9 %, Fe_2O_3 = 74.1 %), colour deep red, nearly or quite uniaxial, negative, n_ω about 2.58, n_ε about 2.43.

Tetracalcium aluminate-ferrite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, CaO = 46.1 %, Al_2O_3 = 21 %, Fe_2O_3 = 32.9 %), pleochroitic with α = yellowish-brown, γ = brown, opt. character negative, moderate axial angle, $n_\alpha = 1.98$, $n_\gamma = 2.08$, spec. grav. = 3.77 [HANSEN, BROWNMILLER, BOGUE (17)]. The aluminate-ferrite forms a complete series of solid solutions with diferrite.

Perovskite ($CaO \cdot TiO_2$, CaO = 41.2 %, TiO_2 = 58.8 %), orthorhombic (pseudo-reg.), $n = 2.34—2.38$. In the cement the mineral appears as finely distributed grains, sometimes in the form of net-works or of skeleton-like shape, isotropic or weakly double refracting. Spec. grav. 4.03. The mineral remains undissolved

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[1] Both minerals in a pure state are known as garnets (Grossularite and Andradite). The former also in tetragonal form constitutes the main part of Sarcolite. A tetragonal structure may also be ascribed to the Andradite when it is present in an isomorphic mixture of Gehlenite-Åkermanite.

[2] SOSMAN and MERWIN, (33).

when digesting the cement powder with 5 % HCl. An analysis of the residue was given by the author in the paper of 1933, but according to the experiences from the present work the material analysed may have been contaminated with glass, adhering the Perovskite grains.

Wüstite (crystallized FeO), reg., isotropic, black (depending on dissolved Fe_2O_3). Spec. grav. = 5.9. Wüstite forms a complete series of solid solutions with MgO [Bowen and Schairer (8)], and by moderate contamination of the latter it becomes brownish translucent. The presence of Wüstite in aluminous cement has not yet been recognized but the chemical relations in FeO-rich varieties make it probable that it does occur. Indeed, its presence in a dark, glass-bearing substance distributed between the ordinary cement minerals and as minute inclusions in them will be shown in this paper.

The Mineral Contents of some Samples of Aluminous Cement Clinker.

A necessary condition for the understanding of the crystallization in cement melts is a knowledge of the species of minerals occurring and their composition. In order to get an idea of this the author some years ago (1933) started a mineralogical investigation of technical cement clinkers. A similar work performed on artificial melts some years earlier (12) had been published by Carstens. In the following some additional notes on four new clinker samples will be added, two of them originating from Sweden (reduced cement), one from France (oxidized cement), and one from Finland (partly reduced cement). It should be observed that the Swedish cements are not ordinary products but represent somewhat extreme species as regards their contents of CaO and Al_2O_3. Also the Finnish cement seems to be somewhat high in CaO as compared with the common product.

The author is much indebted to Director E. Rengade at the Société An. des Chaux et Ciments de Lafarge et du Teil, to Skånska Cement Aktiebolaget in Malmö and to Pargas Kalkbergs Aktiebolag, for samples of cement clinker kindly placed at his disposal.

1. Cement Clinker from Sweden, CaO-poor Species, Reduced Cement. The average analysis, performed by Dr. A. Bygdén, the chemist of the Swedish Geological Survey, is given below.[1]

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[1] In this case as in the following the analyses refer to material from the same specimen as that from which the slides are made.

	Average Analysis	Undiss. in 0.5-*N*. HCl
SiO_2	9.15 %	0.21 %
TiO_2	2.26 »	1.52 »
Al_2O_3	44.39 »	2.77 »
Fe_2O_3	2.29 »	0.78 »
FeO	6.87 »	3.29 »
MnO	0.13 »	0.06 »
MgO	0.54 »	0.30 »
CaO	34.21 »	1.04 »
S	0.49 »	—
	100.33 %	9.97 %
—O for S	0.25 »	
	100.08 %	

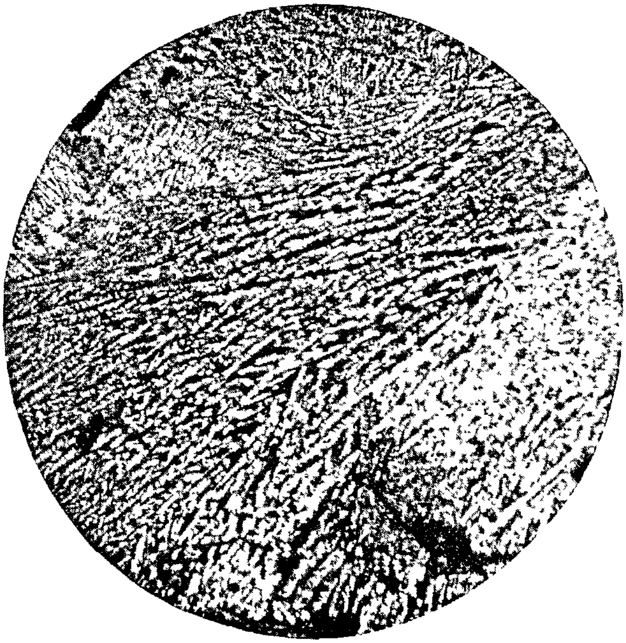

FIG. 4. Cement-Clinker from Valleviken, Sweden. Micrographic intergrowth of monoaluminate (white) and Gehlenite (dark or grey). The smaller dark stripes seen in the monoaluminate are inclusions of Perovskite and glass. For the analysis of the cement see S. G. U. (Swedish Geol. Survey), Ser. C, No. 379, p. 13. The point of the cement when plotted in the diagram of FIG. 8 is given by *a*. Nicols crossed; the diameter of the figure corresponds to about 0.8 mm in the slide.

In the corresponding slide the following components have been recognized: *Monoaluminate, Gehlenite, a dark opaque or seldom translucent glass-bearing substance, Perovskite.* In the slide, two small nodules are also present containing

3:5-aluminate, small isotropic high refracting grains, probably *Spinel*, and a fibrous mineral which may be *Mullite* ($3Al_2O_3 \cdot 2SiO_2$). These nodules seem to represent some poorly mixed remnants of Bauxite. They do not play any noteworthy part in the constitution of the cement. The 3:5-aluminate is restricted to the borders of the nodules (reaction zone) whereas both the other minerals are concentrated to the inner. A dark glass-looking substance, too, is seen in the nodules.

In addition to these constituents the cement contains small sparingly distributed globules of metallic iron. Small amounts of a sulphide, soluble in HCl, is also present, hydrogen sulphide being generated during the dissolving process. This compound is supposed to be FeS.

The Gehlenite evidently appears as two generations (FIG. 5), partly as greater homogeneous and distinctly bounded tables after (001) (phenocrysts) which are sparsely scattered in a denser mixture (the groundmass) in which the main part of the Gehlenite occurs intergrown with the monoaluminate. In the groundmass the Gehlenite assumes the shape of thick rectangular prisms after *c*.

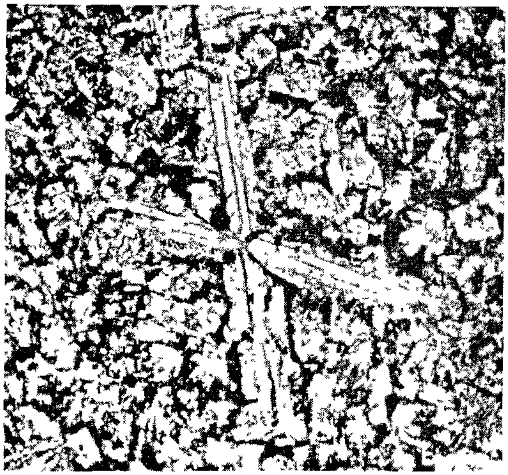

FIG. 5. Cement-Clinker from Valleviken, Sweden, relatively Poor in Lime, Point 1 in FIG. 8. Phenocrysts of Gehlenite forming tables after (001) cut at right angles to this face and enveloped by graphic intergrowths of the same mineral and monoaluminate. The surrounding groundmass is made up by the same minerals intergrown in the same manner (white) and by Perovskite and glass (both the latter dark). Ordinary light. The length of the phenocrysts is about 0.37 mm.

The following properties have been determined on the *Gehlenite*: $n_\omega = 1.675$, $\omega - \varepsilon = 0.012$. The refraction seems to be a little higher in the groundmass than in the phenocrysts. On one border of the slide the Gehlenite shows a distinct pleochroism with ω = blue, ε = colourless and with anomalous interference colours. This phenomenon is developed in the groundmass-Gehlenite only, not in the phenocrysts, but, in connection with the latter, a zonal arrangement can be seen, the phenocrysts being surrounded by an envelope of the pleochroitic substance which gradually passes into the groundmass. The properties determined on the *monoaluminate* are: $n_\gamma = 1.660$, $\gamma - \alpha = 0.020$. This rather well agrees with the pure mineral.

The dark opaque substance and the Perovskite chiefly appear as an interstitial mass between the cement minerals mentioned but they are also seen as minute inclusions in the latter. The dark substance is best studied after dissolving the ordinary cement minerals through diluted HCl. In the residue it appears as small fragments, splinters, or lumps which seldom are translucent and then prove to be an *isotropic brownish-violet or red-violet glass.* In most cases it is not translucent or only in thin edges. Thus it is not possible to decide if the dark substance in reality is homogeneous glass or if it holds minute inclusions of crystallized opaque minerals. The refracting power of the glass is high, distinctly > 1.78.

Ferrite could not be discovered in the slide studied. In any case, the amount of it, if present, must be inconsiderable.

Apart from the Perovskite, perhaps formed very early, the Gehlenite-phenocrysts were apparently the first to separate from the melt, followed later by the simultaneous crystallization of the main mass of this mineral and the monoaluminate. But the crystallization was not complete, and a certain part of the melt was left and congealed in the form of the glass-bearing dark substance. Furthermore, the distribution in the cement of this latter is not even but more ample in some darker *Schlieren* and poorer in the other parts of the slide.

As the glass-bearing residue is of importance for the understanding of the crystallization process, an attempt was made to isolate it. For this reason, fine-ground powder of the clinker was subjected to treatment with diluted HCl (0.5-*N.*). After about 24 hours the residue contained only insignificant remnants of Gehlenite and a few grains of a blue pleochroitic, double refracting unknown mineral ($n > 1.78$), together perhaps 3—4 per cent, the other 96—97 per cent being made up of the glass and Perovskite. Macroscopically, the residue appeared as a black powder and it may chiefly be the glassy substance that gives the cement its dark colour. The residue—amounting to 9.9 per cent of the clinker—was subjected to an analysis by Dr. BYGDÉN, the results of which are quoted above in the second column. The original figures of the analysis were: $SiO_2 = 2.08\%$, $TiO_2 = 15.15\%$, $Al_2O_3 = 27.71\%$, $Fe_2O_3 = 7.80\%$, $FeO = 32.94\%$, $MnO = 0.57\%$, $MgO = 3.03\%$, $CaO = 10.35\%$. If we subtract from the figures obtained the Gehlenite, estimated at about 2 per cent of the residue, the rest can be calculated as 2.31 per cent Perovskite and 7.45 per cent glass, calculated on the total cement. The composition of the glass then becomes:

SiO_2	2.20 %
TiO_2	2.08 »
Al_2O_3	36.19 »
Fe_2O_3	10.47 »
FeO	44.22 »
MnO	0.76 »
MgO	4.07 »
	99.99 %

Thus the glassy substance is mainly composed of iron oxides and alumina, together amounting to nearly 91 %, iron oxides alone constituting about 54.5 %. Evidently this complex contains a great percentage of Wüstite, but, as this compound is not visible in crystallized form, it may enter the dark substance as glass or in a submicroscopical distribution rendering the rest melt its black and opaque appearance. This also makes the high refraction of the glass conceivable.

If we subtract from the average analysis the figures of the Perovskite and the glass, the remainder should correspond to the other minerals recognized in the cement. A calculation performed on this basis must also include the amounts of TiO_2, Fe_2O_3, FeO and MgO remaining after the subtraction of the two named components. Furthermore, metallic iron was estimated at 0.5 per cent (0.64 % as FeO). The calculation gives for the whole cement the following result:

Monoaluminate	57.12	%	
Gehlenite	15.28	»	
Åkermanite	1.63	»	14.46 %
Fe-Åkermanite	8.05	»	
Andradite	4.78	»	
FeS	1.59	»	
Fe (as FeO)	0.64	»	
Perovskite	2.31	»	
Glass	7.45	»	
Rest of uncombined CaO	1.45	»	
	100.30	%	

Accordingly, the Gehlenite amounts to 29.74 per cent and nearly the half of this would be made up by molecules containing FeO and Fe_2O_3. Also 0.74 % TiO_2 is included in this mineral. If we compare this with the optical relations, the introduction of 8 per cent Fe-Åkermanite would cause a rise in the refraction from 1.668 to about 1.679. A similar rising effect would be caused by Andradite and TiO_2 but, on the other hand, the Åkermanite would contribute to lowering the refraction. The double refraction would be little affected though, on the whole, a small rise in it can be expected. As the values of the named properties are $n_\omega = 1.675$ and $\omega - \varepsilon = 0.012$ instead of 1.668 and 0.011, the inclusion of the foreign molecules calculated above would not seem to contradict what can be assumed from the data at hand. Naturally, the calculation cannot be regarded as exact but only as an approximation. Thus it is possible that some minor part of the glass has been dissolved during the treatment of the cement powder with HCl which would somewhat diminish the foreign substances in the Gehlenite. Furthermore, the amount of Fe_2O_3 in the glassy substance is certainly somewhat high as a consequence of oxidization during the strong grinding of the clinker for the analysis.

2. *Cement Clinker from Sweden, Ca-rich Species, Reduced Cement.* Dr. Bygdén's average analysis is shown below:

	Average Analysis
SiO_2	8.25 %
TiO_2	2.28 »
Al_2O_3	42.37 »
Fe_2O_3	1.13 »
FeO	3.18 »
MnO	0.10 »
MgO	0.67 »
CaO	41.75 »
S	0.62 »
	100.35 %
—O for S	0.31 »
	100.04 %

The compounds recognized are: *Monoaluminate, Gehlenite, disilicate, Perovskite and a dark glass-looking substance. Metallic iron* and *iron sulphide* are present as well.

The determined properties of the minerals are: *Gehlenite,* $n_\omega = 1.673$, *monoaluminate,* $n_\gamma = 1.662$ and the axial angle = 54°. Thus the latter mineral agrees well with the pure compound, but the Gehlenite has a higher refraction.

The predominant mineral is monoaluminate. It occurs partly as coarser phenocrysts (Fig. 6) although the number of them is not very great. In the groundmass monoaluminate and Gehlenite form a fine-grained mixture, the amount of the latter mineral being rather small. The Gehlenite always contains some graphic intergrowths of monoaluminate but the latter seems to be homogeneous. The disilicate forms small rounded or elongated grains distributed in the dark interstitial mass and from its boundaries they are seen to protrude into the monoaluminate. A parallel arrangement of several disilicate grains forming an optically uniform group is not rare.

As in the former clinker the dark glassy substance and the Perovskite are concentrated to the interstices between the cement minerals proper but they are also seen in the latter as small inclusions and this impregnation is more abundant than in the foregoing case, rendering the cement a turbid or clouded aspect in the microscope.

In this clinker the monoaluminate has separated before the Gehlenite. It is also evident that the glassy substance represents a late solidified part of the melt but otherwise no information about the order of crystallization is gained from the relations in the slide.

An attempt to isolate the glass was made also here but on account of the intimate impregnation of the cement minerals by the glass and the Perovskite, the procedure was more difficult than in the foregoing case, and only after the powder being treated for 48 hours, being ground anew, had the cement minerals practically disappeared. As it is likely that during this procedure the glass was considerably attacked, no analysis was made of the residue except a determination of FeO. This gave the result, 5.1 per cent calculated on the residue, the amount of which was 6.7 per cent of the whole cement. In another sample of powder treated for 24 hours the total undissolved rest amounted to 7.94 per cent, 6.89 per cent of it consisting of FeO and 26.2 % of TiO_2. Evidently, some solution of FeO must have occurred in the foregoing case. In the second sample the undissolved rest still contained an essential amount of monoaluminate estimated at about 5 %. The content of Perovskite is about 44.5 per cent. Thus the glass should amount to about 50 per cent and the FeO, when calculated on the glass, becomes 13.8 per cent. In this figure Fe_2O_3 is not included and the total sum of the iron oxides would be somewhat greater. In any case it may be concluded that the glass is not so rich in iron oxides in this cement as in the foregoing and the greater part of these oxides may enter the Gehlenite and possibly also the disilicate. The lower content of iron oxides in the glass corresponds with the considerably lower total amount of these substances in the cement (4.31 % against 9.16 % in sample *1*).

A calculation of the cement components is not possible in this clinker. The only thing that can be said is that, on account of its optical properties and because of the relations mentioned above, the Gehlenite must be contaminated by molecules of the same kind as in sample *1*. Possibly also the disilicate contains some FeO.

3. Clinker of Ciment Fondu, Oxidized Cement. The analysis received from Director RENGADE has the composition quoted in the first column below:

	Average Analysis	Undiss. in 0.5-*N*. HCl
SiO_2	4.70 %	0.56 %
TiO_2	1.60 »	0.14 »
Al_2O_3	38.75 »	0.27 »
Fe_2O_3	10.10 »	3.59 »
FeO	8.05 »	4.09 »
CaO	36.60 »	0.19 »
	99.80 %	8.84 %[1]

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[1] Hereto 0.29 % MgO.

The minerals recognized in the slide are: *Monoaluminate, ferrite, disilicate and the usual dark glass.*

The properties determined on the *monoaluminate* are: n_γ = about 1.67, axial angle = 49°. Thus a noticeable difference from the relations in the pure compound (1.661—1.663 and 54°—56°). The *ferrite* is rather ample and of a yellowish-brown or somewhat more reddish-brown colour. It is hardly possible to decide whether one or two kinds of ferrite are represented. The grains are distinctly double refracting but not pleochroitic. Thus, an admixture of Brownmillerite, if it occurs, is not very great.

In the microscope the cement exhibits an aspect often met in aluminous cements, the monoaluminate being developed as great but not homogeneous individuals in which the glassy substance and the ferrite are distributed in the form of small grains arranged in parallel rows or in a feather-like fashion. The content of disilicate is not great. As usual this mineral occurs in the form of small rounded or prismatic, minute grains together with the dark minerals, or protruding into the monoaluminate.

The observations in the slide indicate no apparent order of crystallization in the cement though it may be suggested that the monoaluminate was the first component to separate. The peculiar arrangement of the dark substances may be due to the crystallographical directions in the aluminate. This, *inter alia*, is shown by the fact that the arrangement is the same if the enclosed substances are those present in this case, or if other minerals are present as in cases former described by the author (Gehlenite, disilicate, Perovskite, and glass).

In a fraction treated as usual for 24 hours with diluted HCl the residue consisted of the black, sometimes brown- or red-violet translucent glass. Isolated small high refracting isotropic grains (*n* distinctly greater than that of the glass) possibly represent Perovskite but their quantity is subordinate. Remains of monoaluminate were practically absent. The black powder showed a rather strong magnetism, not found in any other case. A micro-analysis made by Dr. G. ASSARSSON gave the result shown above in the second column. The original figures calculated on the analysed powder were: SiO_2 = 6.1 %, TiO_2 = 1.5 %, Al_2O_3 = 3.2 %, Fe_2O_3 = 37.5 %, FeO = 44.8 %, MgO = 2.8 %, CaO = 2.1 %. The total amount was 9.14 per cent of the whole cement. Thus, the iron oxides here constitute about 82 per cent of the glass. The magnetic power of the powder is explained by the rather high content of Fe_2O_3, but also if we calculate the whole amount of it as Fe_3O_4, there remain about 28 per cent of FeO which may have the form of Wüstite. However, part of the ferric oxide may have originated when grinding the clinker.

After subtracting the oxides of the residue, the remainder of the average analysis was calculated on the minerals identified in the slide, with the following result. For the ferrite it was supposed that only diferrite was present and that it contained an admixture of 20 per cent of Brownmillerite.

Monoaluminate	60.81 %	
Disilicate	11.87 »	
Ferrite	8.39 »	12.78 %
Brownmillerite	3.89 »	
Glass	8.84 »	
Uncombined FeO	3.96 »	
» CaO	1,53 »	
	99.79 %	

According to the calculation, the monoaluminate contains 1.46 per cent TiO_2. It is uncertain whether or not it also contains any FeO or if the excess of this oxide is due to a partial dissolution of the glass during the treatment with HCl. Anyhow, the high refraction and the small axial angle of the aluminate show that it is not pure.

4. Cement from Finland. According to a communication from Pargas Kalkbergs Aktiebolag the melt had been produced in an electrical furnace and under oxidizing conditions, but due to the influence of the coal electrodes a partial reduction may have occurred. The melt contains no metallic iron nor any sulphide but a rather high amount of FeO. The average analysis performed by Dr. G. ASSARSSON gave the results shown in the first column below.

	Average Analysis %	Separated Mineral Fraction %	Undiss. in 0.5-*N*. HCl % of the Clinker
SiO_2	5.19	4.4	0.4
TiO_2	1.71	0.7	0.1
Al_2O_3	39.17	43.6	—
Fe_2O_3	6.33	4.7	1.0
FeO	7.79	5.5	3.0
MgO	0.55	not det.	0.1
CaO	39.34	39.8	0.2
	100.08	98.7	4.8

This cement has a rather peculiar mineral composition. The predominant mineral is unstable 5:3- (3:2-?) aluminate appearing in the slides as thin laths or somewhat broader tables, generally with a subparallel arrangement (FIG. 7). The interstices between the laths are occupied by a yellowish-brown ferrite, and a dark, in the slides opaque substance. When isolated with diluted HCl this latter is found to consist of the usual glassy substance, translucent only in very thin splinters and then showing the same colour as in the foregoing cases and a corresponding, high refraction ($>$ 1.78). The glassy substance is also found as thin fibre-like inclusions or as dendritic formations in the aluminate. Besides these components a little monoaluminate and inconsiderable grains of disilicate were found in the two slides studied.

The properties of the unstable aluminate were given on p. 400. As the mineral is in this case present in unusually great amounts and is developed in a relatively coarse form, an attempt was made to separate a fraction of it from the powdered cement, which was centrifuged in methylene iodide mixed with benzol. The separation—kindly performed by Dr. A. BYGDÉN—was not quite successful in that the mineral could not be obtained in a pure state, but its relative amount was essentially raised and the greater part of the ferrite, as also the monoaluminate and disilicate, could be removed. In the remaining fraction the aluminate formed the predominant part, the remainder being composed chiefly of fragments of the dark glass, adhering aluminate grains. A micro-analysis on the separated fraction performed by Dr. G. ASSARSSON is given in the second column above.

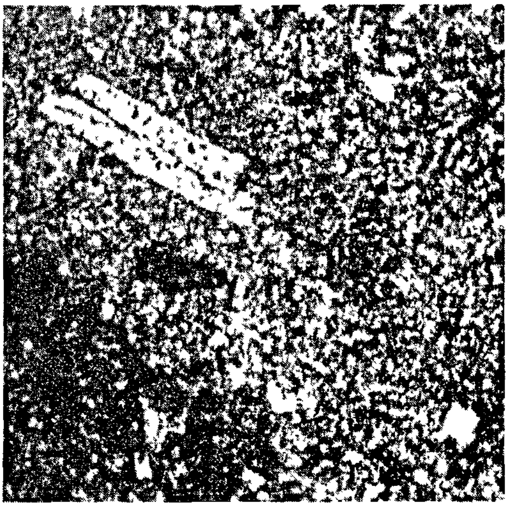

FIG. 6. Cement-Clinker from Valleviken, Sweden, Richer in CaO than That of FIG. 5, Point 2 in FIG. 8. One greater and a smaller phenocryst of monoaluminate in a fine-grained groundmass made up by this mineral and Gehlenite and clouded by minute inclusions of Perovskite and glass. Ordinary light. The length of the great phenocryst is about 0.24 mm.

The third column shows the results of a micro-analysis by the same chemist on a fraction of the glass isolated as before by treatment for 24 hours with 0.5-*N*. HCl. The original figures of the analysis calculated on the residual powder were: SiO_2 = 8.7 %, TiO_2 = 2.5 %, Al_2O_3 = 0.1 %, Fe_2O_3 = 20.9 %, FeO = 60.5 %, MgO = 2.1 %, CaO = 4.1 %. The total amount of the residual glass was 4.9 per cent of the whole clinker and the fraction obtained was free from other impurities than subordinate traces of ferrite.

This glass is chiefly composed of iron oxides and more than 50 per cent of it may consist of Wüstite in a glassy or submicroscopical shape.

An exact calculation of the composition of the unstable aluminate is hardly possible on the basis of the data at hand. If we deduct from the average analysis, the oxides determined in the glass and accept for the monoaluminate and disilicate a fair amount of 4 and 2 per cent, resp., and if we furthermore calculate the remaining Fe_2O_3-content as diferrite, there is left a rest of about 80 per cent which would approximately correspond to the aluminate and whose composition—calculated on 100—is: SiO_2 = 5.1 %, TiO_2 = 2.0 %, Al_2O_3 = 45.6 %, FeO = 6.0 %, MgO = 0.6 %, CaO = 40.8 %. These figures give a molar proportion of SiO_2, Al_2O_3, TiO_2 : FeO, MgO, CaO = 3 : 2.01.

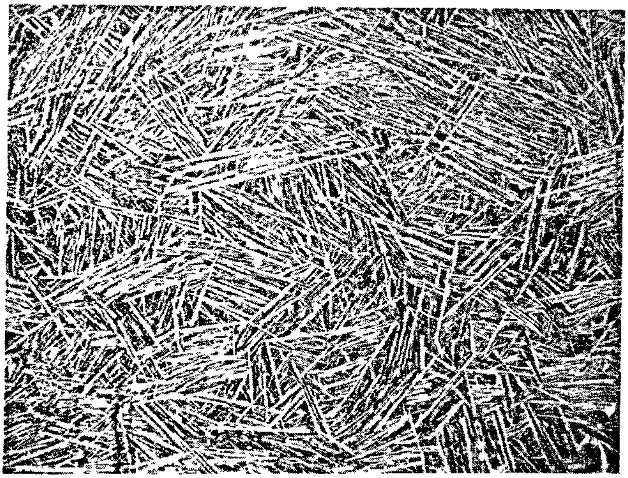

Fig. 7. Cement-Clinker from Pargas, Finland. Numerous needles of unstable 5 : 3 - (3 : 2 - ?) aluminate; between the needles a ferrite or solid solution of ferrite and Brownmillerite and glass, both dark. Ordinary light. The length of the figure is about 4 mm.

This makes the following total mineral composition of the cement:

5 : 3- (3 : 2-?) aluminate	80.2 %
Diferrite	9.1 »
Monoaluminate	4.0 »
Disilicate	2.0 »
Glass	4.8 »
	100.1 %

Of course the calculation is only an approximation. Thus it is probable that not only FeO but also Fe_2O_3 is present in the unstable aluminate. Furthermore, the total amount of the glassy residue may actually be somewhat higher than found, on account of a partial dissolution during the treatment with HCl. Yet, the oxides calculated for the aluminate fairly well correspond to the analysis of the separated fraction, if we remember that this latter is made up of a mixture of the aluminate and a minor quantity of glass. From the relations found we may conclude that the aluminate corresponds to the unstable 5:3- (or 3:2-?) compound though it is not pure but contaminated with foreign substances.

It is rather curious that two cements exhibiting so great chemical similarities as the French Ciment Fondu (No. *3*) and the one just described, can assume so quite different mineral contents.

In the mineralogical description of the four samples there are two points worthy of further mention, the *presence of glassy rest-melts* in the cements and the *occurrence of contaminations in the cement minerals.* Glassy rest-melts have been found in all the samples studied. This raises the question, whether or not late solidified parts of this kind are generally formed in aluminous cements. The circumstance that glass residues have not hitherto been reported can be due to the fact that the glass is rather finely distributed and that any transparency that occurs is hardly detected in the slides unless special attention is devoted to the matter. The writer has reinvestigated the clinkers described by him in 1933 and it was actually possible to demonstrate the presence of a dark glassy substance with the same distribution and the same appearance as that found here. This substance previously either was overlooked, or, in the Ciment Fondu it was supposed to be iron ore minerals. From this the conclusion may be drawn that *glassy rest-melts are common constituents of aluminous cements.* In the cases hitherto studied the quantities of the glass found through isolation with diluted HCl, amount to about 4—10 per cent of the cement. The composition of the glass varies depending on the composition of the cement but an enrichment of iron oxides always occurred. In sample *2* which is poor in iron oxides (4.31 %) the glass contains about 14 per cent FeO besides some Fe_2O_3; in the other cements containing about 9—18 per cent of iron oxides, the contents of the latter in the glass amount to 41—82 per cent. In reduced or partly reduced cements with a considerable FeO-content the chief component of the glass is Wüstite, in a glassy or submicroscopical form. In an oxidized cement, such as the Ciment Fondu, this compound is associated with an essential amount of Fe_2O_3. Here the glass is magnetic but in the former cases this property is weak or absent.

The glass in all samples is shown to be fairly resistent to diluted HCl (0.5-*N.*). A proof of this was given in the description of sample *2*. On No. *3* a similar test was performed with two different samples of the powdered clinker. In one case the powder was treated about 5 hours, in the other for 24 hours. The residue in the two cases amounted to 12.5 and 9.14 per cent, but in the former case the residue still contained an essential amount of monoaluminate. Thus, some further attack on the glass may have occurred during the longer treatment but evidently it was not strong.

The mineral that regularly seems to be contaminated with foreign substances when appearing in aluminous cements, is Gehlenite. That this compound is not pure was shown already in the author's earlier paper although no attempt was then made to calculate its real composition. The liability of this mineral to form solid solutions with Åkermanite in basic open hearth slags and the importance of this fact for the melting process was pointed out by KOCH (20). The chemical relations found here make it probable that the chief impurities occurring in the Gehlenite of the aluminous cements are FeO- and Fe_2O_3-bearing molecules and probably some TiO_2 though also some admixture of Åkermanite may be present.

The relations found in the Pargas-cement (No. *4*) indicate that also the 5 : 3-aluminate can dissolve foreign substances containing the oxides mentioned above. It could not be controlled, whether or not, any contaminations are present in the disilicate—in this case FeO—as the refraction was in no case determinable on account of the small grain of the mineral and the manner in which it occurs.

According to the optical measurements the monoaluminate is less liable to dissolve alien substances. Yet, in the case of the French cement, this mineral shows a refraction distinctly higher than that of the pure mineral, and the axial angle, too, deviates somewhat from the normal. For this mineral we have no earlier experience as to the compounds that possibly may be admixed. As the cement in question is the strongest oxidized it could be supposed that Fe_2O_3 in some form might be dissolved in the aluminate. This would imply that some part of the calculated ferrite would in reality be transferred to the monoaluminate. But there is also a possibility that TiO_2 and some FeO may have been taken up in the aluminate. This and the relations of the unstable aluminate cannot be determined except by experimental research.

A special problem is exhibited by TiO_2. Some minor part of it always seems to be dissolved in the glass. In the relatively SiO_2-rich, reduced cements Nos. *1* and *2*, the main part of TiO_2 is combined with CaO as Perovskite but a residue of about 0.7 and 0.2 per cent remains which probably enters the Gehlenite. In the SiO_2-poor, oxidized or only partly reduced cements Nos. *3* and *4* the presence of Perovskite could not be established with certainty. It could be suggested that a CaO-richer and more easily dissolved compound ($3CaO \cdot 2TiO_2$?) had been formed, but in the slides no corresponding mineral component could be detected. For these reasons, the residue of TiO_2 after subtracting the oxides determined in the glass was supposed to be an ingredient of monoaluminate and unstable 5 : 3-aluminate, resp. It is not known whether TiO_2 in some form can be dissolved by ferrite.

In the foregoing the alkalies have not been included in the discussion. Surely they constitute only a very small part of the cements but they have been shown to play a rather important part in the processes involved by the hydration of the cement. The most probable explanation would appear to be that alkalies are concentrated in the rest-melts but in the case of Gehlenite-bearing cements it can be suggested that some part of the alkalies in the form of $3Na_2O \cdot Al_2O_3 \cdot 3SiO_2$ enter this mineral.

X-Ray Tests.

Most of the minerals in the samples investigated could be determined microscopically and needed no further examination. But in the case of the unstable 5:3-aluminate it was of interest to compare its interferences with the known diagram of the stable compound. No diagram of the unstable compound appears to have been published as yet. Furthermore two samples of the iron-rich glass isolated from the clinkers *3* and *4*[1] were examined in this way. The work entailed by this examination was kindly performed by Cand. Phil. E. YGBERG at the Mineralogical Department of the Natural History Museum in Stockholm. He has submitted the following report on the results arrived at:

"Powder photographs of each of the three samples received from Dr. N. SUNDIUS were made using Cu_{K_α}-radiation ($\lambda_{Cu_{K_\alpha}} = 1.538$ Å) with a filter to absorb the K_β-radiation. In the table below the observed values of $\sin^2\Theta$, d_{hkl} and the relative intensities of all the lines recorded are listed. For comparison similar lists have been added from powder photographs of reg. $5CaO \cdot 3Al_2O_3$ and FeO (Wüstite). The agreement between sample *1a* (the unstable aluminate received from Dr. SUNDIUS) and reg. 5:3-aluminate does not appear great enough to permit the conclusion that both substances are identical. When comparing samples *3* and *4* with FeO (Wüstite) the agreement is greater and there is hardly any doubt that the two former contain Wüstite. In sample *3* (glass from Ciment Fondu) one line of medium intensity ($\sin^2\Theta = 0.272$, $d_{hkl} = 1.4745$) is present which is lacking both in Wüstite and in sample *4*. This line may be due to some admixed substance that is neither Magnetite nor Perovskite. On the other hand it shows better coincidence with a line of strong intensity in the Haematite diagram[2] and on the whole the relations in this and in the diagram of sample *3* indicate that this mineral may be present in the latter."

This investigation confirms the conclusion drawn from the chemical rela-

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[1] The powders used for the photographs originate in all cases from the same fractions as have been analysed.

[2] JUNG and KÖHLER, Chemie d. Erde, 5, (1930), 195.

tions that Wüstite is the chief component in the glassy rest-melts of the iron-rich cements. A further conclusion is that no noteworthy amount of Perovskite is present in the photographed powders.

Sample *1 a*			Reg. $5CaO \cdot 3Al_2O_3$[1]		Undiss. from Sample *4*			Wüstite[2]		Undiss. from Sample *3*		
$\sin^2 \theta$	I	d_{hkl}	d_{hkl}	I	$\sin^2 \theta$	I	d_{hkl}	d_{hkl}	I	d_{hkl}	I	$\sin^2 \theta$
0.042	s	3.752	3.77	m	—	—	—	—	—	2.993	w	0.066
0.061	m	3.114	3.18	m	0.081	w	2.702	—	—	—	—	—
0.071	s	2.886	2.98	s	0.094	m	2.508	2.484	8	2.521	s	0.093
0.077	s	2.771	2.67	ss	0.128	s	2.149	2.149	10	2.149	s	0.128
—	—	—	2.55	m	0.153	w	1.966	—	—	—	—	—
0.099	m	2.444	2.44	s	—	—	—	—	—	1.698	w	0.205
0.109	m	2.329	2.34	m	—	—	—	—	—	1.610	w	0.228
0.117	w	2.248	2.180	s	0.256	m	1.538	1.519	9	1.517	m	0.257
0.131	w	2.125	2.055	w	—	—	—	—	—	1.4745	m	0.272
0.145	m	2.019	1.943	s	0.352	w	1.296	1.295	5	1.294	w	0.353
0.161	m	1.916	1.906	w	0.385	w	1.239	1.238	—	1.235	w	0.388
—	—	—	1.846	w	—	—	—	1.074	—	—	—	—
0.185	w	1.788	1.800	ww	—	—	—	0.984	—	0.981	w	0.615
0.190	w	1.765	1.764	w	0.641	w	0.960	0.959	—	0.960	w	0.641
0.199	w	1.724	1.728	m	0.772	w	0.875	0.876	—	0.874	w	0.774
—	—	—	1.694	w	—	—	—	0.826	—	—	—	—
—	—	—	1.660	s								

The Crystallization Process in Aluminous Cement.

From the fact that the foreign substances present in aluminous cements (TiO_2, FeO, Fe_2O_3, and MgO) react with the pure CaO-Al_2O_3-SiO_2-compounds and enter their composition it may be concluded that the equilibrium relations governing the crystallization in the cement-melts cannot be deduced from the diagram of the pure components. But it would be possible that the deviations actually occurring are small and that the diagram in the main may be used to calculate the final result of the crystallization. This question will be discussed with the help of the data from the cement samples investigated here and before by the author. Unfortunately CARSTENS's results cannot be used in this connection as analyses are lacking.

The points of the investigated cements are plotted in FIG. 8 which is part of the whole CaO-Al_2O_3-SiO_2-diagram. If we compare the positions of the different cements and the initial crystallization products in each of them as found in the slides, it is seen that the beginning separation of the minerals

[1] BROWNMILLER and BOGUE, after LEA and DESCH.

[2] WYKOFF and CRITTENDEN, Z. Kryst., 1926, *63*, 144.

in most cases fairly agrees with the relations in the diagram. Thus, in cements *1* and *2* the first minerals to separate are Gehlenite and monoaluminate (as phenocrysts). The boundary between the stability field of both these compounds must thus lie between these two points. Consequently, the boundary line cannot be much displaced in the system of the two cements. The point *a* represents the Swedish cement described by the author in 1933. In that the first compound to separate was a mineral not belonging to the known cement minerals, and whose composition is still unknown. It is followed by 3:5-aluminate which is bounded to the borders of the nodules of the former, and formed partly at its expense. Both these minerals may constitute some abnormal products in the cement and their quantity also is negligeable. For the rest, the cement is composed of a mixture of monoaluminate and Gehlenite in a graphical intergrowth (Fig. 4). Thus none of them can be shown to precede the other. This would speak for a somewhat lower site of the boundary line between the two stability fields in the cement system, but the dislocation would not be great. It will be noticed that the content of iron in the three cements—which are reduced—is low or moderate ($FeO + Fe_2O_3 = 9.16$ %, 4.31 % and 2.36 %).

In the case of the two French cements (*3* and *b*, the latter described by the author in 1933) the relations are to a certain extent more complicated through the appearance in *b* of a restricted amount of the unstable 5:3-aluminate which may be an early crystallization product. But it is rather possible that in both cements the monoaluminate has begun to separate before the disilicate in accordance with the diagram. On the other hand, the behaviour and the whole mineral content of the cement from Pargas does not at all accord with the diagram, about 80 per cent of it being made up of the unstable 5:3-(3:2-?) aluminate, monoaluminate being represented but sparingly. Furthermore, the relations in the slide indicate a resorption of the unstable aluminate by the latter which would imply that the unstable compound was formed distinctly earlier than the monoaluminate. This all indicates that the unstable 5:3-aluminate, when it occurs, tends to disturb the equilibrium relations of the normal cement system.

The content of iron oxides of the three last mentioned cements is high, amounting to 14.1—18.15 per cent.

If we consider the whole final mineral contents of the cements and compare them with the mineral mixtures that in each case can be predicted from the position of the points in the diagram, we must conclude that generally there is only a partial agreement. From the position of cements *1* and *a* it follows that they should give rise to a mixture of monoaluminate, Gehlenite, and disilicate if final equilibrium is reached. The crystallization would be finished in point I where a resorption of Gehlenite would occur with formation of disilicate. Surely the quantity of disilicate would be small in *1*, but in none of the two cements could this mineral be demonstrated.

If we leave the abnormal cement No. *4* (Pargas) out of consideration, all the remaining CaO-richer cements—Nos. *2*, *3*, and *b*—would at final equilibrium contain mixtures of monoaluminate, disilicate, and 5:3-aluminate. The crystallization would in one case—*1*—pass point I and after the reaction in this point, where the Gehlenite separated would be used up, continue to II. The other cement-melts would directly reach the boundary line between I and II, the remaining solution then continuing to II, where the crystallization would finish. But only monoaluminate and restricted amounts of disilicate have been found in the slides of *2* and *3*, 5:3-aluminate not appearing. In cement *b* 5:3-aluminate is present but in the form of the unstable modification and the manner in which the mineral occurs again indicates an early appearance.

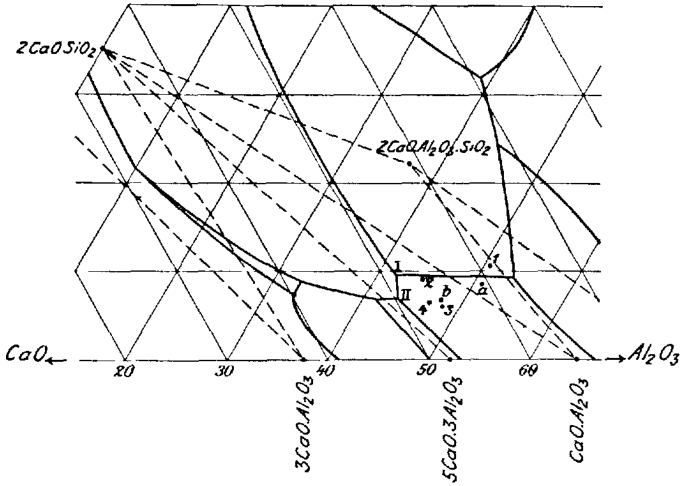

FIG. 8. Position of the Investigated Cement-Clinkers in the CaO-Al_2O_3-SiO_2-Diagram. *a* and *b* the cements examined by the author in 1933.

As a summary we may conclude that the *actually crystallized mineral mixtures generally do not agree with those expected from the diagram of the pure components, the members of the latter richest in CaO not appearing.*

We might suppose this fact to be explained, *e. g.* by lime being stored up during the crystallization in the remaining fluid, which has congealed as a glass. This would correspond to the relations which seem to be generally accepted for the Portland cement, and SOLACOLU had previously proposed a similar supposition for the aluminous cement. The experiences from the rest-melts studied in this work do not speak in favour of this theory as the rest-melts in the cases where they have been isolated and analysed are poor in CaO. The substances enriched are iron oxides and in cement *1* with a medium iron content also aluminium. It is true that the glass may have been somewhat dissolved during the isolation with HCl, but it is not likely that this would involve a complete disturbance of the proportions of the oxides in the residues. Furthermore, direct tests, with White's reagence, on the finely powdered CaO-rich cements *2* and *3* gave a negative result.

Another explanation of the lack of agreement between the actual and theoretical mineral mixture in the aluminous cements would be the influence of the iron oxides and TiO_2 and their capability to combine with and consume CaO as shown in this work not only in ferrites but also in different molecules miscible with the ordinary pure cement minerals. Relations of this kind may be of considerable importance for the mineral building and appear to constitute the chief cause of the failure of the CaO-rich minerals, theoretically expected.

Acknowledgement.

The writer is greatly indebted to Director E. Rengade who kindly placed an analysis of the French cement at his disposal, to Dr. A. Bygdén and Dr. G. Assarsson for valuable analytical work and to Cand. Phil. E. Ygberg for the performance and calculation of X-ray photographs.

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Discussion.

Mr. B. Tavasci:[1]

Melted Cement containing Iron.

Introduction.

