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.

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, $2CaSO_4, H_2O$, readily dissolves in water, forming an unstable solution which is supersaturated in respect to the dihydrate, $CaSO_4, 2H_2O$. 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 $2CaSO_4,H_2O$, 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 $BaSiO_3$, $6H_2O$. The orthosilicate undergoes hydrolysis, forming the hydrated metasilicate, $Ba_2SiO_4 + 15H_2O = BaSiO_3$, $6H_2O + Ba(OH)_2$, $8H_2O$. 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, $3CaO$, SiO_2; calcium orthosilicate, $2CaO$, SiO_2; tricalcium aluminate, $3CaO$, Al_2O_3; pentacalcium trialuminate, $5CaO$, $3Al_2O_3$; 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, $CaSiO_3$, $2 \cdot 5H_2O$, and a hydrated tetra-calcium aluminate, $4CaO$, Al_2O_3, $12H_2O$, 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.