

Proceedings of the First
International Symposium
on the Chemistry of Cement,
London 1918.

TRANSACTIONS
OF THE
FARADY SOCIETY

Volume: XIV
1918

Proceedings on the First International
Symposium on the Chemistry of Cement
London 1918

Reprint Published By
Butterworths Scientific Publications Ltd.
London 1949

CONTENTS

	<u>Page</u>
The Setting of Cement and Plasters. - A General Discussion:	
The Mechanism of the Setting Process in Plaster and Cement. By C.H. DESCH	1
Crystalloids against Colloids in the Theo- ry of Cements By H. LE CHATELIER	8
The Agglomeration of Granular Masses. By F.G. DONNAN	12
The Constitution and Hydration of Portland Cement. By A.A. KLEIN	14
The Setting and Hardening of Portland Ce- ment. By G.A. RANKIN	23
Is the Setting of Cement mainly a Physical or a Chemical Process? By J.G.A. RHODIN	29
Ancient and Modern Mortar. By W.J. DIBDIN..	31
The Effect of the Addition of Suitable Slag on the Setting Properties of Portland Cement. By E. DENY / E.H. LEWIS	36
The Setting of Cement in its Relation to Engineering Structures. By B. BLOUNT ..	41
The Effect of the Addition of Slag to Port- land Cement. By P.C.H. WEST	44
Discussion: W.D. Caroe, A. Binns, W.J. Co- per, Dr. T.M. Lowry, F.C. Hemmings, Dr. W. Rosenhain, E. Hatschek, Dr. H. Borns, S. Rordam, A.C. Davis, T. Hattori, D.B. Butler, E. Deny, E.H. Lewis, Dr. H.C. Desch	46

*The Faraday Society is not responsible for opinions expressed before it by
Authors or Speakers.*

Transactions OF The Faraday Society.

FOUNDED 1903.

TO PROMOTE THE STUDY OF ELECTROCHEMISTRY, ELECTROMETALLURGY,
CHEMICAL PHYSICS, METALLOGRAPHY, AND KINDRED SUBJECTS.

VOL. XIV.

JANUARY, 1919.

PARTS I AND 2.

THE SETTING OF CEMENTS AND PLASTERS.

A GENERAL DISCUSSION.

At the meeting of the Faraday Society held on Monday, January 14, 1918, in the House of the Royal Society of Arts, John Street, Adelphi, London, W.C., a General Discussion took place on **The Setting of Cements and Plasters.**

Mr. James Swinburne, F.R.S., Past-President, was in the Chair, and he introduced the proceedings with the following remarks:—

I may say that the Faraday Society had intended to inaugurate a research into the question of cements and setting generally, realizing its great importance, but there has been great difficulty in this owing to the war, and the Council have considered the best thing they can do is to have a discussion such as we are going to have this evening. The Council have been exceedingly fortunate in getting so very many exceedingly able men to read papers and join in the discussion. I will not take up your time by talking myself, but I will call at once on Dr. Desch to read the first paper.

THE MECHANISM OF THE SETTING PROCESS IN PLASTER AND CEMENT.

By CECIL H. DESCH, D.Sc., Ph.D. (University of Glasgow).

Although the use of calcareous cements dates from a very early period of human history, and has attained to so high a development in modern

times as to have given rise to an industry of the greatest importance, our knowledge of the scientific nature of the materials and processes involved is even yet imperfect, in spite of many excellent investigations covering various parts of the subject. It is convenient, in a review of our present knowledge, to distinguish between the plasters and simple chemical cements, such as the magnesia cements on the one hand, and the lime mortars, Roman and Portland cements, and similar products, on the other. The chemistry of the substances of the first group is now fairly well known, although the plasters manufactured from gypsum have proved to be unexpectedly complex, and there is little doubt that a correct explanation of the principal features of the setting process has been given. The case is different when we turn to the second group. It is only very recently that definite information as to the chemical constituents of Portland cement clinker has been obtained, and even now some points remain in dispute, whilst two distinct explanations of the setting process have been given, and the evidence in favour of either is by no means conclusive. In the present paper an attempt is made to examine these hypotheses and the evidence adduced in their support, and to indicate the nature of the observed discrepancies. The plasters are first considered, on account of their relative simplicity. A short section then follows on the magnesia and similar cements, and the third section is devoted to the setting of lime mortars and the complex cements.

I. Plaster of Paris and Gypsum Cements.

It was shown by Lavoisier in 1765 (1) that the setting of plaster of Paris was essentially a process of recombination of the dehydrated gypsum with the water of which it had been deprived in the process of "burning," and that the strength of the mass after setting was the result of the formation of a confused mass of interlacing crystals. The mechanism of the process was not explained until 1887, when Professor H. le Chatelier (2) showed that the hemihydrate, $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$, readily dissolves in water, forming an unstable solution which is supersaturated in respect to the dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Any particles of the latter salt which may be present, probably in the form of unburnt particles of the original gypsum, act as nuclei, and set up crystallization of the stable dihydrate. It is characteristic of crystals separating from strongly supersaturated solutions that they tend to grow in radial fashion about the nucleus. When the nuclei are sufficiently near to one another, the radiating needles of neighbouring groups interlock, and a mass possessing considerable mechanical strength is obtained, which can only be broken across by breaking the individual crystals. That such a supersaturated solution is actually formed is not only proved by microscopical examination, but was shown by an experiment due to Marignac (3), who shook ground plaster of Paris with water and filtered after a short interval. The filtrate was five times as concentrated as a saturated solution of gypsum at the same temperature, but it soon became turbid and deposited crystals of the dihydrate. In the ordinary setting of plaster the quantity of water is so small as to be capable of dissolving only a minute fraction of the calcium sulphate, but it is sufficient to form a layer of supersaturated solution around each particle of the hemihydrate, and when this layer deposits its excess of dihydrate the remaining water is available for the solution of a further quantity.

It is certain that the above statement corresponds closely with the

main facts of the setting of plaster of Paris of the composition $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$, as prepared by any of the usual technical methods. So far as the writer is aware, only one attempt has been made to explain the setting of plaster as a colloidal process. Rohland (4) has suggested that the water is taken into solution in the salt in a colloidal form, and has extended the same explanation to the caking of other salts when powdered and moistened, but the statement is not supported by evidence, and has not been accepted by others.

There are, however, certain facts which indicate that the setting process is not quite simple. It was observed by Cloez (5) that the heat evolved during the setting appears at two different stages, the initial rise of temperature on mixing plaster with water being followed by a stationary period and then again by a rise of temperature. Moreover, the density of the hydrated plaster is different from that which might be expected from the known properties of calcium sulphate and its hydrates. The hemihydrate has a density of 2.75 and the dihydrate of 2.32, and a calculation shows that the latter compound is formed from its components with a contraction of 7 per cent., whilst in practice an expansion is observed, and it is in fact on account of this property that plaster of Paris finds its application in the making of casts, the expansion enabling it to fill the mould completely, and therefore to take an impression sharply. The setting is found to be accompanied by a contraction, followed by a smaller expansion. The experiments of Davis (6) led him to the conclusion that the crystals of the dihydrate which at first separate are not identical with gypsum, but consist of a second, rhombic modification, which subsequently passes into the stable form. It may also be remarked that a part at least of the expansion is only apparent, and is due to the thrusting apart of the growing crystals, producing a porous mass. This effect is common in the growth of crystals from a supersaturated solution, and its existence is obvious from the familiar porosity of a mass of hardened plaster.

The setting of the various kinds of flooring plaster, consisting largely of soluble anhydrite, is in all probability of a quite similar character, and differs from that of plaster of Paris only in regard to velocity. The addition of other salts may also bring about great changes in the rate of hydration and crystallization of calcium sulphate, potassium sulphate, for instance, accelerating the process, and borax retarding it. Rohland has shown (7) that the accelerators are substances which increase the solubility of gypsum, and the retarders are those which diminish the solubility. Colloidal substances may delay the setting considerably, and these facts are made use of in the preparation of many technical plasters.

II. *Substances the Setting of which resembles that of Plaster.*

It was also shown by le Chatelier that other substances which are capable of forming unstable supersaturated solutions will set in the same manner as plaster of Paris. Thus, anhydrous sodium sulphate dissolves readily in water, and if precautions are taken to prevent too rapid solution and consequent rise of temperature, a highly concentrated solution may be prepared at practically constant temperature. This solution is unstable, and the hydrate separates in characteristic interlocking masses of crystals.

Various cements composed of a mixture of an insoluble metallic oxide and a solution of the chloride or some similar salt of the same metal are

in technical use. For example, a mixture of zinc oxide with a concentrated solution of zinc chloride yields a strongly supersaturated solution, from which the oxychloride slowly crystallizes. Magnesium oxychloride, prepared in a similar manner, forms the basis of many cements, and may be assumed to set by a process of crystallization, although Kallauner (8) considers that the ease with which the chloride is extracted from the solid mass by means of alcohol, and the fact that the free magnesia in the mixture cannot be completely converted into carbonate by carbon dioxide, point to the formation of a solid solution of hydroxide and chloride rather than of a definite oxychloride. A microscopical study of the setting process does not appear to have been made, although it would have some interest in relation to the problem of the dental cements, some of which have an analogous constitution.

Barium metasilicate is another salt which forms supersaturated solutions and is capable of setting when mixed with a small proportion of water. The product is the crystalline hydrated salt $\text{BaSiO}_3 \cdot 6\text{H}_2\text{O}$. The orthosilicate undergoes hydrolysis, forming the hydrated metasilicate, $\text{Ba}_2\text{SiO}_4 + 15\text{H}_2\text{O} = \text{BaSiO}_3 \cdot 6\text{H}_2\text{O} + \text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$. Owing to the comparatively great solubility of the silicate, the setting resembles that of plaster, and the mechanical strength of the product is not comparable with that of a hydraulic cement, although in the case of the orthosilicate the chemical reaction is quite similar to that which constitutes the principal part of the hydration of a Portland cement. The product is crystalline, and consists of interlocking bunches of needles.

III. Lime Mortar and Cements of the Portland Class.

The hardening of a simple lime mortar, composed only of slaked lime and sand with water, is a mere process of desiccation. The calcium hydroxide forms an apparently structureless mass, which may be either colloidal or minutely crystalline, and the cohesion of this mass furnishes the necessary strength. The sand merely prevents the cracking which would otherwise take place during the contraction on drying, by subdividing the lime into thin layers. As time goes on, the calcium hydroxide may recrystallize to a certain extent, whilst those portions of the mass which come into contact with the atmosphere may be converted into the crystalline carbonate, but neither of these changes is essential to the hardening of the cement. There is no chemical reaction between the lime and the sand. On the other hand, when pozzolanic substances are added to the mortar, such as the volcanic earths of the Mediterranean which were used by the Greeks and Romans, the trass and ground tiles which were employed by the Romans in more northern regions, or the burnt brick and ballast added to this day in India, a chemical reaction takes place between the lime and the active or soluble silica which is the essential constituent of all pozzolanic materials, and calcium metasilicate is formed.

Portland cement is a more complex material. The constitution of the clinker has been established by the brilliant investigations of the Geophysical Laboratory staff at Washington. The compounds which are or may be present are tricalcium silicate, $3\text{CaO} \cdot \text{SiO}_2$; calcium orthosilicate, $2\text{CaO} \cdot \text{SiO}_2$; tricalcium aluminate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$; pentacalcium trialuminate, $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$; and free lime, CaO (9). Campbell has recently given reasons for believing (10) that tricalcium aluminate is rather to be regarded as a solid solution of lime in the pentacalcium

trialuminate, but this does not materially affect the present problem. Not more than three of the above-mentioned compounds can be simultaneously present in the clinker in a state of equilibrium, but since the components do not reach the temperature of fusion during the process of manufacture, it is actually possible for small quantities of one or more additional constituents to occur in commercial clinker. It does not appear, however, that clinker made in a rotary kiln departs very widely from the state of equilibrium.

An examination of the ternary equilibrium diagram shows that the clinker will contain a ternary eutectic, there being two such eutectics within the usual range of the composition of clinker. The microscopical examination of transparent sections of clinker does not reveal the presence of any eutectic, but this is simply due to the minuteness of the structure, much overlapping occurring even within the thickness of a thin section. When, however, the specimen is polished on one surface only and lightly etched, as in the examination of metals, the eutectic structure is clearly revealed. The writer has published one such photograph (11) and Mr. T. Hattori, working in the writer's laboratory, has since obtained very beautiful eutectic structures in Japanese clinker. The calcium aluminate which is chiefly present as a constituent of this eutectic is consequently in a finely divided form, and therefore in a condition to react readily with water.

According to the explanation of the setting process put forward by le Chatelier in 1887, the ground cement reacts with water in such a way that the silicates and aluminates are hydrolysed, the stable compounds being the hydrated metasilicate, $\text{CaSiO}_3 \cdot 2.5\text{H}_2\text{O}$, and a hydrated tetra-calcium aluminate, $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$, the excess of lime liberated by the hydrolysis forming calcium hydroxide. Microscopical examination of the reactions of the constituents with water led to the conclusion that the process was strictly analogous with that of the setting of plaster, an unstable supersaturated solution of the basic silicate, for example, being formed initially, followed by rapid crystallization of the stable phase in the form of radiating needles. In reference to this, it should be remarked that the process is largely dependent on the ratio between solid and water, and that in hydration experiments on a microscope slide the quantity of water used is relatively much larger than in the gauging of cement in practice, and that this fact probably accounts for certain discrepancies recorded by different observers.

The alternative hypothesis was proposed by W. Michaëlis in 1893 (12), and expanded in a later paper (13). On this view, whilst the chemical reactions assumed are those which were shown to take place by le Chatelier, the physical conditions are supposed to be different. The hydrated metasilicate is considered to form, not a mass of radiating crystals, but a gelatinous mass or gel, the gradual dehydration of which brings about the hardening of the cement with time. The aluminate crystallizes much more readily than the silicate; but even this is regarded as forming a gel when the solution is sufficiently supersaturated—that is, when the quantity of water is small, as is the case in the practical utilization of cement. The presence of gelatinous material at an early stage of the setting process is readily observed. It has been photographed by Stern (14), and the increase of size of the cement particles by absorption of water and consequent swelling of the gelatinous sheath which forms around them has been described by Ambronn (15) and may be readily confirmed. According to Colony (16), a reaction subsequently

takes place between this early gelatinous material and the remaining constituents of the cement, and a secondary amorphous product is formed, the desiccation of which is the cause of the hardening. At a later stage, crystals of calcium hydroxide, calcite, and zeolites make their appearance (17).

An attempt to distinguish between the various possible colloidal products has been made by Keisermann (18), using the method of staining with organic dyes. The results indicate that the gelatinous sheath consists of calcium metasilicates, which compound also occurs in the form of small needles, whilst the calcium hydroxide and aluminate assume the crystalline form. These staining results with colloids depend largely on the concentrations of the substances concerned, and the writer, possibly not working under precisely similar conditions, has not succeeded in confirming all of Keisermann's results. The dependence of the observations on the size of grain has been pointed out by Wetzel (19). Other experiments in which stains were used led Blumenthal to the conclusion (20) that the metasilicate and aluminate were first formed in a crystalline condition, so that the cement set like plaster, but that a colloidal gelatinous silicate was subsequently formed, and strengthened the mass by binding the crystals together and filling the pores.

The process of setting of the individual constituents, as well as of commercial clinker and artificial mixtures, has been examined in great detail in the laboratories of the U.S. Bureau of Standards (21, 22). The staining method has been applied as a means of identification, and the hydration has been followed under various conditions of temperature and proportion of water. The general conclusion is that the initial set is due to the hydration of the aluminates, and that the only stable hydrated aluminate is the tricalcium salt, the water content of which is variable. Either the 5:3 compound or monocalcium aluminate, if present, undergoes hydrolysis, and the tricalcium salt is formed together with free alumina, the latter separating in a colloidal hydrated form. In presence of an excess of water, the product may be crystalline, as in le Chatelier's original experiments, but with a restricted supply of water an impervious layer of the amorphous material may be formed, retarding the further action of water. The silicates are hydrated much more slowly, the products being calcium hydroxide and an amorphous jelly of hydrated silicate. The hydroxide may be crystalline or amorphous, according to the concentration and to the rate of hydration. The hydrolysis of the silicates is even considered to proceed so far that gelatinous silica is liberated (23). The subsequent conversion of a part of the gelatinous mass into crystals is considered to result rather in a loss than in a gain of strength.

It would appear that conclusions based on the examination of mixtures of ground material with water on a microscope slide must not be applied indiscriminately to the conditions of actual practice. The ratio of water to salts is of the utmost importance in determining the nature of the products, although the chemical reactions may be the same in both cases. An attempt has been made by Von Weimarn (24) to show that the passage from the colloidal to the crystalline condition is a continuous one, and that the difference consists only in a difference of size of the particles. This may be accepted in the sense of considering colloidal materials as being in such a fine state of division that the surface forces are comparable in their effect with those which depend on mass. It is then not difficult to understand that the degree of supersaturation of the solution may

determine whether the product which separates shall have a definite crystalline form or shall be, in the ordinary sense, amorphous. The real nature of the colloidal condition has been unnecessarily obscured by the barbarous terminology which has been adopted by so many writers on the chemistry of colloids, and especially by the school of Wo. Ostwald. Stripped of these uncouth technical terms, the study of colloids appears far less formidable, and it is to be hoped that the present discussion may, by putting in relief the views of the supporters of the two rival hypotheses as to the setting and hardening of cement, lead to a recognition of the true facts of the case, and to an elimination from the subject of the complications which owe their origin largely to a defective terminology.

A final reference should be made to the action of catalysts on the process of setting. Whilst many observations on this point are on record, the subject has not been sufficiently investigated, and affords a promising field for research. The remarkable changes in the velocity of setting which take place spontaneously in commercial ground cements, even when stored out of contact with air, are of great technical importance, and no satisfactory explanation of them has yet been given.

REFERENCES.

1. LAVOISIER : *Œuvres compl.*, iii, 122.
2. LE CHATELIER : Thèse de doctorat, 1887; *Recherches expérimentales sur la Constitution des Mortiers hydrauliques*, Paris, 1904.
3. C. MARIGNAC : *Arch. sci. phys. nat.*, Geneva, 1873, 48, 120.
4. P. ROHLAND : *Kolloid. Zeitsch.*, 1913, 13, 61.
5. C. CLOEZ, *Bull. Soc. Chim.*, 1903, [iii], 29, 171.
6. W. A. DAVIS : *J. Soc. Chem. Ind.*, 1907, 26, 727.
7. *Zeitsch. Elektrochem.*, 1908, 14, 421.
8. O. KALLAUNER : *Chem. Zeit.*, 1909, 33, 871.
9. G. A. RANKIN and F. E. WRIGHT : *Amer. J. Sci.*, 1915, [iv], 39, 1.
10. E. D. CAMPBELL : *J. Ind. Eng. Chem.*, 1917, 9, 943.
11. *The Chemistry and Testing of Cement*, London, 1911. Plate I.
12. *Chem. Zeit.*, 1893, 17, 982.
13. *Der Erhärtungsprozess der kalkhaltigen hydraulischen Bindemittel*, Dresden, 1909.
14. E. STERN : *Zeitsch. anorg. Chem.*, 1909, 63, 160.
15. H. AMBRONN : *Tonind. Zeit.*, 1909, 33, 270.
16. R. J. COLONY : *School Mines Quart.*, 1914, 36, 1.
17. *Ibid.*, also M. VON GLASENAPP, *Chem. Zeit.*, 1914, 38, 588.
18. S. KEISERMANN : *Der Portlandzement, seine Hydratbildung und Konstitution*, Dresden, 1910.
19. *Zentr. hydraul. Zemente*, 1911, 2, 34.
20. F. BLUMENTHAL : *Dissert.*, Jena, 1912; *Silikat Zeitsch.*, 1914, 2, 43.
21. A. A. KLEIN and A. J. PHILLIPS, *U.S. Bureau Stand., Technol. Paper* 43 (1914).
22. P. H. BATES and A. A. KLEIN, *ibid.*, No. 78 (1916).
23. See also G. A. RANKIN : *J. Franklin Inst.*, 1916, 747.
24. P. P. VON WEIMARN : *Zur Lehre von den Zuständen der Materie*, 2 vols., Dresden, 1914.

CRYSTALLOIDS AGAINST COLLOIDS IN THE THEORY OF CEMENTS.

Professor Henry le Chatelier (Paris) sent in a contribution to the Discussion entitled "Crystalloids against Colloids in the Theory of Cements," which was read by Dr. H. Borns.

I have always opposed the theory which attributes the hardening of cements to certain colloidal properties of the material, as being devoid of sense. In a similar way it used to be said that bodies react because they have affinity for each other. Henri Sainte-Claire Deville maliciously remarked that, since affinity was by definition the tendency of bodies to react with each other, that explanation of chemical reactions came down to this: the bodies react because they have the tendency to react. The actual explanation of the hardening of cements is of an analogous kind, I am afraid. People evade defining what they call a colloid, but they seem to take the word in the sense of a body capable of hardening. And then the explanation comes down to this: cements harden because they have the property of hardening. Similar tautologies would easily be avoided if the excellent principle of Pascal were more frequently applied: "Before you announce a statement, begin always by replacing mentally each word by its definition."

After this general remark let us approach the problem more closely. Begin by defining the word "colloid," if that be possible. Graham, the originator of the discovery of the bodies which are thus designated, had recognized the existence of two sorts of different solutions. The one kind gave on evaporation crystallized bodies called *crystalloids* (sea-salt, sugar, etc.), the other gave amorphous gelatinous materials called *colloids* (gelatinous silica, gum, etc.). He further recognized that the crystalloids are diffused when dissolving and that the colloids are not.