The author uses this denomination for melted cements in which iron in a bi- or tri-valent state is present in notable quantities. The study of their constitution offers a great complexity, as, besides the usual elements, lime, silica, and alumina, iron intervenes in its two forms of combination, whereby the system from ternary becomes quinary The fact that not all the binary or ternary systems are known, or at least not in a complete way, suffices to show how far away we are from the knowledge of the whole quinary system, a knowledge which is necessary, if, on the basis of such system, we want to deduce the nature and eventually the quantity of the single constituents which may be present in a cement melted under the said conditions.

A second inconvenience is caused by iron in the study of the constitution of melted cement, namely: part of the constituents are opaque, or at least little transparent, and this is a great obstacle when observing thin sections.

These considerations show that, generally, a complete and accurate determination of the constituents with regard to their chemical and mineralogical nature is not possible.

This necessary preliminary statement having been made, it has been endeavoured to approach, through these researches, the study of one of these cements, made in Italy, containing both ferrous and ferric iron in notable quantities.

Chemical composition of the cement studied:

SiO_2	5.64 %
Al_2O_3	36.80 %
TiO_2	2.00 %
Fe_2O_3	12.58 %
FeO	5.66 %
CaO	35.84 %

An analogous study previously made by the writer [of which the present one is in a certain sense the continuation (3)] on a melted cement of a simplet

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[1] Dott. Ing., Laboratorio Prove Materiali, R. Politecnico di Milano, Milano, Italy.

constitution on account of the practical absence of iron, has been of great utility in the present work.

The method employed, but for some additions, has been the same. The mineralogic and the metallographic microscopes have been used jointly, so as to be able to add the advantages of the one to the other, thereby obtaining concordant results.

The mineralogic microscopic study has been made essentially on thin sections; in a secondary way also on powder when there was a question of ascertaining some index of refraction.

The study by metallographic microscope has been made on specimen duly polished with alumina, usually suspended in alcohol, sometimes in water. Some indication on the respective technique has been given in a previous paper by the writer (4).

The principal etching reagents employed in this second method of study, are the following:

No.	Composition	Temperature of Etching in °C	Time
1	H_2O	100	10—15 sec.
2	$Na_2HPO_4 \cdot 12H_2O$ .... g 2 NH_4Cl .... » 2 H_2O .... ml 100	100	3—5 min.
3	HF 1 : 20	ordinary	1—2 min.
4	Borax 1 %	100	30 sec.
5	Sodium hydroxide 10 % .... ml 40 Sodium phosphate 10 % .... » 10	50—55	45—60 sec.

When interpreting the observations made it has been necessary to bear in mind also the results obtained from two other researches by the writer (5, 6), of which the present one constitutes in a certain sense a completion.

Observations on Melted Cement.

Macroscopic Aspect.

The small blocks obtained by a rough smashing of the solidified mass do not present a uniform aspect. On some of them, as a matter of fact, a distinct crystallization can be observed with a naked eye; in others the aspect is that of a compact mass; besides, a fibrous structure, and finally also some vitreous zones have been observed. The latter are evidently formed on the cooling surface of the melted mass; their thickness is, however, not great; generally it is less than 0.5 cm. The fibrous structure zone is observed under the vitreous zone; its thickness is a few cm, and the fibres are normally directed towards the cooling surface; this is in natural accord with the laws regarding the development of crystals.

General Aspect in Thin Section.

On first observation one can distinguish three principal zones, which can be recognized by their distinctly different optical character. The first is formed by colourless crystals, usually of large dimensions (FIG. 1) of prismatic shape and with fairly strong birefringence: monocalcium aluminate can be easily recognized in them.

FIG. 1. Natural Light.
Magnification 100 ×.

The second zone, in quantity clearly inferior to the preceding one, is characterized by a marked pleochroism and a very weak birefringence. Its optical character is similar to that of Gehlenite; the indices of refraction are, however, relatively higher than those of the pure compound, because its powder immersed in α-mono-brom-naphtalene presents itself clearly in relief. There can also be noted a zonal structure; the external zone of the crystals is usually more birefringent than the inner one. The pleochroism manifests itself by a light yellow-greenish colouration in the direction of the optical axis (negative) and a bluish colouration in the normal direction. In FIG. 1 Gehlenite is visible in the shape of relatively small greyish crystals.

The third zone is, finally, formed by more or less opaque substances, or by others included in them. Several can be distinguished, and among them with certainty: a constituent in small prismatic crystals, and with very strong pleochroism, a constituent of a red-brown colour, isotropic. Other substances are also observed but it is not possible to make a precise distinction of them. They are dealt with below.

Special Observations.

Constituents A and B.—FIG. 2 reproduces the aspect of a specimen, simply polished, under the metallographic microscope.

Both in the grey zone and in the clear one (in the original photograph) a scission in parts of the refracting power can be noticed. Besides, light granules in strong relief are noticed.

FIG. 2. Not attacked.
Magnification 200 ×.

Reactive No. 1 in FIG. 3 brings out, (3), by colouring them more intensely according to their orientation, the crystals of monocalcium aluminate (which we shall call constituent *A*). In this compound its known tendency to twinning can be noticed. It is clearly visible that FIGS. 2 and 3 relate to the same point of the specimen.

In FIG. 4, also relating to the same point, with reactive No. 2 is brought out the Gehlenite (constituent *B*) all covered with white inclusions and of which, on account of the different intensities of colouration, the zonary structure can again be noticed.

In FIG. 5 this fact is more evident in crystals deprived of inclusions.

Constituent C.—With the monocalcium aluminate of FIG. 3 and the Gehlenite of FIG. 4 the grey zone does not yet result wholly covered: there still remain some spots which appear slightly lighter than the rest.

This brings us to the conclusion (4) that the substance in question (constituent *C*) has a slightly higher index of refraction than that of the monocalcium aluminate and of the Gehlenite, namely about 1.7.

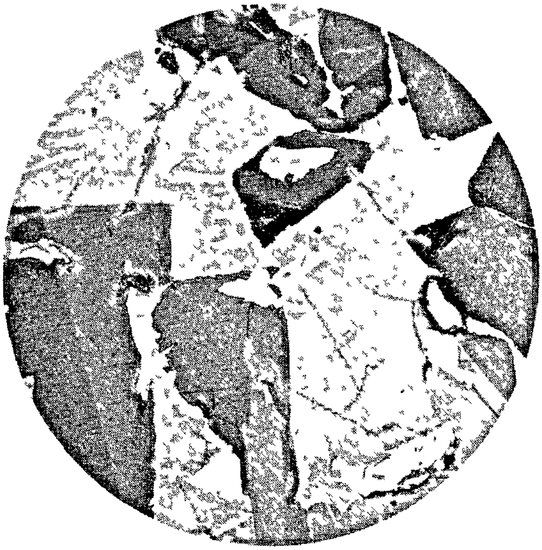

FIG. 3. Etching Reagent No. 1.
Magnification 200 ×.

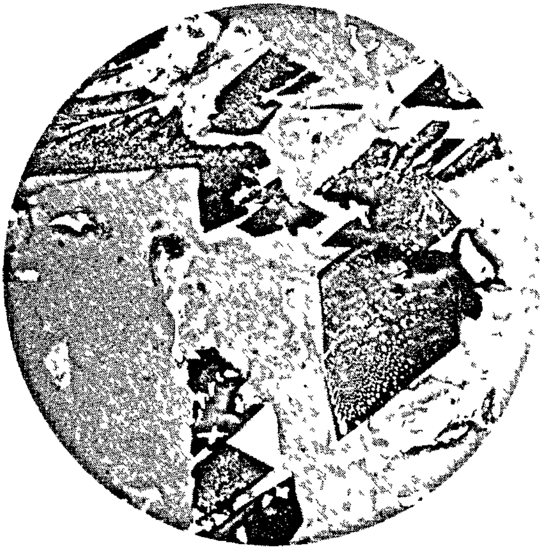

FIG. 4. Etching Reagent No. 2.
Magnification 200 ×.

This substance is coloured (FIG. 6) by reactive No. 4 (it is attacked also by other reactives, for example by No. 5 and No. 1, in the latter case, however, without any noticeable colouration). It presents itself in elongated crystals, sometimes in a bundle, immersed in the clear mass, or usually alongside with the Gehlenite. One of its particular aspects is reproduced in FIG. 7.

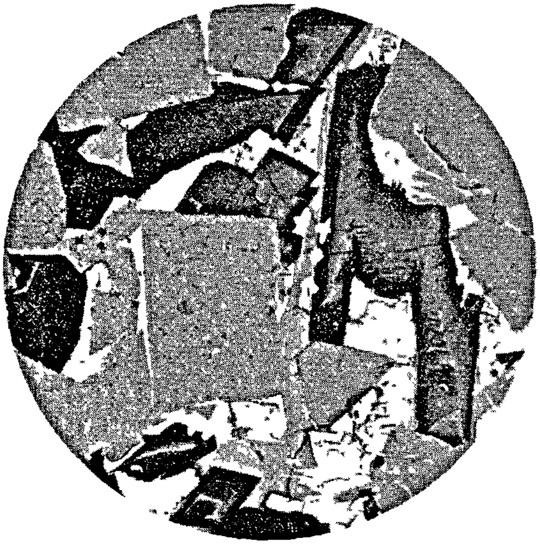

FIG. 5. Etching Reagent No. 2.
Magnification 200 X.

FIG. 6. Etching Reagent No. 4.
Magnification 200 X.

This substance corresponds to the constituent in the form of prismatic crystals of a strong pleochroism, of which mention has been made in the general observations, and which optically, taking into account the uncertainty caused by its pleochroism, which strongly hinders the determinations, results: biaxial, positive, acute bisectrix and optic axial plane parallel to the elongation. Pleochroism α very intense, β less intense azure, tending to greenish; γ olive-green. Birefringence: about 0.010 + 0.015. The indices of refraction seem to be, though by little, all above 1.71.

Let us now try to determine the chemical nature of the constituent *C*. Its optical properties, except for the pleochroism and a slightly smaller birefringence, are similar to those of the silicate bicalcic β. At the beginning it appeared therefore that the constituent *C* could be identified in this compound, some simple considerations of chemical character lead to conclusions which agreed well with this assumption.

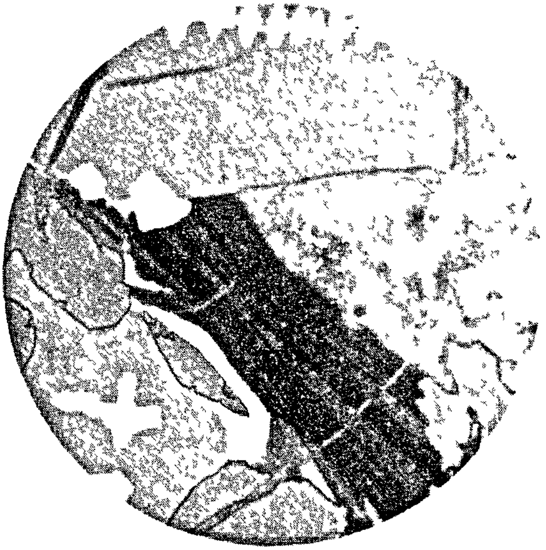

FIG. 7. Etching Reagent No. 4.
Magnification 500 ×.

By an approximate valuation of the single constituents (or of their mixtures) and taking into account the chemical composition of those which are known and of the total composition of the cement, we shall be able to obtain some useful indication as to the unknown constituent.

In our case the monocalcium aluminate constitutes (FIG. 8), in volume, nearly half the melted cement (we may value it at about 45 %); by the same procedure we can value the Gehlenite, also in volume, at about 25 %. The constituents (30 % of the total) which through the metallographic microscope appear lighter in colour can be divided into two parts: one part, about 6—8 %, constituted by Magnetite (constituent *D*) and the rest by compounds containing also calcium oxide, about which more later on. Let us now consider the proportions in volume to those in weight; taking into account the approximate specific weight; let us then compute the quantity of CaO relative to the various constituents and let us subtract it from the total quantity of the cement. If we finally value at about 8—10 % the proportion of constituent *C*, approximate as the preceding calculations may be, we must arrive at the conclusion that this constituent must be very rich in CaO. This fact which agrees with the hypothesis specified above, agrees also with this other one: that the constituent *C* represents the unstable form of $5CaO \cdot 3Al_2O_3$

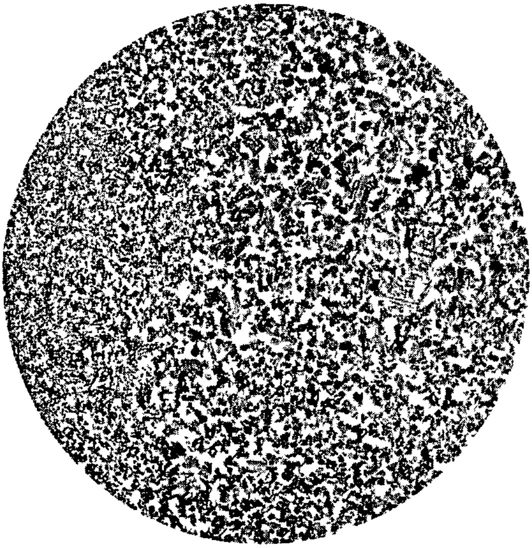

FIG. 8. Etching Reagent No. 1.
Magnification 10 ×.

[several scientists (1) believe that this formula is not quite exact]. This compound in the above-mentioned form, has optical properties which vary with the content of foreign substances, but which can however be compared quite well with those of the constituent *C*. Mainly the marked pleochroism is characteristic of this substance; a particular which had escaped in a first instance the writer's attention. SUNDIUS (2) has quite recently pointed out several aspects of it.

Considering that the bicalcic silicate is not known as a distinctly pleochroic substance and that the constituent *C* is not sensibly attacked by the hydrofluoric acid [in that it differs also from the bicalcic silicate (4)] it can be logically supposed that the constituent *C* represents the instable form of $5CaO \cdot 3Al_2O_3$. It is to be noted that a tempering of the molten cement (in pieces) at 1 100° for some hours causes the total loss of pleochroism both in constituent *B* (Gehlenite) and *C*. Furthermore, the latter becomes turbid in such a way as to be scarcely recognizable.

Constituent D.—It has already been said that this is constituted by Magnetite, without however supporting this statement and without specifying the way in which this constituent presents itself. Cement certainly contains Magnetite, and in relatively large quantities because this can be ascertained by a magnetic test. The chemical nature of Magnetite tells us at once that constituent *D* must be the least easily attacked by micrographic etching reagents: after a certain number of attacks on one and the same specimen, the same constituent must appear in relief on the rest. Furthermore, it must be isotropic if observed by reflection with polarized light.

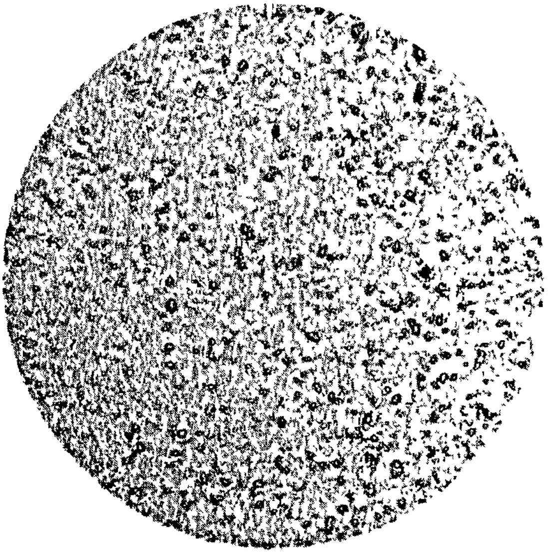

FIG. 9. Not attacked.
Magnification 10 ×.

The granule in strong relief observed on the right side in FIGS. 2, 3, and 4 corresponds to all these requisites. The presence of Magnetite has also been confirmed, as it will be seen later on, by X-ray process.

That this substance is relatively abundant in the cement studied is shown by FIG. 9, in which it appears fairly evenly distributed in the form of small lightly coloured granules in the centre, and dark ones at the periphery on account of the very strong relief.

Constituent *D* was practically unattacked by all the reagents employed in this research.

Constituents E, F.—The largest part of the complex of opaque substances is constituted by an intimate aggregate of two substances, an aggregate which can scarcely be detected without the use of powerful magnification and of reagents capable of bringing it into evidence.

It presents itself on the whole with a very weak relief and with relatively low reflecting power (at least as compared with Magnetite). A distinction between the two constituents, though difficult, is nevertheless possible also with only the water polish, by which it is attacked with slight relief (FIG. 10, in which the contrasts have been increased on purpose to render the foregoing evident). Etching reagent No. 3 attacks (FIG. 11) that of the two constituents (which we shall call *F*) presenting itself in relief, and which has, besides, a slightly stronger reflecting power.

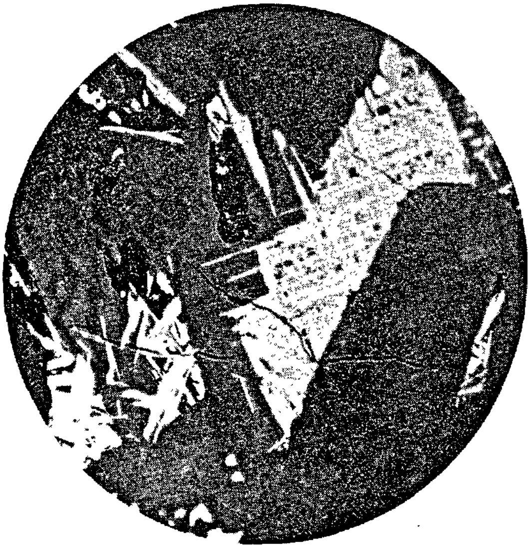

FIG. 10. Not attacked.
Magnification 500 ×.

In FIG. 12 one can observe that reagent No. 5 (after the action of which it is advisable to let a slight polishing action follow) attacks, on the other hand, the other constituent (which we shall call *E*).

These and other micrographic characteristics correspond enough to those of a mixture of solid solution α and β relative to the system $CaO\text{-}Al_2O_3\text{-}Fe_2O_3$ (6). One can therefore identify in *E* the solid solution $\alpha(2CaO \cdot Fe_2O_3 : 4CaO \cdot \cdot Al_2O_3 \cdot Fe_2O_3)$ and in *F* probably the solid solution $\beta(CaO \cdot 2Fe_2O_3 : CaO \cdot \cdot Al_2O_3 \cdot 2Fe_2O_3)$. In respect of some characteristics constituent *F* could be considered similar to the constituent γ found by the writer in the quoted system. The micrographic characteristics of β and γ are very similar; it is therefore easy to mistake the one for the other. However, a tempering at 1 100° for some hours does not cause it to disappear, whereas it would have such action on the constituent γ.

The large dark crystals of FIG. 12 relate to the constituent *C*, the attack of which has not been eliminated by a successive slight polishing.

Another aspect similar to that of FIG. 12, but with a finer structure is shown in FIG. 13. In these two cases the mixture is intimate and uniform; some other time, instead, a clear prevalence of one of the two constituents is noted, and especially of *E* (which has been observed also isolated) or a distinct process of separation of one from the other.

Granules considered as aggregates of the constituents *E* and *F* have also been observed through the mineralogical microscope: their aspect was also similar to that of a mixture of the solid solution observed under the same conditions.

FIG. 11. Etching Reagent No. 3.
Magnification 500 ×.

The same aggregate can sometimes be observed in a thin section: the visible needles are usually yellowish, birefringent and with a positive extinction parallel to the elongation. In a thin section we observe sometimes birefringent crystals, optically negative, with positive elongation and with an absorption $\gamma > \alpha$. These properties correspond to those of the solid solution α, rich of the compound $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$; the crystals indicated differ, however, from the latter through a deeper reddish colouration, which is variable in its intensity.

This may, however, lead to think of another substance with optical properties (excluding the colouration) similar to those of the said solid solution. But if we bear in mind that constituent *E* has been observed (in reflected light) also isolated, and that in thin section also the aggregate of thin needles can sometimes be observed clearly reddish (when it is immersed in the practically opaque mass, in which case a strong illumination is necessary) we must conclude in the negative sense with regard to the above-mentioned hypothesis and assume that the said crystals relate to constituent *E*.

Constituent G.—Mention has already been made in the general remarks of an isotropic constituent having an intense red-brown colouration: we shall distinguish it by the letter *G*. It presents itself generally in a varied dendritical aspect.

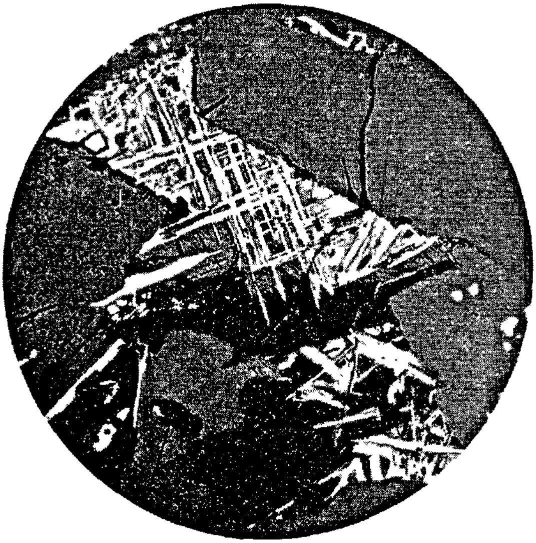

FIG. 12. Etching Reagent No. 5.
Magnification 500 ×.

FIG. 14 (photograph taken with orange-yellow light to lessen the contrasts) shows in thin section one of these aspects. Another one is visible on top of FIG. 7 to the observation with reflected light.

From a careful observation of FIG. 14 one can deduce for constituent *G* a high index of refraction.

Its hardness does not seem to be excessively high, as on the metallographic preparations the relief is poor. Although it has been found also for this constituent a reagent which can attack it (No. 3 at 100° for about 10 sec.) and, therefore, make it distinguishable in reflected light, from other constituents, nevertheless from observations made did not emerge sufficient elements by which the chemical nature could be determined. No natural mineral corresponded to all these characteristics.

At first it has been thought, however, in view of the chemical nature of the cement, of a generic Spinel. Had it been so, the treatment of cement with cold diluted hydrochloric acid (followed by a washing with warm sodium carbonate to eliminate gelatinous silica, if any) should have let them pass into the insoluble residue. It was of course necessary to see that the attack was complete. It has been really observed that constituent *G* was passing into the insoluble residue together with large quantities of Magnetite, the identity of which has been in this case checked by the X-ray method. In a second case the Magnetite was eliminated magnetically from the insoluble residue: the small residue thus obtained, in the form of a dark red-brown colour, showed itself as being formed for the greatest part by constituent *G*. The respective X-ray (the chemical analysis was not possible for lack of material) clearly showed that it was a question of monometric crystals but with one side of the elementar cell of 3.80 Å.

FIG. 13. Etching Reagent No. 5.
Magnification 500 ×.

On the basis of data of structural tables it was possible to exclude at once that it was a case of spinels (the side of which is more than double); instead, the coincidence of the indicated datum with that relating to Perovskite ($CaTiO_3$) was noted. An immediate comparison of the X-ray obtained with that of a sample of natural Perovskite showed the identity: constituent *G* was identified. Evidently, its intense colouration, lacking in natural Perovskite, was hiding its nature.

Other constituents.—By chemical analysis it can be found that constituent G can be present in cement at the utmost in a proportion of about 3.4 %. The remaining constituents, except those already studied, are found in quantities much smaller than that of constituent G, and therefore practically negligible. Nevertheless, it is worth while mentioning them.

In Fig. 10 one can observe, embedded in the aggregate of constituents E and F, some clear small granules of another constituent which, as shown by Fig. 11, is strongly attacked by hydrofluoric acid. Besides its lighter reflective power, it can be distinguished from constituent F also because it can be attacked, unlike the latter, in a few minutes by a mixture of equal parts of hydrofluoric acid 1 : 10 and ethylic alcohol. Furthermore, it is birefringent (observation with light polarized by reflexion).

Fig. 14. Natural Light.
Magnification 500 ×.

Something similar has been observed by the writer in some mixtures with little CaO of the system $CaO\text{-}Al_2O_3\text{-}Fe_2O_3$ (6) brought up to such a temperature as to cause the partial reduction of the iron from the ferric into the ferrous state. There have also been observed (always in negligible quantities) some constituents more reflecting than E and F, birefringent, and sometimes with small relief, some other time with a relatively strong relief.

Structural Varieties.

Already in Fig. 8 it may be noted that the crystalline "grain" does not appear constant, but varies rapidly from one zone to another. At the centre it is rather rough, that is to say of the type reproduced in the preceding FIGS. 1 to 8. It may be opportune to reproduce now some aspects of the same, showing the change-over from the rough form up to a form preceding (it would be better to say: following) the vitreous state. FIGS. 15, 16, 17, 18 (compare with FIG. 2) show this change-over.

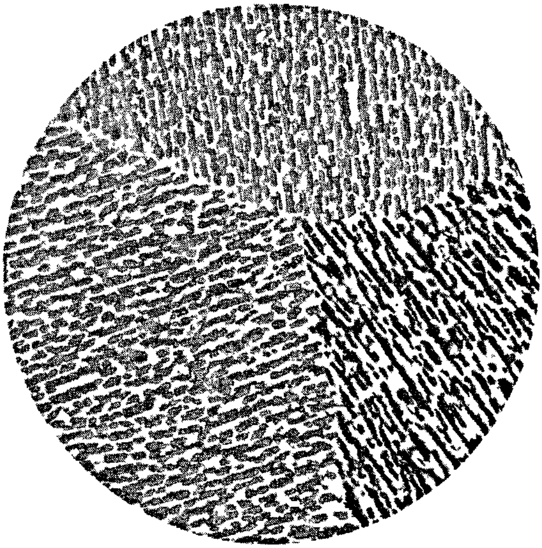

FIG. 15. Etching Reagent No. 1.
Magnification 200 ×.

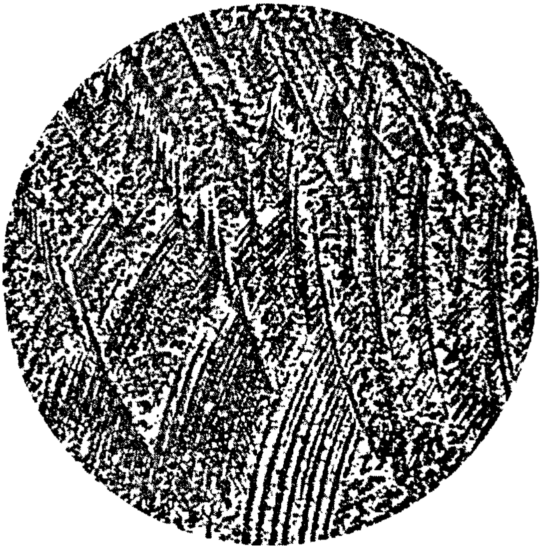

FIG. 16. Etching Reagent No. 1.
Magnification 200 ×.

In FIG. 15 the separation of the constituents is already noticeable. Not so in FIG. 16 (the dark stripes are monocalcium aluminate) and still less in FIG. 17, which represents the fibrous structure mentioned in the macroscopic observations. Finally, in FIG. 18 (the attack with R3 in these conditions, except for glass, always gives the aspect of an attack with R1)

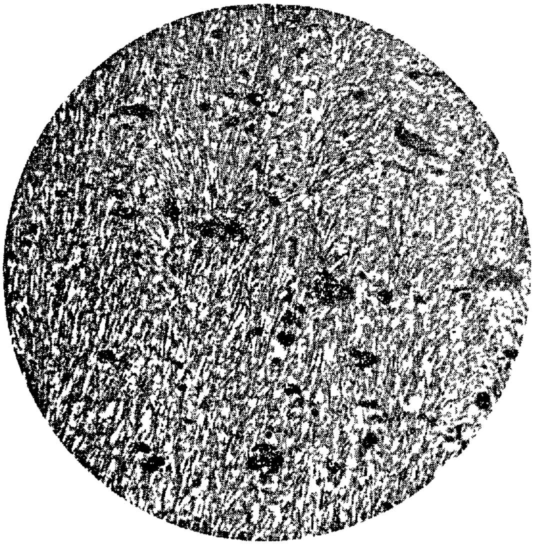

FIG. 17. Etching Reagent No. 1.
Magnification 200 ×.

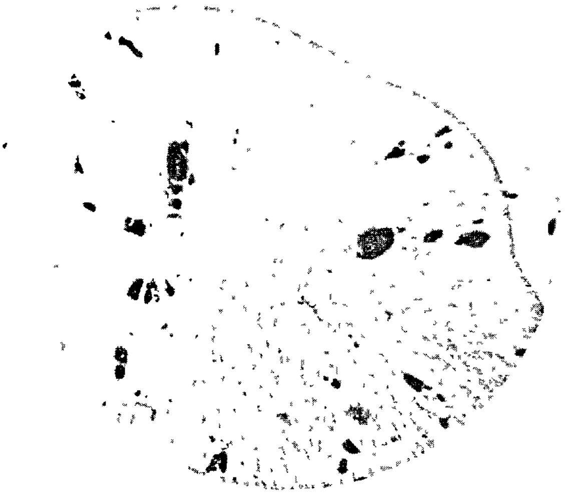

FIG. 18. Etching Reagent No. 3.
Magnification 200 ×.

one can observe the distinct passage into the vitreous zone. Very clearly visible are in this figure the two centres of crystallization; from which start, with a fibrous radiated structure, the microcrystals.

Mechanical Properties.

The molten cement studied can stand in normal tests:

with one day's seasoning	40 kg/cm²	traction
	600 kg/cm²	compression
with 28 days' »	50 kg/cm²	traction
	800 kg/cm²	compression

Summary.

The constitution of a melted cement containing considerable quantities of iron, both in the ferrous and in the ferric state, has been studied. Optical methods of observation, suitably combining those by transparence with those by reflection, have been principally used. In spite of this, it has been sometimes found necessary to have recourse also to chemical and X-ray methods. Taking into account the researches by the writer on the system CaO-Al_2O_3-Fe_2O_3, seven different constituents, which are listed hereunder in order of their frequency, have been found:

monocalcium aluminate, Gehlenite, Magnetite, unstable 5 : 3-calcium aluminate, solid solution of $2CaO \cdot Fe_2O_3$ with $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, solid solution of $CaO \cdot 2Fe_2O_3$ with $CaO \cdot Al_2O_3 \cdot 2Fe_2O_3$, Perovskite. Besides, others, though in negligible quantities, have also been found.

The constituents listed above differ in their properties, in a more or less marked degree, from the respective components in the pure state.

Some structural varieties of the cement studied have been illustrated, and finally some mechanical properties have been pointed out. — *(Translated from Italian.)*

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Mr. F. M. LEA:[1]

In his interesting paper, Dr. SUNDIUS refers on p. 399 to the compounds of lime and titania. A phase equilibrium investigation of the system CaO-

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-$CaO \cdot Al_2O_3$-$CaO \cdot TiO_2$ has recently been completed by NURSE and the present writer. The only calcium titanates found to exist in equilibrium with liquid in this system are $CaO \cdot TiO_2$ and $3CaO \cdot 2TiO_2$. The compound $CaO \cdot TiO_2$ takes up a few per cent $CaO \cdot Al_2O_3$ in solid solution changing in optical character from weakly birefringent (α and γ between 2.35 and 2.40) to isotropic ($n = 2.38$). No evidence of solid solution of $CaO \cdot TiO_2$ in $CaO \cdot Al_2O_3$ was found. The two compounds, $CaO \cdot Al_2O_3$, $CaO \cdot TiO_2$, apart from the limited solid solution mentioned, form a binary eutectic series with eutectic at 22.3 per cent $CaO \cdot Al_2O_3$, M.P. 1 470° ± 5°. It is to be expected that in aluminous cement titania will occur, at least in part, as $CaO \cdot TiO_2$ containing a small amount of $CaO \cdot Al_2O_3$ in solid solution. The compound $3CaO \cdot 2TiO_2$ does not co-exist at invariant points with $CaO \cdot Al_2O_3$ or $5CaO \cdot 3Al_2O_3$, but only with CaO, $3CaO \cdot Al_2O_3$ and $3CaO \cdot Al_2O_3$, $CaO \cdot TiO_2$. Its formation in aluminous cement is therefore unlikely.

Mr. A. TRAVERS:[1]

Estimation of the Aluminates of Lime in an Anhydrous or a Hydrated Cement.

With my pupil, M. F. CLAUSE, I endeavoured to work out a simple procedure to investigate these important constituents.

Struck by the solubility in pure water of the anhydrous monocalcium aluminate, applied by M. SÉAILLES in his separation of the other compounds (silicates, silico-aluminates), we asked ourselves whether this same property could not be extended to all categories of aluminates.

This extrapolation is possible, but only on condition:

1. of operating in boiling water, free of CO_2, and protected from this gas;
2. of preventing all hydrolysis by maintaining a suitable P_H;
3. of remaining below the saturation of tricalcium aluminate hexahydrate, *only stable as substance of deposit in the conditions* of the experiment.

Conditions 2. and 3. are realized as follows:

a. addition of a suitable volume of lime-water (50 mg CaO in 500 ml);

b. dilution such that one remains below the saturation of the aluminate of THORVALDSON (0.3g $3CaO \cdot Al_2O_3$/litre).

In the case of hydrates of aluminate *rich in CaO*, $Al_2O_3 \cdot (3 + x)\ CaO \cdot Aq.$, the addition of lime-water is not necessary.

This very simple method enables one to show:

1. that in *aluminous* cement only $^3/_4$ of the alumina is in the form of $CaO \cdot Al_2O_3$;

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[1] Professeur, Ecole Supérieure des Industries Chimiques, Université de Nancy, Nancy, France.

2. that the "prompt" cements are rich in *tri*calcium aluminate, which explains the rapidity with which they set;
3. that the Portland cement- "*clinker*" contains *tri*calcium aluminate;
4. that the *basic slags* from Lorraine contain only traces of this compound.

The sulpho-aluminate of CANDLOT not being stable at 100°, all the aluminate goes into solution when one treats this salt in the same conditions as the aluminates. — *(Translated from French.)*

MR. N. SUNDIUS (*author's closure*):

The paper of Dr. TAVASCI contains a valuable contribution to our knowledge of the mineral content in the aluminous cements. In most cases the author agrees with him. Only in the case of the presumed Magnetite I have some doubt. It is said to be a relatively abundant constituent, fairly evenly distributed; furthermore, it is found to be isotropic and hardly soluble. If I have some doubt about this identification it is because I have myself in my later work found that what I earlier believed to be Magnetite in the aluminous clinkers could be shown to be a Wüstite-bearing glass. All the properties mentioned above agree with those of the glass. According to my experience glass of this composition is generally present in aluminous cements.

The paper of Dr. LEA is an important contribution to the experimental work necessary for the understanding of the crystallization in aluminous cements. Especially the author was interested by the fact that the experiments did not suggest any other Ca-titanate in the mixtures of the cement than $CaO \cdot TiO_2$ which well agrees with the relations actually found in the clinker. Concerning the monoaluminate and its capacity to dissolve foreign substances the question will not be fully answered until experiments including also iron have been performed.

If the method proposed by Prof. TRAVERS to determine the content of aluminates in a cement is proved to be valid it will offer a good help in calculating the mineral contents of clinkers. Calculations of the minerals in aluminous cement-clinkers performed merely on account of microscopical and chemical tests suggest in most cases somewhat higher values for the content of monoaluminate than corresponding to the boundary value of Prof. TRAVERS but in most cases the differences are small. From the short communication of TRAVERS it does not appear if there is reckoned with the complications introduced by mixtures of different aluminates in the clinker, especially the presence in some cases of the unstable 5 : 3-aluminate and with the influence of contaminations in the minerals.

REACTIONS OF ALUMINOUS CEMENT WITH WATER

BY

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PHIL. DR.

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Introduction.

The reactions of water on high alumina cement are closely related to the properties of the components constituting these technical cements. However, some of these constituents have not as yet been sufficiently investigated; some have not yet been prepared pure of the composition in which they occur in the technical products. The hydration reactions of aluminous cement, have, then, hitherto been studied only in the compounds of the pure components and in the technical products. The connection between these two kinds of hydration reactions will be discussed below. The old formulae of the compounds as given by RANKIN and WRIGHT (29) have been used, as most of the investigations have been made on material prepared according to them. The pure compounds treated below are C_5A_3, CA, C_3A_5, C_2F, C_2AS.

Earlier Investigations.

Hydration of Pure Calcium Aluminates. The reactions of the three calcium aluminates (C_5A_3, CA, C_3A_5) shown as compounds of technical aluminous cement can be treated simultaneously.

The first investigations of the setting reactions of calcium aluminates (MICHAËLIS, FREMY, and others) disclosed their hydraulic properties but the hydration reactions and the hydrated products were not examined in any detail.

LE CHATELIER (22) was the first investigator to study the hydration reactions of the calcium aluminates and their hydrated products. The aluminates, supposed to have the composition CA and C_3A_2, were shaken with one litre of water in portions of 1 and 10 g. An excess of calcium hydroxide was proved in the solutions, after some time, and a great portion of aluminium hydroxide and some crystalline calcium aluminate hydrate was formed. A portion of these aluminate solutions mixed with calcium hydroxide solutions immediately yielded crystalline products. LE CHATELIER concluded from these experiments that the setting properties of the anhydrous calcium aluminates should be referred to supersaturated solutions, which yield hydrated alumina and calcium aluminate hydrates during the setting. CANDLOT (9) also used a supposed calcium aluminate C_3A_2 for shaking with water; the solutions contained $Al_2O_3:CaO$ of a molecular proportion of, after 4 hours, 1:1.2, and after three months, 1:2.5. CANDLOT had other purposes in view than the study of the hydration reactions of the calcium aluminates; the results were therefore not utilized, from this point of view.

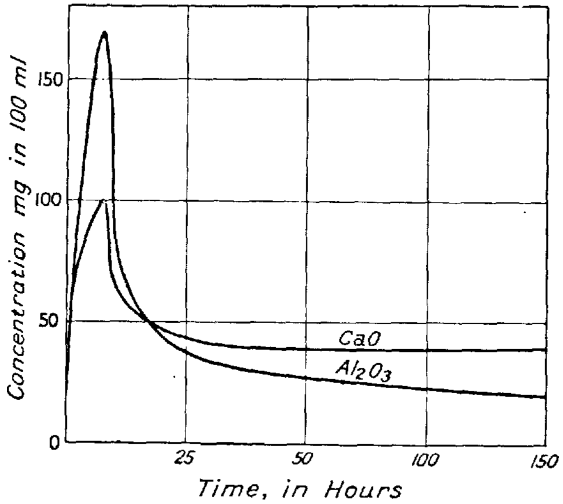

FIG. 1. Solution obtained on Shaking Anhydrous Monocalcium Aluminate with Excess Water (0.5 g per 100 ml). After NORTH (26).

In his investigations NORTH (26) again took up the question of the hydration of the calcium aluminates. During this work the first papers on the three-phase system CaO-Al_2O_3-SiO_2 were published by the Geophysical Laboratory. NORTH used compounds of the supposed compositions CA, C_2A, and C_3A, and shook the powdered compounds with water. The data of the hydrated products are mentioned rather briefly; dicalcium aluminate hydrate [earlier prepared by ALLEN and ROGERS (1)] appeared to be the only crystalline phase in equilibrium with the solutions; the anhydrous monocalcium aluminate yielded alumina and dialuminate hydrate. The most important result is the determination of the variation of the concentration of the solutions, which agrees with that obtained in all later investigations (FIG. 1). Later, BATES and KLEIN (1914) and KLEIN and PHILLIPS (1918) mentioned that alumina and tricalcium aluminate hydrate were the chief hydrated compounds of the anhydrous calcium aluminates. LAFUMA (1925) found a hydrated dialuminatic phase in the hydration of C_3A_5; its composition was $2CaO \cdot Al_2O_3 \cdot 7H_2O$.

WELLS (36) used the anhydrous aluminates prepared according to the investigations of the system $CaO\text{-}Al_2O_3\text{-}SiO_2$ carried out by RANKIN and WRIGHT (29). In his study WELLS used 50 g of the anhydrous calcium aluminates shaken with one litre of water. The variations in the concentrations agree with those found by NORTH (FIG. 2). The hydrated phases were amorphous hydrated alumina and chiefly tricalcium aluminate hydrate, according to the optical determinations of BATES. WELLS also found another optically well-defined phase, a cubic crystal, which was later identified by THORVALDSON and GRACE (34) as tricalcium aluminate hexahydrate.

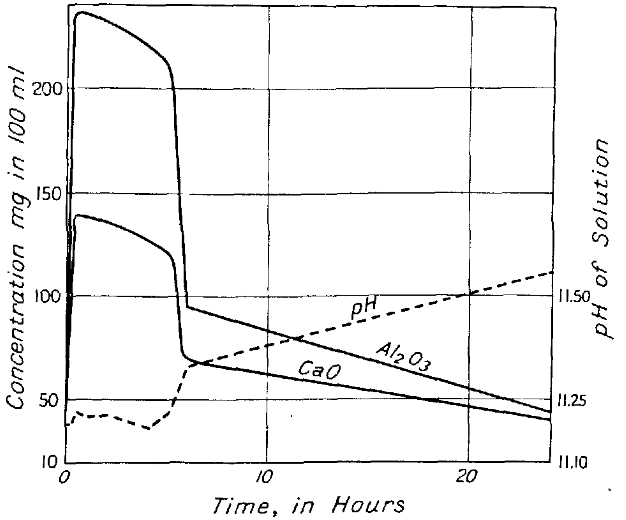

FIG. 2. Solution obtained on Shaking Anhydrous Monocalcium Aluminate with Excess Water (5 g per 100 ml). After WELLS (36).

SCHWIETE and VON GRONOW (32) mentioned that a mixture of anhydrous monocalcium aluminate and calcium oxide yields chiefly dicalcium aluminate hydrate when hydrated at a low temperature. SALMONI (31) used this reaction in his studies of dicalcium aluminate hydrate. KÜHL, THILO and CHI YÜ (20) called attention to the fact that the dicalcium aluminate hydrate first determined by KÜHL (18) as an essential phase in the hydration of aluminous cement is also a chief phase in the hydration of anhydrous monocalcium aluminate.

A study of the hydration reactions was made by ASSARSSON (2, 3, 4). The discussion of the hydration reactions was in this case attacked from another angle; the importance was stressed of a complete knowledge of the conditions in which calcium aluminate solutions yield solid phases. The properties of these solutions must be found in the solutions that surround the clinker grains. Some hydrated products were found, hydrates of mono-, di-, tri-, tetra- and a pentacalcium aluminate (the latter one usually containing a trace of SO_3) and alumina hydrate (Hydrargillite). The deactivation of the anhydrous aluminates and the influence of the varying proportions of anhydrous aluminate to water were emphasized.

In none of the investigations mentioned above was the equilibrium between solids and liquids reached. WELLS (36) carried on his experiments for about one year without, however, proving the real equilibrium.

The results must be seen against the background of the general chemical character of aluminate solutions. Since the first investigations of VON BONSDORFF (8), aluminate solutions have been studied very closely by chemists. The investigations—summaries are given by WELLS (36) and ASSARSSON (4)—show that alumina can be solved into alkali or earth alkali solutions in a concentration such that one equivalent of alkali corresponds nearly to a univalent radical alumina, AlO_4'. These solutions are very unstable; they give off a certain part of their alumina content easily as aluminium hydroxide. Already precipitated alumina catalyzes the decomposition of the aluminate solutions. The solutions thus obtained have an excess of alkali which can be registered as a higher P_H-value. The aluminate occurs mainly as a monoaluminatic ion. Only a very little part of the alumina of the solution can occur dissolved in colloidal form. Some other investigators have been of the opinion that the alumina is present partly or chiefly colloidally solved.

