SVERIGES GEOLOGISKA UNDERSÖKNING

SER. C. Avhandlingar och uppsatser. N:O 357.

ÅRSBOK 23 (1929) N:O 2.

ON THE CONSTITUTION OF HYDRATED PORTLAND CEMENT

BY

G. ASSARSSON AND N. SUNDIUS

With one Plate

Pris 0:50 kr.

STOCKHOLM 1929
KUNGL. BOKTRYCKERIET. P. A. NORSTEDT & SÖNER
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From[1] the work of the Geophysical Laboratory of Washington it is known that the minerals resulting from a mixture of CaO, SiO_2 and Al_2O_3, in the proportions found in Portland Cement, will be trisilicate, disilicate and trialuminate of lime, when the reactions in the melt are complete. At a lower temperature a somewhat larger amount of the disilicate and 5 : 3-aluminate will be formed, the corresponding quantities of CaO being set free at the same time. According to Rankin, these mineral compounds will be the principal ones to be expected in the clinker of the cement, its minor constituents (Fe_2O_3, MgO and alkalis) being neglected. In point of fact a microscopical examination of cement-clinker carried out by P. H. Bates has confirmed this.[2] Nothing but a review of this publication being available, one of the present writers carried out an optical study of the clinker minerals. This investigation will be mentioned here, as it was based on Törnebohm's old slides, which are deposited at the Geol. Survey of Sweden. The principal minerals found in these slides were the same as those named above. Thus Törnebohm's Alit corresponds optically to the lime-trisilicate, the Belit and Felit to the β-disilicate, and the isotropical material, mentioned by him, will for the most part be trialuminate and 5 : 3-aluminate, the substance of the latter being recognisable by its lower refraction power and by the clouded and brownish appearence of the grains, the trialuminate being clear and free of inclusions. Both aluminates are seen in the same slide, but the 5 : 3-aluminate is not always present. Between the Belit and the Felit there is the difference that the substance of the former is somewhat turbid and yellowish, the latter is clear and transparent. Moreover, the Belit is distinguished by an intricate striation, though the substance of the grains is optically uniform. As the optical properties distinctly correspond to those of β-disilicate, the consequence must be that the β-form of the silicate is pseudomorph after the α-modification, while Felit has crystallized in the β-form directly. The Felit is in part transformed into γ-disilicate, easily distinguished by its lower birefraction and by its fibrous consistensy. Very seldom are there seen, together with Belit, really twinned disilicate grains, which may be remains of α-disilicate.

[1] This paper is an abstract from two articles that will appear simultaneously in Swedish in the publication series of the Royal Board of Waterfalls (K. Vattenfallsstyrelsen, Tekn. medd. Ser. B., Stockholm).

[2] Concrete Cement Age (cement mill section) 2, 3 (1913).

Törnebohm's Celit does not correspond to any of the clinker minerals described by Rankin and Wright. In several respects it resembles a dicalcium ferrite,[1] but does not quite tally with this compound, the axial angle being small and the optical character positive. This difference will possibly be due to the replacement of some part of the iron oxyde by Al_2O_3.

The two silicates, the trisilicate and the disilicate, always behave like different minerals, each displaying its own characteristic properties. The latter frequently occurs as small inclusions in the former, but even in this case the two minerals are decidedly different. This fact is not consistent with the view that the trisilicate is a solid solution of CaO in disilicate. In some cases, around the trisilicate grains, there is seen a small outermost border of a somewhat higher birefraction, the composition of which not is known. Even in these slides, however, the two minerals are optically distinctly different. In this paper, therefore, Rankin's view is adopted, that the trisilicate is a separate mineral of the composition $3\,CaO\,.\,SiO_2$.

The hydration products of the separate clinker minerals and of mixtures of them, when treated with water or solutions of calcium hydrate, have been studied by several authors.[2] The products found by them are of two kinds, one consisting of an amorphous mass of hydrosilicate of a composition not definitely known, the other of crystallizing material, calcium-hydrate and hydro-trialuminate. Both the last-named compounds are at first generated as amorphous substances, but tend to assume a crystalline form. When sulphuric acid is present, the double compound sulphate-aluminate is formed too. These constituents would thus be expected in the hydrated cement.