More recently Zsigmondy showed with the aid of the ultramicroscope that the colloidal solutions were not true solutions, but merely suspensions of very finely divided, rigorously insoluble matter. These suspensions are opaque, milky, or transparent, according to the fineness and the abundance of the particles so suspended in the liquid. When their diameter is inferior to the wave-length of light, they allow the light to wend its way through, somewhat as happens in the case of sound with screens of a limited size. The diameter of the true colloids approaches a millionth of a millimetre, and is always much less than a thousandth of 1 mm.

All very minute insoluble bodies give such colloidal suspensions: metals like platinum and silver when pulverized by the electric arc; finely crushed minerals like quartz, alumina, kaolin; completely insoluble chemical precipitates like the sulphides, notably nickel sulphide; or finally the iron tannate used in the manufacture of ink.

But, is there cause to give a particular name to bodies, the only singular

properties—terribly commonplace properties—of which so far are insolubility and fineness?

These very minute bodies possess one quite special and very important property, however, which entitles them to being classed separately, that is the property of absorbing (by snobbery one prefers to speak of *adsorbing* nowadays) the soluble bodies which are held in solution by the liquid with which they are wetted. This absorption, which is frequent with chemical precipitates, is a very grave source of error in analyses. It is true that this property does not strictly characterize finely divided bodies; it manifests itself in identically the same way in porous bodies. Blood carbon, a true colloid, and wood charcoal behave in the same way. From this point of view, colloids and porous bodies must be classed together.

This absorptive power is a particular case of much more general properties which all very fine bodies possess. Chemically a body in the form of an impalpable powder behaves quite differently from the same body in the form of big lumps. There is a special chemistry of colloids and porous bodies. These particular properties are under the immediate sway of surface tension.

The fact has long since been acknowledged that all chemical phenomena depend directly upon diverse forms of energy: heat, electricity, work. The chemical reactions of combustibles liberate heat; the reactions of batteries generate electricity; the reactions of explosives, work. Reciprocally the forces of energy—temperature, electromotive force, pressure—define equilibrium conditions and suppress or attenuate at the same time passive resistances which oppose the reactions, tending to bring the bodies back to the state of equilibrium. The whole of chemistry is only a chapter of energetics.

There is, however, one form of energy of which chemistry does not speak as a rule, that is the surface energy which is measured by the product of the surface tension (or capillary tension) and of the free surface of the body. In magnitude surface tension is generally infinitely small when compared with the other forms of energy. Take the gram-molecule of water, 18 grams, and assume it to have the form of a sphere whose diameter will be 3.3 cm. In contact with its water vapour the sphere will have a surface tension of 0.08 grams per linear centimetre. The surface of the sphere being 34 sq. cm., its surface energy will be $0.08 \times 34 = 2.72$ gram-cm., or 2.72×10^{-3} kg. m., which corresponds to 6.3×10^{-8} kg. calorie. Now the vaporization of a gram-molecule of water absorbs 10 calories, and its combination with lime liberates 10 calories. Its surface energy is therefore only equivalent to the one hundred-millionth part of that quantity of heat, that is to say, absolutely negligible.

If instead of taking the water in the form of a single sphere we divided it into a vast number of little globules, each of one-millionth of 1 mm., their surfaces and consequently their total superficial energy would become 330 million times greater, and thus equivalent to 2 calories; that is to say, the surface energy would be of the order of magnitude of the quantity of heat which water evolves in its various chemical reactions. The surface energy in that case would no longer be a negligible factor.

As regards solids in suspension in a liquid, there is no direct method for measuring the surface tension at the contact between the solid and liquid. Certain indirect considerations lead us to admit, however, that this tension may become a hundred times greater than that of water. The superficial energy will be increased in the same ratio and its influence will become appreciable for dimensions of the order of a ten-thousandth millimetre—dimensions much superior to those of chemical precipitates.

So far our considerations concern solely the grain size without paying

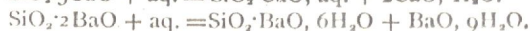
attention to the greater or smaller solubility of the bodies in question. These considerations, however, furnish an immediate explanation of the usual insolubility of the colloids. A solid crystal ground down to very fine grains will certainly have all the properties of colloids, as long as it retains its fineness; but it will rapidly lose the latter, as soon as it is brought in contact with a liquid capable of partially dissolving the substance. The energy of dissolution will be increased by the whole superficial energy of the crystal; there will result an increase in the solubility of the fine crystals, and a super-saturated solution will be produced, from which larger crystals will soon be separated. This fact has very clearly been verified for very fine precipitates of calcium oxalate and barium sulphate. In order to make these precipitates coarser, and thus to prevent them from passing through the filters, such precipitates are kept hot for several hours before filtration.

Every soluble body, even if existing in very fine division, progressively loses its colloidal properties when it is maintained in contact with a liquid in which it is somewhat soluble; its transformation will be all the more rapid, the greater the solubility. It is only insoluble bodies, therefore, which can preserve the extreme state of subdivision which corresponds to the colloidal state. For the same reason, bodies which are properly called colloids never show any discernible crystalline form, because the crystalline orientation supposes a certain mobility of the material within the solvent, be it liquid or gaseous.

We come to the hydraulic mortars. Are the products of their hardening colloidal or are they not? Let us first take the case of plaster. When plaster has set, we can never discern any crystals in the material, even under the strongest magnification of the microscope. That does not prove that no crystals are formed; perhaps they are too small to be recognized. In petrographic specimens, plates less than 0.02 mm. in thickness, one can hardly distinguish crystals less than 0.005 mm. in diameter. By crushing the soft mass under the cover-glass we cannot get below 0.0005 mm. We are thus yet far away from colloidal dimensions. When the humid hydrated plaster is left to itself, crystals begin to become discernible at the end of several weeks; after several years they are sometimes visible to the naked eye. One can see them plainly, in the south of Algeria, on the roots of dead trees which have been transformed into gypsum. We can, moreover, make the crystals in hardening plaster visible from the beginning, when we gauge the plaster with alcoholic water (instead of pure water); the setting is then retarded and the crystals can develop better.

The calcium aluminates, which play an important part in the hardening of rapidly setting cements, are hydrated at the same rate as the plaster, and they give likewise a whitish mass in which crystals are not discernible. If, instead of gauging the aluminate with a little water, we put a few isolated grains of the aluminate into a large volume of water, we observe that the grains soon become surrounded by long crystals of hydrated aluminate, which are always easily visible under the microscope and can sometimes be seen directly by the eye.

Calcium silicate alone causes a difficulty in these considerations, and this is important, because the silicate is the essential element in the hardening of Portland cement. The microscope has never enabled us to see hydrated calcium silicate. Its crystals are certainly very minute; numerous analogies prevent us, however, from denying their existence. The hydration is exactly the same as in the case of barium silicate.



The crystals of hydrated lime are plainly visible, like those of hydrated baryta; they may attain dimensions of several mm. Crystals of barium silicate can always be seen with the aid of a lens, sometimes even with the naked eye. By virtue of analogy we may say that hydrated calcium silicate will certainly crystallize as well; but as it is much less soluble than the barium compounds, the crystals will be too minute to be discernible.

It is not impossible that, initially, the dimensions of these crystals are of colloidal order, as in the moment of formation of the precipitates of barium sulphate and calcium oxalate. I have shown, in fact, that this calcium silicate precipitate absorbs, in the moment of its formation, a certain quantity of lime which varies with the concentration of the liquid. In the course of time the dimensions of the crystals must increase considerably, as in all similar instances. The mechanical resistance does not diminish with time, quite on the contrary. Consequently the colloidal state, which was possible at the beginning, has nothing to do with the hardening of the cement.

To come to an end, I will recall the explanation of the hardening of cements which I gave thirty years ago, and which does not appear to have been weakened yet.

The anhydrous compounds of cements, not being in chemical equilibrium when in contact with water, are more soluble than the same hydrated compounds. For this reason they give rise to the formation of a supersaturated solution from which the hydrated compound may rapidly crystallize. The liquid, being no longer saturated, can redissolve more of the anhydrous compounds, and the whole mass can thus crystallize progressively by passing through a stage of transitory dissolution in a limited volume of water, which, at any given moment, cannot maintain in solution more than a small portion of the total mass of salts present. The crystals which are deposited from the supersaturated solutions always appear in the shape of extremely elongated needles, which have the tendency to group themselves in spherulites about certain centres of crystallization. The entanglement of all these crystals is the only cause of the solidity of the mass. They become welded with one another when the reciprocal orientation is suitable; they adhere by simple contact, as do all solid bodies when really resting upon one another. Finally, friction at the points of contact, even in the absence of all adhesion, suffices to produce a great strength of mechanical resistance, such as is found in all tissues and fabrics whose solidity has no other origin. The finer and the more elongated the crystals, the more numerous the points of contact, and the greater the frictional resistance. The greater the area of contact the more developed the adhesion. The progressive growth of the crystal dimensions by the mechanism which I have suggested increases the part played by adhesion while diminishing that due to friction. A material built up of very wide strips could be very solid if the strips were glued together at their contact surfaces.

THE AGGLOMERATION OF GRANULAR MASSES.

Professor F. G. Donnan, F.R.S., contributed a Paper on "The Agglomeration of Granular Masses," which in the absence of the author was communicated by the Secretary.

I desire in the following note to draw attention to the four principal factors which tend to cause the agglomeration ("caking," binding, setting) of granular masses of material. For this purpose the material must be immersed in a medium which exerts some solvent action, or the granules (crystals, etc.) must be wetted with such a medium. It is necessary, however, to point out that a very small amount, indeed almost a "molecular" layer of such solution, will suffice to cause agglomeration.

1. *Unequally distributed Stress*.—It is well known that if the solid, but not the liquid, be subjected to compressive stress, the solubility will increase. The material thus dissolved will be reprecipitated in contact with unstressed portions of the solid (i.e. unstressed or less stressed granules). In this way the granules become cemented together by the formation of crystalline "bridges" of reprecipitated material. The action of this factor in the agglomeration of granular rock masses has been discussed by le Chatelier. Gravitation suffices to produce the stress.

2. *Unequal Size of Granules*.—It is known that very small particles have a higher solubility than larger particles. The researches of Hulett on gypsum have given us a quantitative measure of this action. Consider now a mass of granules of very different sizes, with their surfaces covered with a thin layer of saturated solution. The spaces between the larger granules will be filled with the "fines." The result is that the layer of solution on a fine particle is not in equilibrium with the layer on a neighbouring large particle, so that re-solution and precipitation (re-crystallization) occur. In this way cementing bridges are formed, and the mass sets (cakes).

3. *Evidence of Unstable or Metastable Forms*.—It is known that at any given temperature and for any given solvent an unstable (metastable) crystalline form has a higher solubility than a stable, or more stable, form. Suppose now that the granular mass consists of a metastable form which is slowly changing into (or which is already partially transformed into) a more stable form. Imagine a metastable and a stable particle in contact. Re-solution occurs at the surface of the former and recrystallization at the surface of the latter, with the result that cementing is produced, just as in the previous cases. Very striking examples of this type of action may be quoted. Thus the formation of the well-known hard boiler-scale is due to the precipitation in the first instance of metastable forms of calcium carbonate or calcium sulphate,

which then change gradually into stabler forms, with resulting cementation and agglomeration. In the case of calcium sulphate we possess already an accurate knowledge of the formation of these metastable forms owing to the researches of van't Hoff and his collaborators. Another striking example is the caking of crystalline salts. Thus the tendency of ammonium nitrate to cake is a well-known phenomenon. Now ammonium nitrate is known to possess a number of different crystalline forms with corresponding transition temperatures. Suppose a mass of ammonium nitrate has been partially, but not quite completely, dried at a temperature above the first transition point. On cooling, the crystals tend to revert to the stable form, with the result that the agglomerating action discussed above comes into play. In order to prevent this we must take care to "dry" it at a temperature *below* the first transition point (which lies at about $38^{\circ}\text{C}.$).

Many other cases of a similar nature could be quoted. Thus, the setting of ordinary plaster of Paris is a well-known case in point, which has been fully discussed from this point of view by le Chatelier.

The reprecipitated (or recrystallized) material in all these cases may be so finely granular as to be practically "colloidal." Indeed, in all cases of setting the phenomena of the colloidal state must be taken into account.

4. *Sheared or "flowed" Crystal Surfaces.*—We may call this the "Beilby effect." Owing to grinding or other shearing actions the surface layers of some of the crystalline granules may have become "amorphous." Such surface layers will possess a higher solubility than the stable crystalline surfaces. Here we have another action which will tend, just as in the previous cases, to produce recrystallization and consequent agglomeration.

Quite apart from the problem of the setting of cements, the factors tending to produce agglomeration discussed in the foregoing are of the greatest importance in technical chemistry. They are not sufficiently known and understood by many of those occupied with industrial problems, so it is hoped that this necessarily brief discussion of them will awaken interest in the subject, by showing that, in the phenomena of setting and agglomeration, we have to deal with most interesting examples of the play of molecular forces, and that the operation of these forces is already fairly well understood.

UNIVERSITY COLLEGE,
January 3, 1918.

THE CONSTITUTION AND HYDRATION OF PORTLAND CEMENT.

Mr. A. A. Klein (Worcester, Mass.) sent in a paper on "The Constitution and Hydration of Portland Cement," which was read by Dr. C. H. Desch.

Portland cement may be defined as the product produced by pulverizing to a sufficient and definite fineness the clinker obtained by an incomplete fusion of a finely ground intimate mixture containing essentially lime, silica, and alumina in certain definite proportions. Iron, magnesium, sodium and potassium oxides are present almost universally in the product, although in the light of recent investigations indications are that these are not at all essential.

Constitution of Portland Cement.

The "whys and wherefores" of cements have been the subject of research and speculation for over one hundred years. Even before Joseph Aspdin took out a patent on the hydraulic lime he called Portland cement, Vicat in France had started his important investigations on the relation of the chemical composition of the stone used as a raw material to the quality of the product derived; on the nature of the constituents produced on burning; and on the chemical and physical reactions involved when limes and cements set and harden with water. Although some of his deductions were proved erroneous by later investigators, many of them are known to be true. He became aware of the fact that the hardening of cement was unlike the hardening of lime in that carbonation of the lime present in cement was not essential to its hardening. He believed likewise that in hardened mortars at least some of the lime was in combination with other oxides besides water, and regarded silica as being the most important one.

Little progress was made in cement investigation for many years after Vicat, although improvement in grinding and burning really revolutionized the product by bettering its quality and uniformity. Progress was made by "hit-and-miss" methods, since no information was forthcoming concerning the chemical reactions involved in the burning of the clinker and in the setting of the resultant cement.

This was largely due to the inadequacy of purely chemical methods as a tool of research. A turning-point was reached when Tornebohm and le Chatelier, working practically simultaneously, employed the petrographic microscope to decipher the constituents of cement clinker and set cement. They were able to identify materials of different optical properties by examining thin sections. For instance, Tornebohm

found four constituents which he called alite, belite, celite, and felite. Of these he considered alite the most hydraulic material, and responsible to a great degree, if not wholly, for the peculiar properties of cement. Neither Tornebohm nor le Chatelier were clear as to the chemical nature of the products they found, nor was Tornebohm's distinction between belite, celite, and felite very lucid. He observed that the amount of alite increased with an increasing lime content. Le Chatelier thought the compound he found which was identical with Tornebohm's alite to be a mixture of tricalcium silicate and tricalcium aluminate.

The application of the polarizing microscope proved an impetus to research on the constitution of cement, and there subsequently appeared several works and several conflicting opinions as to the nature of the minerals found, particularly alite. The reason for this is very apparent when one considers the qualitative petrographic methods used. Firstly, a thin section is practically useless in thoroughly distinguishing between these minerals. It is impossible to obtain a section much thinner than 0.03 mm. even in the most favourable material. Let us now consider that Portland cement is obtained by a process of sintering and partial fusion, that quick cooling is practised to prevent dusting of the clinker, and that the crystals of the compounds themselves formed under the most favourable conditions are very minute and poorly developed and rarely reach a few hundredths of a millimetre in length. With these facts in mind it is readily seen that in Portland cement practice the conditions for coarse crystallization is nil, and it follows that owing to the fineness of crystallization invariably there was overlapping and superimposing of crystallites above others in the thin sections, making the optical observations very indistinct.

Another point, and one which is just as important, was the application of comparatively crude optical tests resulting in the obtaining of rough data. Most of the recent methods for obtaining more accurate quantitative optical constants of artificial products by microscopic methods involve immersed grains. Let us consider that important constant, index of refraction. It is impossible with a thin section to ascertain it more accurately than one in the first decimal place, whereas with immersed grains it may be obtained at least with Portland cement minerals to within an accuracy of 0.003. When one considers the slight optical distinction between tricalcium-silicate and tricalcium-aluminate, two compounds always present in cement, it requires little imagination to see why mixtures of them should have been regarded as homogeneous.

Accordingly, then, there were in general three types of theories concerning the active principle of cement: (1) that it is a solid mutual solution of various calcium silicates and calcium aluminates to which each investigator ascribed formulæ; (2) that it is a definite lime, silica, alumina compound; and (3) that Portland cement is composed of separate silicates and aluminates some or all of which are hydraulic.

There was a time, even very recently, when the solid solution theory was most universally held. In Germany, Tornebohm, Michaëlis, and Schott, among others, came to this conclusion, likewise Glasenapp, at Riga. In the United States, Clifford Richardson* published the results of an exhaustive study, and concluded that the clinker consisted essentially of a solid solution of tricalcium aluminate in tricalcium silicate. He later, however, admitted the error of his conclusions, due, of course,

* *Cement*, 4, 276 (1903)

to the inability of older petrographic methods to decipher extremely fine crystalline products.

Of the investigations which appeared to prove the existence of a ternary compound occurring universally in cement, that of Ernest Jänecke * was the most comprehensive and scientific. The petrographic description of his supposed compound, $8\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, was very qualitative and meagre. The optical constants were not even approximately determined, so that as a basis of comparison with constituents now known to be in cement this description was useless. At any rate, investigations at the Bureau of Standards and at the Geophysical Laboratory concerning the compound $8\text{CaO}, \text{Al}_2\text{O}_3, 2\text{SiO}_2$ have invariably shown that it does not exist, and that a melt of its composition generally crystallizes as $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$.

Finally, of the investigations which led to the conclusion that cement is composed of separate silicates and aluminates, that of the Geophysical Laboratory on the binary systems $\text{CaO}-\text{SiO}_2$, $\text{CaO}-\text{Al}_2\text{O}_3$, $\text{Al}_2\text{O}_3-\text{SiO}_2$ and on the ternary system $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3$ has done most to unravel this problem. In the preliminary report on the ternary system † the constituents of the clinker were enumerated as follows:

"Portland cement clinker within the concentration limits set by Richardson when in equilibrium may exist in the following combinations depending primarily upon relatively small changes in the quantity of lime present:

I.	II.	III.	IV.	V.
CaO	$3\text{CaO} \cdot \text{SiO}_2$	$2\text{CaO} \cdot \text{SiO}_2$	$2\text{CaO} \cdot \text{SiO}_2$	$2\text{CaO} \cdot \text{SiO}_2$
$3\text{CaO} \cdot \text{SiO}_2$	$2\text{CaO} \cdot \text{SiO}_2$	$3\text{CaO} \cdot \text{Al}_2\text{O}_3$	$5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$	$2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$
$3\text{CaO} \cdot \text{Al}_2\text{O}_3$	$3\text{CaO} \cdot \text{Al}_2\text{O}_3$	$5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$	$\text{CaO} \cdot \text{Al}_2\text{O}_3$	$\text{CaO} \cdot \text{Al}_2\text{O}_3$

"Richardson's typical cement corresponds to class II." Furthermore, "If solid solutions are formed, they are very limited in extent, and are not sufficient to affect the optical properties of either silicate, the lime, or the aluminate."

Shortly after this report appeared the Bureau of Standards began an investigation of the constitution of cement, using the optical methods employed at the Geophysical Laboratory for deciphering the constituents. Raw material mixtures which gave clinkers of various diversified chemical compositions were made and studied. Many of these were outside the limits used in cement practice. Different series of clinkers were produced in which, considering MgO with CaO and Fe_2O_3 with Al_2O_3 , one oxide was approximately constant and the other two varied. ‡ Practically all the predictions of the Geophysical Laboratory were verified. Portland cement within the composition limits considered good practice was found to be a mixture of Beta $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{SiO}_2$, and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. Of the three, Beta $2\text{CaO} \cdot \text{SiO}_2$ occurs in the greatest amounts. CaO does not occur except in underburned clinker, and the presence of $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ may result from underburning or from raw material mixture low in lime and high in alumina. Class I, as given in the Geophysical Laboratory report, was never found in the cements even of highest lime content, and it was discovered that a material of such a composition must be burned at higher temperatures than could

* *Zeits. Anorg. Chem.*, 73, 200-22; 74, 428.

† *Jour. Ind. Eng. Chem.*, 3, 1-43.

‡ "Concrete-Cement Age," *C.M.S.*, January 1913, pp. 3-7.

be economically produced. Furthermore, later investigation on the hydration of cement established the undesirability of the presence of free lime in the finished product.

Class II is typical good cement. The constituents of class III were found in abnormally low-limed cements. In all cases of cements of this type "dusting of the clinker" was a serious and frequent occurrence, and oftentimes the yield of undusted clinker was very small. The setting of cements of this class was generally erratic, and the strengths below normal. Classes IV and V were never found in Portland cement.

