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MORPHOLOGY AND MICROSTRUCTURE OF HYDRATING PORTLAND CEMENT AND ITS CONSTITUENTS

**V. CHANGES IN HYDRATION OF PORTLAND CEMENT WITH
AND WITHOUT THE PRESENCE OF TRIETHANOLAMINE AND
CALCIUM LIGNOSULPHONATE**

by
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MORPHOLOGY AND MICROSTRUCTURE OF HYDRATING
PORTLAND CEMENT AND ITS CONSTITUENTS
V. CHANGES IN HYDRATION OF PORTLAND CEMENT
WITH AND WITHOUT THE PRESENCE OF TRIETHANOLAMINE
AND CALCIUM LIGNOSULPHONATE

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(Communicated by G. M. Idorn)

ABSTRACT

Systematic sequential observations with the electron microscope were made of the morphological changes that occurred during the hydration of normal portland cement paste. The specific effect of each of two admixtures, triethanolamine and calcium lignosulphonate, was studied. The hydration products observed were clearly the same as those noted in the pastes of pure minerals or mixtures of these. The morphological changes that occurred appeared to be the same, and the rate of change effected by the presence of an organic admixture was found to be very similar.

SOMMAIRE

Des observations au microscope électronique ont été faites en séquence systématique pour observer les changements morphologiques qui prennent place au cours de l'hydratation d'une pâte de ciment portland ordinaire. Les effets spécifiques de deux adjuvants, triéthanolamine et du lignosulfate de calcium ont été étudiés. Les produits d'hydratation observés étaient nettement les mêmes que ceux observés dans les pâtes de minéraux purs ou des mélanges de ceux-ci. Les changements morphologiques qui ont pris place sont apparus comme étant les mêmes et la rapidité des changements en présence d'adjuvants organiques a paru très similaire.

*Standard cement nomenclature has been used; e.g., w/c = water:cement ratio by weight; $C_3S = 3CaO \cdot SiO_2$; $C_2S = 2CaO \cdot SiO_2$; $C_3A = 3CaO \cdot Al_2O_3$; $C_4AF = 4CaO \cdot Al_2O_3 \cdot Fe_2O_3$.

This is the fifth of a continuing series of papers which report the morphological changes occurring during the hydration of portland cement and its constituents with and without the presence of some organic admixtures. The first four (1-4) dealt with the hydration of the pure mineralogical components of portland cement and a mixture of them. The present paper describes the changes of morphology and microstructure which occur during continued hydration of portland cement paste. The effects of two organic admixtures are observed.

Introduction

Experimental studies of the hydration processes of portland cement and its constituents were reviewed in detail at the Fourth and Fifth International Symposia on the Chemistry of Cement at Washington in 1960 (5) and at Tokyo in 1968 (6-10). Extensive studies of the morphology of cement hydration products have been published by A. Grudemo (11) and many others; these dealt with cement pastes with different w/c^* ratios, and also with products of bottle hydration in excess water. These researchers observed the forms of microstructure and morphology which developed at different times of hydration. Results of these investigations were summarized in papers presented at the Tokyo Symposium.

More recent studies with the scanning electron microscope have extended the supporting knowledge in this field. Among those active in such studies are Diamond (12), Chatterji and Jeffery (13), Williamson (14) and Mills (15).

The previously reported studies in this laboratory were designed to clarify the changes in morphology and microstructure expected to be observed in the more complex portland cement pastes (1-4, 16). Two chemical admixtures were selected in order to determine if the effect of quite alien constituents, which are known to have an effect on the properties of concrete, can be clearly observed and followed by the electron microscope. It was hoped that the taking of electron micrographs on a sequential basis would form the basis of a method to distinguish the effects of different factors on the development of microstructure and, hence, on the mechanical

and physical properties of hardened portland cement paste. The results of the present study of portland cement paste have clearly established the value of this method. The most significant of the findings will be considered here.

Materials and Procedures

A normal portland cement was used, having the mineralogical composition given in Table I.

TABLE I

Mineralogical Composition of Normal Portland Cement

Mineralogical Component	Per Cent by Weight
C_3S	54.2
C_2S	20.7
C_3A	10.0
C_4AF	6.1
SO_3	1.8
Free Lime	1.1
Alkalies ($K_2O + Na_2O$)	0.7
Blaine	3100 cm^2/g

The two organic admixtures used, triethanolamine and calcium lignosulphonate, are the same as those used in the previous studies and their properties are described therein (1-4).

Pastes were prepared on the basis of water to dry powder of 0.5 by weight. Admixture dosages were 0.5 per cent by weight of dry cement. Further characteristics of materials and description of methods and procedures used in preparing and examining test specimens are given in the first two papers in this series (1-2).

At intervals of a few minutes, 1 and 6 hours, 1, 2, 3, 7 and 14 days,

and 1, 2 and 3 months, samples were taken and tested. Hydration was stopped by treating the paste with acetone at about -18°C , and then drying the frozen samples in vacuum.