This result was checked by the present writers by means of a microscopical examination of slides of hydrated cement and concrete. For the preparation of the microscopical slides paraffin oil was at first used, instead of water, but this medium being inconvenient it was exchanged for a saturated solution of calcium-hydroxide in water. As the hydration process in the cement goes on very slowly after the hardening, the chemical influence on the cement of the slides will be negligible. The only probable effect of the contact with the lime-water is the transformation of some small amounts of amorphous calcium-hydroxide into a crystalline state. Before the preparation of the slides the cement was well dried in an exsicator over phosphor-pentoxide.

On examination a slide of hydrated cement is seen to contain a considerable amount of non-hydrated *clinker remains,* which are uniformly distributed in the dense, yellowish gray, hydrated cement mass. The clinker grains remaining in the cement can readily be determined and are found to consist for the greater part of disilicate. Trisilicate also occurs, but most-

[1] Sosman and Mervin, Journ. Wash. Acad. of Sc., Vol. VI, N:o 15 (1916).

[2] S. Keisermann, Kolloidchem. Beihefte, Bd. 1, H. 10—11, 423 (1910), A. A. Klein and A. J. Phillips, Bureau of Standards, Dep. of Commerce, Techn. pap. Nr. 43 (1914).
P. H. Bates and A. A. Klein, Bureau of Standards, Dep. of Commerce, Techn. pap. Nr. 78 (1917) and 197 (1921).

ly as larger fragments, enveloped by clear zones of hydro-silicate. Around the disilicate grains these zones are much smaller and less conspicuous. Grains of clinker aluminate are practically absent. These facts accord with the results arrived at by the treatment of the separate clinker minerals with water, the rate of the hydrolysis of the disilicate being much slower than that of the aluminates and of the trisilicate. An estimate of the clinker grains in a cement $5^1/_2$ months old, and kept in water, gave as a result about 14 vol.-%, of which about 8 % is made up of disilicate, 5—6 % of trisilicate, and the small remainder of the ferritic mineral, and some sporadic remains of trialuminate.

Under the crossed nicols the *calcium hydroxide* of the cement becomes visible. The component is well crystallized but forms homogeneous individuals only to a minor extent. For the most part it fills out the small spaces between the hydrated and partly hydrated clinker grains, but as the substance in neighbouring spaces is often uniformly orientated, it forms in reality larger individuals, which enclose the clinker grains. In this way the calcium hydroxide may contribute not only to the density of the cement but also to its strength.

The *hydro-aluminate* is best observed after treating a slide with a water solution of patent blue. The grains coloured in this way are to some extent amorphous, but for the most part they appear as badly crystallized, fibrous individuals. The fibrous structure is frequently seen arranged radially, and in the central part some small amount of amorphus substance, or in rare cases small remains of clinker aluminate, is to be detected. When most perfectly crystallized, the hydrated alumineous substance exhibits the properties of hydro-trialuminate.

Even when treating the cement in the said manner, the number of aluminate grains observable under the microscope is not great and does not correspond to the figure of Al_2O_3 of the analyses. The explanation of this fact may probably be that the substance in question is in part very finely distributed in the dense hydrosilicatic mass and is not visible in the microscope either. On the other hand, it is possible that the aluminate is isomorphic with the calcium hydroxide and partly mixed with the latter as a solid solution. This assumption is made possible *inter alia* by the similarity of the crystallographical properties of both compounds. No special researches on the subject have as yet been made.

The main part of the hydrated cement, however, is composed of the *amorphous silicate product.* About this it only can be said that it does not contain free hydrous silica, as it does not react to methylen blue. Furthermore, to judge from the varying amounts of crystallized calcium hydroxide in specimens exhibiting similar quantities of clinker remains, it is probable that the hydro-silicate mass may contain some indeterminable amounts of amorphous calcium hydroxide.

Recently the problem of the hydrolysis of the clinker minerals has been attacked in another way by W. M. Lerch and R. H. Bogue.[1] These authors

[1] J. Phys. Chem., 31, 1627 (1927).

determined the hydrolysing curves of the separate, pure clinker minerals. Of special interest for this work are the relations found in the trisilicate. This compound readily gives off a third of its calcium-content, after which the hydrolysis proceeds much more slowly. L. and B. furthermore determined the alkalinity of the water solutions in which the clinker minerals not were hydrolyzed. For the silicates the value of the PH is greater than that of a saturated solution of calcium hydroxide. The same is the case also for the dicalciumferrite. When treated with saturated calcium hydroxide the silicates will thus give off CaO, until equilibrium is established, probably when the remaining hydro-silicate is of about a monosilicatic composition.