The phenomena occurring when a mixture of class II is heated is given in a later work by Rankin.* Although his observations were made only on the pure oxides, they apply to the burning of Portland cement, except that owing to the presence of Fe_2O_3 , MgO , Na_2O , and K_2O in the latter the eutectic temperatures are noticeably lower. Rankin says: "For this purpose, let us follow the reactions which take place when a mixture whose composition is CaO 68.4 per cent., Al_2O_3 8.0 per cent., and SiO_2 23.6 per cent., is slowly heated. This mixture, made up only of the pure oxides lime, alumina, and silica, when properly burned will produce a good Portland cement. When such a mixture is heated, the first change is the evolution of the CO_2 ; the lime then unites with the other components to form the compounds $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and $2\text{CaO} \cdot \text{SiO}_2$ probably in the order named, since the former has a lower melting-point than the latter; subsequently these two compounds unite in part with more lime, and the compounds $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot \text{SiO}_2$ appear. This formation of the last two compounds, a process which goes on very slowly in mixtures of their own composition, is materially facilitated by the circumstance that in the ternary mixtures a portion of the charge has already melted and promotes reaction by acting as a flux or solvent. The temperature at which this flux first appears is $1,335^\circ \text{C}$., the eutectic temperature for the three compounds $2\text{CaO} \cdot \text{SiO}_2$, $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. As the temperature of burning gradually rises above $1,335^\circ$ the relative amount of flux increases, and the rate of formation of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot \text{SiO}_2$ increases accordingly. At a temperature somewhat above $1,335^\circ$ the compound $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ will have completely melted in the flux, and the formation of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ is complete. The substances present as crystals at this stage are $3\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $2\text{CaO} \cdot \text{SiO}_2$, and free CaO . As the temperature is raised still further the amount of flux increases and the rate of combination of $2\text{CaO} \cdot \text{SiO}_2$ to form $3\text{CaO} \cdot \text{SiO}_2$ increases. For finely-ground raw materials of the above composition a temperature of about $1,650^\circ \text{C}$. is required for burning."

The foregoing is, of course, accurate in the case of pure oxides, and Rankin notes the effect on the burning temperature of the presence of the other common oxides. As a matter of fact, investigation by the Bureau of Standards has shown that the burning temperature of the commercial product varies within wide temperature limits. It is possible to obtain a raw material mix which will give a cement passing specifications when burned at $1,250^\circ$ to $1,300^\circ$. This is accounted for, of course, by the fact that in systems involving the same components in general the greater the number of components contributing to a eutectic the lower will be the eutectic temperature. Thus, instead of the flux appearing at $1,335^\circ$, the eutectic temperature of $2\text{CaO} \cdot \text{SiO}_2$, $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ as noted by Rankin, clinkers containing $3\text{CaO} \cdot \text{SiO}_2$ have been burned at less than $1,300^\circ$. In this case the eutectic was probably

* *Journal Franklin Institute*, June 1916.

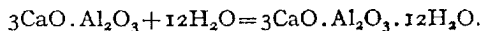
the one between the above compound as well as MgO , Fe_2O_3 , Na_2O , Na_2O , and K_2O compounds or solid solution products.

To recapitulate, the constituents of perfectly burned Portland cement are $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{SiO}_2$, and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. Alite of earlier investigators was apparently a mixture of the latter two compounds, and celite was probably $2\text{CaO} \cdot \text{SiO}_2$ or an intimate mixture of $2\text{CaO} \cdot \text{SiO}_2$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. In actual practice, free lime is usually present in small quantities, and is the constituent which must be blamed when a cement is not volume constant. The compound $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ may also be present, but its presence is not at all derogatory. Of the minor oxides a portion of the Fe_2O_3 exists in cement colouring the compound $2\text{CaO} \cdot \text{SiO}_2$, but the action between them is not entirely understood. The remainder occurs usually as a reddish nearly opaque to black opaque isotropic flux material which sometimes is reduced sufficiently enough to show magnetic properties. Magnesia has been shown by the Bureau of Standards to replace the lime in the silicates and aluminate up to a certain concentration beyond which spinel ($\text{MgO} \cdot \text{Al}_2\text{O}_3$) and monticellite ($\text{MgO} \cdot \text{CaO} \cdot \text{SiO}_2$) are formed.* It was also noted that if properly burned, cement could contain 7-8 per cent. MgO without being affected deleteriously.†

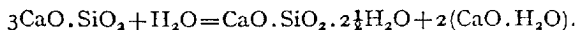
Hydration of Portland Cement.

Having investigated the constituents of cement, the Bureau of Standards undertook to study the hydration of each and every constituent for the purpose of shedding light on the chemical and physical nature of setting and hardening and the nature of the rôle that each constituent played in these processes.

The solution of this problem went hand in hand with the determination of the constitution of cement. Vicat, as has been stated previously in this paper, observed the difference between it and the setting of lime plasters. A clearer conception of the processes was obtained by le Chatelier, Richardson, and others using microscopic methods. Le Chatelier considered that the aluminate of lime in contact with water hydrated and hardened like plaster, according to the equation



To this action was ascribed the initial set of the cement. The later hardening was ascribed, however, to the decomposition of the lime silicate. In contact with water it sets so as to give hydrated monocalcic silicate crystallizing in microscopic needles and calcium hydroxide crystallizing in large hexagonal plates according to the equation



In the investigations of the Bureau of Standards the following compounds were synthesized and studied microscopically for time of hydration and for products of hydration under various conditions of temperature and pressure of the reacting water, $3\text{CaO} \cdot \text{SiO}_2$, Beta $2\text{CaO} \cdot \text{SiO}_2$, Gamma $2\text{CaO} \cdot \text{SiO}_2$, $\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, and $\text{CaO} \cdot \text{Al}_2\text{O}_3$.

* Original Communications, 8th International Congress of Applied Chemistry, v. pp. 73-81.

† "Concrete-Cement Age," *C.M.S.*, September 1914, pp. 706-10.

In addition to this, the hydration of mixtures of two and three of these as well as of cement were studied microscopically.* This work was continued, and sufficient quantities of these products were made to test the compounds and mixtures for time of set tensile strength, etc.† The results of the above investigations have clarified the action of the different cement minerals on hydration and their influence on the strength of the hardened cement. The results may be briefly enumerated.

At early periods the constituents of Portland cement of normal composition and manufacture in the order of their strength-conferring properties are: Tricalcium silicate, tricalcium aluminate, and dicalcium silicate.

With an excess of water, tricalcium aluminate hydrates as the compound $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, where x varies with the drying conditions. 5 : 3 calcium aluminate and monocalcium aluminate, on hydrating, split off amorphous hydrated alumina and form the hydrated tricalcium aluminate. Under conditions of limited water such as encountered in concrete structures, the above crystallized compound does not form immediately, but separates from solution as an amorphous material. In steam at atmospheric pressure a little crystalline aluminate is formed with the amorphous material, still more in the autoclave, and finally, on microscope slides, the hydrated tricalcium aluminate is entirely crystallized. Wherever the amorphous aluminate is formed, it slowly but eventually changes to the crystallized compound.

The hydration of the aluminates begins readily in all cases. With an excess of water the reaction progresses rapidly, and in a few days the aluminates are completely hydrated. With restricted amounts of water, however, the individual aluminate grains become coated with amorphous hydrated aluminate through which further action proceeds with more or less difficulty. Tricalcium aluminate when used alone sets too rapidly and attains too little strength to be of any commercial value as a hydraulic cementing material.

The tests in steam at atmospheric pressure showed that the weakly basic aluminates do not absorb water above 110°C ., while the more basic aluminates absorb water up to 140°C . Furthermore, a specimen of tricalcium aluminate containing high-burned free lime absorbs water even at 175°C .

The nature of the calcium hydroxide, formed by the hydration of free lime with much water, depends upon the fineness of the lime grains and the burning temperature. With coarser lime grains and with highly burned lime the hydration produces a preponderance of crystallized calcium hydroxide. On the other hand, with fine lime grains and with low-burned lime, mainly amorphous hydroxide is formed. Calcium hydroxide crystals are much more inactive chemically than the amorphous variety. White's solution, which attacks the amorphous hydroxide almost instantly, reacts extremely slowly with the crystals. In the autoclave the amorphous variety is not changed, whereas free lime yields according to its fineness and burning temperature crystallized and amorphous hydroxide. The crystals here often grow to large size, depending upon the length of time of reaction, the temperature, and the pressure.

The hydration of the aluminates in limewater reveals the same compounds as in distilled water. No new type of crystals which might

* Klein and Phillips, Bureau of Standards Technical Paper No. 43.

† Betts and Klein, Bureau of Standards Technical Paper No. 78.

indicate hydrated tetracalcium aluminate was observed. There does seem to be an action, however, between the hydrated alumina split off and the calcium hydroxide of the solution, resulting in a greater development of crystallized hydrated tricalcium aluminate.

Aluminates hydrated in the autoclave with an excess of limewater give no new type of compound. The plate crystals of hydrated tricalcium aluminate are rather poorly developed. The addition of dry calcium hydroxide up to 50 per cent. decidedly retards the crystal growth of the aluminates in the autoclave.

The first effect of gypsum solution on the aluminates is to retard the formation of amorphous hydrated material and keep the pores of the material open to the further penetration of water. Specimens hydrated in saturated gypsum solutions show the highest ignition loss after six days. The products of hydration are the same as those with distilled water, with the exception of the additional formation of sulpho-aluminate needles. This new compound is identical for all three aluminates, and its formula is $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot x\text{H}_2\text{O}$. The formation of this compound is only incidental to the initial set, and not the cause of its retardation, since the compound is formed before, during, and after the set. Variation of the gypsum content above and below a certain definite concentration causes a decrease in the setting time. Tricalcium aluminate containing 10 per cent. plaster gains practically no strength after the first period at which it was tested; that is, twenty-four hours.

The problem of initial set is probably one involving the action of small amounts of electrolytes in retarding the coagulation of the amorphous aluminate material. The evidence is in favour of the fact that the aluminates coagulate and separate as amorphous bodies from supersaturated solutions, the rate of coagulation being affected by such small quantities of electrolyte as to preclude the possibility of the reaction being solely a chemical one. Thus with a certain and definite concentration of gypsum, maximum hydration is attained, and at the same time the rate of coagulation is retarded, increasing the time of set.

The sulphoaluminate crystals are broken up in the autoclave, as is also gypsum. Club-shaped crystals are noted with optical constants that suggest a composition between gypsum and anhydrite. With higher temperatures and pressures water is even driven out of the amorphous hydrated aluminate. Gypsum favours the growth of hydrated tricalcium aluminate crystals in the autoclave.

Calcium metasilicate, as well as gamma-calcium orthosilicate, is practically inert with regard to hydration. Beta-calcium orthosilicate is but slightly hydrated in water, until after a considerable length of time. This is manifested by a slight etching of the grains and the formation of a small amount of amorphous material, and crystallized calcium hydroxide. This cement mineral sets too slowly and attains strength too slowly to be of any commercial value when used alone, although at periods beyond twenty-eight days it gains sufficient strength to place it almost on an equality with tricalcium silicate. In mixtures of the beta-orthosilicate and the aluminates the latter show some hydration, while the former is unhydrated after twenty-four hours, at which time cements are exposed hydrated, and the silicate shows quite a little hydration. The slides of beta calcium orthosilicate and aluminates indicate that the hydration of the aluminates proceeds as previously noted. Strength tests on briquettes of orthosilicate containing about 19 per cent. of tricalcium aluminate (which is approximately the amount of

aluminate present in cement) show that the latter adds somewhat to the strength of the former at later periods.

Homogeneous tricalcium silicate was not obtained, the most satisfactory product containing an extremely small amount of free lime, beta-orthosilicate and tricalcium aluminate. Tricalcium silicate acts entirely differently from either beta-orthosilicate or mixtures of beta-orthosilicate and lime, with respect to hydration. It hydrates readily with excess of water, with limited water, and in the autoclave. The products of hydration are identical, and consist of calcium hydroxide crystals and amorphous hydrated silicate. No hydrated calcium metasilicate needles are observed. It sets hard in five hours, and possesses all the important properties of Portland cement, especially those of the rate of setting and strength developed. It shows no sign of disintegration after twenty eight days in water and in the autoclave test. Here the size of the calcium hydroxide crystals depends upon the pressure. In general the greater the pressure the larger the crystals. Mixing tricalcium silicate with beta-calcium orthosilicate has no favourable effect on the hydration of the latter.

Mixtures of tricalcium silicate and the aluminates gauged with water, lime-water, and plaster solution show first the beginning of hydration of the aluminate, followed shortly by the hydration of the silicate. Tricalcium aluminate when used to replace 19 per cent. of tricalcium silicate does not add to the strength of the latter, showing rather a tendency to decrease it at later periods.

The hydration of cements is thus brought about by the formation of amorphous hydrated tricalcium aluminate with or without amorphous alumina, the aluminate later crystallizing. At the same time sulphoaluminate crystals are formed, and low-burned or finely ground lime is hydrated. The formation of the above compounds begins within a short time after the cement is gauged. The next compound to react is tricalcium silicate, whose hydration begins within twenty-four hours. Between seven and twenty-eight days the amorphous aluminate commences to crystallize and beta-orthosilicate begins to hydrate. Although the latter is the chief constituent of the American Portland cements, it is the least reactive compound. The early strength (twenty-four hours) of cements is probably due to the hydration of free lime, the aluminates, and the beginning of tricalcium silicate hydration. The increase in strength between twenty-four hours and seven days depends upon the hydration of tricalcium silicate, although the further hydration of aluminates may contribute somewhat. The increase between seven and twenty-eight days is due to any further hydration of tricalcium silicate and to the beginning of hydration of beta-calcium orthosilicate, but here are encountered opposing forces, in the hydration of any high-burned free lime present and in the crystallization of the aluminate. It is to this hydration that the falling off in strength between seven and twenty-eight days of very high-burned high-limed cements is due, whereas the decrease shown by the high-alumina cements is due to the crystallization of the aluminate.

The dicalcium silicate hydrates to a very granular porous mass which allows of ready egress of solutions, and while it is chemically more resistant to the actions of solutions than the tricalcium silicate, yet it furnishes a great number of voids in which salts may crystallize out of solution, and it is consequently very little able to resist the mechanical action of the "freezing out" (crystallization) of salts from solution.

On the other hand, the hydrated tricalcium silicate with its very dense structure, composed of gelatinous (colloidal) silicate interspersed with crystals of lime hydrate, is probably very susceptible to strains produced by alternate wettings and dryings, colloidal material of this kind being subject to considerable volume change resulting from slight moisture changes.

It appears, therefore, that the composition of Portland cement should be along lines which would not produce a great preponderance of either silicate. The ideal cement should possibly have an excess of the dicalcium silicate, which would give a not too dense hydrated material, gaining strength at later periods. A lesser amount of the tricalcium silicate would furnish the desired early strength and also overcome the excessive porosity of the dicalcium silicate.

It is possible to make a cement that will have the properties of Portland cement by grinding together the previously separately burned constituents in approximately the amounts in which they exist in Portland cement.

The function of tricalcium aluminate in the finished cement is somewhat problematical. A cement with less than 1 per cent. of alumina has all the properties of Portland cement. Such a cement is, however, not a commercial possibility from the manufacturing standpoint, on account of the temperatures and amount of burning involved. It appears, therefore, that the aluminate in the finished cement is of the nature of a diluent or inert material, although it plays an important rôle in lowering the temperature of formation of trisilicate when the clinker is burned.

NORTON COMPANY, WORCESTER, MASS., U.S.A.

THE SETTING AND HARDENING OF PORTLAND CEMENT.

A Paper by Mr. G. A. Rankin (Creighton, U.S.A.), of the Geophysical Laboratory, entitled "The Setting and Hardening of Portland Cement," was read by Dr. C. H. Desch.

In order to understand thoroughly the nature of the setting and hardening of Portland cement, it is essential that one first consider the reactions which result when each of the constituent compounds is finely powdered and mixed with water and also the effect which the admixture of the various constituents has on the nature of these reactions. While there is still much to be learned as to the chemistry of these reactions, sufficient data on the hydration of the individual major constituents have been obtained to enable us to account for the gradual hardening and increase in strength of Portland cement and to indicate the relative value of the constituents as cementing materials.

A statement concerning this matter, based on data obtained at the Geophysical Laboratory in Washington and the Bureau of Standards in Pittsburg, is contained in the following pages. In this, brief mention will first be made as to the constitution of Portland cement clinker, after which the hydration of the constituents will be discussed. In conclusion, a general statement concerning the setting and hardening of Portland cement will be presented.

Portland cement clinker is the result of chemical combination of the three oxides lime, alumina, and silica; but besides these three—which are the essential components—two others, namely magnesia and ferric oxide, always occur to some extent in commercial cement. The average of a large number of chemical analyses of American-made Portland cement shows that more than 90 per cent. of an average Portland cement consists of the three oxides lime, alumina, silica; one would expect, therefore, that its properties are due mainly to the presence of the above three components, and the relatively small admixture of the other oxides exerts at most a wholly secondary influence. Indeed, it has been shown that good Portland cement can be made from the three pure oxides lime, alumina, silica in the proper proportions.

In order to determine the nature and number of the compounds or constituents of Portland cement clinker made from the pure oxides lime, alumina, and silica, a careful study of all possible mixtures of these three oxides when fused was carried on at the Geophysical Laboratory. As a result of this study it was found that if such a pure Portland cement is perfectly burned it is made up of three constituents, namely, dicalcic silicate, tricalcic silicate, and tricalcic aluminate. If the clinker is not perfectly burned, that is, if the chemical reactions are not carried to completion, due to insufficient time or failure to attain a sufficiently high temperature, then two constituents other than the three already mentioned will be present. These two constituents are free lime and the compound $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$.

Without giving in detail the nature of the chemical reactions which result in the formation of the constituents of Portland cement clinker, it may be well to state that of the silicates, dicalcic silicate is the first formed; subsequently this compound unites with more lime in the formation of tricalcic silicate. This reaction takes place with great difficulty, due to the high temperature and length of time required. It is essential, however, that this reaction be carried practically to completion for the production of good cement, since the resulting compound tricalcic silicate is the essential constituent of Portland cement. Of the aluminates the compound $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ is first formed. This compound subsequently unites with lime in the formation of tricalcic aluminate. While it is desirable that this reaction go to completion, it is not necessary for the production of a sound cement. However, the formation of the tricalcic aluminate takes place with such readiness that the reaction between lime and the compound $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ is generally completed before the formation of the tricalcic silicate begins.

The major constituents of Portland cement clinker made up only of the oxides lime, alumina, and silica are, therefore, the three compounds dicalcic silicate, tricalcic silicate, and tricalcic aluminate. The compound $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ and free lime are minor constituents. Each of these compounds has optical properties peculiar to itself which serve to distinguish it from the rest. The several characteristic optical and crystallographical properties were obtained by a study of each compound by itself. These values are constants for the individual compounds in all mixtures made up from pure lime, alumina, and silica; i.e. the final products resulting when such mixtures are heated are present as individuals of constant optical properties and not as solid solutions.

Microscopical examination of commercial Portland cement clinker shows it to be made up largely (over 90 per cent.) of the three compounds tricalcic silicate, dicalcic silicate, and tricalcic aluminate. Free lime and the compound $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ are occasionally present in small percentages. As for the effect of the presence of magnesia and ferric oxide, small quantities of which are always present in commercial clinker, it would appear from the available data that the magnesia is taken up in solid solution by the dicalcic silicate; while ferric oxide is present partly uncombined, in part it unites with lime to form $2\text{CaO}\cdot \text{Fe}_2\text{O}_3$, and it also is taken up in solid solution by dicalcic silicate and the compound $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ to an extent sufficient to colour these compounds.

Having thus briefly discussed the constitution of Portland cement clinker, let us now consider the hydration of the constituents in the following order: Lime, $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$, tricalcic aluminate, dicalcic silicate, tricalcic silicate.

Hydration of Lime.—The action of water on lime varies somewhat, depending on the temperature at which the lime has been burned. Ordinarily an amorphous hydrated material is first formed, which subsequently crystallizes to lime hydrate. When lime occurs in a free state in Portland cement it is high burned, which, if not slowly hydrated by ageing or otherwise, will cause disintegration as the cement hardens. If the percentage of free lime in cement is relatively high, the action of water is very violent, at times being of an explosive nature.

Hydration of the Compound $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$.—When this compound is mixed with about 30 per cent. of water it sets and hardens very rapidly. When moulded specimens are placed in either hot or cold water, however, they disintegrate with great readiness. This is partly due to dissociation, which takes place readily when an excessive percentage of water is present, and partly to the solubility of the $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$. Microscopical examination of this compound

When mixed with a large amount of water shows the rapid formation of an amorphous material about each individual grain. At times this amorphous material will in part crystallize. The available data would tend to show that the crystals thus formed are a hydrate of tricalcic aluminate.

Hydration of the Compound Tricalcic Aluminate.—When tricalcic aluminate mixed with water it sets and hardens rapidly, and while moulded specimens when placed in water remain sound, they develop but little strength, are rather soft, and comparatively soluble in water.

Microscopical examination of this compound when hydrated shows the formation of an amorphous material which at times will completely crystallize. This would tend to prove the crystalline material is a hydrate of tricalcium aluminate.

The Hydration of Dicalcic Silicate.—When dicalcic silicate is mixed with water the action is exceedingly slow, and it is only after a long period of time a matter of several months, that a moulded specimen when placed in water will develop a considerable strength. The specimen remains sound, however, and is not readily soluble.

Microscopical examination of dicalcic silicate which has been shaken for considerable time with an excess of water shows the formation of a coating of amorphous material on the individual grains. It would not appear that its action results in the formation of any hydrated calcium silicate. The amorphous material shows no tendency to crystallize, except that lime which leaches out forms a crystalline hydrate of lime. Thus leaching out of the lime from the amorphous hydrated dicalcic silicate is apparently a process which will continue until amorphous silica alone remains, if a sufficient quantity of water is present for the solution of the lime.

When mixed with the other constituents of Portland cement clinker and taken with water, the hydration of dicalcic silicate is not affected except in the case of dicalcic aluminate, when the rate of formation of amorphous material on the grains of dicalcic silicate is materially increased. This is undoubtedly due to the fact that dicalcic silicate is more readily soluble in a solution saturated with the aluminate, which is itself so readily soluble in water.