Calcium Ferrites. LE CHATELIER (22) pointed out that calcium ferrites can react with water; the experiments did not definitely show, whether or not a chemical compound was really present. LE CHATELIER repeated the experiments of PELOUZE (27) and demonstrated the formation of calcium ferrite hydrate when ferrihydroxide is shaken with calcium hydroxide solution. MARTIN (24) and NAGAI and ASAOKA (1930) also studied the hydration of calcium ferrites; the two latter investigators showed that only the dicalcium ferrite is hydrated. LERCH (23), and LERCH and BOGUE (7) suppose that the amorphous gel, formed when diferrite is being hydrated, is a dicalcium ferrite hydrate. In his detailed examination of the hydration products of the calcium ferrites, HOFFMANN (15) found that the dicalcium ferrite yields tetracalcium ferrite hydrates at 20°, their probable composition being $4CaO \cdot Fe_2O_3 \cdot 14H_2O$, and at 50° of the composition $4CaO \cdot Fe_2O_3 \cdot 7H_2O$; the former is probably identical with the ferrite hydrate prepared by PELOUZE (27). HOFFMANN also determined the lowest concentration of calcium hydroxide at which the tetraferrite hydrate can exist—1 060 mg CaO per l. Between 1 060 mg and 640 mg per l there is probably a ferrite poorer in CaO but not yet determined as to its composition. EIGER (11) found that ferrihydroxide is transformed to tricalcium ferrite hydrate ($3CaO \cdot Fe_2O_3 \cdot 6H_2O$) when shaken with saturated calcium hydroxide solution; the phase formed contains two kinds of crystals, a cubic one ($n = 1.710$) and a hexagonal one ($n = 1.61—1.66$).

Dicalcium Silicate. The dicalcium silicate is hydrated slowly; the hydration products are gels of calcium silicate hydrates. WELLS (36) studied the hydration of dicalcium silicate with calcium aluminate solutions; the hydration appears to be greatly retarded.

Gehlenite. Most of the earlier investigations of the hydration properties of Gehlenite have indicated that this compound does not react with water to any noticeable degree [ENDELL (12), DYCKERHOFF (10), ASSARSSON (3, 4)]. However, VON GRONOW and SCHWIETE (14) hydrated Gehlenite by shaking the compound for some months with water; in this way they got a thixotropic gel. No other studies of this gel have been published.

Hydration of Aluminous Cement. Almost all the earlier investigations of the hydration reactions of aluminous cement were made by shaking a quantity of cement with a great quantity of water. The variation of the concentration of the solutions and the formation of the hydrated products have been studied. In some cases the products of setting cement when hydrated with small quantities of water were studied. The hexagonal crystalline products were supposed to be tricalcium aluminate hydrate [KLEIN and PHILLIPS (16), PULFRICH and LINCK (28), WELLS (36)] or dicalcium aluminate hydrate [LAFUMA (21), KÜHL (18), KÜHL and BERCHEM (19), VON GRONOW and SCHWIETE (14), KOYANAGI (17), ASSARSSON (2, 3)]. The cubic tricalcium aluminate hexahydrate first identified by THORVALDSON and GRACE (34) was found by WELLS (36), KOYANAGI (17), and others. The optically amorphous substance was supposed to be aluminium hydroxide.

Unlike most other investigators, KÜHL and BERCHEM (19) used samples of coarsely ground aluminous cement and obtained the gelous hydration products free from the others. They found a gel containing a great deal of calcium hydroxide, supposed to be adsorptively bound. They also showed that the gel contained a certain amount of silica.

Assarsson (5) used commercial cement samples, but examined the influence of water per unit of cement when the quantities were varied. It was shown that the small accessoric contents of alkalies of the cements examined changed the concentration of the solutions successively when the quantities of water were reduced. The hydration products were shown to include dicalcium and cubic tricalcium aluminate hydrate; the powder photographs of a gel separated from the solutions show the presence of monocalcium aluminate hydrate. In addition some other compounds were found and the hydration of the clinker grains was studied.

Summary of the Results of Earlier Investigations.

Summed up, the results of previous investigations are partly contradictory. One aim of the experiments is to find the agreement between the hydration reactions of the pure anhydrous calcium aluminates and those of the high alumina cement. Though this point is very important, it must in some cases be partly neglected. For all that, the hydration reactions of the anhydrous calcium aluminates must, nevertheless, always be the most important ones in the hydration of aluminous cement.

The Anhydrous Calcium Aluminates. At lower temperatures (5°) the monocalcium aluminate hydrate must be one of the chief compounds of the hydration products. It is found to be a chief compound of the products in the crystallization of the pure calcium aluminate solutions of about monoaluminatic composition. In the hydration of two of the pure anhydrous calcium aluminates (C_3A_5 and CA), a very small quantity of optically identifiable crystalline products can be found. As the solutions contain calcium and alumina of almost monoaluminatic proportion and this proportion predominates in the concentrated solutions at the beginning of the hydration as well as in the solutions of low concentration at the end of the hydration, the chief product must be the monocalcium aluminate hydrate. The anhydrous compound C_5A_3 yields a great deal of dicalcium aluminate hydrate; the gel substance formed at the same time is probably also monoaluminate hydrate. The presence of the dialuminate and monoaluminate hydrates above mentioned is shown by optical and X-ray methods.

At higher temperatures ($> 20°$) the solutions contain calcium and aluminium in monoaluminatic proportions only in higher concentrations. When the hydrated compounds are formed the concentration decreases rapidly, at the end of the reaction the concentration of aluminium more rapidly than that of calcium. A certain excess of free calcium hydroxide is present in the solutions. The hydrated compounds have been demonstrated to be dicalcium aluminate hydrate and aluminium hydroxide (Hydrargillite). The dialuminate hydrate is easily transformed into cubic tricalcium aluminate hexahydrate. This reaction takes place more easily as the temperature rises; at 90° this cubic trialuminate can be formed as a deactivating layer on the surface of the anhydrous crystals. The anhydrous compound C_5A_3 yields cubic trialuminate crystals already at about 20°; in the hydration of C_3A_5 and CA, on the other hand, the cubic trialuminate will be formed only when the temperature is higher than 20°.

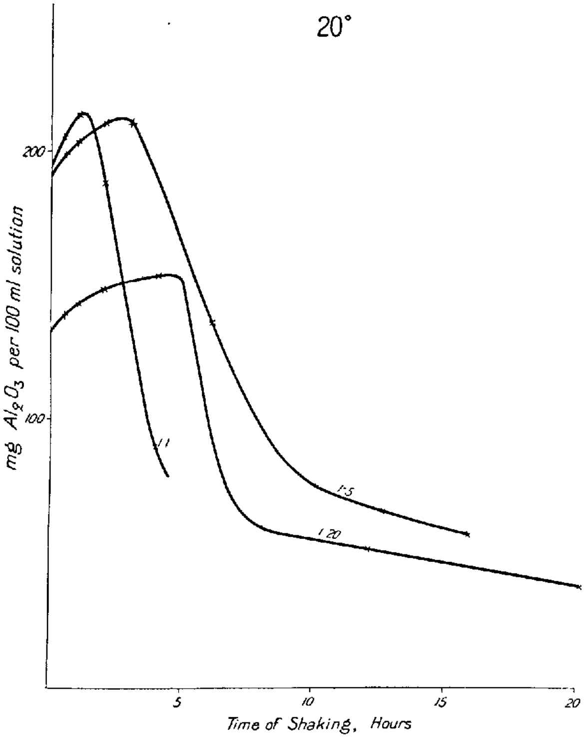

FIG. 3. Content of Al_2O_3 of Solutions obtained on Shaking Monocalcium Aluminate with Varying Amounts of Water at 20°. The Curves of the CaO-Concentration have not been drawn (cf. FIGS. 1 and 2). After ASSARSSON (4).

There are also some other compounds. In the hydration at higher temperatures, there are formed small quantities of a crystal of a hexagonal appearance probably of a tetracalcium aluminatic composition ($\omega = 1.549$, $\varepsilon = 1.527$). The hexagonal plates of the refraction index $\omega = 1.55$, found by WELLS, are perhaps identical with this compound. When the solution acts on the aluminates (especially C_5A_3) at 20° for a long time, there are formed crystals whose refraction indices agree with those of a tetracalcium aluminate hydrate ($\omega = 1.535$, $\varepsilon = 1.520$). There may also be formed small amounts of hexagonal crystals of tricalcium aluminate of the refraction index ω = about 1.530; this ω-index agrees with determinations of THORVALDSON, GRACE and VIGFUSSON (35) of the hexagonal tricalcium aluminate 12-hydrate. When the anhydrous compounds contain traces of sulphate, there are formed some crystals of a needle-shaped pentacalcium aluminate hydrate containing SO_3, the composition of which varies somewhat.

The formation of the hydration products at 20° and higher temperatures has been studied microscopically and with X-rays, hitherto the only methods used. The examinations of the gels in this way have shown that the only aluminium hydroxide occurring with certainty is Gibbsite (Hydrargillite). At 20° there is also formed a gel containing a certain amount of calcium; it consists partly of monocalcium aluminate hydrate. This gel is not found at higher temperatures.

The concentration of the solutions depends very greatly on the relative quantity of water. With a small amount of water, a high concentration is reached more rapidly than with greater amounts. The decomposition of the dissolved aluminate begins sooner with the small amounts of water than with the greater ones (FIG. 3).

The manner in which the anhydrous aluminates are prepared also influences their properties. Some differences in the results published may be attributed to such circumstances. The size of the crystals formed in the melting or sintering of the mixture of lime and alumina influences the reactivity of the aluminates. The anhydrous aluminate pulverized and stored for some time yields solutions of usually more stable kinds and of lower concentrations than the newly prepared aluminate powder due to a formation of a deactivation layer surrounding the crystal grains.

When small quantities of water are used in the hydration, easily dissolved impurities can have a strong influence upon the hydration reactions. The content of alkalies, especially in the aluminates, has a great effect upon the concentration of the solutions and upon the formation of the hydrated compounds. When alkalies occur, the final solution will consist of a mixed alkali- and calcium-aluminate solution.

Dicalcium Silicate, Dicalcium Ferrite and Gehlenite. Dicalcium silicate is hydrated slowly by pure water. When treated with calcium aluminate solutions the silicate is not hydrated [WELLS, (36)]; the grains are probably surrounded by layers of alumina-silica gel causing deactivation.

Dicalcium ferrite yields tetracalcium ferrite hydrate and ferrihydroxide in the beginning of the hydration. When the concentration of the calcium hydroxide of the solutions is small, it is possible that a calcium ferrite hydrate poorer in lime is formed. Probably the dicalcium ferrite is completely hydrolysed by solutions poor in calcium hydroxide.

The hydration of Gehlenite and the products yielded in this reaction have not been investigated in such great detail that a view of the properties of the anhydrous compound can be obtained.

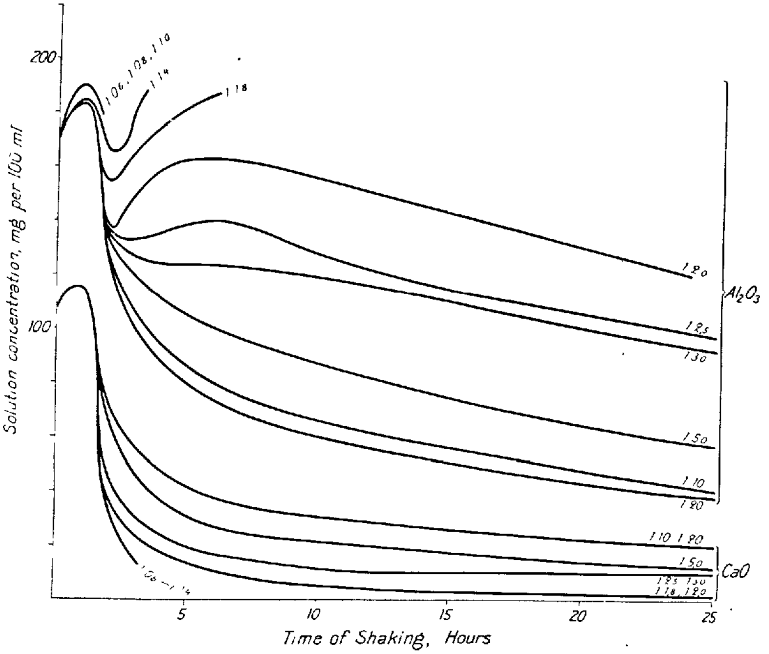

Fig. 4. CaO- and Al_2O_3-Contents of Aluminous Cement Solutions at 20°. Weight-Ratio Water : Cement shown. After Assarsson (3).

High Alumina Cement. The reactions of the anhydrous calcium aluminates appear in the hydration of the high alumina cement when great quantities of water are used, as show most of the earlier investigations. The hydration of aluminous cement in practice, however, takes place with but a limited supply of water. The reactions can be influenced by these circumstances and they may be judged from new points of view. Only a few samples of high alumina cement have been investigated in this way.

The variation of the composition of the solutions when varying quantities of water are used is illustrated in Fig. 4. In this case, a commercial Swedish cement has been used; its mineralogical content is approximately 60 per cent of monocalcium aluminate, 30 per cent of Gehlenite, and 10 per cent of other compounds. The curves show that the concentrations of the solutions depend in a high degree on the quantity of water used. When small quantities of water are used, the final Ca-concentration is lower than when greater amounts of water are used. The variation of the Al-concentration has chiefly the opposite course. The Al-curves have two maximum Al-concentrations, indicating that two reactions overlapping each other take place. When the molecular proportions CaO : Al_2O_3 are calculated the smaller amounts of water are found to contain a concentration of Al_2O_3 considerably exceeding the monoaluminate proportion. This effect increases successively as the quantities of water decrease.

The examinations of the solutions show that a great quantity of alkalies is dissolved during the hydration, and the content of alkalies of the solutions depends very greatly upon the quantity of water used (FIG. 5). The alkalies are slowly dissolved and when small amounts of water are used the final solutions will contain chiefly alkali aluminate, most of the calcium having been precipitated as calcium aluminate hydrates.

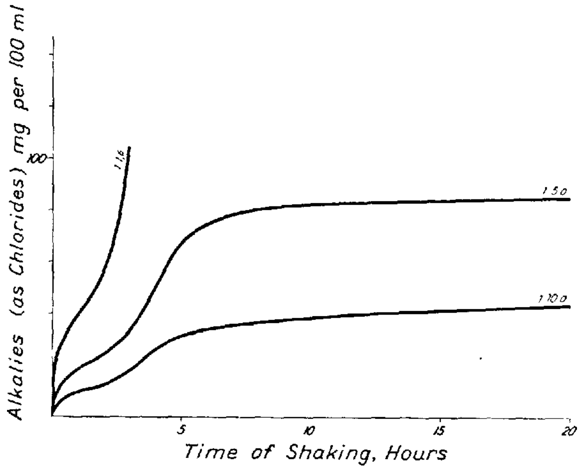

FIG. 5. Alkali Content of Solution of Aluminous Cement. After ASSARSSON (3, 4).

The hydration products formed in the reaction of aluminous cement with water have been only partially identified.

At a lower temperature (20°), dicalcium aluminate hydrate crystallizes. At a higher temperature, the dialuminate is transformed into cubic trialuminate. In addition the monocalcium aluminate hydrate appears at a lower temperature.

Another hydration product is a pentacalcium aluminate with a varying SO_3-content and with refraction indices also somewhat varying ($\omega = 1.487$—1.470, $\varepsilon = 1.480$—1.467). This compound may be found among the hydration products of most sorts of alumina cement. In the hydration of a special Swedish aluminous cement an unknown hexagonal compound appears, of the refraction indices $\omega = 1.498$, $\varepsilon = 1.490$ [Assarsson (2, 4)]. Other calcium aluminate hydrates have also been found. Two kinds of hexagonal crystals with refraction $\omega = 1.535$, $\varepsilon = 1.520$ and $\omega = 1.530$, $\varepsilon = ?$, respectively, corresponding to a α-tetracalcium aluminate hydrate, according to Assarsson, (4), and tricalcium aluminate 12-hydrate, according to Thorvaldson, Grace and Vigfusson (35), have been found in small quantities.

The greater part of the hydration products consists of a gel substance. According to descriptions published of the formation of the hydration products the first attack on the clinker grains is observed as a gel layer with a refraction of about 1.53. During the gradually progressing hydration the clinker grains are transformed into this gel. On the surface of the gel layers, there is formed some gel with a refraction of about 1.48—1.50. Some brown gel lumps are also observed, deriving from the compounds containing ferric oxide; they probably contain mainly ferrihydroxide.

Most of the clinker grains are transformed into gel in this way. Only a few kinds of grains are not attacked. The dark-brown grains of the Wüstite-containing rest-melt (according to Sundius, p. 403) and the perovskite-like mineral [Sundius (33)] are not hydrated. In some cases, the Gehlenite and the dicalcium silicate are hydrated, probably almost completely; there is not found any definitely identifiable residue of these compounds. In other cases, large grains of the Gehlenite remain after the hydration (Assarsson, investigations not yet published). Kühl and Berchem (19) showed that the gel formed in the hydration of aluminous cement contains a great deal of silica. The percentage of silica of the gel was smaller than that of the clinker but a great part was found (Table 1).

Table 1. Composition of the Hydration Products from Aluminous Cement at 12°.
(After Kühl and Berchem.)

Substance	Composition of the Cement Clinker		Composition of the Gel after 77 Days		Composition of the Total Hydration Products after 77 Days	
	per cent	$SiO_2 = 1$	per cent	$SiO_2 = 1$	per cent	$SiO_2 = 1$
SiO_2	7.5	1.0	2.6	1.0	2.4	1.0
Al_2O_3	46.8	6.2	59.0	22.7	56.3	23.2
CaO	41.9	5.6	38.4	14.7	41.3	17.1

The Chemical Character of the Hydration Reactions.

The starting-point for the study of the products formed in the hydration of the anhydrous calcium aluminates must be the conditions determining the properties of the solutions surrounding the grains of the anhydrous aluminates. The hydration taken in this way is to be divided into two stages: firstly the attack of the water on the phase-limit anhydrous compound-solution, and, secondly, the formation of the hydrated compounds of the solutions obtained.

The former stage is a reaction in a heterogeneous system which tends to become homogeneous by increasing the concentration. This reaction has mainly the character of a dissolution. The hydrated part of the crystal is either wrenched away or remains in a position rendering the continued hydration reaction more difficult. The hydration of the anhydrous calcium aluminates depends on the energy content of the system as well as on the properties of the solutions and the hydrated compounds.

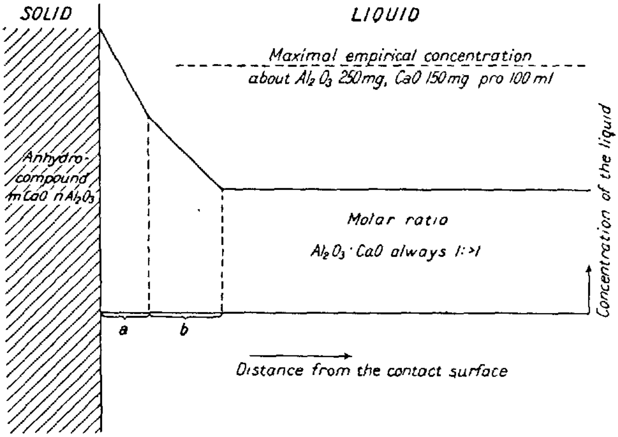

FIG. 6. The Variation of the Concentration in the Contact-Layers at the Phase-Limit Anhydrous Calcium Aluminate/Solution.

The second stage of the hydration process—the formation of the hydrated compounds—plays an important rôle, as the hydrated compounds determine the properties of the setting mass of the calcium aluminates and of the cement.

Starting from these points of view the author made an investigation of the properties of the solutions of calcium aluminate and of the reactions in the hydration of anhydrous calcium aluminates [ASSARSSON (2, 3, 4)].

The conditions might here be discussed in greater detail. The reactions at the phase-limit are illustrated in FIG. 6. We may imagine the surface of the anhydrous grain freshly wet.

At the limit there will be formed a layer of solution which will try to dissolve the compound just in the molar ratio of the anhydrous compound.

However, solutions of pure calcium aluminate can only contain alumina and lime of the ratio one to a little more than one.

As the anhydrous compounds contain alumina and lime of several proportions, the properties of the layers of the solutions at the phase-limit depend on the properties of the solutions formed there and on the composition of the anhydrous compounds. On the wetted surface of the anhydrous calcium aluminates poor in lime, C_3A_5 and CA, there will be formed a layer rich in alumina hydrate. The layer *a* marks this layer. At a certain distance from the grains of the anhydrous compound the solutions formed have the properties derived from the conditions of their formation; thus they are either metastable and easily decomposed or stable. The layer *b* marks these solutions.

The chemical character of layer *a* determines the rapidity of the reaction of water on anhydrous compounds. It contains a certain excess of hydrated alumina or calcium aluminate hydrate solutions very strongly supersaturated with a certain excess of lime.

The solutions formed referable to layer *b* regulate the formation of the hydrated compounds that are yielded in the solutions at some distance from the contact surface. The necessity to know all the properties of the aluminate solutions need not be further emphasized.

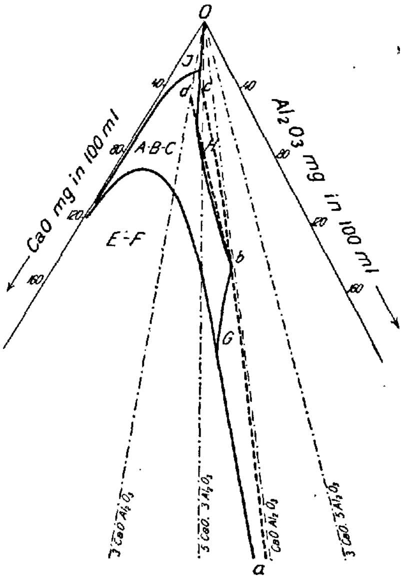

FIG. 7. Solutions obtained on Shaking Calcium Aluminates C_5A_3, CA, and C_3A_5 with Water.—The dotted line *a—b—c* shows the decreasing concentration at 5°, the dotted line *a—b—d* the decreasing concentration at 20°—90°. The letters *A—B—C*, etc., indicate the crystallization areas of solutions of certain properties. After ASSARSSON (4).

The crystallization of the solutions can be indicated as in FIG. 7, which is applicable at the temperatures 5°—90° with very little alteration as the temperature increases. The solutions were made by mixing freshly prepared solutions of calcium aluminate and of calcium hydroxide. The solids were microscopically and analytically examined. The diagram shows the crystallization areas of the solutions of different concentrations. The limits of these areas do not signify concentrations of an equilibrium but only mark the concentration limits of such solutions, all giving the same products.

All solutions of Ca-aluminate must have a certain excess of calcium hydroxide unless they are to be decomposed immediately. Within the area

$CaO \cdot Al_2O_3$—Al_2O_3, therefore, no solutions of pure calcium aluminate can occur. All solutions of pure Ca-aluminate are within the area $CaO \cdot Al_2O_3$—CaO.

The area *I* indicates unsaturated solutions.

The area *A—B—C* marks but slightly supersaturated solutions; the calcium aluminate hydrates crystallize rather slowly in these concentrations.

The solutions of the area *E—F* are strongly supersatured; they yield solids containing crystals and some gel.

The area *H* corresponds to metastable solutions, generally not yielding solids.

The area *G* marks solutions yielding crystals and aluminium hydroxide (Hydrargillite); at a low temperature (5°), however, they form monocalcium aluminate hydrate instead of hydrated alumina.

When the anhydrous Ca-aluminates are treated with water, the grains are surrounded by solutions. The compounds tend to give solutions of a composition corresponding to the composition of the anhydrous aluminates.

A compound of the composition C_3A_5, when dissolved in this proportion, should yield solutions containing an excess of alumina. Such solutions cannot exist; the solution formed can contain only monoaluminate; the excess of alumina remains at the surface of the crystal grains and renders the further hydration more difficult; the process is thus a kind of deactivation. It is well known, that the C_3A_5-compound reacts slowly with water.

The compound CA is dissolved very nearly at its theoretical proportion. To make the solutions stable, however, a little excess of CaO must be present. The grains of the anhydrous aluminate will therefore gradually react more slowly with the water; the excess of alumina at the surface of the grains forms a deactivating layer.

The compound C_5A_3 should give highly supersaturated solutions corresponding to the concentration area *E—F* of FIG. 7. These solutions immediately form calcium aluminate hydrates and some alumina as gel. The anhydrous compound reacts very rapidly with water.

The reactions mentioned above take place at the surface of the crystals—in the so-called diffusion layers. When the solutions have reached a certain concentration or when, for more reason, hydrated compounds are formed, the concentration of the solution decreases rather rapidly (FIGS. 1, 2, and 3). The changes in the concentration of the hydration solutions agree with those in the pure solutions of the concentration area *G*, FIG. 7. At lower temperatures the concentration follows the dotted line *a—b—c*, at higher temperatures the dotted line *a—b—d*. The solids formed in the hydration of the anhydrous calcium aluminates completely agree with those formed in the crystallization of the solutions.

The properties mentioned above refer to the purest materials. When accessory components of any kind are present the reactions are influenced by the disposition of these components to form hydrated compounds. Either these compounds can contain the accessory substance or the conditions of the formation of the hydrated phase can be changed.

The concentration of the solutions formed in the hydration of Swedish high alumina cement has been drawn up in the diagram, Fig. 8. The difference between the pure calcium aluminates and commercial cement is obvious; its connection with the presence of alkalies in the cement has already been mentioned. Other preparations of cement present also other concentration curves. The importance of knowing the influence of the alkalies on the properties of aluminous cement is apparent from the investigations of Rengade, Lhopitailler and de Fontmagne (30).

The products formed in the hydration depend on the special properties of the clinker. The chief reactions of the pure calcium aluminates can always be found,

(lower temp.) monocalcium aluminate (dissolved) →
dicalcium aluminate + Al-hydroxide,

(higher temp.) dicalcium aluminate →
cubic tricalcium aluminate + Al-hydroxide.

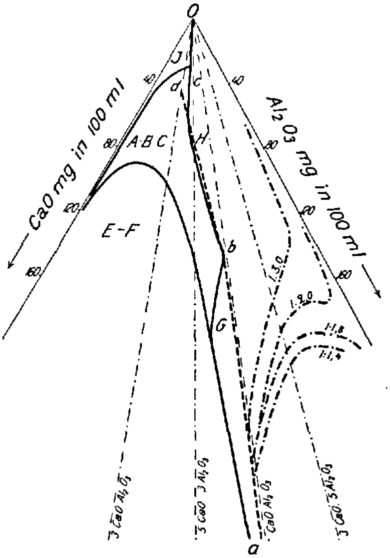

Fig. 8. Concentrations of Al_2O_3 and CaO of Solutions obtained on Shaking Monocalcium Aluminate (dotted line *a*–*b*–*d*) and of those obtained on Shaking High Alumina Cement with Varying Amounts of Water (dotted lines 1 : 1.4, etc.). After Assarsson (2, 3, 4).

A great part of the hydrated aluminates of the aluminous cement is precipitated as monocalcium aluminate hydrate. Probably the amount of this compound depends on the alkalies of the solutions and also on other circumstances during the setting. In some cases parts of a setting aluminous cement contain no microscopically identifiable crystals of dialuminate hydrate, which occurs in other parts as a normal constituent.

Sometimes there is also a difference in the occurrence of other hydrated compounds. It was pointed out that a certain compound of unknown composition was observed in the hydration of a Swedish aluminous cement ($\omega = 1.498$, $\varepsilon = 1.490$). This compound has not been observed in the hydration of other cements.

The data mentioned indicate that the

properties of the various cements depend to a great extent upon the individual properties of the clinkers.

The greater part of the hydration products consists of gels. The investigations hitherto published state that the greater part of the clinker grains is hydrated. The calcium aluminates as well as the Gehlenite and the dicalcium silicate are hydrated.

It has been shown that pure Gehlenite and the dicalcium silicate are hydrated very slowly by pure water. The compounds of the aluminous cement corresponding to these are, on the contrary, hydrated rather rapidly. The explanation has been advanced [ASSARSSON (3)] that the Gehlenite of the cement has taken up in its lattice a certain excess of base (calcium oxide, alkalies), making the melilite-like Gehlenite formed in this way more disposed to hydration. The slowly increasing content of alkalies in the solutions during hydration indicates a slowly proceeding hydration of a certain part of the clinker, possibly originating from a Gehlenite containing some alkalies. The optical anomalies of the clinker compounds [SUNDIUS (33)] might be explained in this way.

The grains of the dicalcium ferrite occurring in the clinker are hydrated slowly. When the CaO-excess of the solutions decreases it is to be expected that the ferrite hydrate rich in lime, first formed, will be gradually hydrolysed, and probably ferrihydroxide will finally be formed. This reaction ought to take place during the setting. The presence of the alkalies may only retard the hydrolysing reaction somewhat, but not obstruct it.

It has already been emphasized that the hydration reactions depend very greatly upon the chemical properties of the layers at the phase-limit. A considerable proportion of the hydration products is precipitated from the solutions; the nature of these compounds can be anticipated after an examination of the properties of the solutions. When the hydrated solids have been formed the concentration of the solutions is low and generally decreases to a certain minimum concentration. The later hydration of the clinker grains therefore depends on the reactions in the diffusion layers at the phase-limit. When pure anhydrous compounds are used the hydration products can be estimated rather easily. On the other hand, the complex system of the technical cement is more difficult to estimate. Some products have been identified by separation from others, but some of them have escaped investigation. Some of the reaction products can be anticipated to a certain extent. At lower temperatures, the monocalcium aluminate hydrate and aluminium hydroxide, at higher temperatures, probably only the latter compound. The influence of these reactions upon the slow hydration of the silica-bearing compounds is more difficult to judge. Probably there occurs a reciprocal precipitation of gels of alumina and calcium silicate hydrates, alumina-silica gels being formed, though not necessarily containing calcium.

The gels mentioned above are subject to ageing in which more stable compounds are formed. These reactions manifest themselves as changes in the volumes of the hydrated cement samples. One of these is the transformation mentioned of the monocalcium hydrate into dialuminate or cubic trialuminate hydrate, when some water, too, is liberated. The gels are also subjected to a syneresis and larger crystals are formed by smaller ones. We know very little regarding these transformations of the cement gels.

When the observations of the hydration reactions of aluminous cement are reviewed it is evident that no reaction formulae of the general hydration course could be drawn up. Some of them we know by studying the individual compounds by themselves; the properties of the technical cement, however, depend on the properties of all the compounds occurring in it. It has been shown that not only the analytical composition of the cement characterizes the properties of each sample of cement; it is also necessary to know the mineral content. On the other hand, there are also certain other properties that play a part in the hydration. The influence of the deactivation due to a thin hydrated surface surrounding the clinker grains has been pointed out above. The size of the grains and the manner in which they occur in the clinker may also influence the properties of the technical products.

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Discussion.

Mr. F. M. LEA:[1]

In his paper on "Reactions of Aluminous Cement with Water", Dr. ASSARSSON refers to the effect of temperature on the hydration products. It is well known that the strength of aluminous cement is considerably reduced by curing at temperatures above normal and this has been attributed to the development of internal stresses, to oxidation of ferrous iron compounds in the cement, or to a change in the hydrated calcium aluminates present. Tests which have been carried out by the writer, and the results of which are now being prepared for publication, have shown that the strength developed by pure calcium monoaluminate is affected by the temperature of curing in a similar manner to that of aluminous cement. Indirect evidence from determinations of density and of the loss on ignition at various temperatures indicates that a transformation of the less basic hydrated calcium aluminates to the compound $3CaO \cdot Al_2O_3 \cdot 6H_2O$ occurs contemporaneously with the fall in strength. It is considered therefore that the primary cause of the fall in strength of aluminous cement on curing at high temperatures is this transformation reaction.

Mr. G. ASSARSSON *(author's closure):*

The observations made by Dr. LEA are in agreement with the general character of the hydration reactions of the anhydrous calcium aluminates. However, it seems that other factors also play a part in the reactions when monoaluminate or dialuminate are transformed into cubic trialuminate. The size of the grains of the hydrated di- and monoaluminate can also be mentioned. But apparently these phenomena do not always cover all possibilities of reaction. Sometimes one is inclined to suppose special forms of hydrated products—perhaps di- or monoaluminate hydrates—which are transformed into cubic trialuminate more easily than the common dialuminate hydrate.

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THE CHEMISTRY OF POZZOLANAS

BY

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Introduction.

Although the use of pozzolanas can be traced back to the ancient Greek civilization, it is only in comparatively recent years that much attention has been paid to the chemistry of these materials and, even to-day, knowledge concerning them is much less advanced than that of, for instance, Portland cement. In the present paper an attempt is made to summarize the existing knowledge of the chemistry of pozzolanas, and while it will be apparent that final conclusions in many cases cannot at present be drawn, it is hoped that such a summary may serve to direct attention to the problems still remaining to be solved. Attention is paid primarily to the more modern work. As, however, the literature on pozzolanas is wide-spread, and in some cases contained in inaccessible publications, the author recognizes that some important papers, to which attention should have been given, may have been overlooked, but it is hoped that other investigators may draw attention to any such gaps in their contributions to the discussions.

Definition and Classification.

The term "pozzolana" was originally applied to the Italian materials of volcanic origin, but in later times its use has spread to cover other materials, which, though different in type, exhibit similar properties, and no useful purpose would now be served by attempting to restrict the term to the natural volcanic earths. The definition suggested is as follows:

Pozzolanas are siliceous materials which, though not cementitious in themselves, contain constituents which at ordinary temperatures will combine with lime in the presence of water to form compounds which have a low solubility and possess cementing properties. It seems desirable to limit the term "pozzolana" to materials in which silica plays an essential part and not to extend it indefinitely to include any substances showing similar properties, as, for example, arsenious oxide. This limitation is admittedly arbitrary, but once the restriction "siliceous" is removed, no further limit can be placed on the extension of the term and it becomes entirely independent of chemical composition. Blast-furnace slag is not considered to be a pozzolana within the terms of this definition, for there is considerable evidence that it is a latent hydraulic cement and that its cementing action does not depend primarily on combination with additional lime.

Pozzolanas can be divided into the following general groups:

1. Volcanic tuffs
2. Diatomaceous earths
3. Certain other highly siliceous rocks (*e. g.* the French Gaize)
4. Burnt clays and shales
5. By-product hydrated silica (*e. g.* Si-Stoff).

The first three groups represent natural materials, but 2 and 3 are usually burnt before use and even 1 is occasionally subjected to heat treatment; Nos. 4 and 5 are usually classed as artificial pozzolanas, the former depending upon burning for the development of their pozzolanic properties while the latter arise as industrial residues. The percentage composition of various typical pozzolanas is shown in TABLE 1. Silica is the main constituent with alumina as the next in order of importance. It may be noted that burnt Bauxite is said by FERRARI (19) to be an excellent pozzolana and LE CHATELIER (44) reported that an example of the use of a bauxite pozzolana in lime mortar is to be found in the ruins at Baux, Rhone Valley, France.

Constitution of Pozzolanas.

Natural Pozzolanas.

The natural pozzolanas of volcanic origin, which consist of tuffs arising from the deposition of volcanic ash and dust, occur both as consolidated porous rocks and in a fragmentary and unconsolidated state. They are materials which have undergone rapid cooling and been subjected to considerable chemical alteration subsequent to their deposition.

Rhenish Trass is a trachytic (alkali felspar) tuff which in thin sections shows an isotropic ground mass containing fragments of primary minerals such as augite, biotite and hornblende together with pumice and particles of the country rock.

The two main Italian deposits are the Roman group and the Flegrean, occurring near Naples. The Roman pozzolanas belong to the leucitic type

Table 1. Composition of Pozzolanas.

	Bacoli (18)	Bacoli (2)	S. Paolo (25)	Segni (66)	Santorin Earth (2)	Santorin Earth (92)	Rhenish Trass (2)	Bavarian Trass (2)	Rumanian Trass (73)	Pumicite (U. S. A.) (14)	Raw Moler (30)	Burnt Gaize (4)	Burnt China Clay (2)	Burnt Clay (2)	Burnt Clay (2)	Burnt Shale (2)	Sistoff (30)	Burnt Hydrated Silica (2)
SiO_2	56.75	55.20	45.50	48.20	63.23	65.20	55.24	57.00	62.52	72.30	66.71	83.85	50.52	58.16	55.52	51.74	45.83	74.00
Al_2O_3	16.92	18.25	15.12	21.91	13.21	12.85	16.42	10.90	11.62	13.30	11.41	8.30	38.35	18.44	20.69	22.43	20.64	9.20
Fe_2O_3	6.34	4.00	12.05	9.55	4.92	6.32	4.60	5.60	1.84	1.40	7.75	3.20	2.35	9.31	7.44	11.21	8.13	1.26
TiO_2	n. e.	0.75	n. e.	n. e.	0.97	n. e.	0.56	0.54	n. e.	n. e.	n. e.	n. e.	1.35	0.85	0.87	0.76	n. e.	2.12
CaO	3.60	2.75	9.33	7.50	3.95	3.15	2.56	6.00	6.56	0.70	2.07	2.43	0.75	3.25	6.28	4.25	2.90	6.05
MgO	0.54	1.13	3.59	3.15	2.10	1.85	1.32	2.18	0.72	0.40	2.20	1.02	0.91	3.91	2.96	1.09	0.74	1.04
K_2O	2.87	10.96	2.15	4.14[1]	2.58	4.19	5.00	1.53	2.89[1]	5.40	n. e.	n. e.	0.78	3.12	1.88	2.46	n. e.	0.74
Na_2O	4.06		3.78		3.90	2.60	4.28	1.76		1.60	n. e.	n. e.	0.52	0.82	0.64	1.16	n. e.	0.70
SO_3	n. e.	0.99	n. e.	0.25	0.65	n. e.	0.14	0.18	n. e.	Trace	1.42	0.65	0.40	1.10	0.68	2.13	4.25	1.29
Loss on ignition	7.18	5.85	8.45	5.30	4.91	3.10	10.08	14.52[2]	13.85	4.20	5.63	0.35	4.03	1.62	2.64	3.16	16.36	4.18

n. e. = not estimated.

[1] Includes other constituents not estimated.

[2] Bavarian Trass contains a considerable amount of carbon dioxide which is included in the loss on ignition value.

The bracketed reference numbers after the name of the pozzolana refer to the source of the analysis.

showing an amorphous ground mass. Leucite, present both as clear unaltered crystals and in a turbid altered form, is the most abundant crystalline component, and augite, and brown mica are also present. A typical Flegrean pozzolana according to Santarelli (63) contains fragments of pumice and trachytic material, the latter having an isotropic ground mass with microcrystals of sanidine and small amounts of plagioclase, augite and magnetite. Much powdered material is also present, yellowish-green in colour and containing small crystals of felspar, magnetite and pyroxenes. Santorin Earth consists mainly of a granular isotropic material mixed with pumice, obsidian, and fragments of crystalline felspars, pyroxenes, quartz etc. Heider separated Santorin Earth into about 20 per cent light pumice floating on water, 60 per cent fine dust and 20 per cent fine sand, of which only the fine dust fraction was an active pozzolana. The activity of this dust is attributed to hydrated silica by Vournazos (92) and earlier investigators.

The source of the pozzolanic properties of trass, the Italian pozzolanas, and other similar materials has been the subject of considerable controversy. It is generally agreed that the active part is the amorphous or vitreous portion, and to a lesser extent the partially altered minerals, and that little activity can be attributed to the crystalline components for these are well defined stable compounds inert to lime. An exception to this is to be found in Tannhäuser's (88) theory attributing the activity of trass to the presence of minerals of the sodalite group, such as sodalite, hauyne and lazurite, and perhaps also in Bach's (3) observation that the fraction of trass insoluble in an acid-alkali extraction gave almost the same strength as the original material; Berl and Urban (7), however, found a contrary result. The activity of the amorphous and vitreous portion does not arise directly from its composition for, apart from the combined water content, the analyses of the different fractions of one pozzolana are very similar and also approach closely to that of the lavas. Three theories which have been advanced to explain the origin of the activity of the non-crystalline materials are as follows:

1. The non-crystalline material is regarded as an alteration product of the original minerals, produced by prolonged exposure, after deposition, to waters containing carbon dioxide and to superheated steam.

2. Pozzolanas originate from materials carried by volcanic eruption from geological strata of essentially clay-like composition; materials that during eruption have undergone calcination sufficient to produce complete dehydration and chemical alteration, but not fusion.

3. The vitreous portion of pozzolanas is essentially a very porous aerogel of high internal surface area.

The first theory has been applied to trass by Michaëlis (55) and later authors, while in a recent paper SANTARELLI (63) attributes the activity of all the Italian pozzolanas to a similar change. The chemical alteration subsequent to deposition is thought to have converted much of the crystalline material into more reactive forms and to have led to the partial removal of basic constituents. In support of this theory SANTARELLI cites the gradual diminution of pozzolanic activity from the base to the top of Italian quarries and the greater abundance of crystalline constituents in the materials of more recent origin. Materials of similar composition, but of more recent eruptions, such as the ashes and lapilli of Vesuvius, show only weak pozzolanic properties.

In the second theory, propounded by GALLO (25), emphasis is laid on the original nature of the erupted material as the main factor in determining pozzolanic properties; these properties are not to be considered as due simply to subsequent alteration, though it is conceded that the active materials have suffered attack and become hydrated and that this has an activating effect. GALLO states, however, that prolonged exposure to atmospheric agents causes a degeneration in pozzolanic properties, a view supported by REBUFFAT (58) who considered that, *ceteris paribus*, pozzolanas are the better the less they have been altered.

The third theory has recently been put forward by PARRAVANO and CAGLIOTI (57) who regard the physical nature of the pozzolana as being of preponderant importance in determining its activity. From a comparison of the gross composition of numerous pozzolanas, of the fractions soluble in 20 per cent HCl followed by 10 per cent NaOH-solution, and of the insoluble fraction which contains the greater part of the crystalline material and some of the vitreous substance, they conclude that the vitreous fraction must be considered as a normal product of solidification of mixtures of silicates having the composition of the pozzolana. This vitreous substance shows no X-ray diffraction pattern and is considered to resemble a desiccated silica gel rather than a glass. Essentially it is regarded as the product of the pulverization of the fused magma by the action of air, water vapour or other gases produced during the eruptions, an "aerogel" of SiO_2-R_2O_3-composition being formed. In support of this theory, these authors prepared a similar product by fusing natural pyroxenes and showed that, as compared with the original pyroxene, it had a much higher solubility in acid-alkali extraction and a much increased rate of absorption of lime. The hydration which subsequently occurs is regarded as a secondary phenomenon and not fundamental to the formation of the vitreous active mass.

On this theory the vitreous mass is regarded as a silica-alumina-iron oxide gel, its properties depending on its physical condition and not on its chemical composition. Thus the soluble fraction from Roman pozzolanas was found to have a composition close to that of Labradorite while that of the Flegrean pozzolanas lay near to that of oligoclase or between that of orthoclase and anorthite. HART (33) found that the portion of Rhenish trass soluble in HCl and Na_2CO_3 had a composition, neglecting the iron oxide, lime, magnesia and minor constituents, approximating to SiO_2 53 per cent, Al_2O_3 24 per cent, alkalies 10 per cent, combined water 13 per cent. He suggested that the main active constituent of trass was therefore a compound of the type of Leucite ($K_2O \cdot Al_2O_3 \cdot 4SiO_2$) in which the K_2O had been partly replaced by combined water.