Between the experiments of Lerch and Bogue and the relations in the hydrated cement, the chief difference lies in the quantity of the water used. In the experiments this quantity was great, but in the cement it is limited. This difference is of very great practical importance, but does not influence the course of the hydration process. A further difference lies in the iron, magnesium and alkali impurities in the cement. The presence of these elements, however, does not play any great part, the solubility of the hydroxides of iron and magnesium being very low. In what form the alkalis are present in the clinker is unknown, but special researches by the present writers have shown that the amounts that are dissolved in water and in solutions of calcium hydroxide are very small and do not appreciably influence the hydrolyzing processes.

In view of the relations referred to in the above, we can imagine the course of the hydrolyzing process during the hardening of the cement about as follows: The first effect of the water on the clinker minerals is a hydrolysis of all of them. As the quantity of the calcium hydroxide dissolved in the water rises to a certain amount, the hydro-trialuminate becomes stable, and this compound is now formed at the expense of all the aluminuous substances. The silicates are not yet in equilibrium and do not reach this state even when the water becomes saturated with calcium hydroxide. The silicates thus continue to give off CaO to the water solution, and calcium hydroxide is deposited from it in a solid state. The same is the case with the ferritic mineral, which is split up into free iron oxide hydrate and CaO. Theoretically, and in the presence of sufficient quantities of water, the alteration of the clinker compounds would continue until they were all altered. The resulting product would then be a mixture of hydro-trialuminate (possibly + sulphate-aluminate), calcium-hydroxide, iron oxide hydrate, and a hydro-silicate, probably of about a monosilicatic composition. This final state is far from being reached in the hardened cement. That this is the case is shown, *inter alia,* by the presence in the hardened cement of considerable quantities of non-hydrated clinker grains.

From the microscopical examination of the cement it is known that the aluminates of the clinker are practically completely hydrated. As the remaining ferritic substance plays an unimportant part, the problem of the

progress of the hydrolyzing effect during the hardening is wholly confined to the silicate complex. As we know the formula for the aluminate, the average composition of the silicate complex could be obtained, if we determined the percentage of free calcium hydroxide present in the cement.

For the determination of the calcium hydroxide, the method of dissolving this substance in glycerine seemed to be applicable. This method was recently tried by Lerch and Bogue for CaO in clinker,[1] and found to be suitable in that case, the calcium bound in silicates, aluminates and ferrite not being dissolved. The chief factor of uncertainty as to the hydrated cement is the water adsorbed by the gelatinous compounds and chemically bound in the hydroxide. All the latter, and at least the greater part of the former, may be free under the progress of the analysis and could be assumed to attack the silicates, producing a too high value of the hydroxide. There is, however, a factor that may counteract this error, namely the slow rate of the hydrolysis of the remaining silicate complex in the cement. Moreover, the possible error may be reduced to a minimum by using large volumes of alcohol. In the researches referred to in the following pages the volume of the alcohol-glycerine solution at the end of the process was about 100 cc, and in this volume the concentration of water attains a max. of 0.1 per cent, even when the cement used has a water-content of 25 per cent. The effect of this water concentration must be small. Another factor of uncertainity is the difficulty of leaching out the last remnants of the hydroxide from the interior of the cement grains. At the end of the operations the remaining cement powder was examined under a microscope, and tested for free lime by White's reagent, but with a negative result. By careful seeking there could be detected small traces of crystallized hydroxide in the innermost parts of a few of the larger grains, but for the rest the compound in question was absent. These small remnants may to some extent counteract the possible error caused by the water liberated. On the whole the value of CaO found may perhaps be a little too high, but does not substantially differ from the correct one. A comparative attempt on pure crystalline calcium hydroxide gave a quite satisfactory result. The rate of the dissolving of the hydroxide was at first very slow, but became more rapid after the addition of a few cc of a solution of ammonium acetate. Compared with the analyzed cement, the rate of the reaction between the glycerine and the calcium hydroxide was slower, probably owing to the presence in the cement of amorphous parts of the hydroxide.

Before the analysis, the cement was dried in an exsicator, crushed until the diameter of the grains was 1 mm, again dried in vacuum (12 mm) over phosphor pentoxide. Lastly it was wetted through with alcohol and dried in vacuum. The sample treated in this way had the following composition.