Hydration of Tricalcic Silicate.—When this compound is mixed with water sets and hardens rather rapidly. Moulded specimens when placed in water remain sound, and within a reasonable time develop a strength comparable with that of the best of Portland cements.

Microscopical examination of hydrated tricalcic silicate shows that an amorphous material is formed similar to hydrated dicalcic silicate. The rate at which this amorphous material is formed in the case of tricalcic silicate is, however, much greater, as is also the rate at which lime can be leached from amorphous tricalcic silicate than is the case with amorphous dicalcic silicate. In either case it does not appear that any definite hydrated calcic silicate is formed, since it is possible to leach or dissolve out the lime, leaving amorphous silica behind from the amorphous material formed from both silicates.

When tricalcic silicate is mixed with the various other constituents of Portland cement and water, it does not appear that the rate of formation of amorphous material is affected.

From the description of the action of water on the constituents of Portland cement, it will be seen that the setting and hardening of Portland cement involve the formation of an amorphous hydrated material which subsequently partially crystallizes; that the initial set is probably due to the hydration of tricalcic aluminate; that the hardness and cohesive strength at

first are due to the cementing action of the amorphous material produced by the aluminate and of tricalcic silicate; and that the gradual increase in strength is due to further hydration of these two compounds, together with the hydration of dicalcic silicate.

Of the three compounds which thus take part in the setting and hardening of Portland cement, the tricalcic silicate appears the best cementing constituent; that is, this compound is the only one of the three which when mixed with water will set and harden within a reasonable time to form a mass which in hardness and strength is comparable to Portland cement. The compound dicalcic silicate requires too long a time to set and harden in order to be in itself a valuable cementing material. The compound tricalcic aluminate, while it sets and hardens rapidly, is rather soluble in water and is not particularly durable or strong.

From this it would appear that the compound tricalcic silicate is the essential constituent of Portland cement. In other words, it is tricalcic silicate which imparts to Portland cement its valuable cementing properties.

In this connection it is interesting to compare the nature of the setting and hardening of tricalcic silicate with an ideal cement which M. Vicat worked out theoretically about one hundred years ago.

M. Vicat, who carried on a very interesting series of experiments in regard to the hardening of cements and plasters, seemed to believe that the lime in cement mortar should be in a state of chemical combination, and that it were best that it should be so combined with gelatinous silica.

When tricalcic silicate is mixed with water to form a mortar, a gelatinous material is formed which is composed of hydrous lime and silica. Whether the lime and silica continue to be chemically combined, or whether the gelatinous material is colloidal, is still a matter of some uncertainty, although it would appear that this material is colloidal.

The similarity between Vicat's theoretical cement and tricalcic silicate is thus apparent.

The basis for Vicat's theoretical reasoning was undoubtedly derived from his observations on the action of hydrated lime when ground with water and pozzolana, a material which contains over 40 per cent. silica, with smaller percentages of alumina, magnesia, ferric oxide, and alkalis. This mixture, commonly known as Roman cement mortar, it would now appear, sets and hardens in much the same manner as tricalcic silicate; in the case of Roman cement the formation of the gelatinous material, which subsequently hardens, being due to the action of lime water on the pozzolana. This action, however, is exceedingly slow, and it requires a much longer time for the completion of the hardening in Roman cement mortar than in mortar containing tricalcic silicate. This is undoubtedly due to the nature of the chemical combinations of silica in pozzolana, which react with water much less readily to form gelatinous silica than is the case of the silica combined in tricalcic silicate. This circumstance, that gelatinous silicate is released with such readiness when tricalcic silicate is mixed with water, is probably the reason why this compound is such a valuable cementing material. Without discussing at length the nature of the cementing value of gelatinous silica, it may be well to state that it seems probable that certain of the toughest sand-stones (ideal concrete structures) are made up of grains of sand originally cemented together with gelatinous silica which was gradually deposited from solution on to the grains of sand and subsequently hardened.

This foregoing discussion, which tends to prove that gelatinous silica is the most essential constituent of a cement mortar, is somewhat speculative. Even so, such speculation is desirable, due to the fact that by formulating

advance theories as to the probable outcome of an investigation one may sooner attain the end.

Let us now consider certain possibilities which might increase the percentage of gelatinous silica in cement mortars. We know at the start in such an investigation that tricalcic silicate is probably the only compound containing silica in combination in such a manner that it is readily released to form a thin coating of gelatinous silica when mixed with water to form mortar. Therefore, until some other compound is discovered in which the silica is combined in such a way that it is more readily available in the gelatinous state, the best way to increase its percentage in cement mortars is to increase the percentage of tricalcic silicate in cement clinker. At the present time an average Portland cement contains about 30 to 35 per cent. of this compound. To increase this percentage is a matter of considerable difficulty.

Pure tricalcic silicate is formed by combination of lime and silica at a temperature of $1,700^{\circ}\text{C}$., which is too high for industrial practice. In order that this compound form readily and at a sufficiently low temperature to become a commercial possibility, it is essential that some low-melting flux be present to facilitate the combination of lime and silica to form tricalcic silicate. At present this flux is to a large extent furnished by the low-melting aluminum aluminates and the small amount of iron oxide and magnesia present in the clinker.

Cements have been made in which the ferric oxide or magnesia has been increased in percentage up to 7 or 8, and while there has been no notable increase in the percentage of tricalcic silicate, these cements are sound and of good strength. The iron cement in particular has been found very useful, since it resists the action of sea water much better than ordinary Portland cement. The reason for this is undoubtedly due to the formation of some chemical combination of the iron oxide with the calcium aluminates which resists the soluble and disintegrating action of sea water. While the nature of this chemical combination is uncertain, it is known that the pure aluminates, particularly the compound $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$, when burned with about 10 per cent. of iron oxide, produce a clinker which when ground and mixed with water is sound and of good strength. A part of this material, even when subjected to the action of steam for a long period of time, shows no sign of disintegrating.

To return to a consideration of the possibility of producing a cement containing a higher percentage of readily hydrated silica than Portland cement now does, it would not appear that it is commercially possible to increase the percentage of tricalcic silicate in order to attain this end. There is, however, at least one other possibility, which may be more practical. This involves the attempt to readily release hydrous silica from some compound containing a higher percentage of silica than the compound tricalcic silicate. This seems not unreasonable, since it will be remembered that dicalcic silicate, while it is practically inactive towards pure water, is quite appreciably hydrated in a solution of the calcium aluminates. It may be that some other solution or electrolyte will be found which will release hydrated silica from this compound as readily as water now releases it from tricalcic silicate.

In conclusion, let us recapitulate the main points contained in this Paper. The value of Portland cement depends upon the fact that when finely powdered and mixed with water an amorphous gelatinous-like material is formed on the individual grains cementing them together. This amorphous material results from the major constituents, tricalcic silicate, dicalcic silicate,

and tricalcic aluminate. Of these constituents, the compound tricalcic silicate is the one which hardens and develops the greatest strength within a reasonable time. This is due to the gelatinous hydrated silica which is readily released when this compound, in a finely powdered state, is mixed with water. This most important constituent, which is the one which formed with the greatest difficulty, makes up about 30 to 35 per cent. of an average normal Portland cement. It may be said, therefore, that the essential process for the manufacture of Portland cement is the formation of this compound, and that any improvement in this process yielding an increased percentage of tricalcic silicate will increase the cementing value of Portland cement. The increase of the percentage of the tricalcic silicate does not appear economically or practically possible, however, at the present time. A more feasible plan of attack for improving the durability of cements would appear to be an attempt to release hydrous silica from some compound such as dicalcic silicate, which contains a higher percentage of silica than tricalcic silicate, by the dissolving action of some suitable electrolyte. Investigation along these lines may ultimately result in the discovery of a cement which will enable us to prepare a concrete closely approaching the ideal : grains of sand cemented together with hydrous silicate—the toughest of sand-tones.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON,
WASHINGTON, D.C., *May 16, 1917.*

IS THE SETTING OF CEMENT MAINLY A PHYSICAL OR A CHEMICAL PROCESS?

Mr. John G. A. Rhodin, F.I.C., read a note entitled "Is the Setting of Cement Mainly a Physical or a Chemical Process?"

Many years ago the writer worked out a process for recovering the potash contained in orthoclase. This process, which has been described many times, involved some rather unexpected theoretical considerations. That the heating of a dry mixture of 100 parts of finely divided felspar with 40 parts CaO (dry slaked) and 40 parts of common salt to a temperature of 900° C. should involve the almost quantitative transformation of the potash in the felspar into KCl was to say the least unexpected. I took it to be the establishment of an equilibrium between the solid phase of two substances and the gaseous one of another. In my specification of 1899 I described the process as a reaction between the lime and the felspar, the NaCl acting as a "semi-volatile" flux. I also suggested that a compound resembling the zeolites was formed. Since then I have found that water vapour also plays an important part in the process, and that the resulting water-soluble salts are alkaline from NaOH. Slaked lime acts more readily than powdered unslaked calcium oxide or calcium carbonate, and the reaction between the anhydrous compounds can be facilitated by passing steam into the muffles. The necessity for calculating the amount of NaCl so as to make the resulting salt hold twice as much NaCl as KCl led to the conclusion that the proportions correspond to an equilibrium between NaCl and KCl vapours at 900° C. I hope to return to this matter at a future date, but I am now forced to confine my attention to the residue after washing out the chlorides. This is a silicate of lime and alumina, which shares with the zeolites the properties of acid solubility and capability of hydration. It hardens slowly in the air, like a very imperfect cement, and it can be easily transformed into a good cement by heating with more lime.

Now, the zeolites have another very remarkable property. If a crystal is heated so as to lose water it becomes dull and non-transparent, but it is restored to its original aspect and properties by simple immersion in water. This is to my mind closely analogous to the setting of cement, viz. the formation of a crystalline form of matter from an amorphous one by simple hydration. The physical state necessary depends on heat treatment below the fusing-points. Zeolites *melt* into a glass without any characteristic of the original mineral. With regard to the setting of cements made from felspar residue, I have watched the phenomenon with the microscope hundreds of times. These cements being white, you can see the setting take place quite easily. The dull white surface alters quite suddenly, and the field of vision changes into a mass of trans-

lucent crystals in a way which gives the impression of an actual movement. These crystals adhere to one another just like the crystals in a sugarloaf. The similarity to the re-formation of zeolite crystals is quite startling.

With regard to the chemical composition of a cement, this might vary very considerably, but the physical condition is common to all cements—a condition of labile molecular equilibrium. This lability may be so great that a cement loses its cementing properties *when stored in a stoppered bottle for twenty-four hours!* Take an actual case. On August 18, 1909, I made a cement by roasting together 200 grams of Brymbo blast-furnace slag, 40 grams Ca(OH)_2 , and 6 grams NaCl in a muffle at just over $1,000^\circ \text{C}$. for one hour. This cement was quick-setting and very strong on the 18th; the next day, viz. the 19th, it had changed in the bottle to a nearly inert powder! I knew even then that Passau's and Colloseus' cements stored badly, but this was supposed to depend upon absorption of water and CO_2 . Well, this was the beginning of a research lasting several years, but finally I hit upon a remedy. Adding quite a small percentage (0.5 per cent.) of aluminium sulphate or alum before firing caused these cements to keep as well as any. Hence the impurities play an important part in cement manufacture. Why aluminium sulphate should improve a slag cement containing all the elements for its formation is a great puzzle. Be it observed, however, that it does not make the freshly burnt cement better; it simply stops it from reverting to inactive silicates. It would be interesting to know whether Professor le Chatelier observed this quick decay in synthetic cements. It does occur with my felspar cements, and the remedy is the same.

We can deduce from these observations that the molecules of a cement are in a state of tension, ready to break up into smaller centres, and that the speed of this breaking up can be diminished by adding substances acting in the reverse way to a catalyser. To decide whether the change is quite as great as that of colloids changing into crystalloids is rather difficult. Anyway, it is a similar phenomenon. A further argument in favour of this conclusion is the fact that fusion spoils all cements, making glassy slags, which no amount of grinding will turn into cement. The comparison with zeolites also shows a way of explaining this theory, if we consider that the loss of water leaves a spongy structure similar to the gold buttons after parting. The constancy of volume of setting sound cements is a further corroboration.

So far, the actual "setting" of cements. The after-hardening is partly a continuation of this process, partly a carbonating process. It is very slow and gradual, but quite perceptible, even after a year or more. With felspar cements I have found sand briquettes increase to a breaking stress of 400 lb. per inch² and more after twelve months, although the cement contained as little as 52 per cent. CaO . As a proof of the above-mentioned preserving effect of alum, I may mention the following: Mr. Benjamin Hannen, of Messrs. Cubitt & Co., had some time ago occasion to send a sample of my white cement to the States. The only sample to be found was contained in a show-bottle, and made by me four years previously. It was found to be as quick-setting as when it was put in. The curious part is that alum affects plaster in the same way, making Keen's cement store well and quick-setting, in contradistinction to German Estrich gyps, which stores badly and sets slowly.

ANCIENT AND MODERN MORTAR.

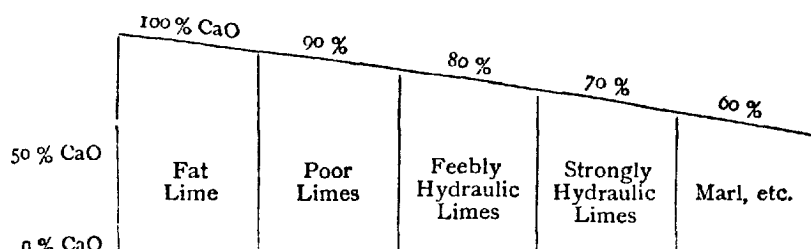
Mr. W. J. Dibdin, F.I.C., F.C.S., read a paper on "Ancient and Modern Mortar."

The comparison between ancient and modern mortars presents many points of interest, amongst which may be more particularly mentioned the quantity of lime used in proportion to aggregate, the character of the aggregate, and the presence of clay. The quantity of soluble silica in some mortars has been quoted as proof of the action of the lime on the flint in the aggregate, but, as will be seen later on, this is entirely fallacious. The strength of certain old mortars has been quoted as if the users possessed methods the art of which has been lost, but there is no evidence that such is the case, as properly compounded modern mortars will within a reasonable time possess strength equal to the best old samples obtainable.

The work carried out by the author for the Science Committee of the Royal Institute of British Architects during the years 1907-8-9-10 following a paper read by him before that Institute in December, 1906, on "The Composition and Strength of Mortars," brought to light many points which had hitherto been but vaguely dealt with.

An important point is that relating to the quantity of lime used. It appears a simple statement to say "1 to 3," i.e. one volume of lime to three of sand. In practice this appears to have been read in different ways. In some instances, the volume of lime is measured as dry unslaked lime as received from the kiln. In others, the lime has been first "dry-slaked" and the required quantity taken from the powdery mass, which has a volume per unit weight of unslaked lime greater than that originally. In some cases the slaked lime is first made into a "putty," kept for a time, and then measured in that condition. For instance, in one case 1 cub. ft. of unslaked lime, after slaking, equalled 1.53 cub. ft., and in another the cubic foot was increased to 1.77, whilst still greater variations have been observed. Hence all statements of proportions of lime to aggregate are generally given in terms of *unslaked* lime, and in stating the results of analyses of mortar the volume of lime is calculated from the percentage of pure CaO on the assumption that the original lime was comparable to a commercial lime containing 80 per cent CaO, and multiplying the weight so found by $2\frac{1}{2}$, to correct *weight to volume*. This is necessarily an arbitrary rule, but it is the only one available, and serves for practical purposes in the absence of definite information. The

variation in the qualities of various limes may be diagrammatically shown thus :



Proportion of Lime in Ancient Mortar.—The analysis of a series of ancient mortars collected for the purpose of the investigation above referred to, by members of the Royal Institute of British Architects and others, the results of which are given at length in the Report to the Science Committee of the Institute, showed that the volume of aggregate to 1 volume of lime varied from 0.4 to 3.7, but in only four instances out of twenty-six was it more than 2, the average of these being about 1, as compared with the modern practice of 3. The best results of a large number of mortars prepared for experimental purposes and kept two years before being tested for crushing and tensile strengths showed, out of 15 samples, that 11 contained 2.0 to 2.5 of aggregate to 1 of lime. Unfortunately, tests with 1 to 1 were not made. It will therefore be seen that in the matter of relative volume the ancient mortars contained larger quantities of lime than is considered permissible in modern practice.

Nature of the Aggregate.—Modern specifications of the aggregate to be used for mortar generally state that this is to be "clean, washed sand, etc." On turning to the results of the analyses of ancient mortars of the twelfth and thirteenth centuries, and that of the London Wall, we find that the proportion of aggregate was not only less, but its character was largely that of gravelly sand with clean ferruginous clay, the quantity of the clay varying up to as much as 19.5 per cent. of the aggregate.

The samples of mortar from Allington Castle, early thirteenth century, collected by Mr. W. D. Caroe, F.R.I.B.A., were particularly interesting. The relative proportions of lime to sand, etc., in three samples were 1 to 1.7, 1 to 1.1 and 1 to 1.9, the observations of Mr. Caroe when sending them being respectively, "Very good indeed," "Not so good as A, but fair," and "In fair condition." The percentage of clean ferruginous clay was respectively 8.6, 3.66, and 4.0 per cent. on the sand, which was fairly coarse, the proportions of coarse sand retained on a $\frac{1}{4}$ -inch mesh being 20, 22 and 12 per cent. respectively. The crushing strength of the first of the three samples was as high as 144 lb. per cubic inch, and that of the second 90 lb. Two other samples from the same building contained lime in the proportions of 1 to 1 and 1 to 1.3; clean red clay in the proportion of 4.5 and 5.7 per cent. of the aggregate, respectively; the crushing strength being 162 lb. and 194 lb. per cubic inch respectively.

Two samples of Roman mortar, viz. from the Pharos, Dover, and a Roman villa at Darenth, contained clean lime and broken brick only; whilst another from Threlfall Castle, near Hythe, contained clean flint and pebbles for the aggregate.

Thus we see that there was no systematic method in the preparation of these early mortars, evidently materials most conveniently obtainable being employed, preference, however, being given to clean ferruginous, clayey, gravelly sand when obtainable.

As showing the character of some of the mortar used after the Fire of London, a sample from Painters' Hall, Trinity Lane, is interesting. This was built by Sir Christopher Wren, who evidently had little time to look after details. The sample was collected by Mr. H. D. Searles-Wood, F.R.I.B.A., and was found to contain lime and grit in the proportion of 1.0 to 0.5. There can be little doubt that a good proportion of this lime was due to the use of old mortar. It was unequally mixed, and contained lumps of lime, some soft and some hard, the "sand and grit" consisting of broken red brick and organic debris, evidently old rubbish from the ruins of the fire, the "earthy matter," clay, etc., in the grit being no less than 15.4 per cent. In this case the crushing strength was 110 lb. per cubic inch.

In comparison with these results, we may now turn to the best results obtained with experimental samples of mortar made with known materials and in proportions of lime to aggregate varying from 1 to 2 up to 1 to 5, and tested after being kept for two years.

					Ratio.	Lb. per cub. in.
<i>White chalk lime</i> gave the best results—						
with Standard Leighton Buzzard sand					.. 1 to 3	=240
..	fine Charlton sand 1 to 2	=300
..	pit sand 1 to 2	=247
..	Thames sand 1 to 2	=297
..	ground brick 1 to 3	=312

<i>Dorking Greystone lime</i> gave the best results—						
with Standard Leighton Buzzard sand					.. 1 to 2	=257
..	with Charlton fine sand 1 to 5	=180
..	pit sand 1 to 2	=333
..	Thames sand 1 to 2	=243
..	ground brick 1 to 3	=162

<i>Blue Lias lime</i> gave the best results—						
with Standard Leighton Buzzard sand					.. 1 to 2	=538
..	Charlton fine sand 1 to 2	=257
..	pit sand 1 to 3	=650
..	Thames sand 1 to 2	=785
..	ground brick 1 to 2	=910

These results show distinctly the reason of the advantage gained by the early builders in fixing their ratio at about 1 to 2 and the use of a coarser aggregate, as we have seen. The modern rush after economy, by reducing the quantity of lime, is very largely responsible for the falling off in quality.

With regard to the presence of clay in the "sand grit," this has received attention. Unfortunately, the experiments were made with ratio of 1 to 3 in all cases, so the results do not compare with the foregoing, but as comparable tests were made with and without the addition of 5 per cent. Red London Clay, they are not without interest.

Ratio 1 to 3.

		Crushing Strength in lb per cub. in.	
		Without Clay.	With 5 per cent. London Clay.
White chalk lime and Standard sand	240	230
" " " " fine Charlton sand	260	70
" " " " pit sand	253	163
Dorking Greystone lime and Standard sand	228	177
" " " " fine Charlton sand	140	82
" " " " pit sand	200	140
Blue Lias lime and Standard sand	188	876
" " " " fine Charlton sand	156	79
" " " " pit sand	650	550

From these results it will be seen that the use of clay when the proportion of matrix to aggregate is 1 to 3 is disadvantageous with white chalk lime and greystone lime, but with blue lias lime a marked improvement is obtained with the Standard sand.