At 2 months hydration time the surfaces of the hydrated cement pastes were etched by ethylene glycol and the treated and untreated surfaces compared. Single-stage replicas from freshly broken surfaces of the paste were made using the platinum carbon technique. The electron micrographs shown are those that depict the average and general morphology. Rarely occurring forms were considered of minor importance and therefore not given attention in this study.

Results and Observations

At the age of a few minutes the cement paste microstructure displayed a loose mixture of unhydrated cement grains; single ettringite-type rods, small rounded particles and crumpled amorphous foils or sheets lay on the surface of the cement grains, and they were considered to be the main forms of hydration products (Fig. 1). With triethanolamine present more ettringite-type rods and small rounded particles appeared, and also amorphous forms were evident (Fig. 2). With calcium lignosulphonate present at this period of hydration, fewer hydration products developed; the major forms were very small, rounded particles, amorphous foils or sheets, and some laths with pointed termination (Fig. 3).

After the cement paste had been hydrated for 6 hours, the main products occurring between the unhydrated cement grains were seen to be ettringite rods, amorphous sheets and small rounded particles. Large unidentified crystals were observed, appearing as possibly foreshortened cubes (Fig. 4). With the admixture triethanolamine, the main hydration products at this time of hydration appeared as irregular plates, probably of low sulphoaluminate, and some single rod-like particles of ettringite (Fig. 5). With calcium lignosulphonate, the short, rod-like crystals of ettringite and the amorphous foils or sheets were the main hydration products at this age (Fig. 6).

FIG. 1

Microstructure of normal portland cement paste, $w/c = 0.5$. Age 5 minutes.

FIG. 2

Microstructure of cement paste with 0.5% triethanolamine, $w/c = 0.5$. Age 5 minutes.

FIG. 3

Microstructure of cement paste with 0.5% calcium lignosulphonate, $w/c = 0.5$. Age 5 minutes.

FIG. 4

Microstructure of cement paste, $w/c = 0.5$. Age 6 hr.

After one day of hydration the microstructure of cement paste displayed a loose mixture of hydration products, among which one could distinguish rods or columns of ettringite, small amorphous fibres of CSH radiating over unhydrated grains of cement, single grains of CAH of twinned, cubic-like forms and unoriented plates of hexagonal CAH (Fig. 7). Very frequently fibrous particles of CSH formed unoriented bundle-like aggregates which were sometimes filled with amorphous materials, thereby forming the flat surfaces (Fig. 8).

In the presence of triethanolamine at one day of hydration an amorphous film of a lace-like form of CSH appeared between the large irregular plates of what was probably low sulphoaluminate; fibres also developed on the surfaces of cement grains. Some of the fibrous, bundle-like aggregates filled with amorphous materials, displayed a sort of wing-like form (Fig. 9). With calcium lignosulphonate, large hexagonal crystals, probably of calcium hydroxide, were present between the amorphous fibres of CSH and the rods of ettringite, which together constituted the major forms of the hydration products (Fig. 10).

When the cement paste had been hydrated for 2 days, the main products appeared to be columns of ettringite and fibres of CSH, as well as twinned aggregates of cubic CAH forming a kind of skeleton structure between unhydrated grains of cement (Fig. 11). With the presence of triethanolamine the platy and fibrous forms of CSH displayed a three-dimensional arrangement (Fig. 12). With calcium lignosulphonate present the microstructure was relatively dense; the main hydration products were radiating fibres of CSH, rods of ettringite, and amorphous material occupying the flat surfaces between the cement grains (Fig. 13).

At three days' hydration with triethanolamine, the platy forms of the hydration products still displayed an angular arrangement of fibrous particles of CSH (Fig. 14). With calcium lignosulphonate the fibrous particles of CSH showed some tendency to a pseudohexagonal arrangement; large rods of ettringite were also present (Fig. 15).

At 7 days' hydration the microstructure of the cement paste was rather dense, and the platy forms of hydration products were often seen to

FIG. 5

Microstructure of cement paste with 0.5% triethanolamine, $w/c = 0.5$. Age 6 hr.

FIG. 6

Microstructure of cement paste with 0.5% calcium lignosulphonate, $w/c = 0.5$. Age 6 hr.

FIG. 7

Microstructure of cement paste, $w/c = 0.5$. Age 1 day.

FIG. 8

Microstructure of cement paste, $w/c = 0.5$. Age 1 day.

FIG. 9

Microstructure of cement paste, with 0.5% triethanolamine, $w/c = 0.5$. Age 1 day.

FIG. 10

Microstructure of cement paste with 0.5% calcium lignosulphonate, $w/c = 0.5$. Age 1 day.

FIG. 11

Microstructure of cement paste, $w/c = 0.5$. Age 2 days.

FIG. 12

Microstructure of cement paste with 0.5% triethanolamine, $w/c = 0.5$. Age 2 days.

have a basic fibrous structure (Fig. 16). With triethanolamine the microstructure of the hydration products and pseudomorphs of cement grains formed a closely knit and massive system; the platy forms still showed an underlying fibrous structure (Fig. 17). With calcium lignosulphonate the microstructure was also close knit and massive, and the hydration products frequently displayed its underlying fibrous structure (Fig. 18).