The active part of natural pozzolanas is regarded by many investigators as having a zeolitic nature, but a discussion of this falls more suitably into a later section.

Natural pozzolanas were stated by ROHLAND (62) to lose all activity on heating to a red heat, but thermal treatment at lower temperatures has in some cases been found beneficial. STEOPOE (74) has found that heating Rumanian trass for one hour at 200° or 500° produced only small changes in its reactivity and rate of strength development in cement mortars, but that after heating at 1 000° the rate at which the SiO_2 and R_2O_3 of the pozzolana combined with lime, as determined by its solubility in cold hydrochloric acid, was much reduced. BURCHARTZ (13) similarly reported that the strength of mortars made with German trass was not adversely affected by heating the trass at 500°. For Santorin earth VOURNAZOS (92) states that after heating at 760° the rate of hardening is reduced to one-tenth and that at 1 000° this material becomes inactive.

Certain of the Italian pozzolanas are subjected to heat-treatment before blending with Portland cement. VITTORI (90) has published data showing that for three Italian pozzolanas (Segni, Paoli, and Bacoli) the optimum temperature of activation is about 700° (3 hours), but also states that the pozzolanas giving the best strengths are those for which the optimum activation temperature is about 300°. Rapid quenching was found to give better results than slow cooling. The elimination of combined water is supposed to give an increased porosity to the pozzolana particles and so facilitate combination. SESTINI and SANTARELLI (67), however, state that the advantages supposed to accrue from the thermal treatment of natural pozzolanas have been much exaggerated. A microscopic and X-ray examination failed to show any change on heat-treatment in the amount, or type, of crystalline material present in natural pozzolanas. FERRARI (19) found that the activity of some Italian pozzolanas was reduced on heating at 150°, and that Santorin earth was unchanged at 300°.

Burnt Clays and Shales.

As a result of investigations in recent years, there is now a considerable knowledge of the natural clay minerals and of their structure, but despite much investigation, the nature of the changes occurring when clays are heated to temperatures between 500° and 1 000° is still uncertain. When the pure mineral Kaolinite is heated, evolution of water becomes rapid at about 500° and a dehydrated product is obtained. The nature of this dehydration reaction has been the subject of much controversy, it being variously held that the kaolin is decomposed to give free alumina and silica; that an anhydrous alumino-silicate of unchanged silica: alumina ratio, Metakaolin, is produced; or that free silica is liberated with formation of an anhydrous alumino-silicate of lower silica: alumina ratio. On further heating an exothermic reaction takes place at about 900°—950°. This can most probably be attributed to a conversion of amorphous alumina into the crystalline γ-form, though many other explanations have been offered, such as the splitting of Metakaolin into its constituent oxides, or a partial liberation of the alumina from the same compound. Again some authors suggest that the formation of γ-Al_2O_3 occurs considerably below 900°. At still higher temperatures Mullite ($3Al_2O_3 \cdot 2SiO_2$) is formed.[1]

The source of the pozzolanic properties of burnt clay cannot at present be settled owing to the uncertainty which still attaches to its constitution. The critical change point occurring at about 500° for Kaolinite, and in some cases at lower temperatures for other clay minerals, can, however, be taken as indicating the point at which development of pozzolanic properties becomes marked, and the 900°—950° change point appears to set an upper limit above which the reactivity becomes small. The properties of a burnt clay pozzolana, whether measured by their rate of reaction with lime solutions or by the strength developed in lime mortars, are, however, by no means constant over the temperature range 500°—950° the optimum burning temperature lying at some point within this range. ANTONEVICH (1) has compared the rates of absorption of lime and also the tensile strength of lime mortars containing clay pozzolanas burnt at different temperatures, and concludes that the optimum burning temperature is about 700°—800°. BUDNIKOFF (12) found from measurements in a diphenyl-methane BUNSEN-calorimeter of the heat of reaction between saturated lime-water and Kaolinite, burnt for one hour at various temperatures, that the activity rose from a low value at 500° to a maximum at 800° and fell to zero at 1 050°. Measurements by the present author of the rate of reaction between burnt clays and lime solutions indicate that pozzolanic properties may develop at temperatures as low as 400° particularly when the burning is prolonged for many hours, and that the subsequent fall at higher temperatures sets in at 800°—900°. At 1 000° the activity was very low. Comparative data on clays burnt in muffle kilns at a

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[1] General summaries of the papers published on the transformation of clay on burning are given by SPANGENBERG (72) and by KRAUSE and WÖHNER (39). Among recent papers there may be mentioned INSLEY and EWELL (35), THILO and SCHÜNEMANN (89).

constant temperature for 1 hour, and on the same clays burnt in a rotary kiln where the time of exposure to the maximum temperature was much shorter, indicate the importance of time as well as temperature of burning. Under the more rapid burning conditions, higher temperatures are required to produce optimum results.

The measurement of the rate of reaction of a pozzolana with a lime solution is not, however, as discussed in a later section, any adequate measure of the value of the material in lime or cement mortars and can be used only as an index of chemical reactivity, and not of cementing value.

The Reaction of Pozzolanas with Lime.

The fundamental property of a pozzolana is its ability to combine with lime and in explanation of this, two theories are advanced, base exchange and direct combination.

The idea that natural pozzolanas behave similarly to zeolitic compounds runs through much of the older literature, being found for instance in papers by authors such as Tannhäuser, Hambloch, and Michaëlis. In more recent investigations further experimental evidence has been obtained by which the relative importance of base exchange as a factor in pozzolanic action can be judged.

Before considering the zeolitic nature of pozzolanas it is desirable to define precisely the meaning to be attached to this term. Hey (34) restricts the zeolites by a rather narrow definition to a group of crystalline solids, hydrated aluminosilicates of mono- and di-valent bases in which the ratio $(R''_1\ R'_2)O : Al_2O_3$ is unity, which are capable of losing part or whole of their water without change of crystal structure, of absorbing other compounds in place of the water removed, and of undergoing base exchange. Considerable variations in the Si : Al-ratio are possible since Si and Al are structurally equivalent to a marked degree. The composition requirement will not be discussed here since, as seen in an earlier section, there is little precise knowledge of the composition of the compounds present in natural pozzolanas, and other compounds are known not conforming to this requirement which show some of the properties of zeolites. There is similarly no evidence available to show what effect dehydration of natural pozzolanas has on the crystal lattices and information is limited to studies of the reversibility of the dehydration such as those made by Fredl (24). From data at present available the similarity of natural pozzolanas to zeolites can only be judged from base exchange characteristics, though this characteristic is of course also shown by some non-zeolitic compounds such as certain of the clay minerals.

BERL and URBAN (7) compared the base exchange properties of two samples of trass with that of a sodium permutite by shaking the ground materials for 72 hours with a 1.14 per cent NH_4Cl-solution. For 25 g material the following results were obtained:

	Sodium Permutite		An Active Trass		A less Active Trass	
Mols. $(NH_4)_2$ removed from solution..	0.02		0.015		0.0055	
Mols. Na_2O found in solution........	0.022	0.022	0.0125	0.016	0.0039	0.0052
Mols. CaO » » »	—		0.0035		0.0013	

An approximate equality is shown between mols. base taken up and liberated, no correction being applied for any water soluble material present. BIEHL and WITTEKINDT (10) by shaking pozzolanas with calcium nitrate and other calcium salt solutions for 24 hours, found that for German trass the amounts of alkali liberated varied from 0—0.5 per cent K_2O, and 0—1.7 per cent Na_2O. A Roman pozzolana gave values 0.23 per cent K_2O, 0.00 per cent Na_2O. The total alkali liberated, calculated to the equivalent molecular quantity of CaO, was in many cases less than the CaO removed from solution and combined by the pozzolana. The difference must be attributed to direct combination of part of the lime, since the alternative explanation of a hydrogen ion replacement seems inadmissible as no zeolites are known containing replaceable hydrogen ions (34). STEOPOE (75) considers that in Rumanian trass the alkalies are zeolitically bound and replaceable by other cations. SESTINI and SANTARELLI (68) using BIEHL and WITTEKINDT's method, concluded that the zeolitic activity of Italian pozzolanas is about equal to that of Rhenish trass, and that the phenomenon of base exchange could play only a secondary part in pozzolanic action. TANNHÄUSER (88) found that on boiling trass with lime-water some 1—2 per cent more alkalies were obtained in solution than when water alone was used, and considered this afforded evidence in support of his theory that the pozzolanic properties of trass were attributable to base exchange with minerals of the sodalite group. Comparative data obtained by the present author on samples of finely ground trass (2 g) shaken with 250 ml distilled water or $\frac{N}{30}$ $Ca(OH)_2$-solution at 25° for 7 days are as follows:

Pozzolanas	Solution	Bases released to Solution g per g Pozzolana				
		CaO	K_2O	Na_2O	Total	Difference
Rhenish Trass.........	$Ca(OH)_2$	—	0.0025	0.0087	0.0112	0.0051
	Water	0.0005	Trace	0.0056	0.0061	
Bavarian Trass........	$Ca(OH)_2$	—	0.0025	0.0089	0.0114	0.0100
	Water	0.0004	0.0001	0.0009	0.0014	

These amounts of alkali liberated by base exchange are of a similar order to those mentioned earlier.

MAFFEI and BIANCHI (49) have studied the liberation of alkalies from one Roman pozzolana (San Paolo) when mixed with lime and made into a paste with water and stored in lime-water for long periods. In a mix containing about 1 part CaO to 2 parts pozzolana the total amount of Na_2O and K_2O liberated after six months was 1.07 per cent by weight of the pozzolana. The amount of alkalies liberated increased with the lime content of the mix and the K_2O was liberated more rapidly than Na_2O.

While the general conclusion to be drawn from the results of most investigators is that base exchange plays but a minor part in the reaction of natural pozzolanas with lime, the evidence for this conclusion is not so decisive as could be desired. Most tests have been made over short periods only (*e. g.* 7 days or less) and it seems desirable that more extended work should be done on lime-pozzolanas pastes stored in air saturated with water vapour for periods of months, since some zeolites show only very slow velocities of reaction. Even, however, if base exchange should prove an important factor contributing to the combination of lime by a pozzolana, it seems doubtful if it can make any contribution to cementing action. In base exchange the lattice of the zeolitic compound remains unchanged and one base ion is exchanged for another fitting into a similar position in the crystal lattice. It is unlikely that this action will be cementitious and indeed normal zeolites show no such cementing properties.

Base exchange plays no essential part in the reaction of burnt clay pozzolanas with lime, for pozzolanas can be prepared from pure Kaolinite containing only small amounts of bases. The author has also found that the removal of the bulk of the soluble salts and replaceable bases from a clay by electrodialysis caused no significant change in the rate of combination of the clay, after burning, with a lime solution.

The course of the combination of lime with pozzolanas has been followed by STEOPOE (76), and later by FERET (16) and by MALQUORI and SASSO (50), the method used depending on the insolubility of the silica of pozzolanas in cold hydrochloric acid ($d = 1.12$) (FLORENTIN method) and the solubility in the same reagent of the lime-pozzolana reaction products. In view of the wide use which has been made, in particular by STEOPOE, of this method in other investigations on pozzolanas, further consideration will be given to it later. As applied in the present connection by the authors mentioned, a pozzolana-lime paste is cured for the required period and the solubility then determined. Data obtained by FERET are shown in TABLE 2. It will be observed that there is a progressive increase with age in the soluble silica and alumina contents of the set lime-pozzolana mixes, but that there is little increase in the content

Table 2. Acid Soluble Constituents of Pozzolanas and Set Pozzolana-Lime Mixes (after FERET).

		Trass	Roman Pozzolana	Bacoli Pozzolana	Burnt Clay
Total per cent in pozzolana	SiO_2	60.0	47.8	57.1	60.1
	Al_2O_3	18.2	17.3	18.3	24.3
	Fe_2O_3	4.1	9.8	4.6	7.2
Per cent soluble in cold HCl ($d = 1.12$)	SiO_2	0.4	1.0	0.3	1.2
	Al_2O_3	10.0	8.3	1.1	4.0
	Fe_2O_3		0.7	0.4	5.0
Lime-Pozzolana mix stored in water at 15°. Per cent soluble in cold HCl ($d = 1.12$) calculated as percentage of pozzolana	1 Week SiO_2	2.4	5.0	2.3	7.9
	Al_2O_3	11.3	11.9	3.1	7.0
	Fe_2O_3		0.7	0.4	6.0
	4 Weeks SiO_2	6.7	8.3	4.5	10.7
	Al_2O_3	11.3	12.9	3.5	12.0
	Fe_2O_3		0.9	0.4	6.1
	26 Weeks SiO_2	13.7	14.1	10.6	14.9
	Al_2O_3	12.5	16.4	5.3	14.4
	Fe_2O_3		1.0	1.0	6.4

of soluble ferric oxide. These results, as well as similar data by MALQUORI and SASSO, indicate that both hydrated calcium silicate and aluminate compounds are formed. Evidence as to the nature of these compounds is to be obtained from the equilibrium relations existing in the system $CaO\text{-}SiO_2\text{-}H_2O$ and $CaO\text{-}Al_2O_3\text{-}H_2O$, and from direct experiments on lime-pozzolana mixes. The two systems mentioned are discussed in another paper presented by BESSEY at the present meeting. It is to be expected that hydrated monocalcium silicate is the least basic silicate that can be formed by the reaction of lime with a pozzolana, as the compound $CaO \cdot 2SiO_2 \cdot Aq.$ can apparently only be formed from a solution in which the $CaO : SiO_2$-ratio is below 1 : 2. The compound $CaO \cdot SiO_2 \cdot Aq.$ seems to a form a solution which is slightly incongruent and to decompose at solution concentrations lower than 0.05 g CaO per litre. In solutions of higher lime concentration this compound takes up lime until at a concentration of about 1.1 g CaO per litre a solid composition of $3CaO \cdot 2SiO_2 \cdot Aq.$ is reached. This lime concentration, which is just below saturation, probably represents also the point at which a more basic silicate ($2CaO \cdot SiO_2 \cdot Aq.$) decomposes. The equilibrium relations of the hydrated calcium aluminates are complex, but the cubic compound $3CaO \cdot Al_2O_3 \cdot \cdot 6H_2O$ is certainly the stable phase in solutions of lime concentration up to 1.08 g CaO per litre. Above this concentration the compound $4CaO \cdot Al_2O_3 \cdot \cdot 13H_2O$, belonging to the monoclinic system, but crystallizing as pseudohexagonal plates, may be the stable phase. The hexagonal compounds $3CaO \cdot$

$\cdot Al_2O_3 \cdot 12H_2O$ and $2CaO \cdot Al_2O_3 \cdot 8H_2O$ are in general only formed in solutions of lime concentration well below saturation.

The reaction between pozzolanas and lime being essentially a surface one between lime in solution and a solid of low solubility with the formation of a solid resultant product, it is unlikely that any equilibrium condition will be reached except after prolonged periods of time and in consequence zoning effects are to be expected, the outer layers initially forming a more basic calcium silicate than the inner core.

Relatively little published work has appeared on the direct study of the lime-pozzolana reaction products. HAMBLOCH (32) studied the microscopic structure of set pozzolana-lime mortars without however reaching any definite conclusions. GALLO (25, 27) observed the formation of hexagonal crystals of a hydrated calcium aluminate in set lime-pozzolana mixes and ascribed them to the compound $3CaO \cdot Al_2O_3 \cdot 10H_2O$, but the criteria adopted would not have distinguished this compound from the hydrated tetracalcium aluminate. More recently MALQUORI (51) has obtained evidence for the existence of the compound $4CaO \cdot Al_2O_3 \cdot 13H_2O$ in set lime-pozzolana mixes. A mix aged for a year when extracted with successive quantities of water showed an arrest point in the lime solution concentration at 1.08 g CaO per litre, pointing to the presence of this compound.

The hydrated calcium silicates present in set pozzolana-lime mixes have not been detected microscopically, which is hardly surprising in view of the general gelatinous nature of these compounds. Some tests made at this Station, however, point to the existence of the compound $3CaO \cdot 2SiO_2 \cdot$ Aq. and the solid solution of this compound with $CaO \cdot SiO_2 \cdot$ Aq. Two hydrated lime-pozzolana pastes aged for 28 days in water were dried and crushed and then extracted with successive quantities of water. The form of the extraction curve obtained by plotting per cent lime extracted against the concentration of lime in the solution at the end of each extraction was similar to that obtained on extraction of hydrated calcium silicates. The amount of lime remaining in the mix in equilibrium with lime solutions of 1.1 and 0.05 g CaO per litre, corresponding to the decomposition points of $3CaO \cdot 2SiO_2 \cdot$ Aq. and $CaO \cdot SiO_2 \cdot$ Aq. respectively, are shown below.

	Burnt Clay Pozzolana	Burnt Shale Pozzolana
1. Total % CaO in lime-pozzolana mix..........	13	13
2. % CaO remaining in solid when concentration of extract solution was 1.1 g CaO per litre	12	10
3. % CaO remaining in solid when concentration of extract solution was 0.05 g CaO per litre	8	7

For the burnt clay pozzolana the ratio of No. 2 : No. 3 is 1.5 corresponding to a change from $3CaO \cdot 2SiO_2 \cdot Aq.$ to $CaO \cdot SiO_2 \cdot Aq.$, and for the burnt shale pozzolana 1.4 suggesting an initial $CaO : SiO_2$-ratio rather below that of $3CaO \cdot 2SiO_2 \cdot Aq.$ More extended work on such lines is, however, required as the results must to some extent be complicated by the presence of hydrated calcium aluminate compounds.

There is no information available as to the possible formation of hydrated calcium alumino-silicates in lime-pozzolana mixes, nor indeed in set cements. An examination of the quaternary system $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}H_2O$ is much needed to ascertain whether such compounds are formed, and, if formed, of the conditions under which they are stable. The knowledge of the ternary systems seems now sufficiently advanced to make such an examination profitable.

The reaction of gypsum solutions with pozzolanas has been studied by several investigators. MECKE (54) has reported the formation of calcium sulpho-aluminate from the action of lime on Si-Stoff containing a considerable amount of sulphates, while BUDNIKOFF (12) has observed the formation of crystals of $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$ in a set paste of burnt kaolinite, anhydrite and hydrated lime. FERRARI (20) has carried out numerous studies on similar mixes and on the action of aqueous lime and calcium sulphate solutions on pozzolanas. A San Paolo (Roman) pozzolana containing 15.67 % Al_2O_3 and 11.9 % Fe_2O_3 showed rapid absorption of sulphate (21). Thus the percentage $CaSO_4$ taken up by the pozzolana when shaken with a solution containing 0.2 g CaO and 0.5 g $CaSO_4$ per gram pozzolana was as follows:

12 hours	1.1 %	10 days	14.4 %
1 day	2.3 %	30 days	20.2 %

FERRARI considers that this high absorption of calcium sulphate cannot be accounted for by formation of calcium sulpho-aluminate as the pozzolana only contained 2.23% of alumina soluble in hydrochloric acid, and suggests that LAFUMA's (40) calcium sulpho-silico-aluminate $9CaO \cdot 4SiO_2 \cdot Al_2O_3 \cdot 7CaSO_4 \cdot 80H_2O$ is formed. It may be noted, however, that LERCH, ASHTON and BOGUE (45) were unable to confirm the existence of this compound, and also that there exists (48, 46) a calcium sulpho-ferrite $3CaO \cdot Fe_2O_3 \cdot 3CaSO_4 \cdot xH_2O$ which may have been formed in FERRARI's experiments.

It has been shown by STEOPOE (77) that magnesium hydroxide reacts with trass in a similar way to calcium hydroxide and that in magnesium hydroxide-trass mixes there is a steady increase with time of the content of SiO_2 and R_2O_3 soluble in cold hydrochloric acid ($d = 1.12$). There is, however, no corresponding hardening and after 28 days the mixed paste was still soft.

It may be noted in this connection that the natural hydrated magnesium silicates such as Serpentine and Talc are themselves soft minerals. Little is known about the hydrated magnesium aluminates, though GALLO (25) observed the formation of crystals similar to the hexagonal plate hydrated calcium aluminates in a mix of alumina gel and magnesium hydroxide. Various natural hydrated magnesium silicates are known and recently JANDER and WUHRER (36) have prepared Serpentine and Talc by the action of water at high temperature (325°—350°) and pressure on mixes of magnesia and silica. STEOPOE (78) has also obtained some indirect evidence of the formation of a hydrated magnesium silicate from the action of magnesium hydroxide on silica gel present in cement mortars decomposed by sulphate attack. The equilibrium relations in the system MgO-SiO_2-H_2O at ordinary temperatures are, however, unknown.

The total amount of lime combined by pozzolanas in contact with saturated calcium hydroxide solution for 150 days was found by MALQUORI and SASSO (50) to be about 30 and 40 g per 100 g pozzolana for Flegrean and Roman pozzolanas respectively. VITTORI (90) also quotes similar figures. Values obtained by the present author for mixes containing a ratio of pozzolana: hydrated lime of 1 : 1 (weight) range up to 50 g per 100 g pozzolana at an age of 1 year. For mixes of higher pozzolana content or with Portland cement the percentage is lower. For example in a pozzolanic cement (60 % Portland cement, 40 % pozzolana) concrete the amount of lime combined by pozzolana after 1 year was about 15—20 per cent by weight of the pozzolana; it was also of the same order in a hydrated lime-pozzolana mix of weight ratio 1:4. STEOPOE (79) has found for trass that the percentage of silica reacting varies with the composition of the mortar and the type (lime or cement), and concludes that there is no definite lime saturation value applicable under all circumstances. Thus the percentages of SiO_2 and R_2O_3 in a sample of Rumanian trass which had reacted in lime and cement mixes after 90 days, as determined by the FLORENTIN method, were as follows:

Mix	0.5 Pozzolana 0.5 Hydrated Lime	$^1/_3$ Pozzolana $^2/_3$ Portland Cement	$^1/_2$ Pozzolana $^1/_2$ Portland Cement
% SiO_2 reacted	30.6	27.0	20.6
% R_2O_3 »	5.1	5.3	4.3

It is evident that to obtain the maximum reaction of a pozzolana it is necessary to have a considerable excess of lime present in order to ensure that no local depletion of lime occurs. Under practical conditions where the ratio of free calcium hydroxide to pozzolana is not high, since it is desired that all the calcium hydroxide shall combine, it seems that a pozzolana will not combine in a year with more than about 20 per cent of its weight of lime.

Pozzolanas and the Resistance of Mortars to Chemical Attack.

The influence of pozzolanas in increasing the resistance of Portland cement mortars and concrete to attack by sea-water, sulphate salt solutions, and other chemically aggresive agencies has been the subject of numerous investigations, but it is proposed here to discuss only one aspect of this question, namely the mechanism of the effects observed.

The original conception of the action of pozzolanas in increasing resistance to attack by sulphate salts and sea-water was that the free calcium hydroxide was combined by the pozzolana to form insoluble and inert compounds. This simple explanation requires, however, elaboration or modification before it can account for all the known facts.

All the calcium compounds present in set cement, or arising from the combination of lime with pozzolanas, are soluble to some extent in pure water, or are decomposed by it, liberating calcium hydroxide, until the hydroxyl ion concentration required to stabilize them is attained. In solutions such as magnesium sulphate where, owing to the small solubility of magnesium hydroxide, the hydroxyl ion concentration is buffered at a low P_H, about 9.9 at 25°, no increase in hydroxyl ion concentration to the point required for stabilization can occur. In addition, for sulphate solutions, the formation of calcium sulpho-aluminate has to be considered, and, for alkali salt solutions, base exchange with the set cement or lime-pozzolana compounds.

The solubilities, or decomposition points of some of the important hydrated cement compounds are as follows:

$Ca(OH)_2$	1.2 g per litre at 25°.
$2CaO \cdot SiO_2 \cdot Aq.$	Probably only just stable in saturated lime solution and liberates CaO to weaker solutions.
$3CaO \cdot 2SiO_2 \cdot Aq.$	Liberates CaO to solutions containing less than 1.1 g CaO per litre.
$CaO \cdot SiO_2 \cdot Aq.$	Liberates CaO to solutions containing less than 0.05 g CaO per litre $P_H = 11$ (approx.). Silica is also dissolved and the solubility is not far from congruent.
$CaO \cdot 2SiO_2 \cdot Aq.$	Cannot apparently be formed by extraction of CaO from $CaO \cdot SiO_2 \cdot Aq.$, but only precipitated from solutions containing excess silica.
$4CaO \cdot Al_2O_3 \cdot 13H_2O$	Liberates CaO to solutions containing less than 1.08 g CaO per litre.
$3CaO \cdot Al_2O_3 \cdot 6H_2O$	Congruently soluble, CaO = 0.20 g per litre.

The compound $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$ is incongruently soluble both in water and salt solution, the data shown below representing therefore the solutions in equilibrium with calcium sulpho-aluminate and its decomposition product alumina.

	CaO	Al_2O_3	SO_3	P_H
Incongruent solubility in water g per litre	0.130	0.035	0.125	10.80
» » » 3 per cent NaCl-solution, g per litre	0.295	0.115	0.230	11.05

In terms of CaO, $CaSO_4$ and Al_2O_3 the corresponding data are:

	CaO	Al_2O_3	$CaSO_4$	P_H
Solubility in water g per litre	0.042	0.035	0.213	10.80
» » 3 per cent NaCl-solution, g per litre ..	0.134	0.115	0.391	11.05

In presence of calcium sulphate the CaO-concentration in solution and P_H required to stabilize calcium sulpho-aluminate are lowered. Thus in a solution containing 0.83 g $CaSO_4$ per litre the equilibrium solution CaO-concentration is 0.022 g per litre and the P_H 10.13.

It is clear from these data that reaction of free calcium hydroxide with either silica or alumina in a pozzolana can only, unless some unknown stable calcium alumino-silicate is formed, result in the formation of lime compounds of relatively greater stability. It must however be remembered that while this might make little difference to the behaviour of a porous cement paste, the effect in a dense concrete of an increased resistance to hydrolysis may still be very marked. The formation of the lime-pozzolana compound also occurs, in cement mixes, subsequent to the hydration of most of the Portland cement and may, therefore, by the formation of protective films, or by blocking of pores, decrease the susceptibility of the hydrated calcium aluminate compounds of the cement to attack. Such an explanation is however open to the objection that many pozzolanas themselves seem to form hydrated calcium aluminate compounds on reaction with lime.

Lafuma (41) has advanced a theory to explain the resistance of aluminous cement to sulphate attack which has also been applied to pozzolanic cements. He suggests that combination between an insoluble set cement compound in the solid state and a substance in solution always causes expansion, but that if the cement compound passes into solution, reacts, and then precipitates as a solid no expansion occurs. In other words, when the solubility of the reacting cement compound is very low the reaction products are formed *in situ* and in crystallizing exert a thrust against the surrounding solids, but when the solubility is higher some diffusion can occur and the solid reaction products be deposited in voids in the mass. It is known that the solubility of the hydrated tetracalcium aluminate is very low in saturated lime solution, and that of the cubic compound $3CaO \cdot Al_2O_3 \cdot 6H_2O$ very low down to lime concentrations below half-saturated. The removal of lime by reaction with pozzolana to give compounds which are in equilibrium with lime solutions below saturation tends therefore to establish the conditions considered necessary for sulpho-aluminate formation without expansion. BLONDIAU (11) has produced evidence in support of this theory, showing that when a pozzolanic cement was completely hydrated, by means of successive regrinding and rehydration, until the lime concentration of the solution in equilibrium with it fell to 0.89 g CaO per litre, little expansion occurred on mixing it with gypsum, though the unhydrated cement showed a large expansion on similarly mixing with gypsum. Though LAFUMA's theory may provide a partial explanation of the resistance of aluminous and pozzolanic cements to sulphate attack, it is doubtful in either case if the mode of crystallization of calcium sulpho-aluminate is the only factor involved. There is, for instance, evidence to show that when set aluminous cement is exposed to sulphate salt solutions little formation of sulpho-aluminate actually occurs. In the supersulphate (slag—gypsum) and sulpho-aluminate (aluminous cement—anhydrite) cements it is true that on hydration calcium sulpho-aluminate is produced in large quantities, and that the set cement shows no expansion, but a reaction involving volume change can easily be accommodated without damage in the setting period when it does not set up internal stresses. The stability of hardened cements, and freedom from expansion when exposed to sulphate solutions, seems to depend primarily on the inhibition of further sulpho-aluminate formation.

In recent years STEOPOE[1] has developed in detail another theory to explain the increased resistance to attack afforded by the use of pozzolanas. As STEOPOE's investigations cover a wide ground it will be convenient to centre the further discussion around STEOPOE's work.

STEOPOE considers that the pozzolana first reacts with lime to form hydrated calcium silicates and aluminates, but that under the action of aggressive solutions these compounds are decomposed again, lime is removed, and ultimately silica and alumina gels remain. The resistance to attack is thus attributed to a complete change in the cement-binding material from an unstable complex of lime compounds to an inert gel. MICHAËLIS (56) showed many years ago that silica gel, and, to somewhat lesser extent, alumina and ferric oxide gels, was capable of developing a high strength. Further indirect evidence is also found from sand-lime bricks where complete carbonation of all the hydrated calcium silicate bonding material, with liberation of all the combined silica, causes an increase rather than a

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[1] Reference numbers 73, 75, 76, 78, 79, 80—87.

decrease in strength. There is, therefore, no difficulty in assuming a bonding action by silica.

This theory which Steopoe applies equally to attack by acidic or pure natural waters, sulphate waters, and sea-water is not new. Rebuffat (59) had made a similar suggestion to explain the low lime contents found in lime-pozzolana mortars which had been immersed in sea-water for prolonged periods. Even in a similar mortar only 20 years old a large fall in lime content was found, and Rebuffat was led to the conclusion that the only important amount of lime remaining in ancient lime-pozzolana mortars was that present as calcium carbonate. Sestini (69) from similar observations has also concluded that pozzolana-lime mortars immersed in sea-water for long periods (nearly 2 000 years) lose a considerable amount of the lime they originally contained, but that the lime remaining is still combined or has been protected from leaching by the action of a protective carbonate coating. He observed that the mortars with the most lime remaining were the stronger and more compact. Rather similar conclusions may be drawn from the analyses given by Giorgis and Cenni (28) of samples of pozzolana-lime mortars which had been completely immersed in sea-water for some 30 years, the samples being taken from various moles and breakwaters on the coast of Italy. Mortars which remained hard and sound were found to have lost from 25—50 per cent of their original lime content, while one mortar, which at the time of sampling was in a crumbly condition, had lost 75 per cent. A very old mortar dating from the time of Nero had, however, lost no more lime than the sound 30 year old mortars, suggesting that in dense mortars the rate of leaching eventually becomes very low.

In this theory no attention is paid to the formation of calcium sulpho-aluminate, causing swelling and bursting of concrete or mortar. It is, however, a common observation that failures of concrete in sea-water are not usually characterized by the swelling found in laboratory tests or in concretes exposed to ground waters containing sulphate salts, but take the form of erosion, *i. e.* a loss of constituents from the mass. This is ascribed to the increase in the leaching action under sea-water conditions produced by wave motion, and also by the increased solubility of calcium hydroxide in presence of sodium chloride. Calcium sulpho-aluminate, though one of the initial products of the reaction of magnesium sulphate on Portland cement, is itself unstable in such a solution, owing to the low P_H-value (9.9) of saturated $Mg(OH)_2$-solution. The author has observed that initially in attack of concrete by sea-water both the MgO- and SO_3-contents of the solid rise, but that later the SO_3-content falls again to a low value. An analysis of four Portland cement concretes exposed to sea-water for some 10 years, after separating part of the aggregate gave the following results:

	Per Cent CaO	Per Cent MgO	Per Cent SO_3	Ratio $\frac{MgO}{CaO}$	Ratio $\frac{SO_3}{CaO}$
A	20.3	0.36	0.60	0.018	0.03
B	16.2	2.9	1.7	0.18	0.10
C	16.4	5.9	2.17	0.36	0.13
D	12.6	5.5	0.93	0.44	0.07

Sample *A* had suffered no attack while *B*, *C*, and *D* had been progressively more attacked. Though the ratios of SO_3 and MgO to CaO are not strictly comparable, as some removal of lime had doubtless occurred by leaching, they serve to show that in samples *B* and *C* a progressive rise in MgO- and SO_3-content had occurred, but that in *D* the content of SO_3 had much decreased again. It appears therefore that, as far as sea-water action is concerned, formation of calcium sulpho-aluminate is probably less important in its effects than those produced by the removal of lime.

The essence of STEOPOE's theory is that the addition of pozzolanas increases the amount of silica gel ultimately remaining as the bonding constituent and so preserves the concrete. As far as attack by sulphate ground waters is concerned, where expansion of the concrete is a characteristic phenomenon, the formation of calcium sulpho-aluminate must, however, be regarded as the prime cause of deterioration and the influence of pozzolanas attributed either to a protective surface effect of the lime-pozzolana compounds, or of the hydrous oxide gels formed by their decomposition, or to the mode of sulpho-aluminate formation as suggested by LAFUMA's theory.

It seems desirable to examine further the evidence put forward in favour of the hydrous oxide gel theory of chemical resistance. STEOPOE has worked in general on neat Portland cement, and Portland cement-pozzolana, pastes made porous by a small addition of calcium carbide. After curing for the required time the material in general is ground and subjected to the action of aggressive solutions. The FLORENTIN method for determining soluble silica (using cold HCl, $d = 1.12$) is applied to determine the amount of hydrated calcium silicates present. STEOPOE has shown that when set Portland cement is allowed to carbonate the soluble silica obtained by this method decreases and concludes that the SiO_2-gel formed is insoluble (80). He similarly finds a decrease in the soluble silica when set cement is attacked by magnesium sulphate solutions and ascribes this also to the formation of silica gel (78). In refutation of the objection that the insoluble product may not be silica gel, but a less basic silicate than that originally present, he shows in one case tested that the insoluble residue from a set cement exposed to the action of magnesium sulphate solution contained no more bases than that from the original set cement. It appears to the present author, however, that further proof of the general validity of the FLORENTIN method for separating silica gel from calcium silicates is required. There is no alkali treatment in this method and its success depends on the silicates all dissolving in the short period (10—15 minutes) allowed in the cold, and filtration taking place before any precipitation of silica gel commences. The crucial point is the rate of solution of the silicate, for any not dissolved in the period allowed is classed as insoluble. MALQUORI and SASSO (50) stated that the FLORENTIN method is only of value for comparative purposes as it does not effect a complete separation of the reacted and unreacted parts of the pozzolana. Further examination of the solubility of the different hydrated calcium silicates, and particularly of samples aged for considerable periods, seems to be essential.

For the powdered porous cement pastes used STEOPOE (82) has shown that the rate of loss of lime to magnesium sulphate solution (1.25 per cent) is substantially unaltered by the substitution of trass for Portland cement if the results are calculated as a percentage of the total uncarbonated lime present. Only in the case of attack by pure water was the substitution of trass found to decrease the rate of loss of lime to the solution. Further the rate of loss of the lime to distilled water, 2.4 per cent NaCl-, 0.45 per cent $MgSO_4$- and 0.55 per cent $MgCl_2$-solutions increased in this order, these solution concentrations being taken to represent those present in sea-water (78). Some confirmatory evidence of the greater rate of loss of lime to sea-water and magnesium sulphate solution than to distilled water is found in the results of GALLO and CAMPANI (26) using mortar briquettes (1 : 4 with standard sand). These results cannot, however, be applied without question to dense concretes where physical structure plays a more important part in determining the rates of solution.

In magnesium sulphate solution STEOPOE (78) finds that the content of insoluble silica first rises, but later commences to fall. He attributes this to a reaction between magnesium hydroxide and silica gel forming a hydrated magnesium silicate soluble in the cold HCl. Further investigation of this reaction and of the conditions of stability of this compound are very desirable. Successive treatments of the ground porous set cement with 2.4 per cent sodium chloride solution were found to cause a progressive increase in the insoluble silica content and a decrease in CaO-content. It may be noted here that the insoluble SiO_2 rose even when the remaining lime content of the set cement was equivalent to a $CaO : SiO_2$-ratio of about 2:1 and when the lime concentration of the extract was far above that required to stabilize hydrated calcium monosilicate. In view of this anomaly it seems important that this work should be further checked using pure set cement compounds.

STEOPOE (78, 82) further puts forward some evidence that in sodium chloride solution some base exchange may take place, Na_2 replacing Ca in the calcium compounds of the set cement, in addition to direct solution of lime. Similar suggestions have been made by numerous earlier investigators, such as MICHAËLIS, SCHWARZ, and REBUFFAT, both in regard to Portland cement and to the lime-pozzolana compounds. STEOPOE (87) supports this suggestion by some analyses of concretes long exposed to sea-water in which an increased alkali content was found, but the reverse change, loss of alkalies, was reported by GIORGIS and CENNI (28). It does not appear possible at present to estimate the importance of base exchange as a factor in sea action, for published analyses of concrete exposed to sea-water do not usually include any determination of alkalies; it is desirable that more data of this type should be obtained. Little direct work has been done on the replacement of lime by alkalies in the hydrated calcium silicates, or aluminates, and this field awaits investigation. A few preliminary tests were made by the author some years ago, but owing to pressure of other work it has not yet been possible to follow them further. On shaking 1 g of hydrated calcium monosilicate for 7 days with 1. 100 ml distilled water, 2. 100 ml 3 per cent NaCl-solution it was found that the CaO-content of the solution was 0.006—0.007 g CaO per 100 ml with water and 0.008—0.0085 with the sodium chloride solution. This result may, however, indicate only an increase in the incongruent solubility of the monosilicate as the values for Na_2 removed from solution were erratic. Reliable conclusions could only be drawn from tests over more prolonged periods of time carried out in gold plated or other inert containers. A similar experiment was made on material obtained by shaking a burnt kaolin pozzolana with N/30 lime-water for 14 days during which period the pozzolana absorbed 8 per cent of its weight of CaO. The product was then shaken with water and 3 % sodium chloride solution for 7 days. The lime-pozzolana product (3 g in 100 ml solution) gave with water a solution containing 0.006 g CaO per 100 ml and with 3 per cent NaCl, 0.029 g CaO per 100 ml, the Na_2O in solution at the same time falling by 0.017 g per 100 ml. It is again not clear, however, that base exchange with the lime-pozzolana reaction product had necessarily occurred for the material used contained unreacted pozzolana and in a blank test on the pozzolana alone an almost similar removal of Na_2O was found. Whether base exchange occurred or not, the results do, however, suggest that the incongruent solubility of hydrated calcium monosilicate is higher in 3 % NaCl-solution than in water. More detailed investigations of the equilibrium of this and other cement compounds with salt solutions are desirable.

STEOPOE (83, 85) has found, in accord with practical experience, that exposure of set cement to carbon dioxide much reduces the rate of attack by aggressive solution, and this is attributed to the "densifying action" of the liberated silica gel. In sea-water, which contains some carbon dioxide, reaction with set cement also occurs to give calcium carbonate initially, but later the more soluble bicarbonate may be formed and leached out. This is considered by STEOPOE (86) to be an additional effect to the other actions mentioned earlier. Doubt may be expressed whether the carbon dioxide content of sea-water plays more than a minor part in bringing about loss of lime and whether in fact its prime effect is not formation of calcium carbonate in the concrete. Solution of lime as bicarbonate can only take place in so far as aggressive carbon dioxide, *i. e.* free carbon dioxide above that required to stabilize the bicarbonate, is present. No data seem to be available on the aggressive carbon dioxide content of sea-water.

The foregoing discussion on STEOPOE's very interesting work, and the associated observations of other investigators, has raised many problems worthy of investigation. No final conclusion as to the general validity of STEOPOE's theory can, in the present author's view, be reached until further confirmatory work has been done.

The Chemical Evaluation of Pozzolanas.

The evaluation of pozzolanas by tests requiring only a short period to carry out is a problem which has attracted the attention of many investigators. It is proposed in the present section to consider briefly various chemical methods that have been used.

It is generally agreed by investigators that the analytical composition of a pozzolana affords no criterion as to its value. The only exception which may perhaps be made to this general statement is that the combined water content has sometimes been considered of significance. Thus a minimum limit to the combined water content is to be found in the German specification for trass. Whatever the value of this limit as far as trass is concerned, and it has been the subject of much controversy in the German literature, it is clear that for pozzolanas as a whole the combined water content is of little practical value for assessing quality.

The oldest test for pozzolanas is that of VICAT in which the rate of absorption of lime from a calcium hydroxide solution is measured. This test, both in its original form and in modified forms as used by later investigators, has some limited value for distinguishing between active and inert materials, but as a general means of classifying pozzolanas it fails. The increase in solid volume of a pozzolana in lime solution, usually known as the flocculation test, has also been shown by numerous investigators to have little value.

Many attempts have been made to assess the value of pozzolanas by their content of material soluble in acid or alkali solutions. Summaries of much of the older work are to be found in papers by FERET (17) and SESTINI (70). The general conclusion reached by these authors, as also by STEOPOE (76), GRÜN (31), GIORGIS and ALVISI (29) and others is that the content of material in a pozzolana soluble in hydrochloric or nitric acid, or in alkali hydroxide or carbonate solution, affords no measure of the strength development in mortars of pozzolanas in general. Further attempts, mostly based on an initial acid attack followed by an alkali treatment, have been more successful in effecting at least partial separation of the active part of natural pozzolanas from the inactive crystalline components. BAIRE's method (5), initial treatment in the cold of 0.5 g pozzolana with 100 ml water and 25 ml 1 : 1-HCl followed, after washing, by digestion with 20 per cent KOH for 20 hours cold and then 4 hours at 50°—65°, the insoluble silica in the residue being determined, has been studied by several investigators. Thus SESTINI and SANTARELLI (66) use this method, but determine the SiO_2 and Al_2O_3 soluble in the initial acid extract as well as that remaining in the insoluble residue, after the KOH-treatment. They state that temperature variations in the KOH-treatment cause marked differences in the results, but that at 50°—65° the amount of silica soluble in the KOH is not, for natural Italian pozzolanas, far short of that which eventually becomes soluble in acid after prolonged reaction with lime. The requirement for an active pozzolana is said to be a high content of SiO_2 and R_2O_3 soluble in the HCl-KOH-treatment, though it appears that this statement refers to the efficiency of the pozzolana in combining with lime and not to the strength developed in pozzolana-lime mortars. No relation is shown between the tensile and compressive strength of a series of Italian pozzolanas and the soluble SiO_2 or R_2O_3. MANUEL DE LA SANTOS (64) states that the soluble silica determined by the BAIRE method is no indication of the value of a pozzolana.

MALQUORI (50, 52, 53) has published a number of papers on the solubility of pozzolanas, comparing the effect of different alkali treatments following an initial acid attack. This author has used two methods: 1. treatment with hot 1 : 1-HCl followed by hot 5 per cent NaOH, 2. treatment with hot 24 per cent HCl followed by 20 per cent KOH. The second method gives rather lower values for the insoluble residue than the first; both give much lower values than the BAIRE method for the Roman pozzolanas, but the reverse is found with those of the Flegrean group. Increase in the KOH-concentration from 20 to 50 per cent in MALQUORI's second method causes a marked decrease in the insoluble residue from the Flegrean (alkalitrachytic) pozzolanas, but not in the leucitic Roman type for which the residue is always low. With inert materials, such as granite and volcanic sands, the residues are always high.

Though the determination of the soluble SiO_2 and R_2O_3 in pozzolanas may have some value when comparing materials of the same type, it must be concluded that, when applied to pozzolanas as a whole, such methods are not a reliable indication of quality, and other methods must be sought.