Under other conditions the use of clay is distinctly advantageous. For instance, greystone lime and Standard sand were used in varying proportions and the blocks crushed at the end of one month, with the following results :

	Crushing Strength in lb. per cub. in.
Standard sand without clay 5 vols., lime 1 vol. ..	= 42
" " + 2½ per cent. clay, 5 vols., lime 1 vol. ..	= 74
" " + 5 per cent. clay, 5 vols., lime 1 vol. ..	= 128
" " + 7½ per cent. clay, 5 vols., lime 1 vol. ..	= 183
" " + 10 per cent. clay, 5 vols., lime 1 vol. ..	= 176
" " + 10 per cent. clay, 2 vols., lime 1 vol. ..	= 223
Lewisham fine sand and natural clay 3 vols., lime 1 vol. ..	= 154
" " " washed free from clay 3 vols., lime 1 vol. ..	= 33

Voids in Aggregate.—An essential factor in regard to the strength of mortar is that relating to the voids, or empty spaces, between the particles. In the case of a mortar made with a sand having 40 per cent. of voids, the crushing strength was found to be only 70 lb. per cubic inch, whilst with a sand having only 23 per cent. of voids the crushing strength was 154 lb. This explains why the proportion of lime, when used with coarse sand, should be in a greater ratio than 1 to 3, 1 to 2 giving far better results.

The suggestion that soluble silicates are formed in the course of time is not borne out in the author's experience. As a test case, a mortar was made with pure lime and clean sand treated with hydrochloric acid, and thoroughly washed. After twelve months it was carefully examined for soluble silica, when not a trace was present. The examination of numerous samples of ancient mortar revealed the presence of no more soluble silica than is normally found in ordinary fresh-made mortar. For instance, the mortar from the Roman Wall, London, contained only 0.30 per cent.; those from Allington Castle, twelfth and thirteenth centuries, only 1.20, 0.70, 1.00, 0.42, 0.84, and 0.68 respectively, and that from the Pharos, Dover, only 0.30 per cent. Certain cases are met with in which the soluble silica is much higher, as at Pembrey Castle, Caernar-

then, thirteenth century, where the soluble silica was as much as 2.95 per cent., and the core of the old wall at Crosby Hall, where 3.8 per cent. was found. Much higher results have been obtained, but in such instances the character of the mortar leads to the conclusion that trass or pozzuolan, etc., had been employed.

The setting of mortar was ascribed by Graham to the fact that "on drying, the mortar binds the stones between which it is interposed, and its own particles cohere so as to form a hard mass solely by the attraction of aggregation, for no chemical combination takes place between the lime and the sand, and the stones are simply united as two pieces of wood are by glue." "From the minute division of the silica and alumina in hydraulic mortar, their combination with lime is more likely to occur than in ordinary mortar. Still, the fixing of the hydraulic mortar seems to be chiefly due to the fixation of the water and formation of a solid hydrate like gypsum." This view entirely agrees with my own experiments, as recited shortly in the foregoing, and I have no doubt that the process of crystallization acts largely in connection with the "setting" of mortar and cement, assisted by aggregation.

THE EFFECT OF THE ADDITION OF SUITABLE SLAG ON THE SETTING PROPERTIES OF PORTLAND CEMENT.

Monsieur E. Deny, I.A.M. (Ghent), and Mr. E. H. Lewis, M.A., presented a paper on "The Effect of the Addition of Suitable Slag on the Setting Properties of Portland Cement," which was read by Mr. Lewis.

We regret that we are not able to communicate results of laboratory research into the setting of Portland cement. Such research it has been impossible for us to undertake in these difficult times. For the last three years we have been responsible for the completion and starting of a plant, which at the outbreak of war was in course of erection, and for the manufacture of cement which in Germany would be called *Eisen Portland*. With a depleted staff it has been necessary to concentrate as far as possible on actual production. Research into this subject has been carried out with great thoroughness by Dr. Passow, whose work on it is well known, and by others. In this country very little research appears to have been done in connection with this class of cement, and we propose only to give certain results which have been obtained in the manufacture of such cement on an industrial scale. These, as far as they go, confirm the results given in Dr. Passow's *Die Hochofenschlacke in der Zementindustrie*.

The slag which we have used comes from blast furnaces in which hematite pig iron is manufactured. It is therefore fairly high in lime, which runs approximately to 49 per cent., the silica being in the neighbourhood of 31 per cent. and the alumina of 15 per cent. It is well known that in the manufacture of hematite pig iron the high lime content is due to the necessity of removing the sulphur from the metal. This sulphur is to some extent removed from the slag in the process of granulation, and the remainder is eliminated in the rotary kiln, so that there is no difficulty in keeping the sulphur content of the resulting cement within the limits of the British Standard Specification, even though the addition of gypsum or plaster of Paris be necessary to control the setting time.

The cement made from blast furnace slag is of course, like other Portland cement, made from limestone and clay. But a portion of the limestone and the bulk of the clay are subject to a double burning, being first passed through the blast furnace. Ninety per cent. of the lime in the slag comes from the limestone used as flux in the furnaces, while roughly 70 per cent. of the silica comes from the ores and 70 per cent. of the alumina from the coal used in Scottish practice.

The splint coal commonly used in Scottish furnaces contains approximately $2\frac{1}{2}$ per cent. of alumina, due mainly to the inclusion of a certain amount of clay from the pavement or roof of the seams. Cement

clinker made from such slag and limestone, on account of its comparatively high alumina-to-silica ratio, gives generally a quick-setting cement. But this property is capable of adjustment by the use of a suitable limestone, and by the addition of properly granulated slag. By these two expedients the setting time can, if required, be reduced to that of a medium- or slow-setting cement. By those who are not familiar with the use of cement made in this way considerable objection is sometimes raised to the addition of granulated slag to the clinker in the finishing mills. Our experience is that such an addition of slag, up to 30 per cent. of the total, not only regulates the setting time of the cement, but adds considerably to its tensile strength. The following figures show the average of the tests taken from all the wagons of cement which have been sent out from the works since the commencement of manufacture.

TESTS OF CEMENT DISPATCHED FROM COMMENCEMENT OF MANUFACTURE
TO OCTOBER, 1917—AVERAGE OF 1,711 TENSILE TESTS.

							Lb. per square inch.
3 days	540
7 days	704
28 days	855

Not only is this improvement possible to the high alumina cement made from clinker, of which such slag and limestone are the constituents, but the effect is the same in the case of Portland cement made from the usual material. In the discussion which followed upon a paper read by Mr. B. J. Day at the Institution of Engineers and Shipbuilders in Scotland, on December 21, 1915, it was stated by a very competent authority that "German Eisen Portland cement was merely a genuine Portland cement adulterated with slag." This statement led us to make experiments to determine the result of adding granulated slag to a standard brand of Portland cement.

The granulated slag which we use has itself well marked setting properties, as the following table shows. It will be noticed that this slag, though high in alumina, gives a slow setting and hardening time.

TEST OF BRIQUETTES MADE WITH GRANULATED BLAST FURNACE SLAG,
SEPTEMBER 29, 1915 (STORED IN AIR).

Tensile Strength.							Lb. per square inch.
3 days	195
7 days	300
28 days	430
2 months	480
4 months	480
6 months	615
12 months	470
18 months	528
24 months	666

Analysis of Slag.

Silica	30.5
Iron oxide and alumina	16.6
Lime	49.4
Magnesia	2.3

TENSILE STRENGTH OF BRIQUETTES GAUGED OF 1 SLAG, 3 SAND, 8½ PER CENT. WATER (STORED IN WATER).

						Lb. per square inch.
7 days	215
28 days	342
3 months	400

The results of tests made with the cement ("Rhinoceros" brand) neat and with the cement mixed in the proportion of 70 to 30 with Wishaw blast furnace granulated slag are given in the following table:

	Neat Cement.	70 % Cement plus 30 % Slag.
Fineness—residue on 180 × 180 ..	10	10 (slag).
Setting time—initial	6 min.	16½ min.
" " final	8 min.	1 hr. 10 min.
Le Chatelier test—mm. expansion..	3	1
Tensile strength—7 days	560	630
" " 28 days	722	793

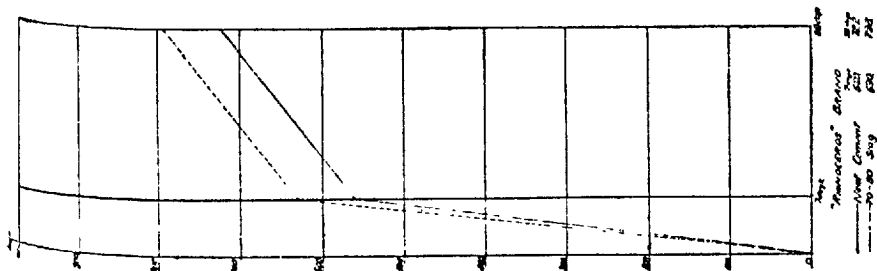
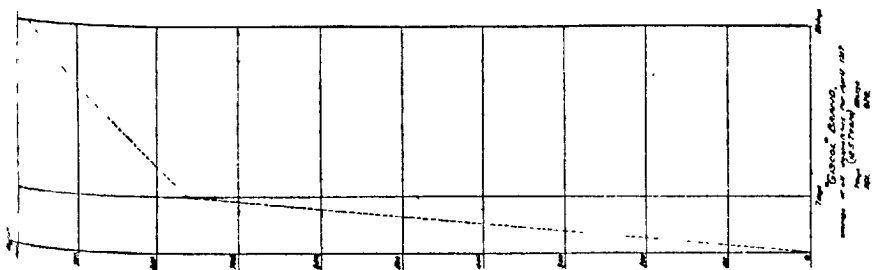
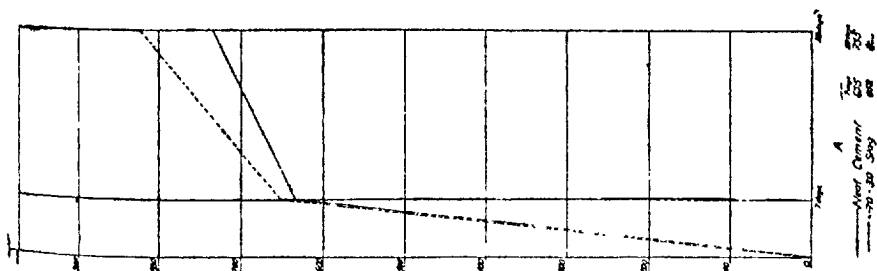
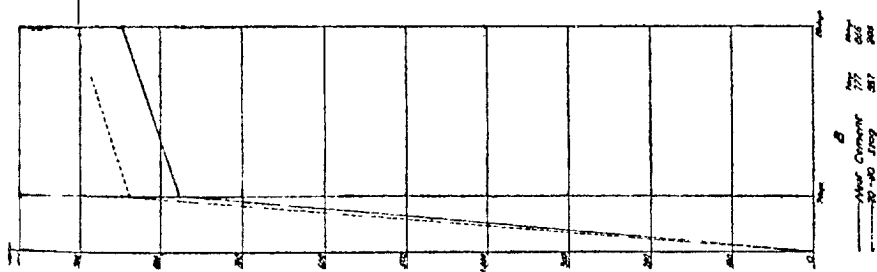
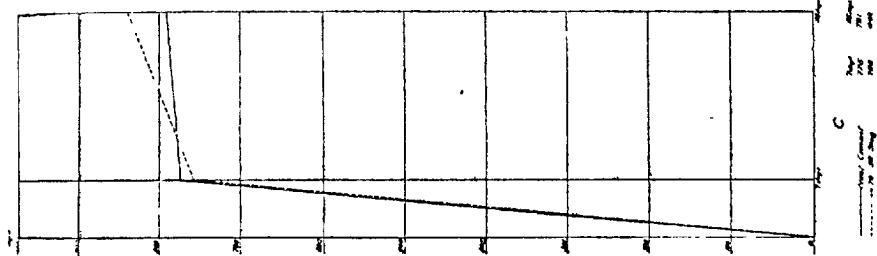
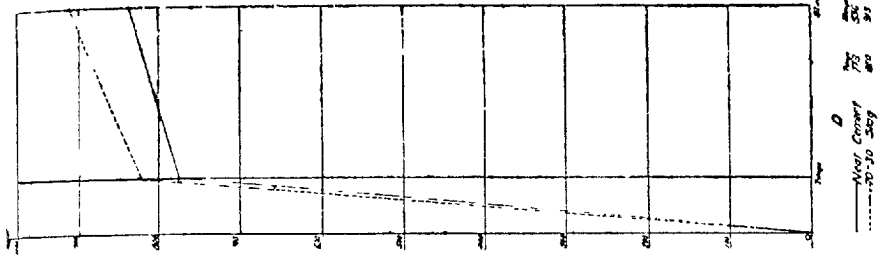
The results of this experiment were so interesting that similar experiments were made with various other well-known brands of cement from England and South Wales, of which the results are given:

A (*Aberthaw*)

	Neat Cement.	70 % Cement plus 30 % Slag.
Fineness—residue on 180 × 180 ..	5.8 per cent.	8 per cent. (slag).
Setting time—initial	20 min.	1 hour.
" " final	5 hr. 30 min.	7 hours.
Le Chatelier test—mm. expansion..	1	1
Tensile strength—7 days	635	653
" " 28 days	735	823

B (*Peter Brothers*)

Fineness—residue on 180 × 180 ..	10.8 per cent.	7 per cent. (slag).
Setting time—initial	50 min.	3 hours.
" " final	1 hr. 40 min.	5 hours.
Le Chatelier test—mm. expansion..	1	½
Tensile strength—7 days	777	837
" " 28 days	846	906



C (*South Wales Portland Cement Company, Ltd.*)

	Neat Cement.	70 % Cement plus 30 % Slag.
Fineness—residue on 180 × 180 ..	10.5 per cent.	7.5 per cent. (slag).
Setting time—initial	2 hours	2 hr. 5 min.
„ „ final	4 hr. 10 min.	3 hr. 50 min.
Le Chatelier test—mm. expansion..	—	—
Tensile strength—7 days	775	758
„ „ 28 days	791	840

D (*"Tunnel" Brand*)

Fineness—residue on 180 × 180 ..	12.7 per cent.	—
Setting time—initial	4 hr. 40 min.	7 hr. 30 min.
„ „ final	6 hr. 40 min.	9 hr. 20 min.
Le Chatelier test—mm. expansion..	1	1
Tensile strength—7 days	778	820
„ „ 28 days	836	913

There is one very interesting point to which we particularly wish to call attention. It is generally admitted that quick-setting Portland cement has less strength after a lapse of time than cement which sets more slowly.

With our cement the high content of alumina makes it possible, contrary to the generally accepted theory, to use without fear of expansion a greater percentage of lime in the clinker than is usual. The result of grinding such a clinker without any addition of raw slag is a very quick-setting cement; but if suitable slag be added such clinker gives a cement of reasonable setting time, which soon attains so great a strength that it has reached 1,300 lb. per square inch at 28 days.

This result is, in our opinion, due to the presence in the clinker of a large proportion of "alite," consequent upon the high percentage of lime, which is greater than could be carried in ordinary Portland cement.

We venture to suggest the explanation that this quick setting and quick hardening are due to the colloid, which is first formed by the hydrolysis of the aluminate of lime and is present to an unusual degree, having a favourable influence upon the subsequent formation of a colloid by the hydrolysis of the silicate of lime. This would corroborate the theory of Dr. W. Michaëlis on the phenomenon of the setting and hardening of cements. It would be of great interest if further research could be carried out upon this point, which is peculiar to cement made in the way we have described.

THE SETTING OF CEMENT IN ITS RELATION TO ENGINEERING STRUCTURES.

Mr. Bertram Blount read a paper on "The Setting of Cement in its Relation to Engineering Structures."

The question of the setting of cements of all sorts has been a subject of investigation for many years, and except in the simple case of plaster of Paris, remains unsettled. As there are many contributors to this discussion who have devoted great attention and much work to the endeavour to decide the true causes of setting, and as at this meeting they will formulate their views, I propose to deal chiefly with the practical aspect as it appears to the engineer.

Before doing this, however, I should like to say a word or two on the present state of the theory of the subject.

In the first place the term cement is elastic, and it is wrong to suppose that colloids like casein should be excluded. Their behaviour may throw light on the mechanism of setting of more important cements. Next, how is one to define setting? Generally it involves hydration, but is the induration due to loss of water, as in the case of clay, to be excluded? I take it that, broadly, setting does not connote hydration, and with this narrower definition we must be content. Taking the typical case of plaster of Paris, it has been established that a supersaturated solution is formed, that interlocking crystals are deposited from it, and that the released water passes on to perform the same function with adjacent particles. This naturally leads to a consideration of whether strontium sulphate and barium sulphate set in the same way. The low solubility of both, especially the latter, would seem at first glance to negative the supposition, but as both are found crystalline in nature, the question is not superfluous. Coming to industrial cements of the Portland cement class, the question is much more difficult. I am not aware that any definite proof has been given that the constituents of Portland cement form supersaturated solutions and set in the manner accepted as true for plaster of Paris. A fair indication of this is found in the fact that there are two schools of thought concerning setting, the one crystalline, the other colloidal. I profess myself strongly neutral, as evidence on each side appears inconclusive, but it may well be that in this discussion the whole matter will be cleared up by those who have had more recent opportunities of experiment than I.

Such theoretical considerations lie at the very root of the matter, and when they have been determined will be as complete a guide to practice as the principles of mechanics are to the design of a bridge. Until this end has been accomplished we must be content with humbler empirical methods.

As setting is a gradual process, there is no such thing in reality as a setting point or setting time. But in practice it is convenient to fix an arbitrary condition which is called the "setting point" and to call the time occupied in reaching this condition the "setting time." With minor cements, such as those of the plaster of Paris class, it is not usual to define the condition or the time rigidly. It is generally sufficient to recognize that ordinary plaster of Paris "goes off" quickly and needs rapid handling, and that other calcium sulphate cements setting more slowly can be manipulated in a more leisurely way and require a considerable time to harden. With the more important cements, of which Portland cement is the chief instance, something less rough and ready is required. In consequence numerous methods have been devised and put into tentative use. One of the most mechanically attractive was that of my friend Professor John Goodman, who in 1887 constructed a machine consisting of a metal trough on which ran a loaded roller pulled by clockwork and having a central fin. The trough was filled with cement and the ends of the roller rolled on the edges of the trough with the fin dipping in the plastic cement. As the cement set, and the roadbed became harder, the fin with its roller was gradually lifted upwards and eventually rode on the surface of the set cement. The rate and time of setting were automatically recorded on a diagram drawn by a pencil passing through the centre of the roller. Certainly a neat idea, but the difficulty common to all methods of determining setting time came in. There was no definite point of time when the fin on the roller ceased to make an impression, and thus the accuracy aimed at by this ingenious machine was greater than the nature of the material allowed.

In practice the only apparatus of any value for determining the setting time of cement is the Vicat needle—or one of its modifications, such as the British standard needle formerly used—which is too well known to need description. By simple means of this kind, cements can be classified quite as closely as their nature allows, having regard to the fact that the setting of cement is not like the setting point of a metal—and that too is a progressive phenomenon—but a gradual process.

Even with this modest standard of attainment the determination of the setting point of cement is beset with pitfalls. Cement is scarcely ever used neat, and yet its setting point is invariably determined neat, and I for one see no means of using any other method. The best that can be hoped for is that a cement with a given setting time will behave with some sort of relation thereto when it is made into mortar or concrete. But consider the difficulties here. An ordinary Portland cement will require about $22\frac{1}{2}$ per cent. of water to make a plastic mass. When mixed with standard sand in the proportion of 1 : 3 it will need about 10 per cent. of water, reckoned on the mixture, in order to make a plastic mass, i.e. roughly double the amount used when it is neat. The mechanism of setting will be very different under these different conditions, but there is more than that. The aggregate, sand, stones, and the like, will be mechanically in the way of progressive hydration; that, however, is a trifle compared with the thermal effect. The setting of cement generates heat, which in large masses and with quick-setting cements may cause a considerable rise in temperature. Indeed, the method of measuring rise of temperature has been suggested as a mode of determining the setting time—chiefly in Germany; anything more lunatic is difficult to conceive. Where the cement is slow setting and the propor-

tion of aggregate is considerable, say 6 or 8 to 1, as it generally is, the rise of temperature is not large unless the cement is so unsound that it contains what is conveniently termed "free lime." That idea may be dismissed with regard to cement made under modern conditions. What is of more moment is the influence of temperature on the rate of setting of cement. If the temperature is high the rate of setting is correspondingly high and may be too high for satisfactory construction.

Cements used in Madras at a tropical temperature and in winter in Canada, obviously are being employed under very different conditions, and it is the business of the cement manufacturer to provide a suitable material which shall act not as it does in a temperate climate, but in the place and under the conditions of actual use; he must be a little proleptic. I admit that the task is a hard one; proleptical tasks mostly are, but that the difficulties can be overcome is shown pretty clearly by results. When not only ordinary concrete but ferro-concrete has to be considered, the difficulties with regard to setting increase rapidly.

A 30-ton block may be made for harbour work and allowed to lie in the yard for six months, and if it does not set hard at once, no one is much the worse, provided that the cement and aggregate are of good quality.

With ferro-concrete the matter is different. A reasonable time must be allowed for such things as piles, as they are not put immediately to use and may lie in the yard, but the ordinary ferro-concrete structure is monolithic, and the engineer responsible for the structure must know the period necessary for proper setting.

To sum up this part of the question of setting of cement in general, it appears to me—to put extant knowledge in the shortest way—that little is known about the mechanism of setting, save in the case of plaster of Paris; that the most important cement, Portland cement, is tested for setting time neat and is never used neat, and that there is no quantitative relation between its setting time neat and its setting time in concrete. The conclusion naturally follows that much earnest and thoughtful work must be done before we can arrive at anything which can be accepted generally as proved, not by authority, or as it were of faith, but *proved*.

THE EFFECT OF THE ADDITION OF SLAG TO PORTLAND CEMENT.

Mr. Percy C. H. West also spoke on "The Effect of the Addition of Slag to Portland Cement."