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[1] Ind. Eng. Chem. 18, 739 (1926).

	1.	2.
SiO_2	18.6	23.0
Al_2O_3	4.5	5.5
Fe_2O_3	2,0	2.5
CaO	52.0	64.2
MgO	1.3	1.6
CO_2	2.6	3.2
	81.0	100.0

1. Analysis of the dried cement.
2. The same figures as in 1, calculated as water-free.

To the figures of 1 there must be added 0.5 per cent of alkalis, determined as oxides, and 0,27 per cent of insoluble mineral grains (quarz, feldspar, etc.). SO_3 is present only in traces.

For the determination of the calcium hydroxide, a sample of 0.5 gr. was pulverized as finely as possible together with 5 cc glycerine (G. = 1.26) and some absolute alcohol. The dissolving out of the hydroxide was performed in a similar manner to that described by the authors referred to above. The grinding of the powder and the boiling with alcohol and glycerine were repeated as long as the solution showed any reaction to $Ca(OH)_2$.

Two determinations performed in this way gave 8.8 and 9.2 per cent of CaO in the whole sample or, calculated on water-free material and on an average, 11.2 per cent.

Starting from this figure, an approximate calculation of the mineral content of the cement can be made. In the cement there is present a considerable amount of lime carbonate, and from the analysis it can be determined at 7.3 per cent.[1] Some minor part of this carbonate may already have been present in the clinker powder used, yet a great part may have been introduced and formed from the water added during the hydration of the clinker. Some part of the carbonate is also formed from the CO_2 of the air during the grinding and storing of the cement. At least the bulk of the latter amounts may have been formed at the expense of calcium hydroxide. Thus at least the greater part of the carbonate should strictly be reckoned as hydroxide, but in the absence of any norm for the division, the whole amount is set down as a separate compound of the cement. The course of the calculation appears from the table 1.

Table 1.

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	CO_2	Total
Figures of the water-free cement	23.0	5.5	2.5	1.6	64.2	3.2	100.0
CaO in $Ca(OH)_2$					11.2		11.2
$CaCO_3$					4.1	3.2	7.3
$3CaO \cdot Al_2O_3$		5.5			9.0		14.5
Fe_2O_3			2.5				2.5
Silicate complex	23.0			1.6	39.9		64.5

[1] This figure and all the figures in the following pages refer to water-free composition.

For the calculation the quite small amount of remaining ferrite in the cement is neglected, and the MgO is included in the silicates. In the silicate complex are included the hydrosilicate of the cement and the remaining unhydrated clinker grains. The figures of the table show the average composition of this complex to be:

$$CaO : SiO_2 = 2 : 1.04.$$

This formula conforms almost exactly to an average disilicatic proportion. As the clinker remains to some small extent include grains of trisilicate, the hydrated silicate mass may be a little richer in SiO_2 than is shown by the average formula. Also there is some uncertainty as to the lime of the carbonate referred to in the above. But even if we admit that as much as half this lime enters into the silicate complex, its formula would not be substantially altered. This estimate, however, is certainly much too high.

This result is somewhat surprising, as most earlier authors seem to have supposed an approximately monosilicatic formula for the hydrosilicate in the cement, though opinions in favour of a disilicate are not entirely absent. The analytically found formula agrees well with the hydrolyzing curves of Lerch and Bogue, also it is in fairly close agreement with the mineralogical relations found in the cement.

From the data arrived at in the above, it follows that the process of the hardening of the cement consists of a hydrating of the aluminates and their transformation into hydro-trialuminate, a decomposition of most of the ferritic substance and a splitting off of one of the CaO-molecules of the trisilicate. These reactions go on relatively suddenly. The ferrite in itself is not very easy to hydrolyze, but its amount is small. The disilicate in the clinker, on the other hand, is but little affected. The further hydrolyses of the still average disilicatic silicate complex proceeds much more slowly. As the silicate complex is not yet in equilibrium with the saturated solution of calcium hydroxide, it should be further decomposed. The fact that it is not, but remains unaltered, must be due to the commencing relative deficiency of water in the hardening cement and to the dense, gelatinous consistency of the hydrosilicate mass, which prevents further reactions.