Amongst the older methods are those of ZAMBONI (94) and GALLO (25) in which the silica becoming soluble after reaction with lime is determined. This method has been further developed by STEOPOE (76) and applied by FERET (16) who has shown that the estimation of the SiO_2 and R_2O_3 in a pozzolana-lime mix which has combined with lime and become soluble in cold 24 per cent HCl ($d = 1.12$) gives a good estimate of the strength development of lime-pozzolana mortars, provided the physical nature of the pozzolana is not such that the amount of water required to give a mortar of plastic consistence is markedly increased. Such a test, however, requires the same period of time as a direct strength test and, though of much interest in the theoretical investigation of pozzolanic action, offers no particular advantages for practical testing. The direct measurement of the amount of lime combined, or of pozzolana combining with lime, under some accelerated condition of test has, however, been advocated as long ago as 1896 by REBUFFAT, as the most desirable method for testing pozzolanas.

Such a step has recently been taken by SESTINI and SANTARELLI (66) who have compared the free lime and soluble silica contents of set lime-pozzolana and pozzolanic (Portland) cement mixes after 6 months curing in water at ordinary temperatures and after an accelerated test in which the mortar is cured for 1 day in moist air, 6 days in water at ordinary temperatures, and then for 48 hours in steam at 100°. The soluble silica was determined by treating a 1-g sample, dried at 100°—110°, with 100 ml 1:1-HCl, filtering and pouring 50 ml boiling 5 per cent Na_2CO_3-solution on the filter. The soluble silica is estimated in the filtrate. For the natural Italian pozzolanas used, a fair relation is shown between the results under the two test conditions, both for soluble silica and free lime. From experience with artificial pozzolanas, however, the present author considers a curing temperature of 100° is too high and prefers a period of curing of 46 hours at 50°. Curing at 100°, and for periods of over 100 hours at 50°, has been found to cause disproportionate development of strength in lime mortars containing poor pozzolanas which at ordinary temperatures only show low strength after six months. Similar discrepancies would probably be found in the soluble silica and free lime content as determined by SESTINI and SANTARELLI. It may perhaps be questioned whether, in any event, this chemical test offers any advantages over a strength test under the same accelerated conditions of curing for obtaining an index of the resistance to chemical attack by sulphate and other aggressive solutions which is produced by the use of pozzolanas. It must be admitted, however, that many investigators prefer a direct chemical test of the lime combined by a pozzolana, or an indirect one of the SiO_2 and R_2O_3 which reacts with lime, but it is necessary that the results of such tests should be correlated with long period sulphate resistance tests before any final conclusion can be reached. In work on both artificial and natural pozzolanas the present author has found that the sulphate resistance, and the increase in strength at long ages, of pozzolanic (Portland) cements can be assessed by short period strength tests under accelerated conditions of curing. The results of this work, which will shortly be published, indicate that the difference in the tensile strength of plastic mortars cured under the following two conditions

1.	2.
1 day in moist air at 18° 6 days in water at 18°	1 day in moist air at 18° 4 days in water at 18° 46 hours in water at 50° 2 hours in water at 18°

is a good index of the two properties mentioned.[1] It seems probable also that compression tests could be similarly used.

The estimation of the amount of free calcium hydroxide remaining in set pozzolana-lime or pozzolanic (Portland) cements has been much used as an indication of the value of a pozzolana. In view of the difficulties attached to this estimation it has been considered desirable to discuss this subject briefly; this is done in the next section which has been written by the author's colleague, Mr. G. E. BESSEY.

The Estimation of Free Calcium Hydroxide in Pozzolana Mixes.

(BY G. E. BESSEY.)

A number of methods, as shown in TABLE 3, have been used to determine the free calcium hydroxide content of pozzolana-lime or pozzolana-cement mortars or concretes. Most of these methods were originally devised for use in determining the free calcium oxide or hydroxide in Portland cements and the errors likely to arise from their application to hydrated materials containing active additions such as pozzolanas need some consideration.

Before discussing the sources of error to which these methods are subject, the conditions under which the determination must be carried out may be considered. A hydrated lime-pozzolana mix may contain hydrated calcium aluminates and silicates and possibly ferrites, together with unreacted pozzolanic material and free calcium hydroxide; a Portland cement-pozzolana mix may contain, in addition, unhydrated cement which may have fresh surfaces

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[1] The author (42) formerly used a 3-day test period with only 24 hours at 50°, but the strength differences under this condition did not differentiate so satisfactorily between pozzolanas of different quality as the above test.

Table 3. Methods used for Estimation of Free Calcium Hydroxide.

Method	Originally described by	Applied to Pozzolanic Mixes by
Sugar	—	Sestini and Santarelli (66, 71)
Glycerol	Emley (15); Lerch and Bogue (47)	Kathrein (37); Rodt (60)
Ethylene Glycol	Schläpfer and Bukowski (65)	Forsén (23); Rodt (61)
Phenol	Konarzewski and Lukaszewicz (38)	Sestini and Santarelli (66, 71) Wittekindt (93)
Lime Solution	Bakewell and Bessey (6); Forsén (22)	Forsén (22); Lea (43)
Calorimetric	Bessey (8)	Lea (43); Vittori (91)

exposed by crushing or grinding samples for analysis. The less basic of the hydrated compounds are hydrolysed or dissolved by aqueous solutions of P_H below about 11.0, while the more basic ones release an appreciable amount of lime to solutions of higher P_H-values. Thus the aluminates require a lime concentration of about half saturation (0.6 g CaO per litre) with a P_H of about 12.0 to make their solubility inappreciable. In the case of the tetra-aluminate, hydrolysis may occur at lime solution concentrations below 1.08 g CaO per litre, but this compound, even though unstable, commonly persists without decomposition at lower concentrations. The compound $3CaO \cdot 2SiO_2 \cdot Aq.$ suffers little hydrolysis in solutions of lime concentration down to about 0.8 g CaO per litre. Extraction with any reagent which gives a P_H much below 12.0 will therefore tend to cause some hydrolysis unless the sample under test contains sufficient free calcium hydroxide to raise the solution P_H to this value. The use of alcohol as a solvent, however, lowers the solubility of the hydrated compounds and reduces the liability to hydrolysis.

The presence of unhydrated compounds in Portland cement-pozzolana mixes prevents the use of aqueous solutions for extracting free calcium hydroxide, since further hydration of the cement compounds with liberation of further free hydroxide might occur during the extraction.

The aqueous sugar solution method, which has frequently been applied to determination of the uncarbonated lime in hydrated limes and lime mortars, has been used by Sestini and Santarelli in tests on hydrated lime-pozzolana mortars. These authors also carried out comparative tests with the sugar and ethylene glycol methods and with a modified phenol method; they found similar results with the sugar and phenol methods, but rather lower results with the glycol method. Various previous investigators had concluded that the sugar method could not be applied in the presence of silicates, and the dissociation constant of sugar ($Ka = 1 \times 10^{-13}$) indicates that P_H-values below that required to stabilize the silicates and aluminates will be maintained. It must be concluded therefore that the method is subject to errors which will probably vary with the accessibility (particle size, etc.) of the hydrated compounds.

The glycerol-alcohol extraction method as described by LERCH and BOGUE is widely used for the determination of free lime in cements. Attempts to apply it directly to hydrated materials have generally led to the conclusion that calcium hydroxide does not dissolve sufficiently rapidly in the reagent to give satisfactory results. KATHREIN used this method to determine the free calcium hydroxide in Portland cement mortars containing pumice and other materials. The results were in the order that might be anticipated for the different materials added and for different curing conditions, but there was no check on their absolute accuracy. RODT (60) also used this method for examining hydrated cements and cement-trass mixes. He found that the free lime contents of all the hydrated materials, including plain Portland cement decreased with increasing age in water storage; this is contrary to the experience of other workers and the result must be attributed to errors in the method of determination. The decrease is probably due to the formation of coarser crystals of calcium hydroxide at longer ages with a corresponding difficulty in obtaining complete solution.

FORSÉN (22) has used the glycerol method after heating the material to be tested to 550° to dehydrate the calcium hydroxide and found that reproducible results could be obtained in this way; he points out, however, that the accuracy of the method could not be assessed, since no exact method of determination was available for comparison. The possible errors in this method are probably similar to those in the calorimetric method mentioned below.

The ethylene glycol extraction method, described by SCHLÄPFER and BUKOWSKI, is a convenient one for free lime determinations in cements and has been widely adopted. These authors consider that it may be applied to hydrated materials satisfactorily, but it has been concluded by the present author (9) that it leads to appreciable errors. The difficulty of obtaining complete solution of calcium hydroxide when in a crystalline state may cause low results, whilst attack of other cement compounds tends to give high results; there is no means of judging for any particular sample which error may be the greater. RODT (61) has applied this method also to hydrated Portland cements and cement-trass mixes; his results were similar to those with the glycerol method and it seems likely that similar errors apply to both methods FORSÉN (23) also mentions the use of this method in a study of special cements for hydraulic structures.

The phenol-alcohol extraction method, proposed by KONARZEWSKI and LUKASZEWICZ, has not been found by the present author to give satisfactory results even with unhydrated cements. Phenol is too strongly acid in reaction for this purpose and tends to cause hydrolysis; its dissociation constant, *Ka* is 1×10^{-10}, as compared with 7×10^{-15} for glycerol and 6×10^{-15} for ethylene glycol. With hydrated materials the hydrolysis errors are likely to be even larger than with unhydrated cements, but may possibly be counterbalanced by errors due to difficulty of solution of crystalline calcium hydroxide, as in the ethylene glycol and glycerol methods. SESTINI and SANTARELLI used the method in work on cement-pozzolana mixes for determining the free lime at short ages; at longer ages they used the sugar method, assuming that hydration of the cement would be complete. WITTEKINDT also used the method on hydrated cement and cement-trass mixes. He found a progressive increase up to 40 weeks in free lime content in a plain Portland cement stored in water, but a decrease in trass-cement mixes.

The lime solution method of extraction of calcium hydroxide was proposed by BAKEWELL and BESSEY for work on lime mortars, particularly when pozzolanas were present, and has been applied to mixes containing both artificial and natural pozzolanas. The method consists of shaking, for 24 hours, a weighed portion of the sample with a half saturated calcium hydroxide solution, in such proportion that the final lime concentration lies between 0.8 and 1.0 g CaO per litre; after allowing it to settle, the increase in lime concentration of the solution is determined. The principal error with materials tested at short ages is probably the further reaction of remaining pozzolanic material with free lime during the course of the extraction. Any appreciable hydrolysis of the hydrated silicates and aluminates is eliminated, if the compound $3CaO \cdot 2SiO_2 \cdot xH_2O$ is considered to be the most basic stable silicate, and any possible hydrolysis of hydrated tetracalcium aluminate is ignored.

FORSÉN has applied a similar method to hydrated cements and cement-pozzolana mixes. The sample is in this case subjected to successive extractions by water for short periods only, the lime in the resulting solutions being determined by titration. The accuracy of the method when applied in this way to cement mixes is doubtful, for as previously mentioned, the unhydrated cement in the sample may yield further calcium hydroxide during the extraction; it is in any case important to maintain the final lime concentration of the solution at above 0.6 g CaO per litre to prevent appreciable solution or hydrolysis of the hydrated compounds.

The calorimetric method, described by the present author for determining the calcium hydroxide in set cements, has been applied by LEA both to lime-pozzolana and cement-pozzolana mixes. The results are concordant and show clearly the effect of varying proportions of pozzolana and of age. VITTORI has also used the method for pozzolanic cements and pozzolana-lime pastes. He found that reaction of the pozzolana with lime during the heating had only slight effects upon the heat of hydration; in LEA's results a small correction is made for this. The more significant errors are probably due mainly to decomposition of certain compounds with liberation of calcium oxide, or combination of other compounds with calcium hydroxide, during the ignition. Some further work is being carried out by the present author on hydrated cement compounds to check further the validity of this method. No definite opinion can however be expressed with regard to its absolute accuracy until this work has been completed or other means of checking the true value of the free calcium hydroxide in hydrated materials is available.

In conclusion, the author considers that for lime-pozzolana mixes the lime solution extraction method gives results which are the most useful for they represent the lime not in combination with alumina, ferric oxide, or silica when in contact with lime solutions slightly below saturation (0.8—1.0 g CaO per litre). It is true that the compound $2CaO \cdot SiO_2 \cdot Aq.$ may be formed at concentrations very close to saturation (above 1.1 g per litre) within a certain range of temperature, but its range of stability appears to be so small that the extra lime it contains probably reacts to all reagents in a manner similar to calcium hydroxide, and may therefore arbitrarily be considered as such.

The position with regard to pozzolana-cement mixes is more difficult and it is doubtful whether any of the methods which have been used give results having any very precise meaning, although they may be consistent in themselves and some of them are valuable for purposes of comparison. A considerable amount of further work is required before the free calcium hydroxide content of a set cement containing pozzolana can be ascertained with accuracy.

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Discussion.

Mr. P. S. HÅKANSON:[1]

With regard to Dr. LEA's excellent and comprehensive paper I just want to make a few remarks. Dr. LEA suggests a method for evaluating the pozzolanas. This method is based on strength determinations, but as the pozzolanas are added chiefly in order to increase the chemical resistance of the concrete, I think that their quality in this respect rather ought to be determined by methods based on chemical considerations.

For a number of years we have been manufacturing a pozzolanic cement in Limhamn, Sweden. We have primarily been interested in increasing the resistance of the concrete against the action of soft waters and for that reason we have found it logical to use an extraction method for evaluating the pozzolana used. After various periods of time specimens cured in carefully sealed tins are crushed and extracted with distilled water. The total amount of calcium oxide present in the sample is determined and then an amount containing 300 mg of CaO is weighed out. This is introduced into a bottle and 250 ml of water are added. After shaking for 15 minutes the liquid is sucked off and a new amount of water introduced. The extractions are repeated for a number of times. The amount of lime removed each time is calculated in per cent of the total amount of lime present. Typical results from tests on an ordinary Portland cement and on a pozzolanic cement made from the same clinker are recorded below.

Lime removed from	*1st*	*2nd*	*3rd*	*4th*	*5th*	*Extraction.*
Portland cement mortar	31.2	11.2	7.1	5.5	4.2	% of total CaO
Pozzolanic cement mortar...	14.2	8.5	6.4	5.2	4.4	% of total CaO

These figures, we believe, indicate fairly well the ability of the pozzolana to increase the resistance of concrete to the action of soft waters. The objection, of course, against making experiments on crushed material is that no credit is given for increase in resistance due to increased denseness. That question, however, has to be considered separately.

With respect to the estimation of free lime in pozzolanic cement mortar I quite agree that it is very difficult. We have worked a good deal with the

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glycol method as described by SCHLÄPFER and BUKOWSKI (2). One weakness of this method, which also has been pointed out by MACPHERSON (1), is that the crystalline calcium hydroxide on ageing becomes less readily soluble. In carefully protected specimens of straight Portland cement mortar we have very often found a considerably smaller amount of free lime after 180 days than after 28 days. Another weakness of the method is that it does not sharply distinguish between free lime and lime combined in certain compounds, as is evident from the following experiments.

A cement mortar sample was subjected to 5 successive treatments with ethylene glycol. Each extract was titrated separately and the following results were found.

Lime found in	*1st*	*2nd*	*3rd*	*4th*	*5th*	*Extraction.*
Portland cement mortar	13.4	2.9	1.8	1.8	1.4	%
Pozzolanic cement mortar...	3.6	1.0	0.7	0.7	0.6	%

As to the calorimetric method, I want to mention an experience we have had. When we first started our free lime determinations we used to dehydrate the samples at 500°. Later we changed over to drying in vacuum at 40° because we found that an appreciable amount of lime was combined during the period of heating. Some results which demonstrate this fact are given below. From these it follows that, when working with pozzolanas, one should be very careful in the use of methods which involve heating.

	% Free Lime in a Sample heated	
	$^1/_2$ Hour at 500°	*2 Hours in Vacuum at 40°.*
Portland cement mortar	13.1	13.1
Pozzolanic cement mortar	0.3	3.1

A test which has been very much criticized as to its value is the determination of soluble silica. Carefully employed, I believe, however, that it gives quite useful information as to the lime combining capacity which can be expected from a pozzolana. In our laboratory the determination is carried out in the following way. The sample is first boiled for one hour with 1:3 hydrochloric acid and then digested on a steam bath for 15 minutes with a 5 % sodium carbonate solution. Both extracts are analysed separately.

If the acid extract does not contain ions such as for instance Ca which may have been present in the sample as silicates, we have found a fairly good relationship to exist between lime combining capacity and the amount of silica found in the alkaline extract. If, on the other hand, the acid extract contains considerable amounts of ions such as Ca, great care should be exercised when judging the results. The method has proven to be especially helpful as a routine method for controlling the manufacture of an artificial pozzolana.

Obviously, the existing methods for the determination of free lime in set mortars are more or less unreliable and for that reason of a limited value for the estimation of the lime combining capacity of pozzolanas.

A better way to attack the problem is probably to employ the same method as Forsén has used in his study of the components, *viz.* to shake a small amount of the material to be investigated in such a large amount of lime solution that the solution remains nearly saturated even since equilibrium is reached. After various periods of time the solid phase is filtered off, washed with alcohol and ether and analysed. All operations, of course, have to be carried out under careful protection against carbonic acid.

The method looks quite promising although as yet we have carried out only a few preliminary experiments.

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Mr. L. Forsén:[1]

It seems to be evidenced by experiments that the hardening of cement is brought about through the dissolution of the components and a following precipitation of the newly-formed hydrates from supersaturated solutions. Therefore, it is tempting to try to explain the pozzolanic reactions in a similar way.

When the active component of a pozzolana is silicic acid, this is probably present in a form soluble in alkaline solutions. If this is the case, silica dissolves and forms calcium silicate hydrates which precipitate owing to their low solubility.

It appears to me that the reason for the reactivity of the silicic acid in pozzolanas might be that this silicic acid, on account of its origin and way of formation, has a more open lattice than quartz and inert silicates. Diatomaceous earth and other such pozzolanas contain remains from animale substances in which the silicic acid has probably been combined in organic compounds. Pozzolana earth contains naturally burnt amorphous products or melts. Si-Stoff, produced from kaolin by careful heating and subsequent

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[1] Dr.-Ing., Chief Chemist, Skånska Cementaktiebolaget, Limhamn, Sweden.

dissolving of the Al_2O_3, contains silicic acid which even water-free is soluble in alkaline solutions.

The chemistry of pozzolanas has not yet been much studied but I believe that even in this field good progress is attainable with the aid of chemistry and maybe also X-rays.

Mr C. D. CRICHTON:[1]

Dr. LEA explained in his paper the difficulties which have been met in obtaining a satisfactory method of testing for pozzolanic value. One test after another has been discarded and the only remaining test is the one he has described, and which might be called the "hot and cold" tensile test.

It consists briefly of testing tensile briquettes made with 3 parts of standard sand to 1 part of pozzolana cement by weight using water to a given consistency which is plastic and not the dry consistency of the English B. S. S. method. One set of briquettes is kept at 18° for 7 days (1 day moist air and 6 days in water) and then tested—this is "the cold" test. Another set of briquettes is kept for 1 day in moist air, 4 days water at 18°, then 46 hours in water at 50° and finally 2 hours in water at 18°. The briquettes are then tested—this is the "hot" test. The difference between the "hot" and "cold" tests is a measure of the pozzolanic value of the cement.

A pure Portland cement tested in this way gave a "hot" test of 320 lb. per sq. in. and a "cold" test of 380 with the difference of —60 lb.

A pozzolanic cement of poor quality gave this result: "hot" = 320 lb., "cold" = 270 lb. Difference = + 50 lb.

A pozzolanic cement of indifferent quality gave this result: "hot" = 350 lb., "cold" = 250 lb. Difference = 100 lb.

A pozzolanic cement of good quality gave this result: "hot" = 500 lb., "cold" = 300 lb. Difference = 200 lb.

It has been suggested that the minimum difference permissible should be 120 lb.

It is essential that this "hot and cold" test should be related to the qualities of pozzolana cements in regard, 1. to the resistance to sulphates, 2. to the ultimate compressive strength of pozzolana cement concrete, and perhaps to other properties.

1. With regard to resistance to sulphates the "hot and cold" test does seem to act as a criterion. This can be seen on FIG. 1. The solution

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[1] Superintendent of Research Department, the Associated Portland Cement Manufacturers Ltd, Gravesend, Kent, England.

was 2 % $MgSO_4$. The expansion line for "good pozzolana cement" is an average of three such cements.

It is perhaps necessary to state that the specimens used for this test were intentionally made very porous. They are made with 4 parts standard sand to 1 of cement and a water : cement ratio of 0.60. Well made, dense concrete is very much more resistant to sulphate action than these specimens.

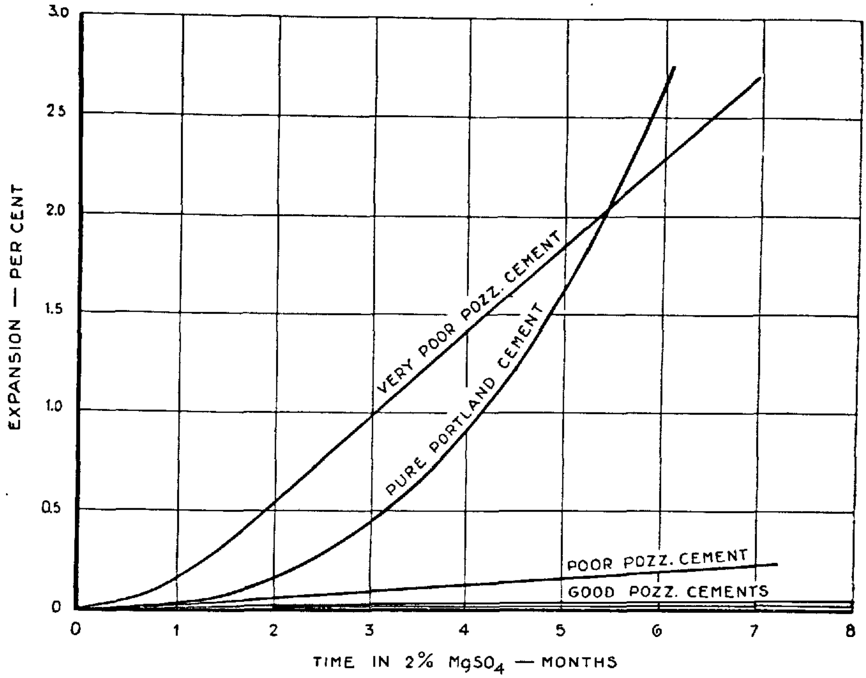

FIG. 1. Expansion of Pozzolana Cements in 2 % $MgSO_4$-Solution.

2. With regard to ultimate compressive strength, the following method was adopted.

It has been ascertained that the strength of concrete cubes is directly proportional to the amount of cement in the cubes, provided the total water in the cubes is constant and the aggregates are of the same quality. This holds true over the range of cement contents which result in a solid compact concrete. The lower limit of cement content is where the original mix is about 8.5 ballast and sand to 1 part of cement, and 0.91 water (22 g cement per 100 cm^3 concrete). In the usual concrete with 4 parts of ballast : 2 parts sand : 1 cement : 0.6 water, where a pozzolana cement is used the proportions may be (say) 4 : 2 : 0.6 pure cement : 0.4 pozzolana. It is inadvisable to compare pozzolana cement concrete directly with a concrete containing the same amount of pure cement, because the proportions for such a concrete would be 10 parts of ballast and sand to 1 cement, and the resulting concrete would not be solid.

Straight line curves of the strength of concrete are obtained by plotting the compressive strength against the cement content of the cubes expressed

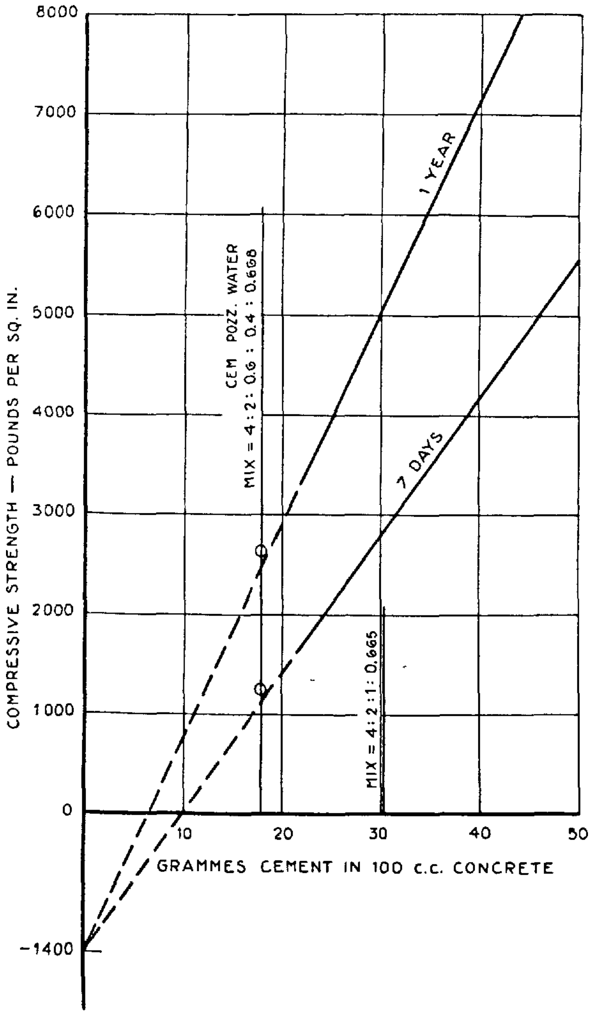

FIG. 2.

in grammes per 100 cm^3 of concrete, the water content being fixed—in the present case the water content was fixed at 20 g per 100 cm^3 concrete. Different straight lines were obtained for different dates but only the 7-days and 1-year are shown on FIG. 2.

The pozzolana concrete was 4 : 2 : 0.6 cement : 0.4 pozzolana : $0.668H_2O$. This concrete has 20 g of water and 18 g of cement in 100 cm^3 concrete. If pozzolana has no strength value in concrete, the strengths at 7 days (see FIG. 2) would be 1 100 lb. per sq. in. and at 1 year 2 400 lb. per sq. in. If the total strength exceeds these figures then the difference between the actual figures obtained and 1 100 (at 7 days) or 2 400 (at 1 year) gives the pozzolanic strength of the cement.

Up to the present, no appreciable deviation from the values of 1 100 and 2 400 have been obtained. The usual deviation has been of the order of 100 or 200 lb. per sq. in. This result is not in agreement with the results of Dr. LEA who obtained substantial increases and, so far, no explanation of this lack of agreement has been offered. Further tests are in hand.

So far, the "hot and cold" test is the best that has been found. It requires, however, 7 days and is not of much use for the control of manufacture.

Mr. CRICHTON would welcome a test for pozzolanic value which would give quicker results. Dr. HÅKANSON's method of determining CaO absorbed is open to the same objection—that it takes 7 days. It is also probable that the lime absorption will vary with the types of pozzolana and cement used.

Mr. W. BÜSSEM:[1]

I should like to make some comments on Dr. LEA's lecture. Dr. LEA left the question open as to what combinations, in the quaternary system of lime, silica, alumina and water, are possible. In the last two years Dr. STRÄTLING has carried out in our Institute a number of experiments in this matter. As the test material for these experiments we chose burnt kaolin, which was burnt in various stages from 400° to 1 100°. First of all very exact grain-size measurements were performed on this material, after which it was subjected to reaction in a shaking-apparatus at 20° with lime solution. At the same time the reaction was followed thermo-chemically, and the heat of wetting, the absorption of the lime and the subsequent chemical reaction of the lime with the desiccated kaolin investigated. It proved that the development of heat did not cease with the absorption of the lime, but continued. After some months the reaction had penetrated a considerable part of the product, and the X-ray analysis of these parts showed that a new crystalline phase had formed. The end-values of the lime absorption finally, after six months, reached the order of magnitude of 3 mols. lime, thus $3CaO$ to 1 mol. desiccated kaolin. The gross composition of the basic body after this lapse of time was $3CaO \cdot Al_2O_3 \cdot 2SiO_2$. The question now was: is this basic body a uniform crystalline phase in this combination or does it comprise several crystalline phases,

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thus, for example, as we originally supposed, calcium aluminate hydrate and calcium silicate hydrate in such a way that the gross composition 3 : 1 : 2 to xH_2O arises? In order to settle this point we proceeded to compare all known minerals and synthetic compounds of this kind and found that no similarity or identity exists. We then made further experiments in which we took other test materials. We took as our starting material either calcium aluminate and calcium silicate mixed with water, or calcium aluminate hydrate and calcium silicate hydrate mixed with water or calcium alumosilicate together with water. And in this connection the following observations were made: when we took as our test product certain anhydrous compounds, as for example tricalcium silicate and tricalcium aluminate with an Al_2O_3: : SiO_2-gross-ratio of 1 : 2 and reacted with water, we also obtained the same basic body. If, on the other hand, we took the corresponding hydrates as our starting material we were unable to carry the reaction further—the hydrates remained completely unchanged. When we chose other test compounds we obtained, in coming from the side poor in alumina, and thus correspondingly rich in silica, a compound having more or less exactly the composition $3CaO \cdot 2SiO_2$. The more alumina was added the more the basic body tended to have the composition of our original compound arising from kaolin; and when we went more to the side rich in alumina and thus poor in silica we found the compound $3CaO \cdot Al_2O_3 \cdot 6H_2O$, thus the cubic tricalcium aluminate hexahydrate. In this way we were able to explain why our basic body that arose out of the kaolin reaction is not homogeneous, but consists, probably, of two phases which we were able to interpret as a ternary calcium silicate hydrate having the composition $3CaO \cdot 2SiO_2 \cdot xH_2O$ and a quaternary Gehlenite hydrate, $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot xH_2O$ respectively. An attempt to change the Gehlenite itself in this way from the anhydrous form to this hydrate was, however, unsuccessful. Even in the autoclave it was not possible to attack the Gehlenite, which accords with the results spoken of by Dr. ASSARSSON in his lecture here to-day. For further confirmation we then heated our basic body from the kaolin reaction, and actually found, on heating to 900°, the presence of the Gehlenite, and on further heating to about 1 100°—1 200° the presence side by side of monocalcium silicate in the α-form, that is to say the so-called pseudo-Wollastonite, and the Gehlenite itself, so that the trial formula is thus confirmed.—*(Translated from German.)*

Mr. T. THORVALDSON:[1]

I was very much interested in Mr. CRICHTON's account of his work on evaluating pozzolanas by means of the effect of admixtures of these on the

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[1] Professor, University of Saskatchewan, Saskatoon, Canada.

expansion of mortars in sulphate solutions. Some years ago we carried out a large number of experiments of this type on some volcanic ashes found in Saskatchewan and other pozzolanic materials. We did not publish our results because we felt that the method was not entirely satisfactory for a general evaluation of these pozzolanas due to the large number of factors affecting the results.

When we arranged mortars, in which a definite fraction of the cement had been in turn replaced with several of these pozzolanic materials, in a series according to the relative effect of the pozzolana on the rate of expansion, the order was not necessarily the same as that obtained when using other ratios of pozzolana to cement, or with mortars differing only in richness of mix, or with a different Portland cement. While we found an optimum admixture of the pozzolana for a given set of conditions this optimum was not necessarily the same for test pieces of another richness of mix or made with another Portland cement. The numerical figures for the evaluation and sometimes even the order differed with the time of exposure to the sulphate solution. The results of separate exposures to solutions of sodium sulphate, magnesium sulphate and calcium sulphate did not always give consistent values nor did exposures to solutions of different concentrations of the same sulphate.

The results may indicate that evaluation of pozzolanas is meaningless except under the exact conditions under which they are going to be used in practice.

Dr. LEA has discussed in his paper the action of sulphate waters and sea-water on concrete more particularly in relation to the effect of the addition of pozzolanas. He observes that the action of sea-water does not produce the swelling typical of the action of sulphates in laboratory tests. The modification of sulphate action by the presence of other substances in solution is rather interesting. We have observed that the presence of salts, which alone do not cause swelling, affects the rate of swelling in sulphate solutions. Addition of sodium hydroxide to solutions of sodium sulphate has a remarkable retarding effect, in some cases almost preventing the swelling completely. We have also found that once the swelling of the mortar in sulphate solutions is well under way, it is very difficult to stop it; thus it may continue to complete disintegration even when the mortar is transferred to distilled water. We find that it is difficult to ascribe the swelling, at least in some of our experiments, to crystallization or to deposition of solids in the test piece. It seems rather that the sulphate causes some change in the cementing "glue" in the mortar specimen and that as a result the swelling continues.

We have made another observation which may have a bearing on this. When dicalcium silicate or tricalcium silicate is shaken with sulphate solutions, the hydrolysis equlibrium is shifted towards greater liberation of lime than in pure water. That is, for a given alkalinity of the liquid phase the hydrosilicate gel has a lower lime:silica ratio when sodium sulphate is present. This might mean that when the mortar specimen is immersed in pure water, the limiting composition of the cement "glue" is that of hydrated dicalcium silicate, while in the presence of sulphates the limiting lime:silica ratio of the gel might correspond to a lower hydrosilicate with essentially different colloid properties. This would also explain the apparent "induction" period observed in sulphate disintegration, and the fact that many factors retarding disintegration (such as steam-curing and the addition of pozzolanas) only increase the length of time before any serious swelling occurs (*i. e.*, the length of the "induction" period). Once the swelling begins, the rate often does not differ much from that obtained in the absence of the retarding factor.

Now the swelling of mortars in sulphate solutions is probably brought about by a combination of several factors. In the case of magnesium sulphate, the deposition of insoluble or slightly soluble substances inside the specimen is probably one of the main factors. Yet, in other cases, expansion takes place without any such cause being indicated by microscopic observation. I would like to suggest that in these cases osmotic forces may be mainly responsible for the swelling, the colloid gel in the mortar setting up differences in the concentration of the ions according to the principles of the DONNAN equilibrium.

Mr. A. TRAVERS:[1]

Some Remarks on the Study of the Permutitic Properties of Certain Cements.

A certain number of authors have wished to see in the pozzolanas and in the basic slags of blast-furnaces, bodies analogous to the permutites, that is to say, 1. possessing the properties of changing cations—valency against valency—2. capable of losing their water, totally or partially, without changing their structure.

It is absolutely necessary, if one wishes to study such a reaction of exchange, to use *perfectly neutral salts;* that is to say, *salts undergoing no hydrolysis.*

The permutites, in fact, can only exist in a rather restricted region, of P_H — 5 to P_H—10.

The *complex* silico-aluminate of the type $M \cdot AlO_2 \cdot nSiO_2$ is in fact destroyed outside these limits; consequently, one ought not to employ:

ammonium chloride (P_H in the neighbourhood of 5)

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[1] Professeur, Ecole Supérieure des Industries Chimiques, Université de Nancy, Nancy, France.

salts of copper (P_H in the neighbourhood of 3), of lead etc., all with an acid reaction, nor *free* alkalis. The alkaline carbonates, on the other hand, do not act on the complex $M \cdot AlO_2 \cdot nSiO_2$ (preparation of *artificial* permutites by *fusion* anhydrous SiO_2 and Al_2O_3 with CO_3Na_2).

BERL and URBAN (1), wishing to show the permutitic properties of trass, used, in my opinion ill-advisedly, NH_4Cl.

According to a number of authors (2) the pozzolanas, when treated with lime-water, would give off alkalies to the solution, but the percentage in weight of freed alkalies remains very low (1 %), and it does not seem that it is the *permutite* reaction that is able to explain the hydraulic properties.

The important fixation of lime (20 to 40 % of the weight of the pozzolana) by *simple addition* seems rather to be responsible for these properties. It is due, in my opinion, to the "free" or uncombined silica of the pozzolanas.

I have not found, on the other hand, any permutitic property in the basic slag from the blast-furnace. In all my experiments I used nitrate of silver, *a neutral salt*, of which the precise estimation allows of a large approximation. There is no exchange of cations. Only at the end of two or three days does one observe a darkening, due to the formation of Ag_2S. The calcium sulphide of the slag, probably engaged in a *complex*[1] only shows the properties of the sulphur ion at the end of this time, while in the free state it is very soluble in water.—*(Translated from French.)*

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Mr. F. M. LEA (*author's closure*):

Dr. BÜSSEM's report that a hydrated calcium alumino-silicate of composition $2CaO_3 \cdot Al_2O \cdot SiO_2 \cdot xH_2O$ is formed by the action of lime solutions on burnt kaolin is of much importance in connection with the mechanism of pozzolanic action. As mentioned on page 475, one difficulty in finding a satisfactory chemical explanation of the increased resistance to sulphate attack obtained by adding pozzolanas to Portland cement has been the alumina content of the pozzolana. If this alumina does not, when it reacts with lime, form a hydrated tetra- (or tri-)calcium aluminate as in Portland cement, but an alumino-silicate more resistant to sulphate attack, this difficulty may disappear. It is important that the stability relations of this new

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[1] Dr. KAEMPFE supposes that it is an aluminate sulphide. Inst. Hochschule Berlin, 1934.

compound should be studied in order to ascertain if it remains permanently stable in contact with saturated lime solutions, or whether it splits into the more basic silicate and aluminate compounds, and to determine if it can form in the setting of Portland cement itself.

Mr. CRICHTON mentions the 50° curing test for pozzolanic cements which was referred to in the paper. A discussion of the relation between the results obtained by this test and the strength development and sulphate resistance of pozzolanic cements will be given in a forthcoming Building Research Technical Paper and is too lengthy to consider here. It may be mentioned that the difference between the strengths obtained under the 50° and 18° curing condition increases as the proportion of pozzolana present in the pozzolanic cement is raised. For good sulphate resistance, which requires an adequate content of pozzolana, the minimum permissible strength difference of 120 lb. per sq. in. suggested by Mr. CRICHTON is rather too low. The test is purely empirical, but has been found to hold for a wide variety of pozzolanas. Data are given by Mr. CRICHTON for one pozzolanic cement indicating that even at an age of 1 year the pozzolana present had made no contribution to strength development. There is, however, much data in the literature, apart from the author's own results, which show that, when good pozzolanas are substituted for Portland cement, the strength obtained at long ages is considerably higher than that to be expected alone from the Portland cement fraction present.

The suggestion by Dr. FORSÉN that the source of the activity of the reactive forms of silica is to be found in a more open lattice structure is interesting and in accord with at least some of the conceptions of the nature of the decomposition of clays on burning. It may also be noted that N. A. SHISHACOW (3) has concluded from electron diffraction patterns that pozzolanas contain randomly distributed two-dimensional crystals (*i. e.* sheets) of composition Si_2O_5.

Mr. HÅKANSON's data on the extraction of crushed set cements with water are in agreement with results obtained by the author which also indicate the greater resistance to leaching of lime shown by pozzolanic cements in comparison with Portland. Similar results have also been obtained from percolation tests on concrete and are discussed in a paper (2) which is now in the press. The estimation of free lime in set pozzolanic cements is admittedly uncertain. In the calorimetric method a correction, as mentioned by Mr. HÅKANSON, is required for the free lime which combines with the pozzolana during the heating. The author has for this purpose used a correction factor determined by extrapolation of a curve relating estimated free lime contents to time of heating, but, though no high precision can be claimed for it, the correction is much less than that suggested by Mr. HÅKANSON's results.

While the estimation of soluble silica by Mr. HÅKANSON's method may be useful as a works' control process when dealing with one particular pozzolana, it seems doubtful if it could be used as a relative measure of quality of pozzolanas of widely differing types.

The author is in agreement with Professor TRAVERS's suggestion that the hydraulic properties of pozzolanas cannot be attributed to base exchange reactions, though, as indicated on page 469, base exchange may play some small part in lime fixation.

Professor THORVALDSON comments that when mortars containing different pozzolanic materials are arranged in order of sulphate resistance, the order found is not necessarily the same when the mortar composition or the sulphate solution used is changed. It is, of course, true that even Portland cements do not always fall in the same order when the test solution is varied.

V. V. KIND (1), from a comparison of the relative resistance of pozzolanic and Portland cement to sulphate attack, has reported that in sodium sulphate solutions up to 10 per cent concentration the pozzolanic cement showed much the greater resistance, as was also the case for magnesium sulphate solutions below about 0.5—0.75 per cent. With magnesium sulphate solutions of higher concentration, *e. g.* above 2 per cent, however, the pozzolanic cement was destroyed even more rapidly than the Portland cement. While the present author's results do not confirm KIND's data, in so far as pozzolanic cements have been found considerably more resistant than Portland cement to 5 per cent magnesium sulphate solution, this may be due to differences in the mortars used for test. While agreeing with Professor THORVALDSON that the relative order in which different pozzolanas are placed by sulphate resistance tests may vary somewhat according to the test conditions, the author considers that it is possible to distinguish by such tests between pozzolanas of value in practice and inferior materials of little value. The observations of Professor THORVALDSON on the inhibition of swelling of mortars during attack when certain other salts are added to the sulphate solution is very interesting and it is hoped it may be studied further. The shift in the hydrolytic equilibrium of the hydrated silicates towards a higher lime concentration when sulphate salts are present, found by Professor THORVALDSON, is confirmed by the results for sodium chloride mentioned on page 480.

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THE PHYSICAL STRUCTURE OF HYDRATED CEMENTS

BY

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Introduction.

As the *raison d'être* of cement lies in its capacity to harden it follows that much interest must be directed to the causes of this hardening. The chemical reactions between cement and water are in this connection the means to the attainment of the end in view, but they are not in themselves sufficient. Lightly burned magnesia, MgO, hardens "hydraulically" with water to form a marble-like mass of $Mg(OH)_2$. Periclase, MgO, in Portland cement clinker will in time, by its hydration, cause expansion of concrete produced from such cement. Magnesia distributed in the clinker glass, again, does not give rise to such unsoundness. It is thus obvious that it is not only the chemical reaction in itself, which is identical in the cases mentioned, but also the way in which it takes place and the resulting structure in the product that is here of importance.

The strength and other technical properties of the hydrated cement, such as shrinkage, elasticity, plasticity, permeability etc., are determined by its physical structure. This, again, is a result of the chemical reactions and the physical conditions obtaining when the reactions take place. By establishing the structure of hardened cement we are enabled to explain the binding power or strength of the cement as well as a number of other properties, and, consequently, to improve the cement and possibly also to find ways to new ones. Taken in this sense the study of the physical structure is a necessary supplement to the chemistry of cement, and it also constitutes an essential link between cement and the concrete manufactured therefrom.

The subject dealt with in this report has been treated both by chemists interested in cement and by engineers interested in concrete. It touches the border-line between the solid and liquid phases and also that between what is known and unknown on the subject in the physical and chemical science of to-day. The author realizes not only the difficulty of giving a satisfactory survey of all the contributions in this field, scattered as they are in various branches of the literature, but also the difficulty of giving a criticism of them that shall be not too vague yet at the same time reliable. Although a retrospect of the question, the more serious study of which is as yet in its infancy, must thus to a certain extent be incomplete, the author hopes that it may nevertheless prove of value for the continued work in this field.

Where not otherwise specified in the following "cement" is understood to mean a Portland cement of normal composition that is assumed to harden in a normal way.

The Hydration Process and the Development of Structure.