We have listened to the paper read by Mr. Lewis and M. Deny with considerable interest. The question of the value of "Iron Portland cement" and its relation to Portland cement has, of course, been a subject of discussion for many years, ever since, as a matter of fact, Lurman, and later Bodmer, prepared cement with the aid of blast-furnace slag.

Michaëlis, and about the same time Erdmenger, in the seventies and eighties, observed the notable results obtained by the addition of pozzuolanic materials to Portland cement mortars, and the publication of the results obtained by them constituted the first blow struck in a battle which is apparently not yet ended.

The publication of a circular by the "Vorwohler" Portland Cement Works, which were selling a Portland cement to which blast-furnace slag had been added, describing their cement as a "Portland cement improved by the addition of silica in an active form," was the next important incident in this conflict.

The Association of German Portland Cement Manufacturers then began to take active steps to show that such additions were adulterations and nothing more. Dyckerhoff was one of the strongest supporters of this view and Jantzen one of the chief opponents. On the other side, too, at a later date was Dr. Passow, to whose work reference has been made this evening.

Of course, the subject has been dealt with at considerable length, and I shall only add very little to what has already been said. I have some experience of the manufacture of cement to which slag has been added, and I must say that that experience as a whole does not confirm the view that the addition of slag is any advantage except, perhaps, in the direction of reducing the cost of production. A good Portland cement is not improved by the addition of slag, although a bad Portland cement may be. In making these remarks I do not wish it to be thought that I would say that an iron Portland cement is a bad cement. On the contrary, I can say it is a thoroughly reliable material. Certain tests have been referred to in which it has been shown that the addition of slag improves cement, but the experiments carried out at the Royal Prussian material testing station do not, on the whole, confirm that view. There may have been instances in which improvements have been effected, but this has not been great. It has been shown, in the paper read this evening, that the addition of slag has the effect of re-

ducing the quick-setting character of the cement, and this undoubtedly it does; in fact, to such an extent, that in many cases it makes the addition of slag disadvantageous. I might mention some cement which came under my notice that had been used during particularly cold and damp weather. It was a cement to which slag had been added to the extent of the usual 30 per cent. The tests of the cement were thoroughly satisfactory; the aggregate was tested with Portland cement, and the results were equally satisfactory. What had happened was that the cement had become so slow in consequence of its being mixed with an aggregate containing a relatively large percentage of calcium sulphate that it swelled to a remarkable degree, and, in fact, dislocated certain walls. It did a considerable amount of damage, and this necessitated carrying out a number of experiments. Taking this particular highly sulphated aggregate and mixing it with Portland cement, and putting the pat, before it had become set, in water, the pat set well, but on using iron Portland cement the pat swelled considerably. A number of experiments of a like nature have been carried out, and a number of experiences of that character have come to my notice, and consequently I think it is a point which should receive some attention at the hands of those people who are interested in the manufacture or sale of iron Portland cement. In order to give an idea of what has been my experience in this matter, I may say that by taking an ordinary Portland cement of good quality and adding an equal quantity of highly basic granulated slag, a cement has been produced which has been slightly, but not considerably, inferior to an ordinary quality Portland cement.

Mr. Lewis referred to the work of Passow and stated that his results confirmed those of Passow. I think Passow's results were those obtained by a person who was interested. They are more or less *ex parte* statements. He has found that the addition of slag is always to be recommended, but other workers have found that that is not the case. I have already mentioned the work of the Royal Prussian material testing station. That work should be carefully considered, and I think the conclusions to be drawn from it would not altogether confirm the views which have been expressed by Mr. Lewis in his paper.

DISCUSSION.

The subject was then thrown open for general discussion.

Mr. W. D. Caroe, F.S.A.: I can only speak entirely from the practical point of view. I came here really as a learner and a listener, and not to impart any information, but if I can direct the minds of the men of science in the direction of some of the practical uses and difficulties of mortars and cements in building I shall feel, perhaps, that I have done some little service to the cause of building. Of course, I am immensely interested in these scientific examinations into such an important item of the building trade as cements and limes. I can, perhaps, give you three practical instances of their value which occur to me at the moment. I happen to have been a member of the so-called "Expert Committee" which had to deal with the stability of St. Paul's Cathedral just before the war, and there we found great difficulty in coming to any definite conclusion until the happy idea was hit upon of calling in Mr. Dibdin to make a scientific examination of the mortar used by Sir Christopher Wren. I will only say briefly that the scientific examination entirely altered our views with regard to the stability of that building. That, I think, is a very remarkable instance of the importance of scientific consideration of practical questions of the kind. I should explain to you in a few words, if one may venture a word of criticism of that great man, that Sir Christopher Wren depended too much on his mortar to sustain the building. The great piers which carry the dome bear a load of about 14 tons to the square foot, and they are composed of a large core of rubble set in mortar and surrounded by but a casing of stone. The result is that the mortar, in finding its level under compression, has sunk more than the stone, and the mortar rubble is thus largely called upon to carry the weight of the building. If that mortar had been a bad mortar, the building would have been in jeopardy. Mr. Dibdin discovered that Sir Christopher Wren's mortar was extraordinarily good, although made of a somewhat "poor" lime. The proportion of lime to sand was very much larger than we find in modern mortar or in any modern specification. I think the crushing strength of the mortar reached something like 600 lb. That is one instance of the importance of scientific investigation.

Another was when I was called upon to erect some buildings at the National Physical Laboratory at Teddington. There I had a scientific testing-house virtually at hand, and all the building materials used were scientifically tested. It was certainly an eye-opener to me to find how apt we are to grope in the dark in our ordinary methods of building and how often in this case did the building materials, not excluding cements, fail to meet the requirements we put upon them.

A third instance is referred to in Mr. Dibdin's paper. He mentions the mortars at Allington Castle, and there the mortar which was most successful, which bore 194 lb. per cubic inch, was a Norman mortar belonging to the eleventh century. It was a revelation to me, brought up on the traditional architect's specification in which clay is rigidly excluded from mortar, to find that mortar could be very much stronger when a certain amount of clay was introduced. That one question alone seems to me to be one in which the Society could serve the great

building trade very materially. There may be pitfalls, so far as I read Mr. Dibdin's paper, in the introduction of clay, because he gives definite instances in which the presence of clay has reduced the crushing strength materially. At the same time there are more instances where it has had the opposite effect, but as I say, we are groping in the dark. Architects rigidly exclude clay from their specifications, and yet here there is evidence that they ought not necessarily to do so, but we ought to know very definitely on what lines clay can be introduced and on what lines it cannot.

If I may just say two or three words on the question of cement, I will rigidly exclude from what I say anything scientific, because I am not equipped to deal with that side. Cement, of course, I look upon in building as one of the most important materials, more particularly now that we are dealing so largely with concrete and reinforced concrete buildings. At the same time, cement can be one of the most dangerous materials upon which we can rely, because it is so easily open to misuse; and that is another direction in which this Society may be able very materially to help us. One of the great dangers or disadvantages, of course, in connection with cement, is its expansion, which was referred to by the last speaker. My own experience is very much what his has been—that in the use of cement to which slag has been introduced there is a distinct danger in the expansion of the cement causing the building to give way. I can instance cases where cement has continued to expand for four or even five years, and as a matter of fact, when I talk to the ordinary builder about the use of cement I always warn him it is not only the result that you get to-day you have to consider; it is the result you will get four or five years hence when chemical actions, possibly, have ceased to take place. That is a matter of extreme importance in connection with the use of cement.

There is another subject for examination, and that is the direct chemical effect of cement upon stone. There are some stones that will not stand cement, or at any rate some cements. The difficulty, of course, we have to contend with in using cement is that in small buildings we cannot afford to test every sample of cement that is sent in, and some hot new cements have the effect of disintegrating the stones which they are supposed to bind together.

I act for the Ecclesiastical Commissioners, and have some large cathedrals and many small buildings under my care, and the ordinary and casual use of cement by the local builder, I regret to say, is one of the greatest dangers to old buildings that can possibly be found. Generally, one finds this occurring. The building is pointed in cement. It may or may not affect the stone, but the result of four or five years' exposure to the atmosphere upon that cement is to detach either one side or the other from the material which it is supposed to bind together. The result is, of course, small hair cracks, which grow larger as the water enters into them and the frost helps to disintegrate them. My own practice accordingly now is to refuse entirely to allow cement to be used in ancient buildings in any manner where one face of the cement so used is exposed to the atmosphere. The best modern cement is a most admirable material to use when all parts of it are able to set at the same rate, but a bad material when any part of it is able to set more quickly than any other part. As an instance of that, there were about 2,500 small cement tabs placed over the cracks in St. Paul's Cathedral, and it was said that 1,500 of them had cracked, thereby indicating that

the building was in motion. Accordingly, Mr. Horace Darwin, whose name I am sure will be received by this Society with approbation, made a very simple experiment. He took a piece of stone about 3 in. thick and 2 ft. square—sound solid stone—and sawed some thin lines across it about 1 in. deep. They varied in width from the thickness of the saw up to about $\frac{1}{4}$ in. wide, and upon that he put some cement tabs. Some of them cracked! Of course, the cracking is due to the fact that where the air can reach both sides of the tab, i.e. across the crack, the setting can take place more rapidly than elsewhere. These are only a few of the small points met with in ordinary practice as to the use, the possible danger, and the importance of cements and mortars.

I am exceedingly grateful to you for inviting me to come here. I have learned a great deal, and much has been said which I cannot claim to fully understand, but if I by any means have succeeded in directing the members of this Society towards some few points of practical use and difficulties where we can rely only upon scientific investigation to help us, I hope that you will excuse me for having brought them to your notice. They are but examples of others that could be named.

Mr. A. Binns: It would be an impertinence on my part if I, as an engineer, were to attempt to address a highly scientific audience on the scientific portion of these papers. I can only attempt to make a few general remarks as an engineer who has had something to do with concrete. As Mr. Blount has pointed out, there is a very great difference between the tests that we may make of neat cement for setting time, where by conventional, and arbitrary apparatus we determine what we call initial and final set, and the actual behaviour of set concrete. From the point of view of the engineer there are two things that he very much desires with regard to the setting time of the cement that he is using. In the first place, it is essential that the concrete shall not begin to set in too short a period—in such a short period that he has not time to carry out the usual operations and manipulations of getting the concrete deposited into its final resting-place. I should think that, generally speaking, for 90 per cent. of concrete used for either reinforced concrete or mass concrete, thirty minutes from the time of gauging the concrete would be ample to get it into its final resting-place in the works. In the second place, the engineer, and certainly the contractor, is very anxious that once the concrete has got into place, the setting and hardening shall continue as rapidly as possible, to enable him with safety to strip his shuttering in the minimum time for use elsewhere on the job, and this is a point which is of special importance now that timber is so difficult to obtain. As Mr. Blount has suggested, the time when one may strike shutters in mass work or reinforced concrete bears only a very obscure relationship to the setting time of the cement as determined by the Vicat needle. I have known cases on a very large scale where "medium" cement has been specified according to the British Standard specification and the contractor has appealed to be allowed to use "slow" setting cement because he found he could strip his shuttering after a shorter period than with medium setting cement, and this has not been a thing lightly determined upon. It has been a case where hundreds of thousands of cubic yards of concrete have been placed, and it is extremely interesting as showing that the co-ordination between the setting time of cement and the setting time of concrete is at least doubtful.

One of the previous speakers spoke of cases where concrete has been

apparently very reluctant to go off. I have known in my experience concrete to be removed from the work because after several days it had not set. For my own information I have kept samples of this concrete, and after some weeks have found it to be as good as any other concrete.

Another speaker made some remarks about the danger of using cement in connection with masonry. I do not use cement much in connection with masonry; but I should like to bear testimony to the marvellous excellence of Portland cement. The improvement in the qualities of cement as supplied for large works, properly tested and fulfilling all the requirements of the British Standard specification, is very considerable compared with twenty years ago. I think we may trace this improvement to the activities of the scientific gentlemen engaged in the production of cement, and I think possibly in no small degree to the fact that we have a British Standard specification, and that every individual engineer has ceased to insist upon his own pet fads and fancies with regard to the quality of the cement he is to use.

There is one other little thing I should like to speak of, because I think that those of us who are actually dealing in cement and using it in very large quantities may possibly be able to make some observations of interest to those engaged in the manufacture of cement. One of the things that disturbs me in the use of cement in large mass work is that we do not get a homogeneous monolithic mass of concrete in large walls. The plane of the day's work where we leave off at the end of the day—we are working usually in layers 3 ft. thick with shutters 6 ft. high—is always a point of weakness. If there is the slightest settlement, that is the plane of horizontal shear. I have some photographs, which I should like to pass round for inspection, showing some concrete at present being cut out of an old mass concrete wall that has been under water for something like thirty-four years. We are blasting out this concrete, and the way it comes out in square blocks like huge blocks of granite is extremely interesting; and even in new work you will find, if there is the slightest percolation through the wall, it is at these planes of the day's work that you are most likely to find the weakness. Another thing that troubles me in connection with concrete is the difficulty with regard to the percentage of water used. We get an excellent cement, but we make a miserably bad concrete. I find that in everyday work the percentage of water used in mixing concrete with the very best mixing machines varies at least 33 per cent. All the good makes of concrete mixers are supposed to have automatic control over the water used, but they are not automatic, and the percentage really varies very greatly. If you break up concrete in which a large excess of water has been used, you will find a honeycomb appearance where the surplus water has been left, and instead of getting a close texture of high density, you get a very bad concrete.

I have prepared specimens of concrete for the purpose of testing. I have taken 12-in. cubes from the actual concrete in use on the work—well over a hundred such specimens—and tested them for crushing strength, and a great number I have tested for percolation. The maximum head of water under which the concrete in my work will be is 35 ft., and I rigged up a tower and put a tank at the top with an arrangement for testing these 12-in. cubes. I have some diagrams showing the effect of this percolation over a period of seventy or eighty days.

There is one other remark I should like to make. In reinforced concrete one notices that if you strip the concrete off the reinforcement

there is a perfect bed of mortar where the iron bar has been. We have taken 2 ft. off the heads of piles containing eight bars in each pile, and cut out the core, showing where the bars had been bedded, and it is a perfect bed of mortar. It seems to me a marvellous thing that you cannot see a stone in the bed. In no single case has one stone touched the metal, and I have made a little experiment by dipping a pebble into mortar and allowing the mortar to set, and you will find that the cement from the mortar will run a perceptible distance up the pebble—as much as $\frac{1}{4}$ in. This may be an effect of capillary attraction facilitated by the fine grinding of cement, but in any case it appears to be a valuable property for the effective sheathing of the reinforcement bars.

Mr. W. J. Cooper: It had been my intention to prepare a paper to present at this meeting, but unfortunately I have been ill, and I hardly expected to be able to be present to-night to contribute to the discussion.

I join issue with a previous speaker who made some remarks to the effect that Portland cement is an extremely dangerous material to use—that the matter of concern was not what happened *now*, but what happened in, say, five years' time. I think that anybody who uses cement of present-day manufacture, adequately looked after in the process of manufacture and properly tested, deserves what he gets if he experiences expansion in after-years. Portland cement, as it is made to-day, can be and is made absolutely free from any danger of future expansion.

The question of the setting of cement is somewhat vexed, and I think that more disputes arise between the user, the engineer, and the manufacturer on questions of setting than on any other point. The manufacturer tests his cement and gets certain results. A certificate is frequently issued to that effect, but the first thing the manufacturer hears is that cement which took two hours to set when it was tested at the works takes two minutes or two days on the job. In the result, the matter is referred to a third party, who usually obtains quite different results from those of the manufacturer, engineer, architect, or the party using it. That is a point on which very valuable research work might be carried out.

The setting properties of Portland cement and of other cements of a like nature sometimes vary in a more or less obscure manner, for reasons very difficult to find, and I think a most profitable field of research might be in the direction of probing these properties and endeavouring to find some cause for the phenomena, and, having found the cause, to find some means whereby the setting time can be definitely assured under more or less similar conditions. Mr. Blount pointed out that work in a tropical country like India and in a country like Canada in the winter is carried out under very different conditions. No one could expect a sample of the same cement to set alike under both these conditions. In countries like ours, where temperature differences are comparatively slight, the differences in the rate of setting are often great, and a reason has to be assigned for these differences and a cure found for them. I feel convinced a cure will be found if the subject receives the attention it deserves.

Dr. T. Martin Lowry, F.R.S., referred to the setting of ammonium nitrate, which he had investigated somewhat fully. The conclusions reached as to the cause of the caking were substantially the same as those now suggested by Professor Donnan. The fundamental cause was recrystallization, e.g. after passing through a transition-point, after working, and perhaps merely as a result of minute subdivision. One remarkable point is that caking after passing through a transition-

point could be stopped absolutely by drying with phosphoric anhydride. Under certain conditions recrystallization might lead to disintegration instead of caking.

As these observations appeared to be capable of very wide general application, an application had been made by the Faraday Society to the Department of Industrial and Scientific Research to initiate a research on the caking and disintegration of salts and other crystalline materials. This research had been carried on very successfully during the past year by Mr. F. C. Hemmings, who might be asked to give to the meeting a brief account of the work he had done. The research had been undertaken in part with the idea that it might serve as a prelude to a more difficult research on the setting of cements and plasters, and in view of the many points requiring further investigation which had been brought to light by the present discussion, it was a matter for consideration whether the Council should not take action at an early date to initiate a systematic research on the setting of cements and plasters, in order to make use of the very valuable experience which had already been gained through Mr. Hemmings' work on the caking of salts.

Mr. F. C. Hemmings: With regard to the theory of the setting of plaster of Paris, there is one point that needs consideration: is it necessary to assume that the whole mass is converted into the dihydrate? The quantity of water added in the first place is very small, and much of this is used up in the formation of the dihydrate from the hemihydrate, and consequently very little will be left for the process of re-solution. Is it not sufficient to assume that the dihydrate will be deposited in the interstices of the tiny particles and hence cause the whole mass to set?

A further point that has not already been mentioned is the great improvement that is effected in the setting of "dead-burnt" plasters by grinding. I think the explanation of this is on the lines upon which Dr. Lowry has spoken, i.e. the change that is produced by "working," and the consequent increase in the solubility of the substance.

There is one suggestion that I should like to put forward in relation to crystalline growth. We all know that crystals will grow if surrounded by a saturated solution which is in contact with the atmosphere, and it is quite possible that this fact has a considerable bearing on the question of setting. As growth proceeds the spaces between the particles gradually become obliterated, and a compact mass is formed.

To come to Professor Donnan's remarks, the principles enunciated in this paper do not seem to be very widely appreciated on the commercial side, but they are entirely in harmony with our own laboratory and factory experience. The presence of a solvent medium has been shown to be absolutely essential for the setting of crystalline salts, though mere traces of solvent will produce the effect. The degree of solubility and the quantity of solution retained in the interior of the crystals are also important factors, and I have no doubt that the setting and disintegration of ammonium nitrate crystals, as mentioned by Dr. Lowry, can be largely attributed to these causes.

The effect produced by the presence of free solvent is well illustrated by the specimens of copper sulphate which we have here. Crystalline hydrates, when ordinarily prepared, show the same tendency to agglomeration as do soluble salts in general, but when such a compound is partially dehydrated, a very fine granular product is obtained which shows no tendency whatever to set, if moisture is excluded. In this case there is no possibility of the presence of free water for the formation

of a film of solution around the particles. On the other hand, if the anhydrous compound is exposed to air saturated with water vapour an expansion which causes "bulging" is produced. This appears to continue until the salt is fully hydrated, and when this point has been reached, the substance gradually *sets* to a hard solid block, and the setting is accompanied by considerable contraction. In this case the setting commences as soon as there is the possibility of the presence of *free* solvent.

Although we have not yet been able to investigate the causes of the setting of calcareous cements, we feel that the processes of solution and recrystallization play a very important part in these phenomena.

Dr. Walter Rosenhain, F.R.S.: The setting of cements is a subject of very great interest, and that interest has been considerably increased by the remarks of the two last speakers, dealing with a point to which Professor Donnan had already referred. Mr. Blount had, incidentally, mentioned it also.

The point of view which I would like to put forward is that the setting of cement appears to be one of a whole class of phenomena of an analogous character, and I would like to extend this analogy still further, to include the setting of metals when they solidify from fusion. That is a very familiar phenomenon, but we should realize that it is really a phenomenon of setting very like that of plaster or cement, not because we have a liquid setting into a strong, hard solid, but because we see in it the formation of an aggregate of coherent crystals instead of merely a heap of loose crystals lying upon one another, and an aggregate of crystals adhering powerfully to one another is very much what we have in a plaster or cement after setting. The welding of two pieces of metal to one another is, in the same sense, a phenomenon of "setting"; it is again a case of crystals which have been placed in juxtaposition and have adhered powerfully. Our whole conception of these phenomena depends upon this: What is the mechanism by which crystals in such an aggregate adhere to one another? I think that we can dismiss at once the idea of mere frictional adhesion due to any sort of interlocking. We have cohesion due to that cause in textile fibres, but there the explanation lies in the very term "fibres"—i.e. structural units which are very long compared with their thickness, so that frictional adhesion between intertwined units may become very large compared with the strength of any one unit. But our knowledge of the micro-structure of crystalline aggregates, whether metals or minerals or cements, at once disposes of such an analogy—the crystals may in some cases be elongated in shape, but never to any extent justifying the term "fibre" or affording sufficient frictional contact to account for the cohesion between them. Frictional adhesion, therefore, cannot account for the fact that, even in crystalline aggregates made up of equi-axed crystals, the inter-crystalline cohesion is generally considerably stronger than the cohesion within the crystals themselves, so that when the aggregate is forcibly broken, fracture occurs across the crystals and not along the crystal boundaries. It would be interesting, incidentally, to know from Dr. Lowry or the other speakers whether this rule applied to the crystal aggregates formed by such substances as ammonium nitrate.

