

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 is 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 any considerable strength. The specimen remains sound, however, and is not readily soluble.

Microscopical examination of dicalcic silicate which has been shaken for a 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 this 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. This 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 shaken with water, the hydration of dicalcic silicate is not affected except in the case of tricalcic 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 it sets and hardens rather rapidly. Moulded specimens when placed in water remain sound, and within a reasonable time develop a strength comparable to 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 cements in water, it does not appear that the rate of formation of amorphous tricalcic silicate is affected.

From this 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 alkalies. 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 sandstones (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 a 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 calcium 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 5 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,

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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 sandstones.

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