Dry cement is a powder mixed with air and in a high degree aggregated.[1] The size of the cement particles varies on an average from some fractions of a micron to rather more than 100 microns with a distribution-maximum of about 10—20 microns. The specific surface is of the order of magnitude 2 000 cm^2 per g. The cement particles are as regards their chemical composition not homogeneous. During the grinding of the cement clinker the harder clinker components remain to a greater extent in the coarser particles while the more easily ground components tend rather to be found in the finer particles (14, 60). The gypsum added to regulate the setting time and which is especially easily ground is also most fine of grain. The separate particles are further for the most part unhomogeneous and consist of several different clinker components.

When cement is mixed with water the particles are rather quickly wetted and disaggregate, forming a suspension in the water. The thickness of the suspension depends on the proportion cement : water. When the suspension is left standing, a settling takes place, in which connection the water is separated above the suspension. In a fat cement-water-mixture separation of the water may be quite insignificant, in a lean mixture, on the other hand, it may be considerable (29, 11, 26). The result is a loose sediment of the coarser particles with the finest particles still in suspension in the intermediate spaces. The structure thus obtained constitutes the point of departure for the continued development and may be designated *structure A*. So far we may, with a certain justification, assume that the specific cement qualities of the particles play a subordinate rôle, and that the structure would on the whole have been the same if the particles had not consisted of cement but had been inert in relation to the water.

The hydration of the cement, which began as soon as the particles were

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[1] The aggregation of the particles can to a certain extent be counteracted by intensive mixing and the addition of air, as takes place in practice in the transport of cement through pipe-lines. A very effective disaggregation can be obtained by mixing cement with SiF_4-gas. After this mixing the cement has for a time a strikingly fluid appearance and dusts heavily.

wetted with water, continues now within the frame constituted by structure *A*. According to FORSÉN in a report to this Meeting (21), the hydration process is in essentials as follows.—The cement components go into solution in the same stoichiometric proportions as the water-free components. Supersaturated solutions are here formed, from which the "cement-glue", amorphous $Ca_2SiO_4 \cdot 4H_2O$, is precipitated. The dissolution of the components is delayed by the formation of a semipermeable film of aluminates rich in lime almost immediately round the cement particles. — Tricalcium silicate, which is the chief source of dicalcium silicate hydrate, gives as a by-product calcium hydroxide, which is separated in the form of small crystals. Other hydration products such as double salts of calcium aluminate etc. may be ignored in this connection, and the reader is referred to the reports to the Meeting that deal in detail with the reaction with water of the cement and of the components of cement.

The mechanism of the precipitation of $Ca_2SiO_4 \cdot 4H_2O$, the "cement-glue" is not clear. The silicate hydrate appears in an apparently amorphous state but may very conceivably consist of extremely small crystals. It seems probable that these are in this case needle-shaped, cf. BESSEY (4). The precipitation may be conceived to take place in different ways.—1. It may take place near the cement particles in such a way that newly formed hydrate successively pushes the earlier precipitated hydrate masses to the side. An envelope is formed, that grows from within.—2. It may also take place in such a way that the silicate solutions pass through the earlier precipitated hydrate layer and build upon this from without.—3. A further possibility would be that during a first phase the hydrate formed a colloidal solution that coagulated to a gel, upon which the continued hydration would take place within the frame of this gel. It would then be possible to look upon this gel as a 2nd structure, and the continued building-up within this as a 3rd structure, according to a suggested terminology by POWERS (55).

Probably the most likely solution, however, is that in reality several of these alternatives enter into the process, either simultaneously or on different occasions according to the circumstances. Doubtless the result implies throughout a successive thickening around the cement grains until these have been completely converted or continued hydration has become impossible on account of the density of the hydrate layer. In the present survey the structure built up by the hydration products is designated *structure B*, which is thus formed in conjunction with a breaking down or consumption of structure *A*.

Structure *B* does not constitute a final stage. It is changed successively in consequence of continued hydration of the remains of the cement particles (in which connection chemical changes may occur, influencing both the continued hydration and the old structure), as a result of ageing (crystal enlargement, gel-coarsening), as a result of temperature changes, as a result of moisture changes (drying, or moistening and periods of these), as a result of external chemical influence (carbonation etc.), and as a result of external mechanical influences (loading and unloading).

Volume Relations and Speeds of Reaction.

The volume relations in connection with the development of structure *A* are shown in Fig. 1 (26). The heavy lines show the separation of water in various groups of cement. The dashed line indicates absolute cement volumes in per-cent values of the whole system cement + water. In the case of average water : cement ratios and a moderate separation of water, the water volume in structure *A* is in round numbers twice the cement volume.

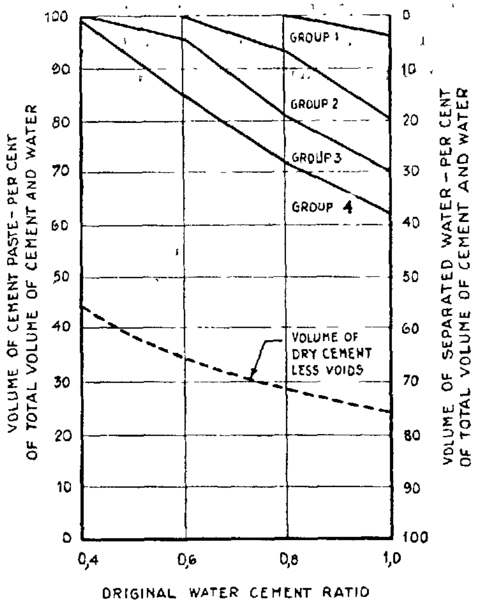

Fig. 1. Water Separation of Different Types of Cement. Group 3 represents typical standard Portland cements. (Giertz-Hedström.)

A contraction of the system cement + water takes place on hydration of the cement. The contraction may easily be measured by means of a suitable dilatometer arrangement, and this again is a convenient method of following the hydration of the cement. Such measurements were carried out by Le Chatelier (44). More recently, there have been measurements by Gessner (24), Neville and Jones (50), Powers (54), Berchem (3), and others. Fig. 2 shows the course of contraction, with about 75 % addition of water, of the most important components in Portland cement clinker.

The contraction of the system cement + water must involve a reduction of the external dimensions of the system, an additional filling with water, that is absorbed into the system, an increase in and formation of new pores in the system or several of these effects simultaneously. One or the other of these may predominate according to the circumstances.

Within the system the hydration entails an increase in the volume of the solid phase and a decrease in that of the fluid phase. It has been attempted to estimate the magnitude of these volume changes, but the result will vary according to where the line between the solid and fluid phases is drawn. This question is treated in greater detail later. Here it will be sufficient to give some examples.

When CaO, with specific gravity 3.31, takes up a molecule of H_2O to form $Ca(OH)_2$, with specific gravity 2.23, the volume of the solid phase increases by 96 %. At the same time there is a contraction of the system calcium oxide + water by 5 %.

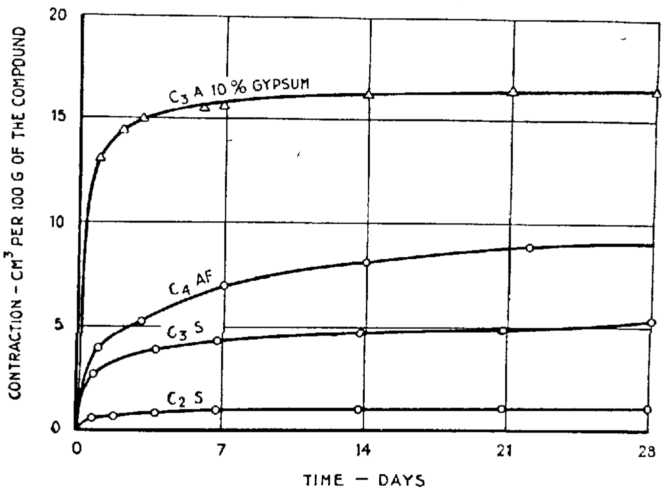

Fig. 2. Contraction on Hydration of Portland Cement Clinker Components. (Powers.)

Eiger (20) gives the following data for two cement clinkers.

	Specific Gravity, unhydrated	Calculated Spec. Grav., 100 % hydrated	Fixed Water, (diff. 110°—1 000°) in 100 % hydr. Sample % of Clinker
Clinker A	3.20	2.26	19.6
» C	3.14	2.20	18.8

This would imply that the clinker samples had, by taking up about 20 % water, increased their volume by about 70 %. These data should, however, be taken with some reservation on account of the assumptions on which the calculations are based and the difficulties of measuring. The figures thus show, for the system cement + water, an expansion instead of a contraction. The figure 70 % may, nevertheless, as will be seen later, be taken as indicating the right order of magnitude of the volume increase.

The reaction velocity in the hydration of cement, expressed as an average for the cement particles and the cement components, may be determined by measuring some of the physical or chemical effects accompanying the hydrations.

The swelling of the cement or the formation of new solid phase has been investigated by HÄNSEL, STEINHERZ and WAGNER (32), DUBRISAY (18), and others, the viscosity changes of the cement suspension by GESSNER (24), DORSCH and DEUBEL (17), and others, and the changes in its electrical conductivity by GESSNER (24), BOHLIN and BRUND (7), DORSCH (16), and others. These measurements, that are chiefly of importance as giving information concerning the first hydration period, confirm that the hydration and development of a new solid phase begin immediately after the addition of water.

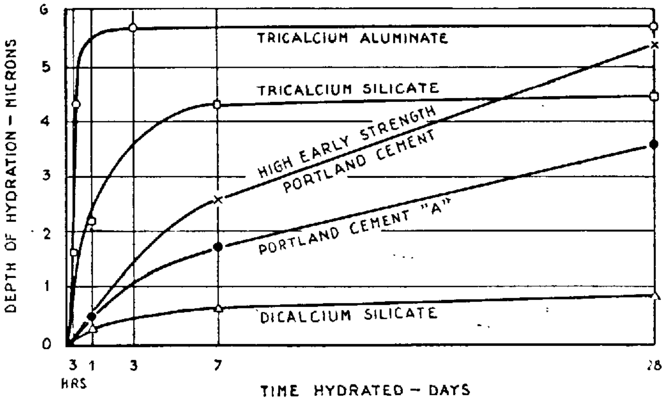

FIG. 3. Depth of Hydration of Portland Cement and Portland Cement Components. (ANDEREGG and HUBBELL.)

Conclusions regarding a greater part of the hydration period are enabled by measurements of the contraction—cf. above (24, 50, 54, 3) — of the specific gravity of the hydrated cement, carried out by EIGER (20), BERCHEM (3), and others, of the heat development, carried out by LERCH and BOGUE (46), HONUS (28), POWERS (54), and others, of the water-fixation measured in various ways, which will be discussed later, and of the optical properties as carried out by ANDEREGG and HUBBELL (1). With a knowledge of the value of the respective degrees of hydration for unhydrated and completely hydrated cement it is possible, by using the data obtained, to calculate the average degree of hydration. If, further, the original distribution of grain-sizes in the cement is known, or if grains of equal size are used, the average depth to which the hydration has penetrated may be calculated. Calculations of the average deformation of the grain distribution curve in such cases have been made by WERNER and GIERTZ-HEDSTRÖM (65) and EIGER (20). FIG. 3 shows some optically obtained values of depth of hydration for Portland cement and Portland cement components.

Hydration data calculated in this way are in so far incorrect as they do not take account of the various speeds of reaction of the cement components and the distribution of these components over various particle sizes. They give, however, a valuable approximate picture of the course of the hydration.

A summary of the section here dealt with gives, in round numbers, the following schematic picture of the hydration of cement. Cement and water form in the initial stage a suspension in which the solid phase takes up $^1/_3$ of the volume and the fluid phase $^2/_3$ of the volume. By hydration to 100 % the solid phase increases in volume to about $^2/_3$ and the fluid phase decreases to about $^1/_3$. Simultaneously with this a contraction of the system by 5 % takes place. The hydration penetrates to a depth of 0.004 mm in 28 days, after which time more than $^3/_4$ of the cement has been hydrated. In this process the cement particles have become smaller, so that some grains have completely disappeared but remains of the larger grains are still left.

Methods for the Investigation of the Physical Structure of Hardened Cement.

Macroscopic Observations.

Certain macroscopic observations are in themselves sufficient to enable some conclusions as to the physical structure of hardened cement. So, for example, its permeability indicates that bound cement has a porous and not a compact structure. Its ability to absorb water indicates the presence of a capillary structure, and its shrinkage and swelling on drying and moistening provides a striking analogy with the conditions obtaining in irreversible gels.

Further phenomena of interest are the course of the elastic and plastic deformation, the capacity of cement to re-harden on crushing and fresh mixing with water, its resistance to the action of frost, the way in which its strength is conditioned by factors such as moisture and temperature etc.

The macroscopic observations enable us, firstly, to draw direct conclusions as to the structure of hardened cement, and secondly, to confirm or refute various theories regarding this structure. The author will return to these questions later, although rather briefly, as it may be sufficient merely to indicate them in the present report.

Microscopic Examinations.

With the aid of the microscope it is possible to get a considerably more detailed picture of the physical structure of hardened cement than by macroscopic observation. Practically all research-workers since Le Chatelier (44) and Törnebohm (63) have used this instrument. Reference may here be made to investigations by Kühl (38), Sundius and Assarsson (57), Colony (15), Parker and Hirst (51), Berchem (3), Brown and Carlson (12), and others, who have used ground samples of hardened cement (or concrete) with normal water content. Many investigations of the hydration of cement in the presence of large quantities of water have also been carried out. In the latter case, however, the conditions for the formation of the normal structure are altered so considerably that the right interpretation of the result is exceedingly difficult. It is, therefore, best for the present to leave these latter investigations out of account.

Microscopic studies of ground samples of hardened cement consistently show that it normally contains unhydrated remains of the original cement grain embedded in an amorphous mass, often called the "cement gel", in which one finds numerous crystals of calcium hydroxide and, in certain cases and to a lesser extent, also crystals of other kinds such as calcium sulphoaluminate etc. The amorphous mass constitutes the main part of the hardened cement and is undoubtedly the component from which the cement mainly derives its strength.

The *"cement gel"* may be considered as consisting of a calcium silicate hydrate of a composition approximately corresponding to $2CaO \cdot SiO_2 \cdot 4H_2O$, Forsén (21). The composition of the silicate may be modified by surface adsorption or by lack of lime. It is a hydration product of the tricalcium silicate and dicalcium silicate of the clinker. To a lesser extent one also finds other gel-like products, the formation of which is conditioned by other component parts of the cement, and which are of importance for the course of the setting of the cement. While it is possible with the aid of microscopic methods to identify the various crystals in the clinker remains and the new crystalline formations, it has not hitherto been possible to penetrate the structure of the so-called "cement gel". The resolving power of the microscope is not sufficient to reveal the extremely fine structure of this main product of the hydration and it has proved necessary to employ other more indirect methods of investigations.

The *calcium hydroxide* is a product of the hydration of the tricalcium silicate. It is easily observable under the microscope in hardened cement and is generally formed in hollow spaces and in connection with the clinker remains. Lime-fixing additions to the cement diminish the quantity of the calcium hydroxide.

It seems not to be produced to any considerable extent in the case of the hydration of the dicalcium silicate in a limited amount of water.

The *clinker remains* contain all the original constituents of the clinker, but, in other proportions, according to the various speeds of reaction to water of the constituents. It is often possible to distinguish a hydration zone around the single grains, probably indicating a thickened layer of hydration products.

The microscopic investigations carried out by Brown and Carlson (12) give many clear data as to the development of the structure which may here be reproduced as follows.—The cement gel has a considerable tendency to fill comparatively very large intergranular spaces of up to 50 to 100 microns in size. The gel seems not to develop as an even envelope around the clinker grains but grows abundantly in the intermediate spaces offering the greatest freedom for growth. Its porosity varies with the water content used, so that a denser gel is obtained with lower water content and a more porous gel with higher water content. Not even when magnified a thousand times, is it possible to observe any channels in the gel. The calcium hydroxide crystals decrease in number and are more evenly distributed in the samples with lower water contents. They appear not to crystallize within the gel mass. The pores of the gel seem to remain open and serve as channels. A comparison between tricalcium silicate and dicalcium silicate that have been left to hydrate for $1^1/_2$ years shows an almost complete hydration with strong gel formation and quantities of calcium hydroxide crystals for the tricalcium silicate, and for the dicalcium silicate a far from complete hydration with practically nothing but gel as hydration product. Despite the different degrees of hydration both the hardened silicates showed almost equal values as regards strength and these were in both cases high. The trisilicate, however, had already attained 60 % of this strength after 7 days, at which stage the disilicate had not yet any perceptible strength.—Brown and Carlson (12) have also investigated the effect of steam-hardening and addition of pozzolana.

X-Ray Analysis.

X-ray examinations of hardened cement have so far given little beyond a confirmation of what has been shown by the microscope. The presence of clinker remains and crystallized calcium hydroxide is thus confirmed, Brandenberger (9). The structure of the main mass, the "cement gel", is, however, such as to give, at least for the present, no clear guidance in the X-ray diagrams. This may be due to its lacking a crystalline structure or other regular fine structure, or to the crystals being so small or deformed (for example bent needles) that no definite interferences are obtained. Berchem and Brandenberger (3) have found that a sample of tricalcium silicate, that has been hydrated for a long period and from which by means of extraction about $^1/_3$ of the lime content has been removed, no longer shows any of the tricalcium silicate lines, which supports the view of dicalcium silicate hydrate as a hydration product of tricalcium silicate. They have also found, in such samples, some new lines probably to be ascribed to the dicalcium silicate hydrate, which even in samples which have been stored at high temperatures for long periods seem to appear only in very moderately developed crystals. (Reference may also be made to page 389 of this book.)

Considering the continual improvements that are being made in X-ray technique we have every reason to expect that it will in the future contribute much more to the structural investigation of hardened cement.

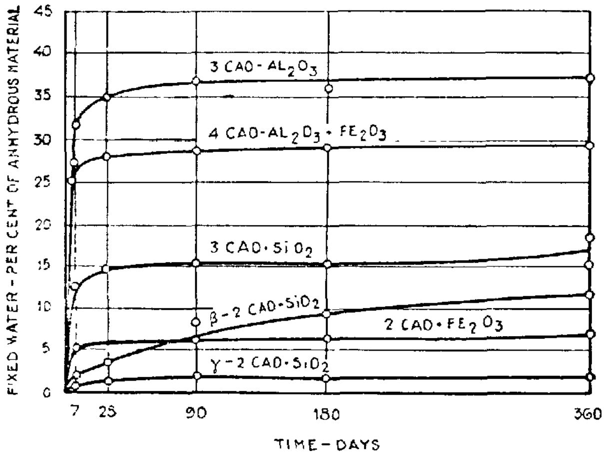

Fig. 4. Fixed Water of Hydrated Clinker Compounds at Various Ages. (Bogue and Lerch.)

Measurement of the Water-Fixation.

From the chemical point of view the hydration of cement is a complex reaction process resulting in a number of new water-containing compounds. From the structural point of view, however, water is engaged in the hydrated cement also otherwise than solely as hydrate water. It is in this respect possible to distinguish at least 5 different functions of water. There is free water that is only enclosed in the hardened cement and whose vapour-pressure is somewhat reduced as a result of dissolved substances, but which is otherwise practically identical with pure water. A certain amount of the water is fixed by the dissolved and solvated substances and more or less firmly attached to these. Further, a part of the water functions as capillary-bound water with a vapour-pressure varying according to the degree of dryness of the cement and the size of the capillaries. A certain amount of the water is further bound by adsorption at the surfaces of the solid phases and is found engaged in varying degrees according to its nearness to the surfaces and the nature of these. Finally, there is chemically bound water engaged in the chemical structure of the solid elements.

It is obvious that investigations of the water-fixation in hardened cement can give various data concerning its physical structure, and such investigations also constitute a very valuable indirect method of approach as regards this structure.

The simplest way to get an idea of this water-fixation is to heat up the hardened cement to different temperatures and then ascertain how much water it retains. Such measurements have been carried out by many investigators. Among the more recent of these may be mentioned those by WORK and LASSETER (73), BOGUE and LERCH (6), LEA and JONES (43), and WILSON and MARTIN (69). FIG. 4 shows the water-fixation in various clinker minerals determined as the difference in weight on heating up to 105° and 850°.

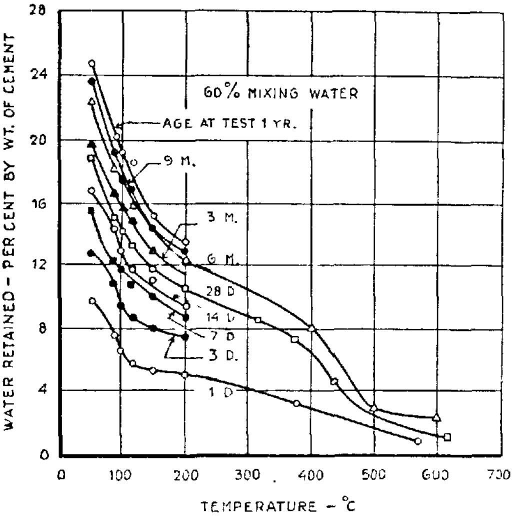

FIG. 5. Water retained by a Hydrated Portland Cement at Varying Temperatures and Ages. (WILSON and MARTIN.)

Such measurements of the fixation of water give in the first place an idea of the degree of hydration, expressed as a mean value. By determining the amount of water retained in connection with a series of different temperatures a more detailed picture of the water-fixation is obtained. FIG. 5 illustrates a series of such experiments.

The results obtained from the heating experiments are to some extent arbitrary in so far as the moisture of the air and the length of time taken for the heating are independent variables. In connection with experiments with isobar heating of hydrated cement and of separate compounds as carried out by KRAUSS and JÖRNS (36) and KRAUSS and PRÜSSING (37), this source of error is eliminated. The chief drawback in connection with the heating experiments, however, is the influence of the heating upon the water-fixation and the structure. This disadvantage is lessened in proportion as the temperatures used are lowered, but, in this case, the measurements also become more difficult and more dependent on the moisture in the atmosphere.

By means of drying tests, where the atmospheric moisture is kept constant in each separate experiment but successively varied from experiment to experiment, one obtains vapour-pressure—water-content curves that enable more detailed conclusions as to the structure without its being necessary to employ temperature changes. Such experiments have been performed by JESSER (33), GESSNER (24), GIERTZ-HEDSTRÖM (25) and BERCHEM (3). FIG. 6 shows curves obtained in connection with drying experiments over a period of a year on originally 1 month old cement prisms in closed containers.

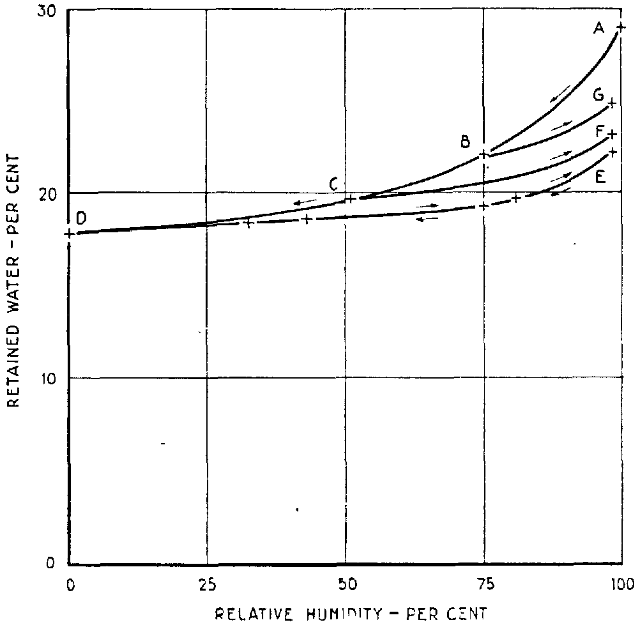

FIG. 6. Vapour-Pressure—Water-Content Curves for a Hydrated Portland Cement. (JESSER.)

The curves obtained are strikingly analogous with corresponding curves obtained for silica gel. In order to obtain final equilibriums, however, very long experimental times are required, which is unsuitable for a material like cement. FIG. 7 shows curves for some different binding agents obtained on brief exposures of crushed samples to the influence of circulating air.

In FIG. 7 the circles indicate the water content of the material at the beginning of the experiment. The difference between the crystalline hardened gypsum and the gel-containing cement is striking. The interpretation of the breaks for the cement at about 40 % relative moisture is uncertain. It seems, however, reasonable to suppose that they represent a favoured capillary dimension in the material.

TABLE I gives an idea of the connection between the results obtained by means of heating and by means of drying (short-time experiments with crushed samples). Data from the heating tests at low temperature are of course uncertain.

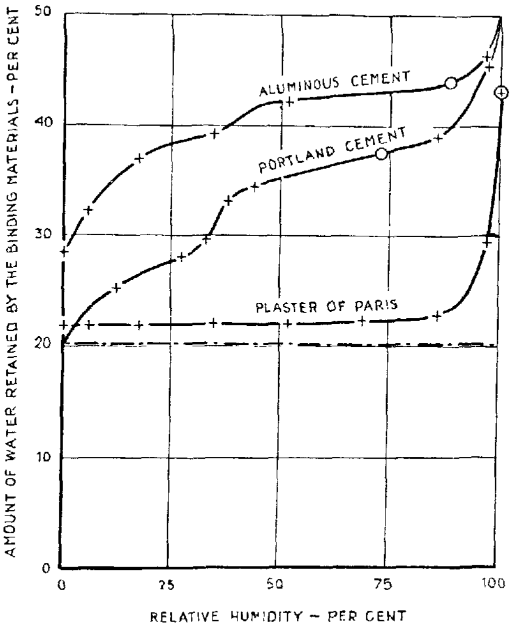

FIG. 7. Vapour-Pressure—Water-Content Curves for Hydrated Cements. (GIERTZ-HEDSTRÖM.)

Attempts have been made to determine the water-fixation also in other ways. WORK and LASSETER (73) have carried out extraction with absolute alcohol, distillation with benzol, toluol, and xylol in comparison with heating tests. BÜLL (13) has carried out extractions with dioxan in connection with a detailed discussion of the manner of fixation of the water in inorganic substances. Freezing tests have been performed by GIERTZ-HEDSTRÖM (25) and v. GRONOW (27). In all these tests the treatment is comparable with a reduction of vapour-pressure, that is, to say, a form of drying out, but with the addition of a different complication for each method. A good critical discussion of the various water-fixation measurements has been given by LEA (41).

Table 1. Water retained by Hydrated Cements on Drying and on Heating. Age of the specimens 10 days.

(GIERTZ-HEDSTRÖM. Unpublished data.)

Drying Relative Humidity %	Heating Temperature	Portland Cement Retained Water %[1]	Aluminous Cement Retained Water %[1]
—	110	11.6	17.4
—	90	11.9	18.2
—	70	13.9	23.4
0	—	15.6	26.4
—	50	14.9	29.6
—	30	16.5	32.8
10	—	20.1	34.2
30	—	22.0	36.5
85	—	34.1	43.8
99	—	42.9	49.3

[1] Calculated on anhydrous materials.

A more detailed discussion of the importance of the water-fixation measurements in determining the hydration of hardened cement is given below.

In connection with what has been said above some tests regarding the hydration capacity of cement with different relative moistures should be mentioned. JESSER (33) reports that Portland cement and aluminous cement stop hydrating when the relative moisture falls below 80—90 %. RODT (56) has found a slight and limited hydration, less than 1 %, with a relative moisture under 50 %, and up to 2 % hydration with 60 % moisture, but thereafter a successively increased and continued hydration with moisture contents of 60, 70, 80, and 90 %.

Theories Concerning the Physical Structure of Cement.

Two main theories to explain the physical structure of cement or its capacity to harden have been advanced, namely, the theory of an interweaving of crystals propounded by LE CHATELIER (44) and the theory of a thickening of colloidal gels by "innere Absaugung" by MICHAËLIS (49). LE CHATELIER also on a later occasion made a contribution in defence of his theory (45); and MICHAËLIS's theory has been defended by KÜHL (39) and others.

Each of the theories is in so far justified as both crystals and colloidal substances play a part in the hardening of cement and one can point to hardened products whose strength is dependent solely on crystals and others whose strength is conditioned solely by colloids. It is, however, as yet probably impossible to say which of them gives the best picture of the real structure, and both are in any case to be regarded as rather crudely schematic.

It has been shown in the foregoing that the most important constituent part of hardened cement may be assumed to be an apparently amorphous, porous and gel-like mass, with the ideal stoichiometric composition $2CaO \cdot SiO_2 \cdot 4H_2O$. The crystal theory can thus not be maintained unless one admits that the crystals may be of colloidal order of magnitude. This LE CHATELIER has done, but then it must also be admitted that colloidal effects, such as gel formation, etc., may arise. It seems, however, at least to the author, difficult to imagine that "innere Absaugung" of the "cement gel", according to MICHAËLIS, should cause the cement to harden. If no additional water is supplied to the system cement-water it is of course to be expected that the contraction accompanying the hydration will cause a compression of the system as a result of capillary effects in the surfaces limiting the system. This compression must, however, be comparatively slight, as in hardened cement prepared with normal water content and not specially dried out we have, even after a long period, water with a vapour-pressure only slightly differing from the vapour-pressure of free water. It might be thought that suction takes place in the interior of the mass, but this assumption meets the objection that, as we know, the cement gel is at least for the most part very porous and takes up and gives off water both easily and quickly. Nor is it probable that the effect mentioned is due to a suction of the gel layer nearest the cement grain. Certainly it may probably be assumed that there is an interior comsumption of water at the surfaces of the grains, but this is then accompanied, in point of volume, by a still more considerable formation of new solid phase that results in a thickening of the gel layers the nearer to the surface of the grains they lie. The channels that may be imagined in the gels are thus narrowest close to the cement grains and extend outward. A suction that should compress the gel layer is then difficult to imagine. Nor does the circumstance that the hydration of the cement grains is brought, after a time, to a stand-still need to be explained by a thickening of the nearest gels by suction. The blocking of the surfaces of the grains caused by the formation of new solid phase is quite sufficient as an explanation. It would probably be more justified to speak of an inner compression than of an inner suction.

The question as to whether the apparently amorphous hydration products are to be designated as gels or not depends upon the definition given to this concept. FREUNDLICH (22) defines gels as "kolloiddisperse Gebilde, die aus einer festen und einer flüssigen Phase oder vielleicht aus zwei zähflüssigen Phasen bestehen, und die, obwohl sie sehr flüssigkeitsreich sein können, Form und Zusammenhalt, also elastische Eigenschaften haben". If this definition is accepted, the designation "gel" for the hydration products in question is undoubtedly correct. It is, however, obvious that this definition fits many different structures and that there may be good reason to classify these in various sub-types.

Although it has not yet been possible definitely to establish a crystalline structure in the constituent parts of the cement gel, such a structure is by no means out of the question. SVEDBERG (59) mentions that by means of X-ray analysis it has been established that many gels are built up with crystalline material, although it is often necessary for them to age or be heated up before interference lines occur. Purely amorphous solid substances are, moreover, to be regarded as a rarity. Pending further investigation it is reasonable to assume, as a working hypothesis, that the elementary constituents of the cement gel are crystalline. This is, too, in conformity with the view that the structural material of the gel has a definite stoichiometric composition (21).

In this case one arrives at a combination of the theories of LE CHATELIER and MICHAËLIS in that the crystals are at the same time also colloids and *vice versa.* On the other hand, however, it is more difficult to accept the notion of an interweaving of crystals or of an inner suction as an adequate explanation of the hardening.

A number of other more or less different theories have been advanced as to the nature of the hardening. Reference may be made to the theory of the calcium hydroxide as the source of the strength of cement, supported by TIPPMANN (62) and others, to theories based upon analogies with zeolites by LAFUMA (40) and others, to capillary-force theories, such as that by WÜRZNER (74), to FREYSSINET's germ-theory (23) and to the theory of the hardening as an electro-static surface phenomenon, by JESSER (34). The author does not here propose to go through all the pros and contras of the various theories, which in a number of cases are very clear, but will endeavour, in the light of available data, to explain what the theories may actually be based upon.

It is, to begin with, definitely established that the cement gel alone can impart considerable strength to the hardened cement. See, amongst others, BROWN and CARLSON (12). As will emerge later, the calcium hydroxide may probably be assumed to contribute in a certain degree to the strength of cement (6), and if so, then probably also other new crystalline formations.

The water-fixation measurements, especially the water-content—vapour-pressure curves, enable a number of conclusions regarding the structure of hardened cement. It has thus been ascertained that the water in the hardened cement is found fixed in all degrees from hard-bound water with a vapour-pressure practically equal to zero to free water in equilibrium with air of 100 % humidity. In this interval a certain vapour-pressure does not necessarily correspond to a certain type of water-fixation, but, for example, chemically bound, surface-adsorbed and capillary-bound water may conceivably be characterized by the same vapour-pressure. In connection with quick drying tests by GIERTZ-HEDSTRÖM (25), FIG. 7, it seems, however, probable that the water-fixation curves will give a rough picture of the types of water-fixation. In the diagram the water content with vapour-pressure = 0 probably corresponds in essentials to chemically bound water. The part of the curve beginning thereafter at vapour-pressure = 0, which bends off in the direction of the abscissa, is probably to be regarded as representing the surface adsorption of water, the break in the curve the capillary-bound water in the typical capillaries of the material, and the remaining part of the curve the water enclosed in the coarser pores. It is, in this case, scarcely probable that a distinct dividing line between chemically bound and surface-adsorbed water would be drawn, so that it seems reasonable to take these groups together and assume that their quantity is approximately represented by the value of the curve at the beginning of the break, that is, to say, at a relative humidity of about 30 %. It is probably also justifiable to draw a line in the neighbourhood of 100 % relative humidity, for example 95 %, when the water on the curve to the right of this line could be called free water. The classification thus obtained would for the case reproduced in FIG. 7 for Portland cement be as follows. Chemically bound and surface-adsorbed water 0—30 % relative humidity. Water in the capillaries typical of the material 30—40 % relative humidity. Water in coarser capillaries 40—95 % relative humidity. Free water 95—100 % relative humidity. Such a division is of course to a large extent arbitrary and perhaps not fully adequate, but it is of value for a survey of the water-fixation proportions and their practical significance.

By means of known formulae it is possible to calculate the capillary dimension corresponding to a certain vapour-pressure, provided that the absorbed fluid layer on the capillary walls may be neglected. FIG. 8 shows how the capillary radius (in microns × 10^3) calculated in this way varies with the relative humidity. The capillary pressure corresponding to these capillary dimensions is also included in the diagram (25).

According to such a calculation the capillary radius typical of Portland cement and aluminous cement given in FIG. 7 would be rather more than a thousandth part of a micron.[1] It is, however, certain that the assumption upon which the calculation is based is not correct when we come down to these capillary dimensions—see for instance WILSDON, BONNELL and NOTTAGE (68), so that the capillary dimensions corresponding to these vapour-pressures must be taken as bigger. The import of the dimension given is illustrated by the fact that one molecule of water is of the order of magnitude one quarter of a thousandth part of a micron.

With the aid of determinations of the water-fixation and contraction the increase in volume in the solid phase produced by the hydration can be cal-

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[1] For laminar capillaries a laminar distance of a thosuandth part of a micron.

culated. BERCHEM (3) gives the following data for a Portland cement that had been hydrated for 2 months.

Contraction on hydration of 100 g cement with 37.30 g water—6.4 cm³.
Spec. grav. of non-hydrated cement—3.08, *i. e.* volume of 100 g cement—32.5 cm³.

Relative Humidity, %,	By 100 g Cement Retained Water, g,
0 (0.05 mm Hg)	22.4
31 (5.4 » »)	30.6
46 (8.0 » »)	35.1

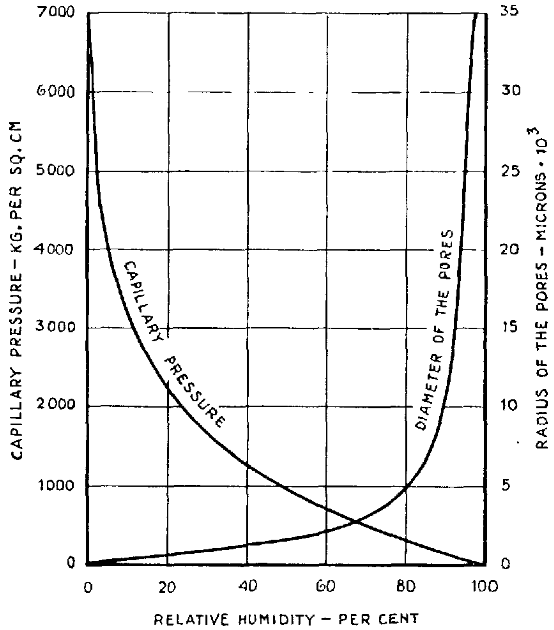

FIG. 8. Capillary Dimension and Capillary Pressure calculated to correspond with Various Relative Humidities.

Assuming that the volume contraction refers to the hardest bound water (of the system cement + water) and with reference to the above suggested classification of water-types on the basis of vapour-pressure, one gets, with the figures given:

Volume of unhydrated cement	32.5 cm³	=	100 %
» » cement + chemically bound water	48.5 »	»	150 %
» » do. + surface-adsorbed water	56.7 »	»	175 %
» » do. do. + water in smaller capillaries	61.2 »	»	190 %

These values are conditioned by the assumptions made, which are both approximations and open to criticism. Such a calculation gives, however, a useful picture of the volume relations.

The chemically bound water and the free water belong to the solid phase resp. the fluid phase, and may therefore be regarded as functioning in accordance herewith. The manner in which the intermediate types of water function is, however, less clear. They borrow, of course, features from both the solid and the fluid phases. One can, following the example of DE WAELE and LEWIS (64) and others, employ the term "pseudosolid" fluid layer in connection with the surface-adsorbed water. The changed properties of this surface layer in relation to free water are manifested in depolymerization, changed dielectricity constant, capacity to function as a lubricating agent on the solid surface etc. These conditions have been studied by a large number of research-workers. Reference may be made to works by BRIGGS (10), JONES and GORTNER (35), and HÜTTIG (31), as also to numerous publications, especially in Kolloid-Zeitschrift, the Journal of Physical Chemistry, the Journal of the American Chemical Society and the Canadian Journal of Research.

By ascertaining the properties of water bound in various ways and by establishing the water-fixation in hydrated cement in greater detail it will be possible to throw considerable light on the structure of hardened cement and its significance for the practical use of cement. It is, for example, already possible to discern certain approximate relations between the structure and the technical properties, which will be touched upon later.

The cause of the hardening of cement may already be partly explained as the increase in volume of the solid phase and the diminished porosity resulting from this. Doubtless the capacity of the new-formed gel to adhere to other solid objects and its capacity for coherence in itself also play a very important part. It seems reasonable to assume that the separate gel particles have an adherent capacity even when they are still surrounded by a film of water, and also that this later disappears and is replaced by a direct contact between the particles, and also between these and the other solid phases present.

The hydraulic hardening of cement, that is, to say, its capacity to harden under water and to be in water indefinitely, is dependent on the chemical conditions, 1. that the hardening reactions are hydrations and can thus take place under water, and, 2. that the hydration products are little soluble and can thus remain undissolved in water. Further, the following physical conditions are essential to the hardening, 3. that the hydration shall take place at such a moderate rate that the new-formed solid phase does not cause expansion at the commencement of the reactions, and, 4. that the hydration shall cease when the structure has become so dense that further increase in the volume of the solid phase cannot be allowed.

Factors influencing the Physical Structure.

The physical structure of hardened cement is dependent on a very large number of factors. It is not possible in this connection to touch upon all of them, nor to treat them in any detail. The following enumeration may, however, serve to illustrate the complexity of this dependence and to indicate some of the more important relations.

Cement and Special Additions.

The chemical composition and physical structure of unhydrated cement are of course the dominating factors. In this connection one must take into account the type of cement (Portland cement, aluminous cement, slag cement etc.), variations in the type (*e. g.* the content of trisilicate, disilicate etc. in Portland cement), the physical distribution of the cement components in the clinker (size of crystals, homogeneity etc.), the degree of grinding (distribution of grain-sizes, shape of grain), the distribution of the cement components in different grain-sizes, hydration and other chemical reactions on the surface of the cement particles during the storing of the dry cement etc.

Additions to the cement may be of great importance for the physical structure. As well as the additions that enter into the constitution of the cement, such as gypsum, pozzolanas etc., such additions as calcium chloride, additions altering the surface tension (*e. g.* Tricosal and TDA), admixture of foreign binding agents etc. also exert an influence. In this connection account should also be taken of the effect of sand and stone and impurities entering in the manufacture of concrete.

Water Content.

The water content used in the preparation of cement influences the spacing in structure *A* and thus also in structure *B*. The degree of hydration depends on the water content and, as a rule, rises simultaneously with this. This is also of importance for the course of the chemical reactions in that it thins out the system and also exerts an indirect influence on the development of the structure, for example by modifying the rise of temperature. All the technical properties are in a high degree dependent on the water: cement figure.

Age.

The physical structure is very largely dependent on the time factor. A statement of age, reckoned from the addition of water to the dry cement is thus of fundamental importance in characterizing the structure. The hydration as the main factor proceeds with time, whereby structure *B* is successively built up. During this process the chemical reactions may also change in character in that regulating additions are used up, which, again, may react upon the old structure.

Simultaneously with these processes, although very slowly, an ageing of the already formed parts of structure *B* is going forward. Little is known of this process, but there is every reason to believe, and observations support this belief, that it takes place. The cement gel is in its colloidal form not a final stable product, but must, by gel coarsening and crystalline growth, go the same way as other inorganic colloids in nature.

Temperature.

The temperature obtaining during the process of hydration effects the chemical reactions both as to kind and rate, as also the development of the structure in other respects. Mention may here be made of the generally favourable influence of high temperature on short-time strength and of low temperature on long-time strength. The ageing of the structure is affected by higher temperatures and is accelerated thereby, probably in a considerable degree. An extremely powerful change in the normal storing conditions is constituted by steam-curing, to which what has just been said applies in an especially high degree. High temperatures accompanied by loss of water content have a breaking down effect on the structure. At very low temperatures structural change may take place as a result of freezing.

Moisture.

During the hydration a consumption of water occurs which, if not adequately compensated by addition from without, involves a diminishing of the availability of the water in the system. To illustrate how this may be of importance it may be mentioned that the water-tightness of concrete pipes, for example, is considerably better if they are stored in water than if they are stored in moisture-saturated air.

If water is taken away fram the system by drying, the availability of the remaining water is still more diminished and may finally lead to the stopping of the hydration altogether. The same effect may be obtained by freezing, instead of drying, a certain amount of the water. In both cases the vapour-pressure sinks in the remaining water.

In the course of drying, capillary forces arise which compress the cement gel, which undergoes structural changes of both reversible and irreversible nature. On very strong drying the chemically bound water is also driven off.

On moistening and thawing, a number of the processes mentioned take place reversibly and the continued hydration is facilitated. Drying and moistening repeated at intervals (as also freezing and thawing) may conceivably have a considerable influence on the structure.

External Chemical Factors.

Among the external chemical factors may be mentioned carbonation, dissolution and influences of saline solutions, which are all able to change the normal structure in a high degree. It would, however, take us too far to go into these questions in detail, for although of great importance they do not, strictly speaking, belong to the consideration of the normal physical structure.

External Mechanical Factors.

It may be mentioned in passing that external mechanical factors such as loading and frequently repeated series of this, especially if they are allowed to act for a long period, may influence the physical structure in a way that may have importance from the practical point of view.