If, then, we may dismiss frictional adhesion as an adequate explanation of crystal adhesion, what is the mechanism of this adhesion? Some few years ago, guided by ideas very far indeed removed from the subject under discussion this evening, I put forward the hypothesis that the adhesion of crystals in metals is due to the presence between

them of a film of amorphous material or—what is really the same thing—of material in the undercooled liquid condition. That hypothesis seemed at first a little difficult to accept, and it met with a good deal of opposition and criticism, but it has now gone a very long way towards a very wide, if not general, acceptance, because one new fact after another has been discovered which finds a ready interpretation or explanation by that theory. The facts brought forward to-night throw further light on the mechanism of crystal adhesion and tend to support the probability of the "amorphous cement" theory. We may regard the cement as consisting, at one stage, of solid grains or crystals lying surrounded by a liquid solution of certain constituents. This liquid then undergoes solidification as the result of the removal of water—either by percolation or by chemical action, such as the hydration of some of the solid material present. If the film of liquid is thick enough, this solidification may take place by crystallization, but if it is very thin it may—by analogy with the phenomena in metals—congeal in an amorphous condition. Even if there is crystallization, in the last resort the final thin films of liquid between the crystals will still solidify as "undercooled" or supersaturated liquid. It is these amorphous films or layers which give to the whole mass its great stiffness and strength, since strength and hardness appear to be essential properties of undercooled liquids. The hardness and strength of such undercooled liquids, and indeed of all amorphous substances, including the colloids, to whose "hardness" sarcastic reference has already been made this evening, can be explained in a perfectly reasonable and scientific manner. The softness and ductility of crystalline materials—such as the ductile metals—is due to the fact that crystalline structure implies a certain geometrical arrangement of the atoms or molecules, and this results in some degree of weakness in certain of the geometrical planes. Consequently, crystals have cleavage or gliding planes along which displacement or rupture can occur relatively easily—layers of atoms are able to slide over one another under the action of forces which would be far too small to tear them apart bodily. In the amorphous substance, however, this geometrical arrangement of the atoms or molecules is absent; sliding of layers cannot as a rule occur at all, and any displacement must be either of the nature of very gradual flow or sudden and complete rupture. This is characteristic of such typical amorphous undercooled liquids as glass or sealing-wax.

The analogy between inter-crystalline cohesion in metals and in cements or other crystalline aggregates could be carried much further, but it would take too long to go into details. I merely wish to bring the idea forward for consideration. We have a theory which has proved useful and fruitful in explaining the setting of metals, and it may perhaps prove applicable to the analogous phenomena met with in the setting of cements and other crystalline aggregates.

Mr. E. Hatschek: I should like to add a few remarks to what Dr. Desch has said with regard to the rival theories of crystalline and colloidal structures and setting. Dr. Desch pointed out very clearly that the difference between Le Chatelier and Michaëlis is that one worked in dilute and the other in concentrated solution, and this is practically the whole difference, and accounts for their divergent results and conclusions. It is well known, especially from the work of von Weimarn on about two hundred different substances, that slightly soluble compounds may be obtained either as gels, as the familiar crystalline

precipitates, or as sols, simply by an appropriate choice of the concentrations of the reacting solutions. Thus, barium sulphate may be obtained as a clear gel by using concentrated solutions of two exceptionally soluble salts, viz. barium thiocyanate and manganous sulphate.

I would even go a step farther and point out that the two theories are not only compatible but even complementary. It is perfectly possible that the first product of a reaction may be a gel consisting of ultra-micro-crystalline elements, and that this may gradually assume a coarser crystalline structure owing to the intermediate true solution of the reaction product. With substances as slightly soluble as, say, barium sulphate the process would necessarily be very slow, but cases are known where the gel is transformed into microscopic crystals in the space of a few days or even hours. One has been described by W. Doehle,* who obtained the mercury salt of a sulphonic acid which formed gels in concentrations as low as 1 : 300. The gel gradually breaks up and the salt crystallizes out, the process being irreversible. The other, even more striking, case is that of camphoryl phenyl thiosemicarbazide, one of the substances obtained by Dr. M. O. Forster in his studies on the camphane series, which I have investigated.† This substance has a true solubility of about 0.5 per cent. in cold absolute alcohol, but is very soluble in boiling alcohol. If the latter solution is allowed to cool slowly, the substance crystallizes out in large simple crystals. If, however, the solution is cooled suddenly, it sets to a beautiful gel recalling silicic acid gel. This gel is not stable, but in a short time—hours, or at most days, depending on temperature and concentration—the gel exudes liquid, while at the same time the substance crystallizes out. The crystals thus formed, as I should like to emphasize specially, are all twins or more complicated aggregates.

We have here an instance in which gel formation and subsequent crystallization succeed each other with striking rapidity, owing to the high true solubility of the substance in the cold solvent. Intermediate cases between this and the transformations requiring years, or possibly centuries, can no doubt be found by a careful study of solubilities.

As regards Professor le Chatelier's general remarks on colloids, I should like to be allowed to say that the observations on the first page of his paper appear to be cancelled by those on the second. In the former he labours to show that the special treatment of the colloidal state is unnecessary, while in the latter he gives a very clear statement of the factors, notably the effect of large "specific surface," which have made it, if not necessary, at least eminently desirable, to study the colloidal state specially.

Dr. H. Borns: Perhaps I may be permitted to comment on two points in M. le Chatelier's paper. In the first instance, I do not understand how the author's considerations of grain size are to furnish any explanation of the usual insolubility of colloids. Secondly, I fail to follow his argument on the hardening of cements. He says: "The anhydrous compounds are more soluble than the hydrated compounds; they give rise to the formation of a super-saturated solution, from which the hydrated compounds may rapidly crystallize. The liquid, being no longer saturated, can redissolve more of the anhydrous compound. . . ." Would not the solution remain saturated after having deposited crystals?

* *Ueber Derivate des Benzothiazols*, Dissertation, Leipzig, 1912, pp. 14, 61.

† *Koll. Zeitschr.*, xi., p. 158, 1912.

And how are the progressive crystallization and the transitory solution of which he speaks to go on without the aid of some periodical factor, of which there is no mention?

Mr. S. Rørdam (*communicated*): I heard with great interest the discussion on the setting properties of Portland cement, and particularly that on the paper read by Messrs. E. Deny and E. H. Lewis.

I have myself had occasion to experiment with an addition of blast furnace slag to Portland cement, and have carried out series of tests on mixtures of Portland cement with the particular kind of slag of which Messrs. Deny and Lewis are speaking. As I cannot altogether subscribe to the results obtained by the authors, and as it appears to me that there are good reasons to warn people who are not altogether familiar with the testing of cement against drawing too far-reaching conclusions from the results given in the paper, I desire to make a few comments on this point.

First of all, it will be noticed that all the tests given are obtained from briquettes gauged of neat cement, and that in none of the four cases, A, B, C, D, for which curves are given have the corresponding tests with briquettes gauged with a mixture of cement and sand been given. These neat tests are by no means a good criterion of what would have been obtained by a mixture of sand and cement or by concrete in which the cement has been used. Anybody who is familiar with cement testing will know that the neat strengths obtained with a finely ground and in every way first-class cement are very often unsatisfactory, and a consumer is not justified to form an opinion on the qualities of a cement he proposes to use until he has seen the tensile or crushing strengths of sand briquettes.

In the laboratory with which I am connected, I have had an opportunity to make a series of tests on the identical materials mentioned under the heading D in the paper. As a result of extensive tests I have found that under no circumstances does an addition of the slag improve the strength of the cement to any appreciable extent, and that under certain conditions a very marked decrease takes place.

My tests were carried out with briquettes gauged from one part of Portland cement or Portland cement slag mixture (70 to 30) and three parts of standard sand in accordance with the requirements of the British Standard Specifications for Portland cement. The briquettes were divided into two batches, one stored under water in the usual way, and the other batch kept in a moist atmosphere during the storing.

The briquettes were tested for tensile strength after 7, 28, and 90 days' storing, and the results obtained are given graphically under A and B (Fig. 1). A represents the results of the wet-storing, B those of the dry-storing tests.

It will be seen that after 90 days' storing under water there is only a slight difference in the strength of the Portland cement and the cement slag mixture. When the briquettes have been stored in a moist atmosphere instead of under water there is a considerable difference between the strengths in the two cases, and the cement slag briquettes thus stored are not only inferior in strength to the Portland cement briquettes stored under the same conditions but also to the corresponding cement slag briquettes stored under water.

This decrease in the strength of the cement slag briquettes when exposed to the air is probably partly due to the oxidation of the slag which takes place, and which is clearly shown by the appearance of the

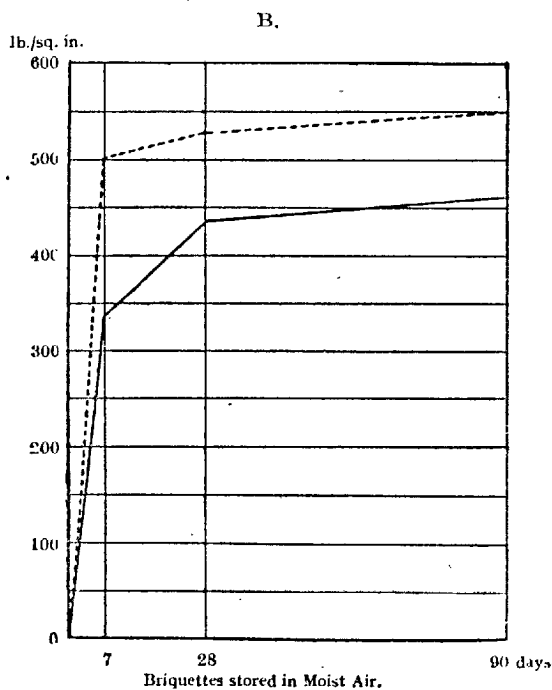
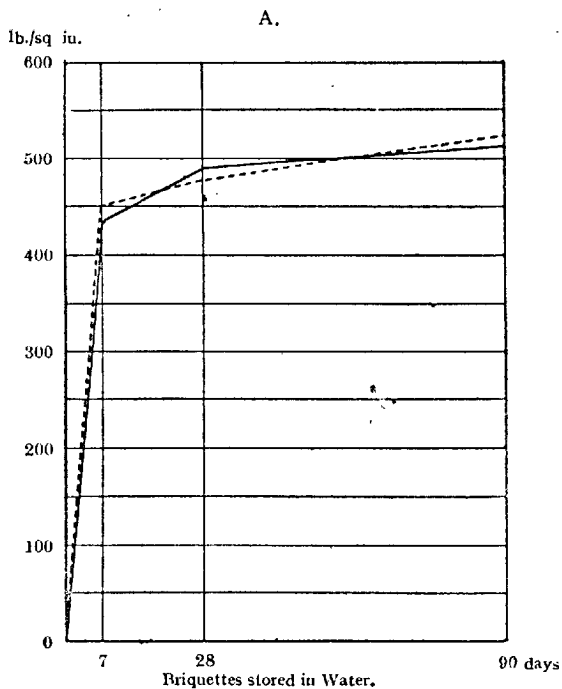


FIG. 1.

----- Briquettes 1 : 3 Portland Cement.
 ————— Briquettes 1 : 3 Cement Slag (70/30)

briquettes; those which are stored under water are still after 90 days quite black inside from the contents of ferrous sulphide formed, whereas those exposed to the air have already after three or four days' storing assumed a uniform grey colour right through. The tests mentioned in the paper do not show this action of the air, because the oxidation naturally is reduced to a minimum when the neat briquettes are stored under water.

I think all cement experts will agree that it is by no means unreasonable to demand that test briquettes shall show good strengths after storing in a humid atmosphere. By far the majority of Portland cements are used on land and the hardening takes place, not under water, but in the air, which is even, very often, far from being humid. The German Standard Specification for Portland cement takes this into account by specifying that briquettes of cement which is intended for use otherwise than under water shall be kept one day in a moist atmosphere, six days under water, and thereafter 21 days in the air.

If the same were to be specified in the British Specifications I have every reason to believe that an admixture of slag and Portland cement would give quite different results to those mentioned in the paper. I do not wish to state that an addition of slag will in no case improve a Portland cement; for instance, a lightly burnt and not too strong cement might be improved, but I feel quite certain that a high-class Portland cement, well burnt and well ground, is in no case improved by an addition of slag and that, on the contrary, such a mixture will make a good Portland cement less suited for many purposes.

Mr. A. C. Davis (*communicated*): The contention of Messrs. Deny and Lewis that the addition of granulated slag to Portland cement clinker produces a cement of superior quality to that produced from clinker alone is weakened by the omission from the tables given in the paper of tensile tests of cement and sand mixtures.

There are many who will remember that results of a similar order to those given by Messrs. Deny and Lewis could be presented by the defenders of "Kentish rag" adulteration of cement, and, indeed, it must be admitted that sometimes, within certain limits, the grinding of an inert material with Portland cement clinker tends to reduce the expansion test and to increase the neat tensile test. But the fallacy is immediately exposed when the tensile tests of a 3-sand, 1-cement mixture are exhibited, as these are reduced as the proportion of the adulterant is increased.

It is not intended to deny, however, that granulated slag has certain pozzuolanic and even cementitious properties and it may well be that the mixtures of clinker and slag reported upon by the authors would show tensile tests for sand briquettes better than those of pure cement free from slag.

What the cement user has to decide is whether it is worth while to risk the sometimes disastrous effects of sulphur in cements (especially as sulphides, which is the form in which sulphur chiefly occurs in slag) which have been adulterated with granulated slag for the sake of obtaining a slightly stronger cement at, presumably, lower cost.

Where the cement is to be used for reinforced concrete, the decision will not require a moment's thought for any one who has had before him concrete blocks made with slag cement, which have been burst by the swelling of steel rods embedded in the blocks.

With plain concrete, the temptation to use the adulterated cement is more difficult to resist when the price is appreciably lower, but many

contractors have found that it is cheaper in the end to pay the price for the unadulterated article rather than contend with the delays in hardening that frequently attend the use of slag cements and cements adulterated with slag.

It appears to be common ground between the "crystalloid" and "colloid" schools that set cement derives its adhesive and cohesive qualities largely from the presence of low-lime compounds, or even, as suggested by Rankin, of hydrous silica, although other experts will not agree with Rankin that the hydrolysis goes so far as to result in hydrous silica, as concurrently with the silica hydrate of lime would be produced, and the two substances cannot long exist together, as fairly rapid combination takes place. It is clear, however, that the set cement also contains hydrated lime, and no evidence has been presented to show that this hydrated lime is other than inert. We have therefore the anomalous position that, as the only known means of securing strength in their products, cement manufacturers are compelled to include the highest possible proportion of lime in their cements that is compatible with constancy of volume, while in the resultant concrete a large proportion of the lime is nothing more than a diluent.

In their efforts to reach the maximum lime content, manufacturers are forced to grind their raw materials finely at considerable cost, and, the clinkering temperature of high limed mixtures being high, the cost of calcination is also heavy. It is well, then, that the attention of chemists should be constantly directed to this anomaly, which requires the manufacture of cement to be burdened with an excess of a constituent which is costly to manipulate and which is ultimately found to be a diluent.

The production of low-lime cements has occupied the attention of many workers, but unfortunately the basis of their experiments and operations has invariably been blast furnace slag, with its inevitable content of sulphur as sulphide. So tainted at the source, such low-lime cements have seldom been judged upon their merits as cement, but have been condemned, and rightly so, on account of their sulphur content, with its possibilities of disaster.

The elimination of sulphur from slag has not proved a practical proposition up to the present, and it would tend to more rapid progress if this source of raw material for low-lime cement production were abandoned. The ordinary sources of raw material, such as chalk, limestone, clay, and shale, could be used for low-lime cement production, and there would still be considerable scope for economy in cost of production, for three reasons: firstly, there would probably be no necessity for extreme fineness of grinding the raw materials; secondly, there would be less carbonate of lime to dissociate, and consequently less heat absorbed, and thirdly, the low-lime mixture would require a considerably lower temperature of calcination.

The results obtained from Passow and Collos slag cements offer much encouragement to the investigator aiming at the production of low-lime cement. These slag cements, containing about 45 per cent. of lime, had no difficulty in complying with the requirements of the British Standard Specification for tensile tests when mixed with sand, and for constancy of volume tests, and they thus satisfied two of the most important requirements of the cement user; but they are ruled out entirely by their content of sulphur, their tendency to slow hardening, and the frequent faculty of losing their cementitious properties with age.

The sulphur difficulty can be avoided by abandoning slag and starting with "clean" raw materials, and the investigator of the future is then faced with problems of slow hardening and failure to keep, before low-lime cements can be made a marketable commodity.

Mr. T. Hattori (Formosa) wrote that he had found the microscopical examination of cement clinker of great value in determining the quality. The alite grains in well burnt clinker had sharp outlines, but in insufficiently burnt clinker the alite grains were rounded and indefinite. The proportion increased with the percentage of lime, and its distribution was uniform in good clinker, but irregular in a product of bad quality. Alite was more readily attacked by water or dilute hydrochloric acid than celite, but less readily by dilute hydrofluoric acid. The latter reagent was to be recommended for etching, as clinker often contained clusters of white granules which might be mistaken for alite. Deep etching with hydrofluoric acid coloured the alite, but left these granules quite unchanged. Their nature was now under investigation.

Hardened cement was found under the microscope to consist of a mass of unaltered grains (residual clinker) embedded in hydrated material. The unaltered grains were much harder than the ground mass, so that the hardness and strength of a neat cement briquette was proportional to the percentage of grit which it contained. This would be a reason why the strength of neat briquettes made from finely ground cement was usually low. On the other hand, fine cement had a great sand-carrying capacity and made a dense mortar, so that the strength of such cement-sand briquettes was high. No proportional relation existed between the strength of neat cement and of mortar made from it, and it was therefore desirable that tests of neat cement should be deleted from specifications and replaced by tests of cement-sand mortar.

Mr. D. B. Butler (*in a communication received May 2, 1918*) wrote regretting his inability to be present at the discussion. The papers presented for discussion were extremely interesting, and covered a very wide range. With regard to the setting process of cement, to which most of the contributors had devoted their attention, there appeared to be two schools of thought, one supporting the crystalline theory, of which M. le Chatelier was the chief exponent, and the other the colloidal theory; personally he was inclined to the view that neither party had fully established their case, although he had a distinct leaning to the crystalline theory. Some fifteen years ago he spent a good deal of time in microscopic research on this subject, but unfortunately without any definite results. He found that when subjected to water Portland cement certainly formed definite crystals, some needle shaped, and some a peculiar flat irregular shape, resembling the small wings of an embryonic moth. Owing to pressure of other work, these researches unfortunately had to be abandoned, but so far as they went they certainly favoured the crystalline theory of setting of Portland cement.

The communication of Mr. T. Hattori, of Formosa, as to the results of his microscopic researches, was very interesting, more especially his examination of set cement, which he found to consist of unaltered grains (residual clinker) embedded in hydrated material. This confirms the writer's researches contained in a paper on the "Finer Grinding of Portland Cement," published in 1898 in the *Proceedings of the Institution of Civil Engineers*. Photomicrographs accompanying this paper showed very clearly the unaltered grains of clinker embedded in a white crystalline mass of hydrated material, which further goes to support the crystalline theory of setting.

Whatever may be the action which takes place, whether crystalline or colloidal, or a combination of the two, the setting action of Portland cement is, at the present moment, very imperfectly understood, and opens up a wide field for research. One thing is very certain, that the setting time of cement as at present manufactured is a somewhat variable quantity; it is no uncommon thing in the writer's laboratory to find a cement which, as received from the manufacturer, has an initial set of, say, one hour, while after 24 hours' aeration, as prescribed by the current British Standard Specification, the initial set quickens up to, say, ten minutes, the atmospheric and other conditions being exactly the same in each case. This point was touched upon by Mr. W. J. Cooper, who pointed out the difference between the setting-time results obtained by the manufacturer at the works, by the user on the job, and by the referee or third party, which last is the usual rôle of the writer. These differences, when not to be explained by differences of the conditions under which the tests are carried out, are probably traceable to the action of the atmosphere on the sulphur compounds present, whether inherent in the cement itself or added by the manufacturer for specific purposes. The researches and conclusions of Candlot on this subject some twenty years ago still hold good in the writer's opinion.

With regard to the effect of the addition of slag on Portland cement discussed in Messrs. Deny and Lewis's paper, it is by no means surprising that it results in a slower setting cement, as claimed by the authors. The initial setting properties of slag are extremely slow and feeble, and therefore the addition of any marked quantity of slag would have the same effect as the addition of a similar quantity of inert material, such as sand, and retard the setting time accordingly.

As has been pointed out by one or two others, the authors of this paper omit the usual 3 to 1 sand-mortar tests, and only quote neat tests in support of their contention as to the favourable effect of slag on Portland cement. This may be altogether misleading, since 15 or 20 per cent. of finely ground sand, or other inert material, may be added to cement without materially affecting its strength when tested neat, but when tested as a mortar, of the usual 3 to 1 composition, the prejudicial effect of a mixture of the inert material is indicated at once by a marked diminution in cementitious value. This point was very clearly brought out by the writer in some researches as to the effect of Kentish Rag and other admixtures on the strength, etc., of Portland cement, when this subject was agitating the cement world in 1895-6 (see *Proceedings, Society of Engineers*, 1896). On this point the writer agrees with the remarks of Mr. Rørdam, that the addition of slag cannot improve good Portland cement, but may improve an indifferent one. There is also the question of the sulphur compounds in the slag, which are generally in excess of that allowable in Portland cement proper, and might very conceivably prove a source of danger; several instances have come under the writer's notice in which the sulphur compounds of slag used as an aggregate for concrete making purposes have led to disastrous results.