Thus, the cement does not represent a chemical system in equilibrium. On the contrary, each increase of the water-content will cause a continued hydrolysis of the silicate complex and a generation of more lime hydroxide. That the cement can, nevertheless, exist unchanged for many years, even when immersed in water, is wholly to be attributed to the density of its structure and of the hydrosilicate.

2—291034. *S. G. U. Ser. C. N:o 357. Assarsson and Sundius.*

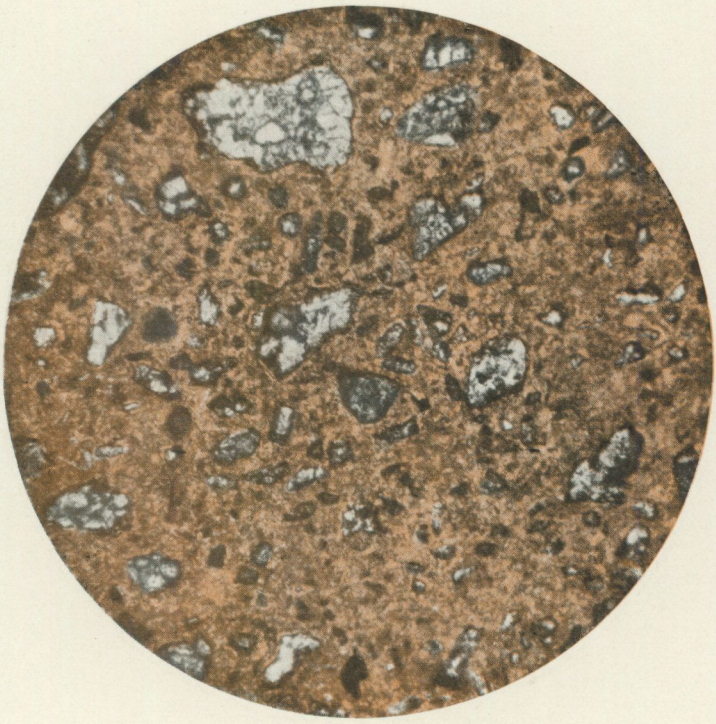

Fig. 1. Thin section of hydrated cement, seen in ordinary light. Magn. 120 x. The hydrated parts of the cement are printed in red leaving the intact clinker remains visible.

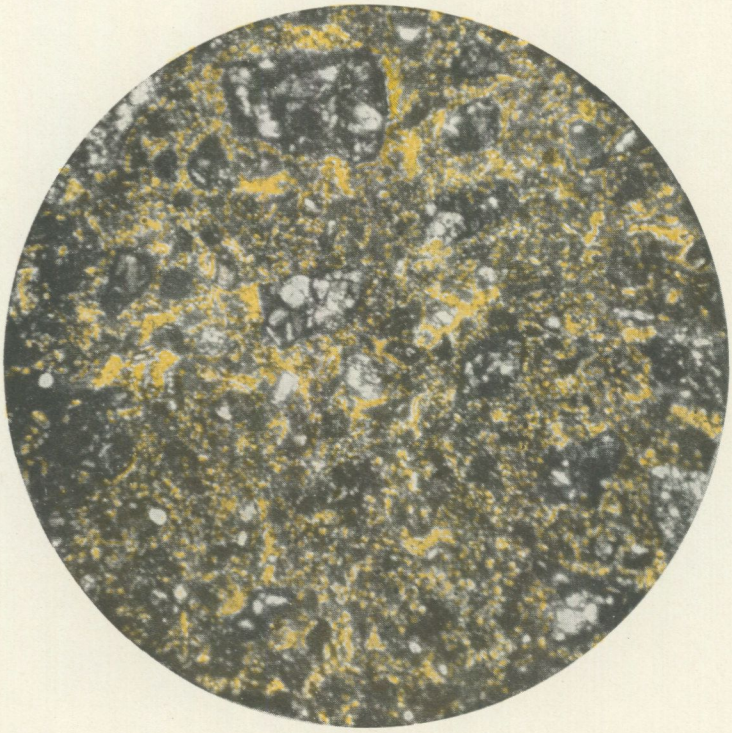

Fig. 2. The same figure as in 1, seen in crossed polarized light. The figure is intended to show the distribution in the hydrated mass of the calcium hydroxide, which is coloured yellow. The quantity of the hydroxide however appears to be greater on the reproduced photograph than it is in reality owing to the halation produced by the interference light of the grains. The position of the clinker remains is distinguishable if the figure is compared with nr. 1.

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