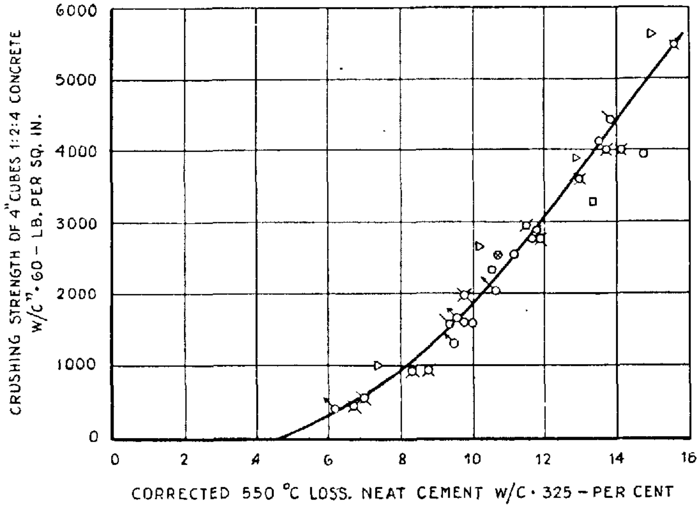

Fig. 9. Relation between Crushing Strength and Rate of Hydration. (Lea and Jones.)

Relations between the Physical Structure of Cement and its Technical Qualities.

Strength.

The dependence of the strength on the physical structure, especially the degree of hydration, has interested many research-workers. Reference may be made to works by Werner and Giertz-Hedström (65, 66), Work and Lasseter (73), Woods, Starke and Steinour (71), Eiger (20), Bogue and Lerch (6, 46), and Lea and Jones (43).

Fig. 9 shows the relation between strength and degree of hydration for 10 different cements according to Lea and Jones. The composition of these cements varies considerably. An individual course for the different cements can be distinguished, but the test-values are all closely grouped around the mean-value curve. Werner and Giertz-Hedström, Work and Lasseter, and Eiger have in different ways likewise found that even very different cements give on the whole the same strength on the same increase in volume of the solid phase and the same degree of hydration.

Although it is thus possible as a first approximation to regard the strength as a function of the degree of hydration and independent of the kind of cement, this can obviously not be the whole truth, as emerges for instance from the spreading of the test-values. On the study of the clinker components of Portland cement Bogue and Lerch (6) found considerable differences as regards the relation between water-fixation and strength. Fig. 10 shows water-fixation and strength in tricalcium silicate and dicalcium silicate. The curves *1* refer to fixed water (at 105°) of calcium hydroxide and silicate gel together and the curves *2* to the fixed water of the silicate gel alone.

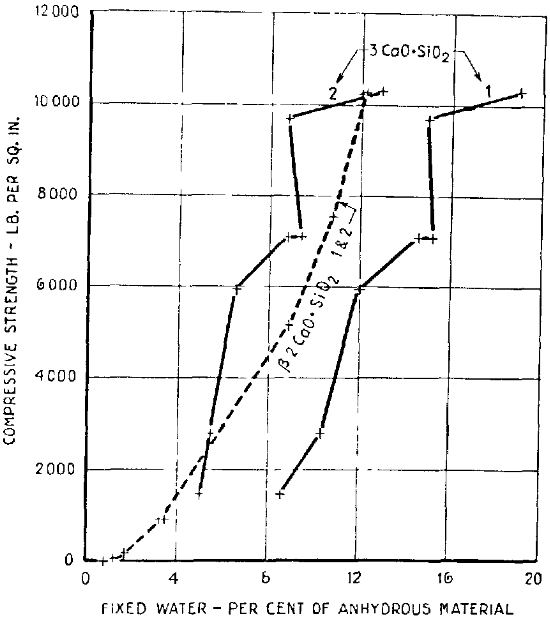

Fig. 10. Relation between Compressive Strength and Fixed Water of Tricalcium Silicate and Dicalcium Silicate. Curves marked *1* indicate fixed water given as loss of water on heating to 1 000° C. Curves marked *2* indicate fixed water less water combined in $Ca(OH)_2$. (According to data by Bogue and Lerch.)

These test-values indicate that the silicate gel, which is the sole cause of the hardening in dicalcium silicate, is also chiefly responsible for the hardening in tricalcium silicate, but is to a certain extent helped here by calcium hydroxide.

Available data indicate, as regards the relation between the degree of hydration and compressive strength, other factors being kept constant, that a certain degree of hydration must first take place before any strength can be counted upon, and that thereafter approximately linear proportionality obtains between the continued hydration and the strength. (LEA and JONES's FIG. 9, and EIGER's FIG. 10, 1937.) If the original compactness and the increase herein caused by the hydration are calculated, one finds, analogously, that the compactness must attain a certain value before any strength can be counted upon, but, hereafter, the strength increases approximately with the square of the increase of the compactness (WERNER and GIERTZ-HEDSTRÖM's FIGS. 8 and 9, Zement 1931, and EIGER's FIG. 14, 1937). The existing data are as yet too incomplete to allow of a more precise indication of the actual relation. It seems, however, reasonable to expect that, when more material is available, it will be possible to establish general relations that with fair precision will allow of the calculation of the strength in any concrete on the basis of the hydration data of the cement.

Elastic and Plastic Deformation.

There is as yet little in the way of data that would allow of any conclusions as to the relation between the physical structure and the elastic and plastic deformation. It is, however, obvious that there must be such a relation. FREYSSINET (23) has advanced theories on the subject into which it is not proposed to enter here, as available subject-matter is rather limited.

The modulus of elasticity depending upon the hydration, analogously with the strength, has been dealt with by WERNER and GIERTZ-HEDSTRÖM (66).

Shrinkage and Swelling.

It has long been clear that the shrinkage of hardened cement on drying and its swelling on subsequent moistening are determined by the properties of the cement gel. WOODS, STARKE and STEINOUR (72) have referred to the shrinkage in certain test-conditions as a function of the calculated mineral composition of Portland cement. WERNER and GIERTZ-HEDSTRÖM (66) have tried to find a general relation for different cements between the volume percentage of loosely bound water (chiefly capillary-bound water) and the shrinkage. During that part of the drying period in which free water is being given off, no appreciable shrinkage, under suitable test-conditions, takes place. BERCHEM (3) also refers to the shrinkage as chiefly determined by the quantity of loosely bound water. FIG. 11 shows the course of shrinkage in Portland cement, aluminous cement, and tricalcium silicate. From FIG. 11 it may be seen that, as regards Portland cement, the shrinkage does not commence until a large part of free water has been removed.

LUCAS (47) states that the variation in length on shrinkage is proportional to the relative humidity except in very dry air. DUTRON (19) has given a series of data for non-reinforced and reinforced concrete and attempted to set these in relation with the volume increase on hydration and the capillary forces thus arising. Reference may also be made to investigations and theories by POGÁNY (53), v. TERZAGHI (61), and FREYSSINET (23).

According to JESSER (33), the shrinkage and loss of water on drying is only partially reversible and very analogous with the conditions in silica gel. BRADY (8), however, has found a considerable reversibility simultaneously with a certain hysteresis effect in the shrinkage of cement-mortar in connection with variations in relative humidity from 0—100 %. In both cases, however, the test-periods were extremely long, one year and more, so that the result may be assumed to have been blurred by, amongst other things, the continued hydration.

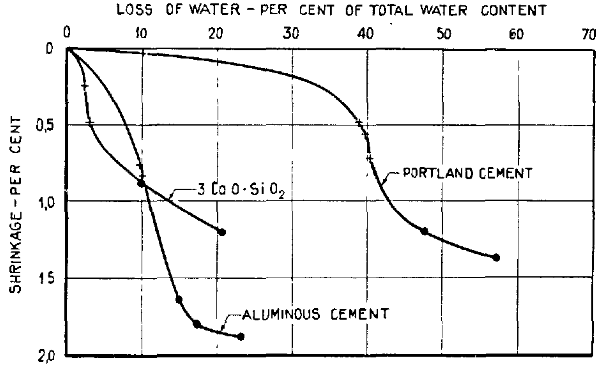

FIG. 11. Shrinkage and Loss of Water of Portland Cement, Aluminous Cement and Tricalcium Silicate. (BERCHEM.)

As regards the nature of the shrinkage, it may be mentioned that WHITE (67) has performed an experiment with treatment of a dried sample of hardened cement with benzol and water. The benzol-soaked sample showed no swelling; on subsequent soaking in water, however, this sets in. The sample absorbed, though, considerably less benzol than water. WHITE gives data that clearly show how the capacity of hardened cement to shrink and swell is retained even after periods of more than 20 years. The range of the variations in length increased in this connection, which is explained by continued hydration of the cement.

Permeability.

The permeability is determined, besides by coarser pores and hollow spaces, originating largely in connection with the preparation of concrete, also by the capillaries of the hardened cement. As these are an integral part of the structure of cement, it follows that hardened cement, and therefore also concrete, even if in the mechanical sense they are impermeable, always retain, under normal conditions, a certain capillary permeability. This is due to the structure of the hardened cement and is an expression of its porosity. WERNER and GIERTZ-HEDSTRÖM (66) have tried to find a relation between the capillary porosity and the volume percentage of free water + loosely bound water. This question has, however, been little investigated. Reference may also be made to an account by POGÁNY (52).

Chemical Resistance.

The chemical resistance is, as regards concrete, to a considerable extent dependent on its structure, especially its impermeability. Even as regards hardened cement the physical structure must be taken as an essential factor for the resistance. Of importance in this connection are the permeability, the structure of the gels (especially the silica gel) that remain after chemical attack and which may constitute a protective layer, and the structural changes caused in the surface layer by carbonation in the air. A more detailed treatment of these questions cannot, however, be given here.

Besides the references to the literature given in the foregoing, reference may also be made to publications by BOGUE (5), HOUWINK (30), LEA and DESCH (42), and LYNAM (48), where surveys are given of earlier views of the course of the hydration, the structure of various solid bodies, the general chemistry of cement and concrete, as well as volume changes and deformation of concrete, respectively.

Summary.

The study of the physical structure is an important supplement to the purely chemical investigations and constitutes the basis for an understanding of the function of cement and its application in concrete.

In the system cement + water, the cement particles form a first structure *A*, within the frame of which the hydration reactions take place and the new structure, *B*, is built up simultaneously with the breaking down and consumption of *A*. The rate of hydration and the volume changes accompanying it are in this connection of fundamental importance.

The physical structure of hardened cement can be studied in macroscopic observations, and by means of microscopic examinations, X-ray analysis and measurement of the water-fixation. The microscopic examinations give a good picture of the general development of the structure, but do not reveal

the structure of the cement gel, the most important product of hydration. It is to be expected that X-ray analysis will in this connection be of great service later. The water-fixation measurements constitute a very good indirect means of establishing the average structure.

The crystalloid and colloid interpretations of the structure of cement each give a valuable but crude picture of the hardening process. As it is quite conceivable that the constituent parts of the cement gel are extremely small crystals the two theories are not necessarily irreconcilable. Inner suction as a cause of the hardening seems not very plausible. The hardening may be considered as caused by the increase of the solid phase, chiefly by the development of the cement gel, and by the capacity of this gel for coherence in itself and adherence to other solid phases. A more detailed picture cannot as yet be given of the causes of these properties in the cement gel, but it seems reasonable to suppose that the separate gel particles have a capacity for adherence even when they are surrounded by a film of water, and that this afterwards disappears and is replaced by direct contact between the solid phases. Added strength may be obtained on drying hardened cement by the capillary forces thus arising.

The physical structure is determined by numerous factors, chiefly the kind of cement, but also in a very high degree by attendant circumstances such as water content, age, drying etc. A complete discussion of these matters has not been attempted, as this would mean dealing with the whole chemistry of cement and manufacture of concrete.

There are very obvious relations between the physical structure of hardened cement and its technical properties. Approximate relations have been given regarding strength, shrinkage, and permeability. Available data are not sufficient to enable a precise statement of these relations, but it may be expected that it will ultimately be possible to calculate the technical properties of concrete with fair accuracy on the basis of the structural and hydration data of the cement.

It has not been possible to give a complete survey of all the questions. That which has been gone through in the foregoing, however, shows a rich and fruitful field of work. Research in this field is as yet in its infancy, but definite progress has been made in several respects. Thus, in the 20 years that have elapsed since the cement discussion in the Faraday Society, the water-fixation measurements have been introduced and X-ray methods have begun to be applied. There is, then, reason to hope that the study of the physical structure, which can now be based upon further progress in the chemistry of cement and concrete construction, may also be able to render valuable service to these scientific fields in return.

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74. WÜRZNER, K. — Zement, 1932, 243; 1934, 572.

Discussion.

Mr. P. SCHLÄPFER:[1]

In his valuable survey Mr. GIERTZ-HEDSTRÖM also mentions the shrinkage measurements which I have carried out in our laboratory in collaboration with my assistant, Dr. BERCHEM. The figures quoted are fairly high. This is due to the fact that we used very small test samples, 10 × 10 × 30 mm in size. These measurements show quite definitely that shrinkage also depends on the ratio of volume to surface. If the surface is large, the shrinkage measurement will result in higher figures. Therefore, in all investigations concerning shrinkage the conditions under which the measurements are made, must always be specified.

Mr. F. M. LEA:[2]

In his very interesting paper Mr. GIERTZ-HEDSTRÖM refers briefly to the relation between the physical structure of set cements and the properties of shrinkage and creep, or plastic flow. The mechanism of these effects is at present a subject of controversy. Two main theories have been advanced to explain the change in volume of set cement with changes in water content. The one theory, put forward by FREYSSINET is based on considerations of capillary effects, while in the other theory the changes are regarded as due to volume changes in the bonding cement as it undergoes dehydration and rehydration. In FREYSSINET's theory (2) it is considered that such volume changes can be directly connected with changes in the negative pressure under which water is held in a capillary system. Briefly FREYSSINET suggests that, on exposure of a mortar or concrete to an atmosphere of a given relative humidity, the amount of water held in the capillaries becomes so adjusted as to fill them to a point where the curvature of the water meniscus is that required to give a reduced vapour-pressure equal to that of the surrounding air. When the relative humidity of the environment is changed, the amount of water in the capillaries alters, and with it the curvature of the water meniscus, so as to maintain an equilibrium between the vapour-pressure of the water and that of the surrounding air. From the application of THOMSON's equation, the radius of curvature of the meniscus for a given reduced vapour-pressure is calculated, and then, assuming that the surface tension of the capillary water may be taken as that of water in bulk, the negative pressure of the capillary water is calculated. This negative pressure may be regarded as equivalent to

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[1] Professor, Dr., Eidgenössische technische Hochschule in Zürich, Zürich, Switzerland.

[2] D. Sc., F. I. C., Building Research Station, Garston, Herts, England.

an induced compressive stress on the concrete, and variations in it to variations in the induced compressive stress producing corresponding changes in elastic deformation. FREYSSINET considers therefore that, on exposing a concrete to an atmosphere of lower relative humidity than that with which it is in equilibrium, water is lost from the capillaries, the negative pressure of the remaining water rises, the induced compressive stress increases and the concrete suffers a decrease in volume, *i. e.* it undergoes drying shrinkage.

Attractive as it may appear at first sight, FREYSSINET's theory is open to many serious objections and the classical picture of capillary condensation on which he relies, must, in the light of modern knowledge, be regarded as of doubtful validity. Even if we disregard such uncertain points as the applicability of THOMSON's equation to small capillaries in which the vapour-pressure of water is appreciably reduced, and the assumption that, when the negative pressure of the contained water increases, the effect of this increase on the induced compressive stress may not be more than offset by a reduction in the percentage area in any cross section which is filled by water, there still remain other more serious objections. In FREYSSINET's theory the surface tension changes of the solid, and the effect of sorption of water on the solid-air interfacial tension, are entirely neglected, though in magnitude these effects are probably greater than those arising from the capillary condensation theory.

Thus, in the case of charcoal BANGHAM (1) has shown that the expansion of this material on sorption of vapours is directly proportional to the surface energy lowering up to the point where liquid film formation occurs, and that above this point there is little further expansion even though the bulk of the sorption takes place beyond this point.

To what extent volume changes in concrete can be attributed to changes in the solid-air interfacial tension, as found in the case of charcoal, must be regarded as at present an open question, but it seems clear that the FREYSSINET-theory cannot in its present form be maintained.

FREYSSINET's theory of creep, or plastic flow is an elaboration of his shrinkage theory. It is considered that, when a concrete in equilibrium with its surrounding atmosphere is subjected to a compressive stress, it first undergoes a compressive strain which produces a deformation of the capillaries accompanied by a displacement of water outwards. The new position of the water meniscus is assumed to correspond to a capillary diameter larger than the initial value, and the negative pressure of the contained water is therefore decreased. The effect of this is to reduce the induced compressive stress, thus partially offsetting the effect of the applied external stress. The deformation of the concrete is then less than that which would have been found had capillary effects been absent. Since, however, the water meniscus is now of lesser curvature than the original value, there is no longer an equilibrium between the concrete and the surrounding atmosphere. In FREYSSINET's words, the applied compressive stress has had the effect of raising the "humidity condition" of the concrete. If the surrounding atmosphere is maintained at its original humidity, water slowly evaporates from the concrete until the water meniscus has returned to a point where its reduced vapour-pressure is again equal to that of the surrounding atmosphere. The negative pressure of the capillary water rises, the induced compressive stress increases and the concrete undergoes further deformation, and this, in FREYSSINET's theory, is the mechanism of creep.

This theory, it is clear, is open to any of the objections that can be brought against the shrinkage theory from which it is developed. Further, in a concrete immersed in water and fully saturated, no change in negative pressure of the capillary water is possible, for it is already zero, and under such conditions creep should not occur. This is contrary to the experimental evidence.

No data are available by which the alternative hypothesis, in which shrinkage and moisture movement are attributed to dehydration and rehydration effects, can be judged. That dehydration and rehydration of the set cement do occur is clear and it seems likely that these must be accompanied by volume change. As an analogy there need only be mentioned the marked changes in lattice spacings found with some of the clay minerals when their water content is altered. Possibly any final explanation may involve the effects both of changes in interfacial tension and of combined water content. It should also be noted that the drying shrinkage of mortars or concretes can be divided into two parts, the one the initial shrinkage which is irreversible and occurs on the first drying, and the other the roughly reversible movement which takes place on subsequent wetting and drying. The irreversible movement is probably best attributed to the formation of the set cement compounds initially in an expanded unstable condition and their tendency to decrease in volume as they approach the stable state. As a rough analogy the well known behaviour of silica gel can be cited.

Bibliography.

1. BANGHAM, D. H. — Trans. Faraday Soc., 1937, *23*, 805 and earlier papers.
2. FREYSSINET, E. — Une révolution dans les techniques du Beton. Paris, 1936. Librairie de l'enseignement technique.

Mr. A. EIGER:[1]

If you permit me, Mr. Chairman and Gentlemen, I will make a short statement which might be a suggestion for applying a rather simple but, I think, very

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[1] Inz. Dr. n. t., Mazowiecka 7, Warszawa, Poland.

promising method for what I might call "getting into the hydrated cement". Some years ago I was interested in determination of the hydration rate and to check it by examination of the strength of very finely reground pastes.[1]

You know the work of the Japanese investigators centrifugating cement clinkers. I tried to apply this method to hydrated cement gel, basing on the following assumptions.

If it was possible in the mentioned research to separate the minerals in clinker so as to get fractions of such content of each, that they could be identified by X-rays, the same could only be easier done in hydrated cements, due to the differences in specific gravity of the hydrates *viz.:*

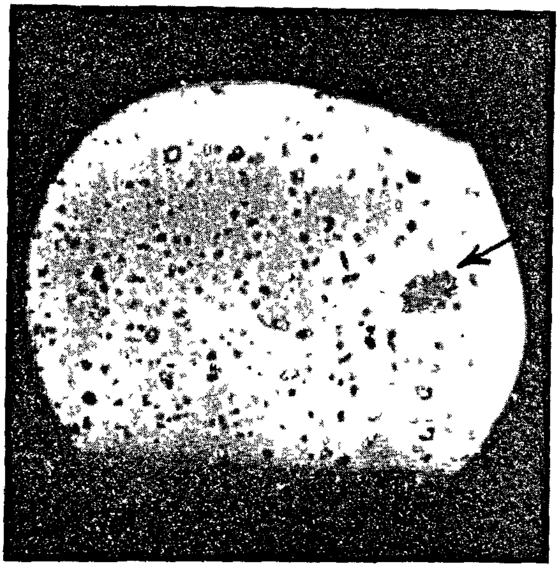

FIG. 1. Photomicrograph of Hydrated Cement ground in a Colloidal Mill.

(FIGS 1, 2, and 3 are made by Mr J. GOTLIEB in Prof. Dr. ZAWADSKI's Institute of Inorganic Technology in Warsaw.)

C_2SH_n	2.10—2.15
CH_2	2.24
C_3AH_6	2.52
C_3FH_6	2.80
unhydrated	3.15

This separation can only take place if the gel is ground as fine as possible, in order to separate the hydrates one from another, which is more difficult than in clinker, the most hydrates being gels in form of layers. The next

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[1] Erhartung und Festigkeit, Zement, 1932.

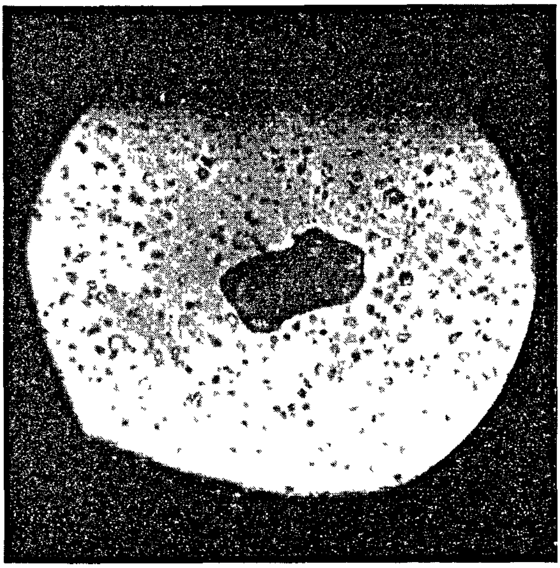

FIG. 2. Photomicrograph of an Unhydrated Alite Crystal obtained by Centrifugalization from Ground Hydrated Cement.

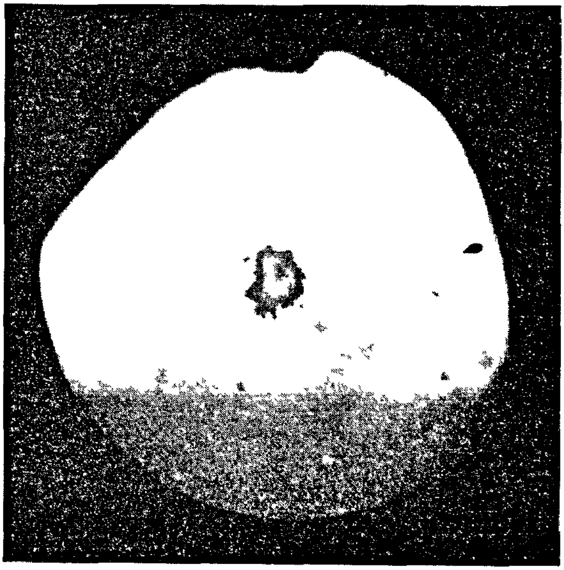

FIG. 3. Photomicrograph of an Alite Crystal attacked by Water and obtained by Centrifugalization from Ground Hydrated Cement.

problem was how to stop hydration at a certain moment and the question was, whether—when the surfaces increase to such an enormous extent—new reactions would take place.

The results of a series of preliminary tests, carried out with the kind help of Messrs. Z. SOBIERAJ and J. GOTLIEB, can be resumed as follows.

The samples were dried at 105° and ground in benzene in a Rossetti colloidal mill, giving a suspension of grains of an average dimension of 5—6 microns, though greater grains containing all the compounds were still present (FIG. 1).

The samples were centrifuged at 3 500 r.p.m. in mixes of $C_2H_2Br_4$, CH_2I_2 and C_6H_6 of the specific gravity which was necessary to separate the hydrates. The differences between the fractions so obtained and the original composition were of the same range as in the research stated. The suspension behaved really like a colloid, the great viscosity being responsible for so small a separation. Further tests will be run with a centrifuge of 15 000 r.p.m.

FIG. 2 shows an alite crystal (twin) unhydrated while in FIG. 3 we see an alite hexagonal crystal still keeping its form, but attacked by water on the whole surface, showing a dark gel layer all around.

I thought it interesting to state this method, because, if it will work satisfactorily, and there are no reasons why it should not, it can give a picture of what is really happening *in the paste* while cement is hydrated at any moment of the hydration.

I would think it worth while if this method be tried out at two or three laboratories at the same time, the exchange of experiences shortening the unavoidable time until the method will give the results it promises.

Mr. D. G. R. BONNELL:[1]

I cannot let this meeting pass without complimenting Mr. GIERTZ-HEDSTRÖM on his paper dealing with the difficult problem of the physical structure of set cement. Although this Symposium has dealt mostly with the phase-rule aspect, yet it must be realized that the physical properties of the set cement must be thoroughly investigated before a complete understanding of the properties of the final products can be reached.

In the investigation of this problem physico-chemical methods, which have been developed during the study of other problems, have been applied, and it is on this aspect that I should like to sound a note of warning.

In set cement and concrete one is dealing with a system which is undergoing change during ageing and therefore it becomes extremely difficult to reproduce the system and conditions. This is particularly so when dealing with the vapour-pressure—water-content relationship. In this case, care

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[1] Dr., Building Research Station, Garston, Herts, England.

must be taken to ensure that the sample investigated is a typical sample of the material and that the physical structure is not destroyed. This immediately introduces the difficulty of obtaining true equilibrium values since, generally, diffusion of water through the material is slow, while, on the other hand, in order to avoid complications due to ageing, rapid determinations are essential. It is, indeed, extremely doubtful, whether the present methods of determining vapour-pressure relationships give satisfactory values.

For this reason alone, the curves obtained for the vapour-pressure—water-content relation in set cements may be considered to be of doubtful value although there is the further point that the interpretation of such curves without considerable information regarding the pore-size distribution, is a matter of extreme difficulty.

Another method which has been fairly extensively used for determining the state of the water present in the set concrete is the determination of the freezing point of the water present. From the determination of the amount of water freezing at any particular temperature conclusions have been drawn as to whether the water is "free", held by surfaces forces, or is present as "combined" water. This, too, is far from being a satisfactory method since, even when it is assumed that the effect of the salts present may be calculated, it is well-nigh impossible to eliminate super-cooling. It is extremely difficult to differentiate between the effect of super-cooling and the lowering of the freezing point due to surfaces forces. Further, in the present state of our knowledge, it cannot be assumed that the melting temperature of the frozen water can be taken as its freezing temperature because the effects of surfaces forces on the solid ice probably differ considerably from those on the liquid previous to freezing.

These difficulties, of course, apply equally to the investigation of the effect of structure on the properties of other porous building materials and it seems that, if these problems are to be satisfactorily solved, new methods and technique will have to be devised and developed. In the meantime, however, owing to the high complexity of the system studied, great care must be exercised in interpreting the results obtained with the known methods.

Mr. S. GIERTZ-HEDSTRÖM (*author's closure*):

As Professor SCHLÄPFER pointed out, it is absolutely necessary, when reporting on shrinkage measurements, to exactly specify the conditions prevailing during the experiments, something which until lately was very seldom met with, however, at least in the literature on the experiments.

I am entirely in agreement with Dr. LEA that FREYSSINET's theories respecting changes in volume of concrete and their dependence on capillary effects may be criticized from several points of view. While so doing, however, we should compliment Mr. FREYSSINET on his temerity in tackling this complex problem. He has undoubtedly done a great service to research in this domain by directing the attention of both engineers and chemists to the question. Though capillary actions do not constitute the sole cause of volume changes as declared by FREYSSINET, yet they must be considered as playing an important part in the processes. Their signs need not thereby necessarily be those indicated by him. As Dr. LEA has stated, account must also be taken of the surface tension of the solid, volume changes resulting from dehydration and rehydration etc. There are indeed numerous factors which must be taken into consideration. We are only on the threshold of the study of this very complex problem, just as we are when it is a matter of the physical structure as a whole. The complexity of the problems, however, cannot daunt us, since they are of vital significance for the scientific application and utilization of the cement in concrete.

Dr. EIGER referred to an interesting work by Japanese investigators to distinguish the hydration products on the basis of their different specific weights. I should very much like to have further information on this method, which, as far as I have understood, is still under development. Dr. EIGER himself has made trials with a very interesting method of following the hydration process by measuring the changes in the mean specific weight of the hydrated cement, which method I have referred to in my paper. We must for the present try out all available means of getting an insight into and progressively obtaining a clearer comprehension of the physical structure of the hydrated cement. I am convinced that the two methods above mentioned will be of a great value in this respect.

Dr. BONNELL's warnings are very much to the point in this connection. The interpretation of the results obtained by means of physical investigations on the systems available here must be done with the greatest care. I will frankly admit that I made use of the existing results, especially of vapour-pressure measurements, rather much in my paper. Nevertheless, it was done with open eyes and with all due reservations, and the motive was to attempt to throw some light, though maybe at this stage somewhat distorted in nature, over the building-up of the structure. For our subsequent work it is surely of service to have working theories even though we may be aware of the risk that we shall have to discard them later. I, for my part, am entirely in accord with what Dr. BONNELL says here of the desirability of new methods and new investigation practice.

HOMAGE TO THE MEMORY OF THE LATE HENRY LE CHATELIER

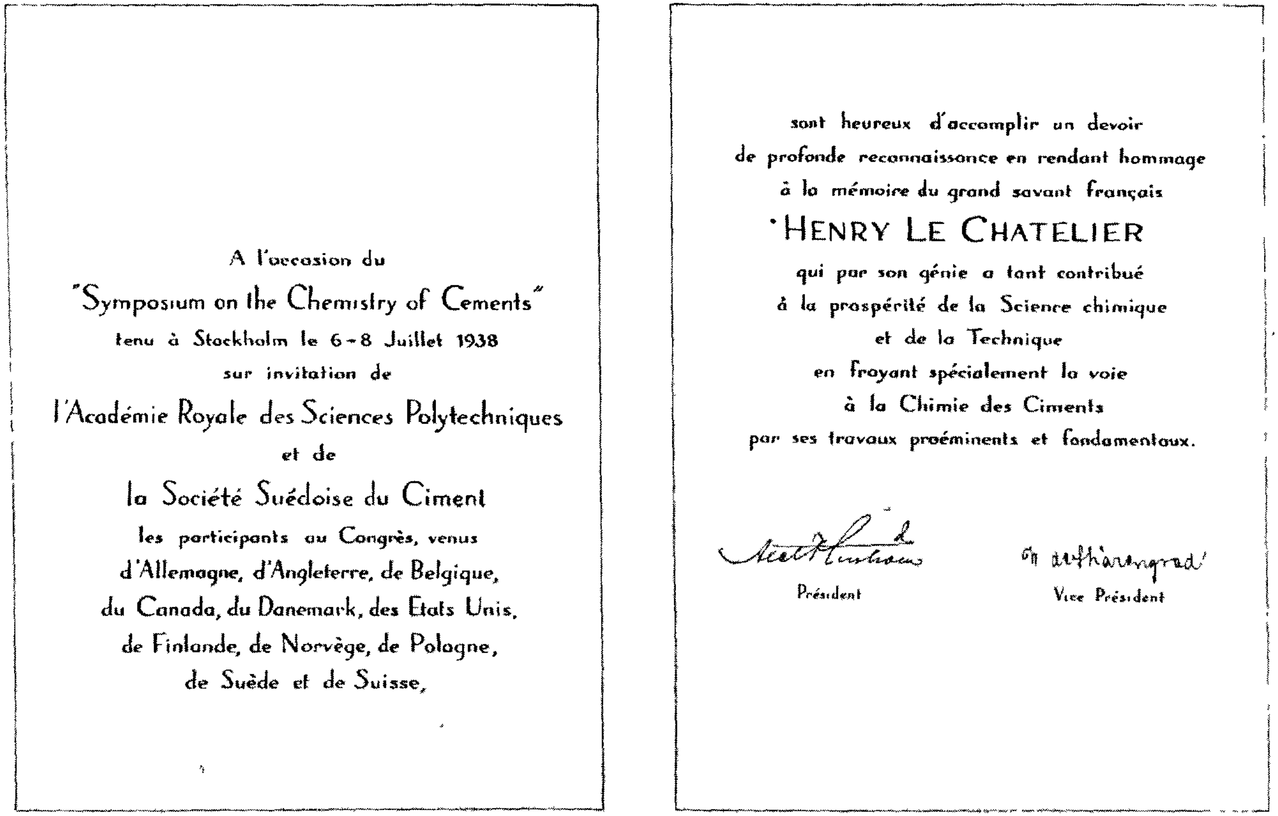
SPEECH BY

Dr. R. H. BOGUE.

Mr. Chairman, Gentlemen.

Cement chemists cannot gather and discuss the problems of cement chemistry without thinking of the man whom we have come lovingly to recognize as the father of cement chemistry, HENRY LE CHATELIER, formerly of the Sorbonne. Physical chemists generally think of him as one of the great savants of physical chemistry and know him best for his contributions to thermodynamics, particularly, perhaps, for the law that has come to be known as the principle af LE CHATELIER. But cement chemists think of him for other reasons. His works on the chemistry of Portland cement are of fundamental importance. Through microscopical and chemical studies he has demonstrated that the clinker contains a number of different minerals of which the tricalcium silicate is the bearer of the hydraulic properties. He has also demonstrated that gypsum, calcium aluminates, and Portland cement attain their set through a crystallization from supersaturated solutions. He was one of those men who believe that we cannot intelligently control industrial processes until we know the nature of the things with which we are dealing.

For these reasons, Mr. Chairman, I suggest that we send a resolution to the Rector of the University of Paris — indicating the honour and respect with which we hold the name of LE CHATELIER. After that resolution has been read by the Secretary I move that we have an unanimous rising vote of approval.



A l'occasion du
"Symposium on the Chemistry of Cements"
tenu à Stockholm le 6-8 Juillet 1938
sur invitation de
l'Académie Royale des Sciences Polytechniques
et de
la Société Suédoise du Ciment
les participants au Congrès, venus
d'Allemagne, d'Angleterre, de Belgique,
du Canada, du Danemark, des Etats Unis,
de Finlande, de Norvège, de Pologne,
de Suède et de Suisse,

sont heureux d'accomplir un devoir
de profonde reconnaissance en rendant hommage
à la mémoire du grand savant français
HENRY LE CHATELIER
qui par son génie a tant contribué
à la prospérité de la Science chimique
et de la Technique
en frayant spécialement la voie
à la Chimie des Ciments
par ses travaux proéminents et fondamentaux.

Président

Vice Président

Address to the Memory of the Late HENRY LE CHATELIER delivered to the Rector of the University of Paris.

THE INTERNATIONAL SUBCOMMITTEE ON SPECIAL CEMENTS FOR LARGE DAMS

At the Symposium a communication was made on the International Subcommittee on Special Cements for Large Dams. The following is an abstract of the statements made on this occasion.

Mr. B. HELLSTRÖM[1], Chairman of the Committee, reminded his hearers that the World Power Conference started in 1924 and that the closely allied International Commission on Large Dams was formed in 1930. At this time special cements — "Silikatcement" in Sweden and "Low Heat Cement" in the U. S. A. — had just come to use for the construction of gravity dams and similar hydraulic works. As a general interest in the matter was apparent an International Subcommittee on Special Cements for Large Dams was formed in 1934 to study special cements and to develop methods for testing them with respect to properties of particular value for their use in hydraulic structures. The Subcommittee had investigated several questions in regard to this kind of cements, in particular methods of testing. To the second Congress, in Washington 1936, the Subcommittee presented a report covering its work up to that date (1). The countries represented in the Subcommittee were Australia, Belgium, Czecho-Slovakia, France, Germany, Great Britain, India, Italy, Japan, Norway, Sweden and the United States. Mr. HELLSTRÖM pointed out that any country which is a member of the International Commission on Large Dams can join the Subcommittee on Special Cements simply by appointing two members, one engineer and one chemist. He also wished those interested welcome to the next meeting of the Subcommittee to be held in Vienna the 26th of August, when reports of the national committees were to be discussed and further work was to be decided upon.

Mr. A. EKWALL[2], Swedish member of the Committee, informed the meeting that the national committee in Sweden had proposed that the question of special cements should be dealt with at the next Congress on Large Dams in 1940. He hoped that this would be the case and stressed the importance of special cements not only for large dams but also for hydraulic structures in general, *e. g.* harbours, locks and ordinary structures for hydraulic power development, where water-tight concrete was a necessary condition for good durability.

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[1] Civ. Ing., Vattenbyggnadsbyrån (VBB) A.-B., Stockholm, Sweden.

[2] Chief Engineer, the Royal Board of Waterfall, Stockholm, Sweden.

Mr. F. M. LEA[1], British member of the Committee, spoke about the test methods which had so far been the main object of the committee's work. At the next meeting in Vienna reports from various countries would be discussed. The British Committee on Special Cements was submitting two reports, one dealing with the solubility of cements, the other with methods of determining their fineness. Dr. LEA gave a review of the contents of these reports the results of which indicated that solubility tests might be used for comparative purposes and that the fineness methods tested gave surprisingly close values. He hoped for a general agreement at the Vienna meeting on the principle for calculating the specific surface from grain-size determinations.

Mr. R. H. BOGUE,[2] from the United States, mentioned that the first low-heat cement in U. S. A. was used in the construction of canyon dams five or six years ago. Since then low-heat cement had been used for several structures and also an intermediate cement (a moderate-heat cement) had become rather popular. It had been a general feeling that the latter type might perhaps be better suited for most of the large structures. There were also some other types of special cements used for special purposes in the United States. Mr. J. L. SAVAGE, Chairman of the U. S. Committee for Special Cements, was now organizing the committee for co-operation and research in this respect.

Mr. W. EITEL[3], German member of the Committee, underlined the importance of the question of special cements and said that the committee was taking its work very seriously. On behalf of the German committee he bade those present heartily welcome to the meeting in Vienna and hoped for a large attendance and for valuable discussions.

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[1] D. Sc., F. I. C., Building Research Station, Garston, Herts, England.

[2] Dr., Research Director, Portland Cement Association Fellowship at the National Bureau of Standards, Washington, U. S. A.

[3] Professor, Dr., Kaiser-Wilhelm-Institut für Silikatforschung, Berlin-Dahlem, Germany.

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1. Interim Report on Methods of Testing Cement in Regard to Heat of Hydration, Action on Cement by Water Percolating through Concrete, Shrinkage, Permeability and Workability. — Submitted by the INTERNATIONAL SUBCOMMITTEE ON SPECIAL CEMENTS FOR LARGE DAMS, April 1936. (To be obtained from the Central Office of the International Commission on Large Dams, 5 Avenue Friedland, Paris 8, France.)

SURVEY OF CONTENTS

The International Meeting on the Chemistry of Cements, designated Symposium on the Chemistry of Cements, was held in Stockholm from 5th to 8th July, 1938. The PRESIDENT of the Meeting, Professor AXEL F. ENSTRÖM, President of the Royal Swedish Institute for Engineering Research, and the VICE-PRESIDENT, Consul W. DE SHÀRENGRAD, President of the Swedish Cement Association, recall in the *preface* (p. V) that a similar meeting was held once previously, in London in 1918, and that developments since then have been of such importance that a further meeting was now regarded as justified. The Royal Swedish Institute for Engineering Research and the Swedish Cement Association were the sponsors of the Stockholm Meeting and the two Institutes are of opinion that publication of the proceedings of the Meeting, as is now taking place, should be done in order to make generally available the surveys, data and views presented on this occasion by leading investigators in various parts of the world and which may be taken as constituting the best authoritative picture to be obtained of the present standpoint of science in this domain.

A brief *review of the events of the Meeting* is furnished by the SECRETARY, Mr. S. GIERTZ-HEDSTRÖM, on pages 1—7. Mention is made of the excursions undertaken in conjunction with the Meeting, and a chronological report of the proceedings is given. Papers had been submitted in advance, and the sessions were devoted to discussion of these papers. Two introductory lectures were delivered, one by Professor T. SVEDBERG and one by Professor J. A. HEDVALL. The discussions were conducted by Professor T. THORVALDSON, Professor W. EITEL, Dr. F. M. LEA, Professor P. SCHLÄPFER, and Dr. R. H. BOGUE. Subsequent to the Meeting written supplementary contributions to the discussions were also received, and those who took part in the discussions were given opportunity to revise their contributions. The papers and the discussions appertaining to them will be found in the proceedings.

A *list of the persons invited to and taking part in the Meeting* will be found on pages 8—11.

Professor T. SVEDBERG in his introductory address "The Study of Giant Molecules by Means of Ultracentrifugal Sedimentation, Diffusion and Electrophoresis", (pages 13—41), describes the experimental technique developed at his institute for the study of high molecular substances. Particulars are given of the principle and the construction of the apparatuses for ultracentrifugal sedimentation, diffusion and electrophoresis; and examples of results achieved are presented, mainly in respect of organic substances. The sphere of investigation is of great general interest, and the technique employed must be regarded as having a certain prospect of being applicable to cement research.

Professor J. A. HEDVALL's introductory address "Reactions between Substances in Solid State, with Special Regard to Systems Containing Silica", (pages 42—58), touches directly on a number of problems of the chemistry of cements. Professor HEDVALL deals especially with the way in which reactions of this kind are governed by the changes of the lattice from ionic type to anhydride type, by crystallographic transitions, by the state of the reacting substances, by crystallographically different surfaces and by foreign substances in the lattice. A number of inorganic reactions are cited as examples, some of which come from the chemistry of cements.

Following the introductory addresses come the surveys prepared for the Meeting of different sections of the chemistry of cements, together with the discussions relating to them.

The discussions opened with Dr. R. H. BOGUE's paper on "Constitution of Portland Cement Clinker", (pages 59—98). This treats generally of the progress in the question of constitution since the previous Meeting (1918) with the following aspects in more detail:—Investigation of clinker by means of polished sections and reflected light.—Recent investigations of complex systems, the components of which have crystallized in conditions of equilibrium, with sub-sections: clinker compounds, alkali components and calculation of compounds at crystalline equilibrium.—The composition in corresponding systems when crystallization has been arrested, with resultant glass forming and changed crystallization. In this the nature of the glass phase is dealt with, along with approximate determination of glass content and estimation of the composition when crystallization is arrested.—The effect of the constitution on the behaviour of the cement, especially as regards unsoundness due to magnesia for different glass contents of the clinker, to free lime and to tricalcium aluminate, as also heat generation for various glass contents.—Annexed are formulae by L. A. DAHL for calculating phase composition of clinker with normal crystallization to an estimated glass content.

The *discussion* (pages 99—140) on Dr. BOGUE's paper comprises contributions by Dr. M. A. SWAYZE, Dr. T. W. PARKER, Dr. B. TAVASCI, Dr. N. SUNDIUS, Dr. E. BRANDENBERGER, Prof. W. EITEL, Mr. R. G. FRANKLIN, Dr. F. M. LEA, Dr. L. FORSÉN and *the author*.

In the succeeding paper "X-Rays and Cement Chemistry" (pages 141—168), Dr. W. BÜSSEM treats of X-ray analysis as an aid in cement research. Following a survey of the fundamental principles of crystal chemistry there is given an account of the chemistry of crystals of the different anhydrous cement compounds, commencing with general observations, especially concerning the theory of "active" and "inactive" calcium ions, and proceeding to detailed data on the different compounds. Then come descriptions of the X-ray characteristics of the lime-alumina-silica-ironoxide-hydrates, and finally the possibilities of improving present X-ray methods are surveyed.