Monsieur E. Deny and Mr. E. H. Lewis (*reply communicated April 30, 1918*): Messrs. Rørdam, Davis, and West misunderstood our paper if they thought that we pretended that all slag mixed with all cement will give good results. A slag of a suitable chemical composition and physical constitution appreciably improves the quality of nearly all cement, but chiefly cement which has been specially made for that purpose.

We agree with Messrs. Rørdam and Davis that sand tests rather

than heat tests should determine the industrial qualities of the product. We have only given the latter, because we had intended to discuss the question of strength only from a technical point of view, and because in Great Britain the British Standard Specification attaches great importance to these tests.

Our sand tests, not only in tension but also in compression, confirm those which we have given for neat cement. But to give more weight to our tests we refer to the comprehensive experiments of Dr. Passow set out in his book, *Die Hochofenschlacke in der Zementindustrie* (Wurzburg: A. Stubers Verlag (Curt Kabitzsch), 1908).

The sand tests quoted below have been reduced to pounds per square inch.

SAND TESTS 1 : 3 (p. 21).

	TENSION.						COMPRESSION.			
	3 Days.		7 Days.		28 Days.		7 Days.		28 Days.	
Hardened in 70% Clinker } 30% Slag }	Water	Air	Water	Air	Water	Air	Water	Air	Water	Air
	189	178	253	260	310	239	2,873	3,314	4,531	4,253

SAND TESTS AT 360 DAYS. IRON PORTLAND CEMENT 70 : 30 (p. 43)

Ratio, Cement : Sand ..			Hardened in Water.			Hardened in Air.		
			1 : 3	1 : 5	1 : 7	1 : 3	1 : 5	1 : 7
V. Tension	704	542	392	1,141	929	617
Compression	8,192	4,608	2,660	9,060	5,604	4,210
VI. Tension	686	505	382	1,047	792	365
Compression	7,965	4,409	2,973	8,463	4,978	3,655
VII. Tension	646	439	351	1,077	790	515
Compression	7,723	3,456	2,247	7,865	4,921	3,399
VIII. Tension	684	378	354	1,115	791	409
Compression	6,486	3,086	2,361	7,035	4,338	2,859

PORTLAND CEMENT WITH 30 PER CENT SLAG. SAND TESTS 1 : 3
(p. 54).

	TENSION.						COMPRESSION.			
	3 Days.		7 Days.		28 Days.		7 Days.		28 Days.	
Hardened in	Water	Air	Water	Air	Water	Air	Water	Air	Water	Air
II.	218	310	309	408	473	486	4,708	5,277	4,850	5,291
III.	202	267	303	408	388	441	3,812	4,494	4,679	4,765

The accompanying diagrams are taken from those given on page 50.

It is shown that not only do the sand tests confirm those which we have given, but that sand tests, both tensile and in compression in free air, are in nearly every case higher than those in water, contrary to Mr. Rórdam's single test.

Mr. Rórdam's tests in water confirm ours, but his single test in air is in complete contradiction, not only with the test made by us with the same slag, but with practically all the experiments quoted by Dr. Passow.

Mr. Rórdam is at fault in drawing a general conclusion from an isolated test. He also refers to a decrease in strength in his test, while his curve shows an increase of 130 lb. from 7 to 90 days for a 70 : 30 mixture, against an increase of 45 lb. for pure cement under the same conditions and after the same interval. Looking a little more closely into his diagrams, we note that the sand tests of his pure cement stored in air for 7 and 28 days are 505 and 525 lb., an increase of 20 lb., against the British Standard Specification requirements of $\frac{10,000}{505} = 19.8$ lb. Stored in water they give 451 and 478, an increase of 27 lb., against the British Standard Specification requirements of $\frac{10,000}{451} = 22$ lb. The 70 : 30 mixture gives under the same conditions in air 332.5 and 435, an increase of 102.5 lb., against the required $\frac{10,000}{332.5} = 30$ lb., and in water 432.5 and 492.5, an increase of 60 lb. where 24 lb. are required. These results are sufficient to combat his statement of a decrease in strength due to an imaginary oxidation of the slag. But they show that the addition of our slag to his cement improves the quality by regulating the hardening and bringing it more into line with the British Standard Specification requirements.

In reply to the very serious objection made by Mr. Davis concerning the sulphur contained in our cement, we submit on pp. 67 and 68 the results of tests made by Messrs. Henry Faija & Co., dated November 23, 1915.

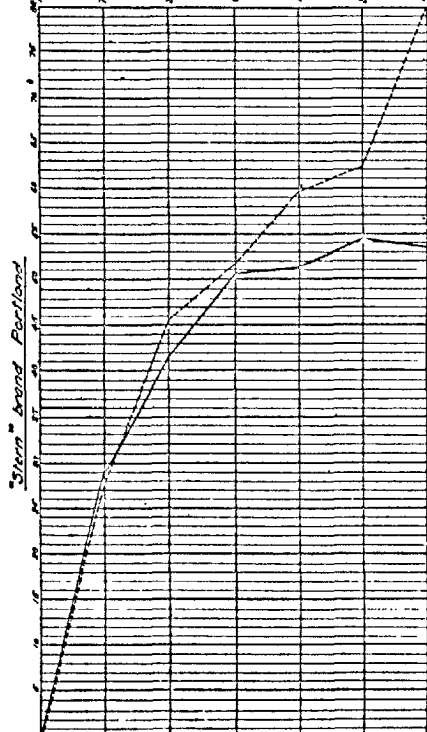
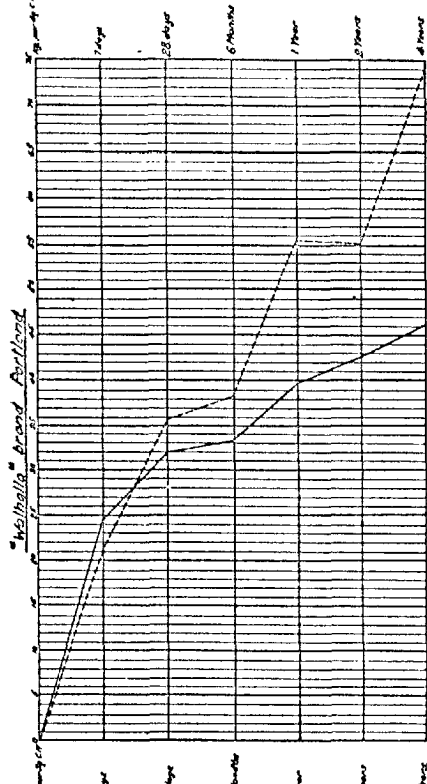
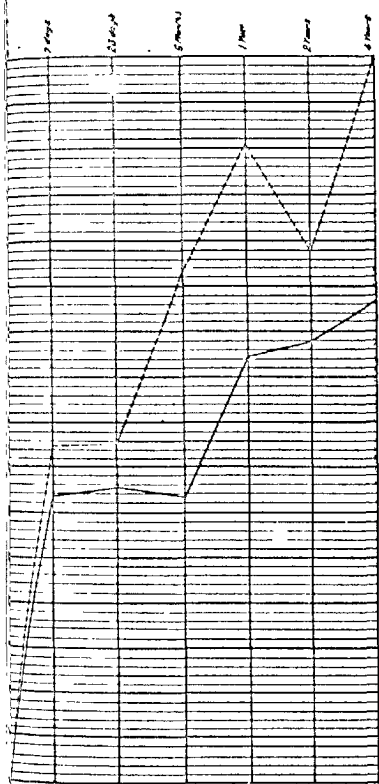
These tests and analysis show that the sand tests at 7 and 28 days are all that could be desired and considerably exceed the requirements of the British Standard Specification, nor is there any exposure of adulteration. They also show that the total sulphur calculated as sulphuric anhydride is well below the limit imposed by the British Standard Specification, being 2.07 per cent., against a limit of 2.75 per cent.

In every other point the tests comply with all the requirements of the British Standard Specification, although in our opinion these are not at all suited to modern conditions.

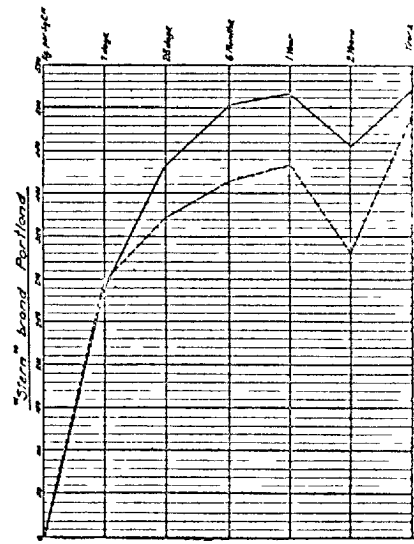
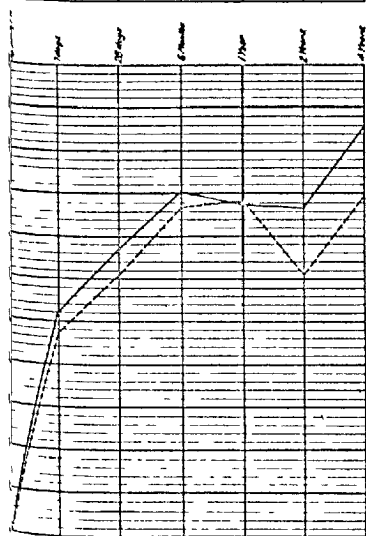
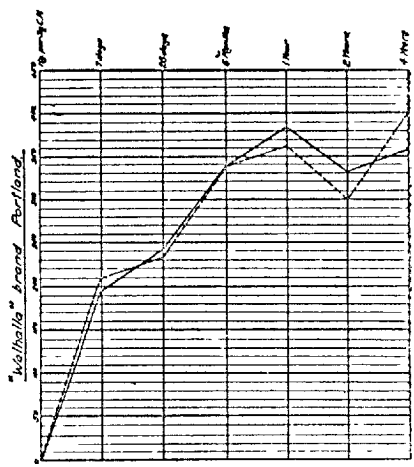
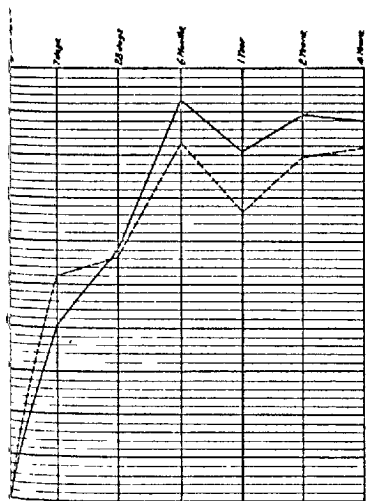
We agree with Mr. Davis that an excessive quantity of sulphur might be disastrous, although no such excess is present in the product under discussion. But the following experiments made on a large scale prove without doubt that the fears expressed by Mr. Davis are groundless in the case of properly made "iron Portland" cement.

1. The example quoted by Dr. Desch, the concrete pier at Skinningrove (described in the *Journal of the Iron and Steel Institute*), which, although made with "slag cement" containing probably a higher proportion of sulphur than "iron Portland," is still after thirty years perfectly sound.

2. The tests extending over a period made by F. W. Taylor and Sandford E. Thompson in America, and given in *Pratique de la Construction en Beton et Mortier de Cement armés ou non armés*, translated by



TENSILE TESTS OF DIFFERENT CEMENTS
 MIXED WITH 30% GROUND WATER-GRANULATED SLAG
 1 OF THE MIXTURE TO 2 OF SAND
 ——— WATER
 - - - - - WATER + CEMENT



CONVERSION TABLES OF DIFFERENT CEMENTS
 MIXED WITH 30% GRAVEL AND 1% SAND
 FOR THE MIXTURE TO BE USED
 IN THE MIXTURE TO BE USED
 IN THE MIXTURE TO BE USED

Specification Requirements.

Maximum, 14 per cent.

Maximum, 1 per cent.

Minimum, 450 lb.

Minimum, 200 lb.

Not less than 3'10.

	INITIAL.	FINAL.	
	Minimum.	Minimum.	Maximum.
Quick Setting	2 min.	10 min.	30 min.
Medium	10 min.	1 hour	3 hours
Slow	30 min.	3 hours	7 hours

Maximum expansion.

After 24 hours' aeration 10 millimetres
 Or after 7 days' " 5 "

BRITISH STANDARD SPECIFICATION.

(Fourth Issue, March 1915.)

Residue when sifted through a No. 180 by 180 sieve, 6·7 per cent.
 Fineness { Residue when sifted through a No. 76 by 76 sieve, 0·1 per cent.

TENSILE STRENGTH PER SQUARE INCH :
NEAT CEMENT.

Water used for gauging 26·35 per cent.
 briquettes placed in water 24 hours
 after gauging. Strain applied at the
 rate of 100 lb. in 12 seconds in a
 standard testing machine.

Seven Days' Test.

No. 1 broke at 510 lb.
 " 2 " 510 "
 " 3 " 550 "
 " 4 " 525 "
 " 5 " 535 "
 " 6 " 545 "

Average, 529 lb.

TENSILE STRENGTH PER SQUARE INCH :
SAND TEST.

Three parts of standard sand to one of
 cement, by weight, gauged with 9·37
 per cent. of water. The briquettes
 were placed in water 24 hours from
 gauging, where they remained until due
 for testing, when they were broken in
 a standard machine, with the following
 results :

Seven Days' Test.

No. 1 broke at 380 lb.
 " 2 " 360 "
 " 3 " 345 "
 " 4 " 365 "
 " 5 " 370 "
 " 6 " 365 "

Average, 364 lb.

Specific gravity 3'113

Setting properties : initial, 8 minutes ;
 final, 65 minutes.

Soundness by the } After 24 hrs. aeration 1 mm.
 Chatelier method } " 7 days " — "

Not exceeding—	
	3'0 per cent.
	1'5 per cent.
	3'0 per cent.
Total sulphur calculated as sulphuric anhydride	2'75 per cent.

Minimum, 2 ; maximum, 2'85.

NEAT TEST.

Minimum increase on 7 days' test :
 Strength at 7 days $\left\{ \begin{array}{l} + \frac{40,000}{\text{Strength at 7 days}} = 604 \text{ lb.} \\ = 529 \text{ lb.} \end{array} \right.$

SAND TEST.

Minimum increase on 7 days' test :
 Strength at 7 days $\left\{ \begin{array}{l} + \frac{10,000}{\text{Strength at 7 days}} = 391 \text{ lb.} \\ = 364 \text{ lb.} \end{array} \right.$

BRITISH STANDARD SPECIFICATION—continued.

CHEMICAL ANALYSIS.

Water	0'66
Carbonic anhydride	nil
Insoluble residue	0'25
Silica	23'69
Alumina	10'37
Oxide of iron	1'07
Oxide of manganese	0'49
Lime	59'97
Magnesia	1'84
Total S as SO ₃ , 2'07 per cent.—	
Sulphur as sulphide	0'55
Sulphuric anhydride	0'70
Alkalies and loss	0'68

100'27

Deduct O equivalent to S .. 0'27

100'00

Hydraulic modulus, 2'15.

Twenty-eight Days' Test.

Briquettes, both neat and sand, gauged and treated as previously described, were broken at the expiration of 28 days from gauging with the following results :—

NEAT TEST.

No. 7 broke at	610 lb.
„ 8 „	595 „
„ 9 „	630 „
„ 10 „	605 „
„ 11 „	595 „
„ 12 „	640 „

Average, 612 lb.

SAND TEST.

No. 7 broke at	455 lb.
„ 8 „	470 „
„ 9 „	440 „
„ 10 „	480 „
„ 11 „	495 „
„ 12 „	440 „

Average, 463 lb.

M. Davis, editor of *Revue générale de la Construction*, pp. 407, § 21 ; 408, § 25 ; 409, § 26 ; 411, § 33.

3. A chimney in reinforced concrete, 57 metres high, built in Wishaw Steel Works, which has been in use at high temperatures for nine months and is showing no sign of deterioration.

Our paper, as we said before, had not for its object the provocation of a quarrel between commercial interests, but rather the promotion of a technical discussion, in order that we might arrive at a definite scientific



explanation of the facts which we have quoted, and at the same time stimulate further research.

Our hopes are already realized ; for the experiments and the explanations given in Mr. G. A. Rankin's most interesting paper confirm all our tests and reply to our suggestions.

(a) Thus, the presence of a high percentage of aluminates in our raw material (slag) acts as a flux in the formation of a high percentage of tricalcic silicate, the principal component of Portland cement.

(b) The high percentage of tricalcic silicate in the mixture explains the high tensile strength obtained.

(c) The high percentage of tricalcic aluminate in the clinker by its catalytic action assists the activity of the dicalcic silicate (which is inert in other cements), both in the clinker and the slag when finely ground together in suitable proportions. This action explains the long continued increase in strength of cement with proper slag added.

(d) The activity of setting caused by the presence of aluminates is regulated by their action on the dicalcic silicate contained in the clinker and the slag.

This is a technical explanation, going further than we had expected, of the facts put forward, which justifies our contention that the mixture of suitable slag and clinker in the proper proportion is an improvement and not an adulteration.

The suggestion that our clinker contained a large proportion of "alite" has been confirmed by Dr. Desch, who kindly made a microscopic examination and photograph (see accompanying figure). Another very important improvement resulting from the addition of a certain quantity of slag, which acts as a pozzuolan, is the increased power of resisting the action of sea-water. Disintegration of the best Portland cements due to this cause takes place in a comparatively short time.

Mr. Davis suggests that research should follow another course. We think that he makes a mistake in advocating the manufacture of a low-lime clinker. He will not thus produce the tricalcic silicate and tricalcic aluminate which are, as explained by Mr. Rankin, so necessary for the desired reactions. This has already been shown by the manufacture on a large scale of cement in France and Belgium from materials low in lime. They require only a low temperature for burning and are easily ground. The final product, known as Roman cement, is quick setting, but seldom exceeds a tensile strength of 100 lb. per square inch at 7 days (neat cement). It is used specially for marine work, where setting in a few hours time is essential, and although low in tensile strength resists admirably the destructive action of sea-water.

Dr. C. H. Desch replied as follows to the discussion:—

The question as to whether the setting of a cement itself is a colloidal or a crystalline process has not been dealt with very much in the discussion, mainly, I think, because there are few people in this country who have done any work on that particular subject. The setting of cements has been studied almost exclusively in the United States and France. Experimental work has not been done here, but we have some interesting information bearing on it by analogy from the study of other substances. As regards the main point at issue between the supporters of the colloidal hypothesis and Professor le Chatelier, I think it is very clearly established, as was said by Mr. Hatschek, that we are dealing largely with a difference of terms ; that whether one regards the jelly as a mass of extremely minute interlacing particles or not is not of very much importance. At any

rate, the essential point is that in the colloidal substance the particles are extremely small, and therefore the surface forces are very important. When you come to crystals of perceptible size, such as in the crystallization of sodium sulphate, the surface forces are very small relatively to the forces of cohesion. In the case of the ultra-microscopic particles in the colloid, the surface forces are large in proportion to the forces of cohesion, and when that fact is fairly grasped it is seen that there is no great question of fact at issue between the two views. Dr. Rosenhain's remarks on setting are extremely interesting in bringing into comparison such entirely different phenomena as the setting of metal and of cement, and there is a close analogy. In the setting of metals, on Dr. Rosenhain's hypothesis, we are dealing with particles very close together becoming united by exceedingly thin films. These films, in the case of cements, are often of greater dimensions than the particles from which they start, so that we have a mass of considerable thickness and not a mere inter-crystalline film. As has been pointed out, the essential difference between cases of recrystallization and of the setting of a colloidal mass lies in the solubility. The substances which occur in cements after setting are substances of very low solubility. It is quite possible that the original substance present in clinker is of comparatively high solubility, but the solution formed by it is unstable and the stable products finally obtained are of extremely low solubility.

In the paper by Mr. Lewis and M. Deny is raised the question whether tricalcium silicate might be formed in the first stage of the operations in the blast furnace. I think that can be answered. Tricalcium silicate is only formed in cement containing a high percentage of lime; during the time the material is in the blast furnace the percentage of lime is much too low for its formation. It is formed in the second stage, when more limestone is added to the silicates. Mr. West doubted whether a good Portland cement was improved by the addition of slag. I think the experiments of Mr. Lewis and M. Deny prove that clearly. They started with good brands of Portland cement and obtained considerable improvement by adding slag. It always seems to me that must be so. When Portland cement sets, lime is liberated in the process. If you can introduce into that a substance capable of combining with the lime owing to the presence of soluble silica, i.e. a pozzuolanic substance, you will expect to get an increase of strength, just as lime mortar derived its great strength from pozzuolan in Roman times. There is no better pozzuolanic substance than finely ground granulated blast-furnace slag, and if you have that mixed with Portland cement, you will expect an increase of strength, because the lime, set free, combines with the silica and forms calcium silicate. The objection made by some people to adding slag is due to the danger of expansion afterwards on account of the high proportion of sulphur. Undoubtedly if you have a high proportion of sulphur you may get expansion, but very much depends on the way in which the sulphur is combined. I have seen excellent blast-furnace slag cement made by the old process which shows no expansion, and such cements are particularly suitable for use under sea water. There is the well-known case of the jetty at the Skinningrove Ironworks which Mr. Hutchinson built thirty years ago with old blast-furnace slag before the matter was investigated very much. That stands in the sea now perfectly, when I believe other jetties made of Portland cement have been badly damaged. The amount of sulphur can be regulated very closely, and in the best iron-Portland cements is little more than in Portland

cement. My impression is that there is a very great future for the manufacture of cement from blast-furnace slag, which will have the effect of disposing of a great deal of extremely troublesome waste material; but care must be taken in its manufacture and the specification must be very rigid.

Mr. Caroe's interesting remarks point to certain problems in connection with setting which deserve careful investigation. Prominent among these is the destructive effect of cement on certain building stones. From every point of view it is to be hoped that the Society will be able to carry out its proposal to subject the problem of setting to a thorough investigation.