The *discussion* (pages 169—177) on Dr. BÜSSEM's paper comprises contributions by Mr. G. E. BESSEY, Dr. A. EIGER, Dr. E. BRANDENBERGER, Prof. T. THORVALDSON, and *the author.*

The two introductory addresses and the discussion of the two above papers took up the first day of the Meeting, which thus was chiefly devoted to questions regarding the constitution of clinker and investigation methods. The theme for the second day of the Meeting was the chemistry of cement hydration. The first paper was that of Mr. G. E. BESSEY on "The Calcium Aluminate and Silicate Hydrates" (pages 178—215). First giving a tabular survey of the recognized hydrates, the author deals with the system CaO-Al_2O_3-H_2O, with sub-headings: methods of preparation (direct synthesis, hydration of the anhydrous calcium aluminates and precipitation methods), properties of the hydrated calcium aluminates (optical properties, water contents and dehydration, crystal structure etc.) as also solubility and phase equilibria. The system CaO-SiO_2-H_2O is then treated with corresponding sub-sections.

The *discussion* (pages 216—230) on Mr. BESSEY's paper comprises contributions by Dr. B. TAVASCI, Prof. T. THORVALDSON, Dr. G. ASSARSSON, Prof. A. TRAVERS and Dr. A. ZAHABI as well as *the author.*

In his paper "The Calcium Aluminate Complex Salts" (pages 231—245), Mr. F. E. JONES makes a survey of the recognized complex compounds of calcium aluminates with other salts, which compounds were not dealt with in the above paper by Mr. G. E. BESSEY. The paper of Mr. JONES is similarly divided into: methods of preparation, properties of the complex aluminates and solubility and phase equilibria. No contributions to the discussion were submitted in connection with this paper.

"Portland Cement and Hydrothermal Reactions" is the title of Prof. T. THORVALDSON's paper (pages 246—267), which deals with the conditions of hydrothermal treatment of Portland cement and its components. The paper comprises the following sections: hydrothermal synthesis of hydrated silicates of calcium, hydrothermal reactions of the anhydrous calcium silicates, summary on calcium hydrosilicates, hydrothermal synthesis of calcium hydroaluminates, hydrothermal changes of tetracalcium aluminoferrite and dicalcium ferrite, and in conclusion hydrothermal treatment of Portland cement and concrete (effect on strength and other physical properties and on resistance to sulphate action).

The *discussion* (pages 268—269) on Prof. THORVALDSON's paper comprises contributions by Dr. L. FORSÉN and *the author.*

Prof. P. SCHLÄPFER's paper "Effect of Water on Portland Cement", (pages 270—284), which formally covers the whole of the ground treated in detail by Messrs. BESSEY, JONES, THORVALDSON and FORSÉN, is more in the nature of a general survey. Following an introduction, an account is first given of the effect of water on single clinker components, calcium silicates (including the influence of the amount of water, temperature and grain-size), calcium aluminates and tetracalcium aluminoferrite ("Brownmillerite") and then of how one may interpret the action of water on Portland cement regarded as a whole.

The *discussion* (pages 285—297) on Prof. SCHLÄPFER's paper comprises contributions by Mr. G. E. Bessey, Dr. G. HAEGERMANN and *the author.*

Dr. L. FORSÉN's paper "The Chemistry of Retarders and Accelerators", (pages 298—363) deals chiefly with that section of the chemistry of the hydration of Portland cement, which is technically termed setting time regulation, but concerns also the chemical reaction mechanism of the reaction of cement with water, as also the influence of accelerators, retarders and destroyers on the progress of hardening. Following a survey of earlier work the author gives an account of a series of new investigations carried out by himself. These concern both components (research methods, the behaviour of the components in water, experiments with aluminate components, experiments with silicate components) and cements (setting time of various cements, composition of the liquid phase of the mortar, combination of gypsum during the hardening of cement, heat of hydration and water combination, influence on setting time and strength of Portland cements and blast-furnace slags, the influence of humus, surface precipitates). The detailed experimental material is collated in a special appendix with 66 tables.

The *discussion* (pages 364—394) on Dr. FORSÉN's paper includes contributions by Mr. C. PONTOPPIDAN, Dr. R. H. BOGUE, Dr. A. EIGER, Dr. F. M. LEA, Mr. G. E. BESSEY, Mr. P. S. ROLLER, Prof. A. TRAVERS, and *the author.*

Concerning all the papers dealing with the hydration of cement and the compositions thereby formed (Mr. BESSEY's, Mr. JONES's, Prof. THORVALDSON's, Prof. SCHLÄPFER's and Dr. FORSÉN's papers) it applies that for natural reasons they touch on each other's domains, and particularly that the discussions pertaining to them concern more than the paper to which these have been attached editorially.

For the third and last day of the Meeting there was assigned a more mixed programme, comprising aluminous cements, pozzolanas and the physical structure of hardened cement. The first paper, that of Dr. N. SUNDIUS on "The Mineral Content of Aluminous Cement", (pages 395—421), deals with questions of the constitution of aluminous cements. It comprises: chemical composition of aluminous cement, minerals in the aluminous cement in general, the mineral contents of 4 aluminate cement clinker samples specially studied, X-ray tests, and the crystallization process in aluminous cement.

The *discussion* (pages 422—440) on Dr. SUNDIUS's paper includes contributions by Dr. B. TAVASCI (a detailed contribution entitled "Melted Cement Containing Iron"), Dr. F. M. LEA, Prof. A. TRAVERS, and *the author.*

The next paper, by Dr. G. ASSARSSON on "Reactions of Aluminous Cement with Water", (pages 441—458), deals with the hydration conditions of this cement. It is divided into: earlier investigations (hydration of pure calcium aluminates, calcium ferrites, dicalcium silicate, Gehlenite, hydration of aluminous cement), summary of the results of earlier investigations (the anhydrous calcium aluminates, dicalcium silicate, dicalcium ferrite, Gehlenite, high alumina cement) and the chemical character of hydration reactions.

The *discussion* (page 459) on Dr. ASSARSSON's paper comprises contributions by Dr. F. M. LEA and *the author.*

"Te Chemistry of Pozzolanas", (pages 460—490), is the title of a paper by Dr. F. M. LEA, which furnishes a survey of the varying and nowadays increasingly numerous pozzolanic materials. It is divided into the following sections: definition and classification, constitution of pozzolanas (natural pozzolanas, burnt clays and shales), the reactions of pozzolanas with lime, pozzolanas and the resistance of mortars to chemical attack, the chemical evaluation of pozzolanas, the estimation of free calcium hydroxide in pozzolana mixes (by G. E. BESSEY).

The *discussion* (pages 491—504) on Dr. LEA's paper comprises contributions by Mr. P. S. HÅKANSON, Dr. L. FORSÉN, Mr. C. D. CRICHTON, Dr. W. BÜSSEM, Prof. T. THORVALDSON, Prof. A. TRAVERS, and *the author.*

The last paper at the Meeting was prepared by Mr. S. GIERTZ-HEDSTRÖM on "The Physical Structure of Hydrated Cements", (pages 505—533) and constitutes to a certain extent a link between the pure chemistry of cements and concrete engineering. Its sub-sections are: the hydration process and the development of structure, volume relations and speeds of reaction, methods for the investigation of the physical structure of hardened cement, theories concerning the physical structure of cement, factors influencing the physical structure and relations between the physical structure of cement and its technical qualities.

The *discussion* (pages 534—541) on Mr. GIERTZ-HEDSTRÖM's paper comprises contributions by Prof. P. SCHLÄPFER, Dr. F. M. LEA, Dr. A. EIGER, Mr. D. G. R. BONNELL, and *the author.*

All the addresses and papers are provided with their own bibliographies. In addition there is at the conclusion of the book a *name index* and a *subject index* dealing with the book as a whole.

During the Meeting tribute was paid to the memory of the pioneer of cement research, the Frenchman HENRY LE CHATELIER in a speech by Dr. R. H. BOGUE and in an *address of homage* from the Meeting to the University of Paris. These are reproduced on pages 542 and 543.

On one of the days of the Meeting a *communication* was given concerning the International Sub-Committee for Special Cements for Large Dams. In this connection Mr. B. HELLSTRÖM, Mr. A. EKWALL, Dr. F. M. LEA, Dr. R. H. BOGUE and Prof. W. EITEL spoke. Brief extracts from these speeches will be found on pages 544 and 545.

EXPOSÉ SOMMAIRE DU CONTENU

La réunion internationale consacrée à la chimie des ciments, "Symposium on the Chemistry of Cements", a eu lieu à Stockholm le 6—8 juillet 1938. Dans la préface (p. V), le PRÉSIDENT de la réunion, M. le professeur AXEL F. ENSTRÖM, président de l'Académie Royale Suédoise dês Sciences Polytechniques, et M. le consul W. DE SHÀRENGRAD, VICE-PRÉSIDENT de la réunion, président de l'Association Suédoise de Ciment, rappellent qu'une réunion analogue avait eu lieu à Londres en 1918 et que le développement dans ce domaine de la science a été si considérable qu'une nouvelle réunion a été jugée désirable. Les invitations à la réunion de Stockholm émanent de l'Académie Royale Suédoise des Sciences Polytechniques et de l'Association Suédoise de Ciment. Ces deux organismes sont d'avis que la publication du présent compte-rendu de la réunion soit utile afin de porter à la connaissance générale les exposés du développement, les données et les opinions présentées au cours de la réunion par des savants éminents des différentes parties du monde. On est fondé à croire que ces matériaux donnent la meilleure idée autoritaire de l'état actuel de la science, dans ce domaine, qui peut être obtenue à présent.

M. S. GIERTZ-HEDSTRÖM, SECRÉTAIRE de la réunion, fait un *sommaire schématique de la réunion,* (p. 1—7), où l'on mentionne les excursions organisées en conjonction avec la réunion ainsi que son abrégé chronologique. Les rapports ont été présentés d'avance, et la réunion fut réservée à leur discussion. M. T. SVEDBERG et M. J. A. HEDVALL ont inauguré la réunion par deux conférences introductoires. Les discussions ont été conduites par MM. T. THORVALDSON, W. EITEL, F. M. LEA, P. SCHLÄPFER et R. H. BOGUE. Après la réunion, on a reçu plusieurs contributions additionnelles à la discussion, et les participants aux discussions pendant la réunion ont eu des occasions de reviser leurs contributions. Les rapports et les discussions y relatives sont reproduits dans le présent compte-rendu.

On trouvera aux pp. 8—11 une *liste des personnes invitées a la réunion et des participants.*

M. T. SVEDBERG décrit, dans sa conférence introductoire sur «L'étude des molécules gigantesques au moyen de la sédimentation par centrifuge ultra-rapide, de la diffusion et de l'électrophorèse», (p. 13—41), la technique expérimentale, développée dans son institut pour l'étude des substances aux molécules très grandes. Il expose les principes de la sédimentation par centrifuge ultra-rapide, de la diffusion et de l'électrophorèse et explique la construction de l'appareillage utilisé à ce but. En outre, il cite des exemples pour illustrer les résultats obtenus, en particulier en ce qui concerne les substances organiques. Le domaine de ces recherches présente un grand intérêt général, et il paraît que la technique expérimentale employée dans ces essais pourrait, dans une certaine mesure, être appliquée à l'étude des ciments.

La conférence introductoire de M. J. A. HEDVALL, intitulée «Les réactions entre les substances en phase solide, considérées particulièrement au point de vue des systèmes contenant de l'acide silicique», (p. 42—58), touche directement plusieurs problèmes relatifs à la chimie des ciments. M. HEDVALL traite spécialement les relations entre les réactions de ce genre et la transformation du réseau du type ionique en type-anhydride, l'état des substances réagissantes, les différences cristallographiques entre les surfaces et les substances étrangères dans le réseau. Il cite plusieurs réactions inorganiques à titre d'exemple, dont quelques-unes proviennent de la chimie des ciments.

Les conférences introductoires sont suivies par les rapports des différentes sections de la chimie des ciments, préparés pour la réunion, et les discussions y relatives.

Les discussions commencent par le rapport de M. R. H. BOGUE «La constitution du clinker de ciment Portland», (p. 59—98). Ce rapport traite en général des progrès réalisés dans la question de constitution depuis la réunion précédente (1918). Les matières suivantes sont discutées d'une manière plus détaillée:—Étude des clinkers au moyen des plaques minces polies et de la lumière réfléchie.—Recherches récentes sur les systèmes complexes dont les composants se sont cristallisés dans les conditions d'équilibre, avec les sous-divisions: composés des clinkers, composants alcalins et le calcul de la constitution lors de l'équilibre de cristallisation.—Composition des systèmes analogues dans les cas où la cristallisation a été suspendue, formation de verre et cristallisation modifiée qui en résultent. Ici, on traite séparément la nature de la phase vitreuse, la détermination approximative de la teneur en verre et le calcul de la composition dans le cas de la cristallisation suspendue.—Le rôle de la constitution au point de vue des propriétés du ciment, particulièrement en ce qui concerne l'inconstance du volume, causée par la magnésie, tenant compte des teneurs variables en verre, par la chaux libre et par le trialuminate de calcium, et pour ce qui concerne la chaleur d'hydratation en fonction de la teneur en verre.—Dans un appendice, on trouvera des formules de L. A. DAHL pour le calcul de la composition du clinker dans le cas de cristallisation normale jusqu'à une teneur en verre calculée.

Les *discussions* (p. 99—140) du rapport de M. BOGUE contiennent des contributions par MM. M. A. SWAYZE, T. W. PARKER, B. TAVASCI, N. SUNDIUS, E. BRANDENBERGER, W. EITEL, R. G. FRANKLIN, F. M. LEA, L. FORSÉN et *l'auteur.*

Dans le rapport suivant «Les rayons X et la chimie des ciments» (p. 141—168), M. W. BÜSSEM traite de l'analyse au moyen des rayons X dans ses applications aux recherches sur les ciments. Un exposé des principes fondamentaux de la chimie des cristaux est suivie par une analyse des différents composés du ciment au point de vue de la chimie des cristaux, commençant par quelques observations générales relatives surtout à la théorie des ions de calcium «actifs» et «inactifs». Dans la suite, on trouve des données détaillées sur les différents composés. Puis on décrit les caractéristiques, au point de vue des rayons X, des hydrates des composés de chaux, oxide d'aluminium, dioxide de silicium et oxide de fer. Le rapport se termine par un abrégé des possibilités de perfectionnement des méthodes actuelles utilisant les rayons X.

Les *discussions* (p. 169—177) de rapport de M. BÜSSEM contiennent des contributions par MM. T. THORVALDSON, A. EIGER, E. BRANDENBERGER, G. E. BESSEY et *l'auteur.*

Les deux conférences introductoires et les discussions des deux rapports susmentionnés constituaient l'ordre du premier jour de la réunion qui fut donc, pour la plus grande partie, consacré aux questions relatives à la constitution du clinker et les méthodes utilisées dans les recherches. Le sujet de la deuxième journée de la réunion était la chimie de l'hydratation du ciment. On a commencé par le rapport de M. G. E. BESSEY «Les hydrates de l'aluminate de calcium et du silicate de calcium» (p. 178—215). Après avoir passé en revue les hydrates connus dans des tableaux, l'auteur traite le système CaO-Al_2O_3-H_2O sous les rubriques suivantes: méthode de préparation (synthèse directe, hydratation des aluminates de calcium ne contenant pas d'eau et méthodes utilisant la precipitation), propriétés des aluminates de calcium hydratés (propriétés optiques, teneur en eau et déhydratation, structure cristalline etc.), la solubilité et les équilibres des phases. Ensuite, on traite le système CaO-SiO_2-H_2O sous les rubriques analogues.

Les *discussions* (p. 216—230) du rapport de M. BESSEY contiennent des contributions par MM. B. TAVASCI, T. THORVALDSON, G. ASSARSSON, A. TRAVERS, A. ZAHABI et *l'auteur.*

Dans son rapport sur «Les composés complexes de l'aluminate de calcium», (p. 231—245), M. F. E. JONES donne une liste des composés connus de l'aluminate de calcium et d'autres sels composés qui ne sont pas traités dans le rapport susmentionné par M. G. E. BESSEY. Le rapport de M. JONES est divisé d'une manière analogue en chapitres suivants: méthodes de préparation, propriétés des aluminates complexes, solubilité et équilibres des phases. Ce rapport n'a pas donné lieu aux discussions.

«Le ciment Portland et les réactions hydrothermales» est le titre du rapport par M. T. THORVALDSON, (p. 246—267), qui s'occupe des conditions se présentant lors du traitement hydrothermal du ciment Portland et de ses composants. Le rapport comprend les chapitres suivants: synthèse hydrothermale des silicates de calcium hydratés, réactions hydrothermales des silicates de calcium ne contenant pas d'eau, sommaire relatif aux hydrosilicates de calcium, synthèse hydrothermale de l'hydroaluminate de calcium, modifications hydrothermales du tétraaluminate-ferrite de calcium et du biferrite de calcium, et, pour conclure, le traitement hydrothermal du ciment Portland et du béton (influence sur la résistance et sur les autres propriétés physiques de même que sur la résistance contre l'attaque des sulfates).

Les *discussions* (p. 268—269) sur le rapport de M. THORVALDSON contiennent des contributions par MM. L. FORSÉN et *l'auteur*.

Le rapport de M. P. SCHLÄPFER, «Influence de l'eau sur le ciment Portland», (p. 270—284), couvre formellement le domaine entier qui est traité d'une manière détaillée par MM. BESSEY, JONES, THORVALDSON et FORSÉN. Son caractère est plutôt généralement sommaire. L'introduction s'occupe d'abord de l'influence de l'eau sur les composants individuels des clinkers, silicates de calcium (entre autres choses, rôle de la quantité d'eau, de la température et de la grandeur des grains), aluminates de calcium et tétraaluminate-ferrite de calcium (»Brownmillerite»). Ensuite, l'auteur discute l'interprétation de l'influence de l'eau sur le ciment Portland, considérée dans sa totalité.

Les *discussions* (p. 285—297) sur le rapport de M. SCHLÄPFER contiennent des contributions par MM. G. E. BESSEY, G. HAEGERMANN et *l'auteur*.

Le rapport de M. L. FORSÉN «La chimie des rétardateurs et des accélérateurs du ciment», (p. 298—363), traite, en premier lieu, la partie de la chimie de l'hydratation du ciment Portland qui est connue dans la technique sous le nom de réglage de la durée de prise, mais qui touche aussi au mécanisme chimique des réactions entre le ciment et l'eau ainsi que l'influence des accélérateurs, des rétardateurs et des destructeurs sur le processus de durcissement. L'auteur passa en revue les travaux plus récents, dans ce domaine, et décrit ensuite une série des recherches nouvelles, effectuées par lui-même. Ces recherches se rapportent d'une part, aux composants (méthodes d'essai, la conduite des composants dans l'eau, essais sur les composants d'aluminate, essais sur les composants de silicate) et d'autre part, sur les ciments (durée de prise des divers ciments, composition de la phase aqueuse du mortier, fixation du gypse durant le durcissement du ciment, chaleur d'hydratation et fixation de l'eau, influence sur la durée de prise et la résistance du ciment Portland et des laitiers de haut-fourneau, influence de l'humus, precipites). Les données expérimentales très détaillées sont réunies dans un appendice spécial comprenant 66 tableaux.

Les *discussions* (p. 364—394) sur le rapport de M. FORSÉN contiennent des contributions par MM. C. PONTOPPIDAN, R. H. BOGUE, A. EIGER, F. M. LEA, G. E. BESSEY, P. S. ROLLER, A. TRAVERS et *l'auteur.*

Une remarque générale s'impose au sujet de tous les rapports qui traitent de l'hydratation du ciment et des composés qui en résultent (savoir, les rapports de MM. BESSEY, JONES, THORVALDSON, SCHLÄPFER et FORSÉN.) Pour des raisons tout naturelles, ces rapports empiètent un peu les uns sur les autres. En particulier, il est à noter que les discussions y relatives portent non seulement sur les rapports sous lesquels la rédaction les a rangées, mais encore sur plusieurs autres.

Le programme de la troisième journée de la réunion, qui en fut aussi la dernière, était plus hétérogène. Il comprenait le ciment fondu, les pouzzolanes et la structure physique de ciment durci. Le premier rapport sur «La constitution minérale du ciment fondu», (p. 395—421), par M. N. SUNDIUS s'occupe des questions relatives à la constitution du ciment fondu. Le rapport comprend les chapitres suivants: la composition chimique du ciment fondu, remarques générales sur les minéraux contenus dans le ciment fondu, composition minérale des 4 échantillons de ciment fondu soumis à une étude spéciale, essais aux rayons X et processus de cristallisation du ciment fondu.

Les *discussions* (p. 422—440) sur le rapport de M. SUNDIUS contiennent des contributions par MM. B. TAVASCI (contribution assez détaillée, intitulée «Ciment fondu ferreux»), F. M. LEA, A. TRAVERS et *l'auteur.*

Le rapport suivant par M. G. ASSARSSON «Les réactions entre le ciment fondu et l'eau», (p. 441—458), traite des conditions d'hydratation de ce ciment. Le rapport se divise en chapitres suivants: recherches plus récentes (hydratation des aluminates de calcium purs, des ferrites de calcium, du bisilicate de calcium, du Gehlenite, hydratation du ciment fondu), sommaire des résultats des recherches plus récentes (aluminates de calcium ne contenant pas d'eau, bisilicate de calcium, biferrite de calcium, Gehlenite, ciment à teneur haute en aluminium), caractère chimique des réactions d'hydratation.

Les *discussions* (p. 459) sur le rapport de M. ASSARSSON contiennent des contributions par M. F. M. LEA et *l'auteur.*

«La chimie des pouzzolanes», (p. 460—490), est le titre du rapport par M. F. M. LEA qui contient une description des diverses matières pouzzolaniques dont le nombre augmente de plus en plus. Ce rapport comprend les chapitres suivants: définition et classification, constitution des pouzzolanes (pouzzolanes naturelles, terres cuites et ardoises), réaction entre pouzzolanes et chaux, l'influence des pouzzolanes sur la résistance du mortier de ciment contre les attaques chimiques, essais chimiques sur les pouzzolanes, détermination de l'hydroxide de calcium libre dans les mélanges pouzzolaniques (par M. G. E. Bessey).

Les *discussions* (p. 491—504) sur le rapport de M. Lea contiennent des contributions par MM. P. S. Håkanson, L. Forsén, C. D. Crichton, W. Büssem, T. Thorvaldson, A. Travers et *l'auteur*.

Le dernier rapport présenté à la réunion est celui de M. S. Giertz-Hedström. Il est intitulé «La structure physique du ciment hydraté» (p. 505—533) et constitute, en quelque sorte, un lien entre la chimie de ciment pure et la technique du béton. Il contient les chapitres suivants: le processus d'hydratation et le développement de la structure, les conditions relatives au volume et les vitesses des réactions, les méthodes utilisées pour l'étude de la structure physique du ciment durci, les théories concernant la structure physique du ciment, les facteurs qui influent sur la structure physique, les relations entre la structure physique du ciment et ses propriétés techniques.

Les *discussions* (p. 534—541) sur le rapport de M. Giertz-Hedström contiennent des contributions par MM. P. Schläpfer, F. M. Lea, A. Eiger, D. G. R. Bonnell et *l'auteur*.

Tous les rapports et conférences sont pourvus d'une notice bibliographique individuelle. En outre, on trouvera, à la fin du compte-rendu, une *table des noms* et une *table analytique des matières* se rapportant à l'ouvrage entier.

La réunion a rendu hommage à la mémoire du pionnier de la science des ciments, le grand savant français Henry Le Chatelier, par un discours de M. R. H. Bogue et une *adresse commémorative* envoyée par la réunion à l'Université de Paris. Ces documents sont reproduits aux pp. 542 et 543.

Pendant la réunion, on a donné quelques *informations générales* sur le sous-comité international sur les ciments pour les grands barrages. Ont parlé à cette occasion: MM. B. Hellström, A. Ekwall, R. H. Bogue et W. Eitel. On trouvera de brefs extraits de leurs discours aux pp. 544 et 545.

INHALTSÜBERSICHT

Die internationale Zementchemietagung, "Symposium on the Chemistry of Cements", wurde in Stockholm am 6—8 Juli 1938 abgehalten. Der VORSITZENDE der Tagung, Herr Professor AXEL F. ENSTRÖM, Präsident der Königlichen Schwedischen Akademie der Ingenieurwissenschaften, und deren STELLVERTRETENDE VORSITZENDE, Herr Konsul W. DE SHÅRENGRAD, Vorsitzender des Schwedischen Zementvereins, erinnern im *Vorwort* (S. V) an eine ähnliche Tagung, die schon einmal früher, im Jahre 1918, in London stattgefunden hatte. Seitdem hat die Zementchemie eine so bedeutende Entwicklung durchgemacht, dass eine neue Tagung als berechtigt angesehen wurde. Die Einladung dazu ging von der Königlichen Schwedischen Akademie der Ingenieurwissenschaften und vom Schwedischen Zementverein aus, und diese beiden Körperschaften sind der Ansicht, dass die Veröffentlichung der Tagungsverhandlungen, wie sie jetzt vorgenommen wird, erwünscht sei, damit die Übersichten, Angaben und Auffassungen, die bei dieser Gelegenheit von hervorragenden Forschern aus verschiedenen Teilen der Welt vorgelegt wurden, und die wahrscheinlich das beste massgebende Bild vom Stande der Wissenschaft auf diesem Gebiet geben, das gegenwärtig erhalten werden kann, zur Kenntnis der Öffentlichkeit gebracht werden.

Eine schematische *Übersicht über den Verlauf der Tagung* aus der Feder des GESCHÄFTSFÜHRERS der Tagung, Herrn S. GIERTZ-HEDSTRÖM, ist auf S. 1—7 zu finden. Darin werden die im Zusammenhang mit der Tagung vorgenommenen Ausflüge erwähnt, und es wird über den zeitlichen Verlauf der Tagung berichtet. Die Berichte sind im voraus eingereicht worden, so dass die Tagungszusammenkünfte der Erörterung dieser Berichte gewidmet waren. Zwei einleitende Vorträge wurden von Herrn Prof. T. SVEDBERG und Herrn Prof. J. A. HEDVALL gehalten. Die Erörterungen wurden von den Herren Prof. T. THORVALDSON, Prof. W. EITEL, Dr. F. M. LEA, Prof. P. SCHLÄPFER und Dr. R. H. BOGUE geleitet. Nach der Tagung wurden einige weitere Diskussionsbeiträge eingereicht, und den Teilnehmern an den Tagungserörterungen wurde Gelegenheit geboten, ihre Beiträge zu überprüfen. Die Berichte und die dazugehörigen Erörterungen sind im vorliegenden Tagungsbericht wiedergegeben.

Ein *Verzeichnis der zur Tagung eingeladenen Personen und der Tagungsteilnehmer* befindet sich auf S. 8—11.

Prof. T. SVEDBERG beschreibt in seinem einleitenden Vortrag, »Untersuchung von Riesenmolekülen durch Ultrazentrifugen-Sedimentierung, Diffusion und Elektrophorese», (S. 13—41) die Versuchstechnik, die in seiner Forschungsanstalt für das Studium der hochmolekularen Stoffe entwickelt wurde. Es wird darin über die Grundlagen der Sedimentierung mittels der Ultrazentrifuge, Diffusion und Elektrophorese sowie über die Ausführung der dafür verwendeten Geräte berichtet. Es folgen einige Beispiele für die dabei erreichten Ergebnisse, besonders hinsichtlich organischer Stoffe. Das Untersuchungsgebiet ist von grossem allgemeinen Interesse, und es ist anzunehmen, dass die dabei angewendeten Verfahren möglicherweise auch in der Zementforschung Verwendung finden können.

Der einleitende Vortrag von Prof. J. A. HEDVALL, »Reaktionen zwischen Stoffen im festen Zustande mit besonderer Berücksichtigung der kieselsäurehaltigen Systeme», (S. 42—58), berührt unmittelbar mehrere Fragen der Zementchemie. Prof. HEDVALL behandelt insbesondere die Abhängigkeit derartiger Reaktionen vom Übergang des Gitters vom Iontyp zum Anhydridtyp, von kristallographischen Umwandlungen, vom Zustand der reagierenden Stoffe, von kristallographischen Oberflächenverschiedenheiten sowie von Fremdstoffen im Gitter. Mehrere anorganische Reaktionen werden als Beispiele angeführt, von denen einige aus der Zementchemie stammen.

Nach den einleitenden Vorträgen folgen die für die Tagung ausgearbeiteten Übersichten über die verschiedenen Abschnitte der Zementchemie und die dazugehörigen Erörterungen.

Angefangen wird mit dem Bericht von Dr. R. H. BOGUE über »Die Zusammensetzung des Portlandzementklinkers», (S. 59—98). Dieser Bericht behandelt im allgemeinen die Fortschritte in der Lösung der Konstitutionsfrage seit der vorherigen Tagung (1918). Ausführlicher besprochen sind folgende Abschnitte: — Untersuchung von Klinkern durch Polierschlieffe und reflektiertes Licht. — Neuere Untersuchungen über komplexe Systeme, deren Bestandteile sich unter Gleichgewichtsbedingungen kristallisiert haben, mit Unterabteilungen: Klinkerverbindungen, Alkaliverbindungen und Berechnung der Mineralienverteilung bei Kristallisationsgleichgewicht. — Zusammensetzung der entsprechenden Systeme bei Hemmung der Kristallisation, mit Glasbildung und veränderter Kristallisation als Folge. Hier werden für sich behandelt: Charakter der Glasphase, annähernde Bestimmung des Glasgehaltes und Berechnung der Zusammensetzung bei gehemmter Kristallisation. — Bedeutung der Zusammensetzung für die Eigenschaften des Zements, insbesondere im Hinblick auf die Volumenbeständigkeit, die von Magnesiumoxid bei verschiedenem Glasgehalt, von freiem Kalk und von Trikalziumaluminat verursacht wird, sowie auf die Wärmeentwicklung bei verschiedenem

Glasgehalt.—In einem Anhang werden Formeln von L. A. DAHL für die Berechnung der Klinkerzusammensetzung bei normaler Kristallisation bis zum berechneten Glasgehalt angegeben.

Die *Erörterung* (S. 99—140) des Berichts von Dr. BOGUE enthält Beiträge von Dr. M. A. SWAYZE, Dr. T. W. PARKER, Dr. B. TAVASCI, Dr. N. SUNDIUS, Dr. E. BRANDENBERGER, Prof. W. EITEL, Herrn R. G. FRANKLIN, Dr. F. M. LEA, Dr. L. FORSÉN und vom *Verfasser*.

In seinem darauffolgenden Bericht »Röntgenstrahlen und Zementchemie», (S. 141—168), behandelt Dr. W. BÜSSEM die Röntgenanalyse als Hilfsmittel der Zementforschung. Nach einer Übersicht über die Grundlagen der Kristallchemie berichtet der Verfasser über die Kristallchemie der verschiedenen Zementverbindungen, beginnend mit allgemeinen Beobachtungen, insbesondere hinsichtlich der Theorie »aktiver» und »inaktiver» Kalziumionen, wonach ausführliche Angaben über die verschiedenen Verbindungen folgen. Sodann werden die Röntgenkennzeichen der Hydrate der Kalk-Aluminiumoxid-Kieseldioxid-Eisenoxid-Verbindungen beschrieben, und zum Schluss werden die Verbesserungsmöglichkeiten für die gegenwärtigen Röntgenverfahren besprochen.

Die *Erörterung* (S. 169—177) des Berichts von Dr. BÜSSEM umfasst die Beiträge von Herrn G. E. BESSEY, Dr. A. EIGER, Dr. E. BRANDENBERGER, Prof. T. THORVALDSON und vom *Verfasser*.

Die beiden einleitenden Vorträge und die Erörterung der zwei genannten Berichte bildeten den Verhandlungsstoff des ersten Tages der Tagung, an dem man sich somit vorwiegend mit den Fragen der Klinkerzusammensetzung und deren Untersuchungsverfahren beschäftigte. Der Gegenstand des zweiten Tages war die Chemie der Zementhydratisierung. Zuerst kam der Bericht von Herrn G. E. BESSEY über »Kalziumaluminat- und Kalziumsilikathydrate», (S. 178—215). Nach Übersichtstafeln über die bekannten Hydrate behandelt der Verfasser das System CaO-Al_2O_3-H_2O mit Unterabteilungen: Darstellungsweise (unmittelbare Synthese, Hydratisierung der wasserfreien Kalziumaluminate und Fällungsverfahren), Eigenschaften der hydratisierten Kalziumaluminate (optische Eigenschaften, Wassergehalt und Dehydratisierung, Kristallaufbau usw.) sowie Löslichkeit und Phasengleichgewicht. Dann wird das System CaO-SiO_2-H_2O mit entsprechenden Unterabteilungen besprochen.

Die *Erörterung* (S. 216—230) des Berichts von Herrn BESSEY enthält Beiträge von Dr. B. TAVASCI, Prof. T. THORVALDSON, Dr. G. ASSARSSON, Prof. A. TRAVERS und Dr. A. ZAHABI sowie vom *Verfasser*.

Herr F. E. JONES gibt in seinem Bericht »Die komplexen Kalziumaluminatverbindungen», (S. 231—245), eine Übersicht über die bekannten komplexen Verbindungen von Kalziumaluminat mit andern Salzen. Diese

Verbindungen sind im erwähnten Bericht von Herrn G. E. BESSEY nicht behandelt. Der Bericht von Herrn JONES ist dem genannten ähnlich eingeteilt: Darstellungsweise, Eigenschaften der komplexen Kalziumaluminate sowie deren Löslichkeit und Phasengleichgewichte. Zu diesem Bericht sind keine Diskussionsbeiträge eingegangen.

»Portlandzement und hydrothermale Reaktionen» ist der Titel des Berichts von Prof. T. THORVALDSON, (S. 246—267), wo die Verhältnisse bei hydrothermaler Behandlung von Portlandzement und dessen Bestandteile erörtert werden. Der Bericht ist wie folgt eingeteilt: hydrothermale Synthese von hydratisierten Kalziumsilikaten, hydrothermale Reaktionen der wasserfreien Kalziumsilikate, Zusammenfassung über Kalziumhydrosilikate, hydrothermale Synthese von Kalziumhydroaluminaten, hydrothermale Veränderungen von Tetrakalziumaluminatferrit und Bikalziumferrit, sowie zum Abschluss hydrothermale Behandlung von Portlandzement und Beton (Einfluss auf Festigkeit und andere physikalische Eigenschaften sowie auf Beständigkeit gegenüber Einwirkung von Sulfaten).

Die *Erörterung* (S. 268—269) des Berichts von Prof. THORVALDSON enthält Beiträge von Dr. L. FORSÉN und vom *Verfasser.*

Der Bericht von Prof. P. SCHLÄPFER »Einwirkung von Wasser auf Portlandzement», (S. 270—284), deckt formell das ganze Gebiet, das in seinen Einzelheiten von BESSEY, JONES, THORVALDSON und FORSÉN behandelt wurde. Dieser Bericht ist in der Hauptsache als eine Übersicht gehalten. Nach der Einleitung wird erst die Einwirkung des Wassers auf die einzelnen Klinkerbestandteile besprochen. Dazu gehören Kalziumsilikate (u. a. die Bedeutung der Wassermenge, Temperatur und Korngrösse), ferner Kalziumaluminate und Tetrakalziumaluminatferrit (»Brownmillerit»). Sodann wird darüber berichtet, wie man die Einwirkung des Wassers auf Portlandzement als Gesamterscheinung deuten soll.

Die *Erörterung* (S. 285—297) des Berichts von Prof. SCHLÄPFER umfasst die Beiträge von Herrn G. E. BESSEY, Dr. G. HAEGERMANN und vom *Verfasser.*

Der Bericht von Dr. L. FORSÉN, (S. 298—363), »Die Chemie der Abbindeverzögerer und der Abbindebeschleuniger» behandelt zunächst denjenigen Abschnitt der Hydratisierungschemie des Portlandzements, der in der Technik als Regelung der Abbindezeit bezeichnet wird, der aber auch den chemischen Mechanismus der Reaktion zwischen Zement und Wasser sowie den Einfluss der beschleunigenden, verzögernden und zerstörenden Stoffe auf den Abbindungsverlauf berührt. Nach einer Übersicht über die früheren Arbeiten berichtet der Verfasser über eine Reihe neuer, von ihm ausgeführten Untersuchungen. Diese beziehen sich einerseits auf Bestandteile (Untersuchungsverfahren, Verhalten der Bestandteile im Wasser, Versuche mit Aluminatbestandteilen, Versuche mit Silikatbestandteilen), teils auf den

Zement selbst (Abbindezeit verschiedener Zemente, Zusammensetzung der Wasserphase des Mörtels, Gipsbindung während der Erhärtung des Zements, Wärmeentwicklung und Wasserbindung, Einfluss auf die Abbindezeit und Festigkeit des Portlandzements und der Hochofenschlacken, Einfluss von Humus, Fällungen). Die ausführlichen Versuchsunterlagen sind in einer besonderen Beilage mit 66 Zahlentafeln zusammengestellt.

Die *Erörterung* des Berichts von Dr. FORSÉN (S. 364—394) umfasst Beiträge von Herrn C. PONTOPIDDAN, Dr. R. H. BOGUE, Dr. A. EIGER, Dr. F. M. LEA, Herrn G. E. BESSEY, Herrn P. S. ROLLER, Prof. A. TRAVERS und vom *Verfasser.*

Alle Berichte, die die Hydratisierung des Zements und die dabei gebildeten Verbindungen behandeln (Berichte von Herrn BESSEY, Herrn JONES, Prof. THORVALDSON, Prof. SCHLÄPFER und Dr. FORSÉN) greifen aus natürlichen Gründen auch etwas ineinander, so dass ihre Gebiete sich zuweilen überschneiden. Daher ist besonders zu beachten, dass die dazugehörigen Erörterungen weitere Gültigkeit haben als für den jeweiligen Bericht, dem sie von der Schriftleitung zugeordnet wurden.

Das Programm des dritten und letzten Tages war etwas mehr gemischt. Es umfasste Aluminatzement, Puzzolanerden und die physikalische Struktur des erhärteten Zements. Der erste Bericht von Dr. N. SUNDIUS über »Mineralgehalt des Aluminatzements« (S. 395—421) beschäftigte sich mit der Zusammensetzung des Aluminatzements. Der Bericht umfasst: chemische Zusammensetzung des Aluminatzements, Allgemeines über Mineralien im Aluminatzement, Mineralgehalt 4 besonders untersuchten Aluminatzementprobe, Röntgenversuche und Kristallisationsverlauf beim Aluminatzement.

Die *Erörterung* des Berichts von Dr. SUNDIUS (S. 422—440) umfasst Beiträge von Dr. B. TAVASCI (ein ausführlicher Beitrag unter dem Titel »Eisenhaltiges Schmelzzement«), Dr. F. M. LEA, Prof. A. TRAVERS und vom *Verfasser.*

Der nächste Bericht von Dr. G. ASSARSSON über »Reaktionen zwischen Aluminatzement und Wasser«, (S. 441—458), behandelt die Hydratisierungserhältnisse bei diesem Zement. Der Bericht ist in folgende Abschnitte eingeteilt; frühere Untersuchungen (Hydratisierung reiner Kalziumaluminate, Kalziumferrite, Bikalziumsilikat, Gehlenit, Hydratisierung von Aluminatzement), Zusammenfassung der Ergebnisse früherer Untersuchungen (die wasserfreien Kalziumaluminate, Bikalziumsilikat, Bikalziumferrit, Gehlenit, Zement mit hohem Aluminiumgehalt) und den chemischen Charakter der Hydratisierungsreaktionen.

Die *Erörterung* (S. 459) des Berichts von Dr. ASSARSSON enthält die Beiträge von Dr. F. M. LEA und dem *Verfasser.*

»Chemie der Puzzolanerden», (S. 460—490), ist ein Bericht von Dr. F. M. LEA betitelt, der eine Übersicht über die verschiedenartigen, nunmehr immer zahlreichere Puzzolanstoffe enthält. Er ist in folgende Abschnitte eingeteilt: Begriffsbestimmung und Klassifizierung, Zusammensetzung der Puzzolanstoffe (natürliche Puzzolanerden, gebrannte Tonerden und Schiefer), Reaktionen zwischen Puzzolanstoffen und Kalk, die Bedeutung der Puzzolanstoffe für die Fähigkeit des Zementmörtels chemischen Angriffen zu widerstehen, chemische Untersuchung der Puzzolanstoffe, Bestimmung des freien Kalziumhydroxids in Puzzolanmischungen (von G. E. BESSEY).

Die *Erörterung* (S. 491—504) des Berichts von Dr. LEA umfasst Beiträge von Herrn P. S. HÅKANSON, Dr. L. FORSÉN, Herrn C. D. CRICHTON, Dr. W. BÜSSEM, Prof. T. THORVALDSON, Prof. A. TRAVERS und vom *Verfasser.*

Der letzte Bericht der Tagung war von Herrn S. GIERTZ-HEDSTRÖM ausgearbeitet. Er ist betitelt »Die physikalische Struktur des hydratisierten Zements» (S. 505—533) und bildet gewissermassen ein Bindeglied zwischen der reinen Zementchemie und der Betontechnik. Die Unterabteilungen sind wie folgt: Hydratisierungsverlauf und Entwicklung des Aufbaues, Volumenverhältnisse und Reaktionsgeschwindigkeiten, Verfahren für die Untersuchung des physikalischen Aufbaues des erhärteten Zements, Theorien über den physikalischen Aufbau des Zements, Faktoren, die auf den physikalischen Aufbau einwirken, und Beziehungen zwischen dem physikalischen Aufbau des Zements und dessen technischen Eigenschaften.

Die *Erörterung* (S. 534—541) zum Bericht von Herrn GIERTZ-HEDSTRÖM umfasst die Beitrage von Prof. P. SCHLÄPFER, Dr. F. M. LEA, Dr. A. EIGER, Herrn D. G. R. BONNELL und vom *Verfasser.*

Jeder Vortrag und Bericht ist mit seiner besonderen Literaturübersicht versehen. Ausserdem wird man am Ende dieses Gesamtberichtes ein *Namenverzeichnis* und ein *Sachverzeichnis* finden, die für das gesamte Werk gelten.

Auf der Tagung wurde das Gedächtnis des Wegbereiters der Zementforschung, des grossen französischen Gelehrten HENRY LE CHATELIER gefeiert, und zwar durch eine Rede von Dr. R. H. BOGUE und durch eine von der Tagung an die Universität Paris gerichtete *Gedächtnisadresse,* siehe S. 542 und S. 543.

Während der Tagung wurde eine allgemeine *Mitteilung* über den Internationalen Unterausschuss für Sonderzement für grosse Talsperren gemacht. Dabei sprachen Herr B. HELLSTRÖM, Herr A. EKWALL, Dr. F. M. LEA, Dr. R. H. BOGUE und Prof. W. EITEL. Kurze Auszüge aus diesen Ansprachen sind auf S. 544 und 545 wiedergegeben.

NAME INDEX

The Index covers pages 1—545 with the exception of List of Invited and Participants on pages 8—10. References to Bibliographies are printed in *italics*.

SUBJECT INDEX

The Index covers pages 13—545. References to subjects dealt with at some length are printed in *italics*.

As the nature of the present publication would make it impracticable to draw up a complete set of references to all subject-matters, the Index has on the whole been restricted to comprise references to individual chemical compounds, to which a limited number of systematical references has been added. — *See also the detailed Contents!*