At age 14 days the cement paste had a massive and dense microstructure; it was made up of pseudomorphs of cement minerals and hydration products in the form of plates, fibres or irregular semi-amorphous habits (Fig. 19). In the presence of either triethanolamine or calcium lignosulphonate the microstructure was quite similar to that with no admixture present except that between the platy fibres and amorphous irregular forms of the hydration products, twinned cubic crystals of hydrogarnet could be distinguished (Fig. 20).

At ages of 30 and 60 days all cement pastes, with or without an admixture, showed the same type of dense, massive, unoriented microstructure made up of pseudomorphs of cement grains and the various forms of hydration products (Fig. 21). The cement paste was etched with ethylene glycol for 30 minutes; after etching, only a skeleton structure of fibres and plates remained of the microstructure that had been evident at earlier stages of hydration (Fig. 22).

After 3 months' hydration the microstructure with no admixture present was similar to that with triethanolamine present. Both displayed a massive, closely knit, unoriented structure of pseudomorphs of cement grains and several forms of hydration products (Fig. 23). The only difference with calcium lignosulphonate at that time of hydration, was the occurrence of more plates of striated cleavage (Fig. 24).

Under the conditions of these experiments, hydration products began to form as soon as the dry cement came in contact with water. The presence of triethanolamine clearly accelerated the formation of hydration products and the calcium lignosulphonate apparently retarded it. This was the case also with the simpler systems (1-4). For example, with the

FIG. 13

Microstructure of cement paste with 0.5% calcium lignosulphonate, $w/c = 0.5$. Age 2 days.

FIG. 14

Microstructure of cement paste with 0.5% triethanolamine, $w/c = 0.5$. Age 3 days.

FIG. 15

Microstructure of cement paste with 0.5% calcium lignosulphonate, $w/c = 0.5$. Age 3 days.

FIG. 16

Microstructure of cement paste, $w/c = 0.5$. Age 7 days.

FIG. 17

Microstructure of cement paste with 0.5% triethanolamine, $w/c = 0.5$. Age 7 days.

FIG. 18

Microstructure of cement paste with 0.5% calcium lignosulphonate, $w/c = 0.5$. Age 7 days.

FIG. 19

Microstructure of cement paste, $w/c = 0.5$. Age 14 days.

FIG. 20

Microstructure of cement paste with 0.5% calcium lignosulphonate, $w/c = 0.5$. Age 14 days.

FIG. 21

Microstructure of cement paste with 0.5% triethanolamine, $w/c = 0.5$. Age 2 months.

FIG. 22

Microstructure of cement paste with 0.5% triethanolamine, $w/c = 0.5$. Age 2 months. The surface was etched with ethylene glycol for 30 minutes.

FIG. 23

Microstructure of cement paste, $w/c = 0.5$. Age 3 months.

FIG. 24

Microstructure of cement paste with 0.5% calcium lignosulphonate, $w/c = 0.5$. Age 3 months.

accelerator present, the ettringite formation existed up to 2 hours, after which only the low sulphate form appeared. With the set-retarder, however, the ettringite persisted almost to two days before giving place to the low sulphate form.

The hydration products observed in the portland cement paste were clearly the same as those observed in the pastes of pure minerals (1-4), and the morphological changes that occurred appeared to be the same also. In the cement paste, as well as in the pure mineral pastes, the rate of change was affected by the presence or absence of the organic admixtures used.

The important changes in the morphology of the hydration products of cement, as for example, the change from the hexagonal CAH to the cubic CAH, or the change from ettringite to the low sulphate form of calcium sulphoaluminate, could be observed very clearly. In fact, most changes were as clear in the cement system as in the simpler systems, and sometimes were even clearer.

Although no major hydration products developed in the cement paste that did not also occur in the pure compound pastes, some differences observed are of interest, and indicate the usefulness of the sequential observation method in studying variables. With this particular normal portland cement, the formation of hydrogarnet was observed, whereas this product was absent in the simpler systems with gypsum present (1-4, 17). In the cement paste large hexagonal crystals of CH appeared at 6 hours when no admixture was present, at 1 day when the calcium lignosulphonate admixture was present, and not at all when the admixture triethanolamine was present. At later stages of hydration the well-formed CH crystals observed in the first two instances were no longer in evidence.

In the hydration of the portland cement used in these tests it appeared that the basic skeleton structure of the hardened cement paste had been essentially formed at 7 days. The changes occurring after this time consist mainly of the "filling-in" of the looser structure with additional hydration products which appear amorphous in nature (6). The microstructure, mainly CSH, then continues to become more dense and massive. Again, the rate at

which each change takes place is affected by the admixture present, and presumably can be affected by other factors not studied in this investigation. Size and crystal habits also depended on the admixture present. The occurrence of a new form of hydration product characterized a separate stage in the hydration process. It appears, then, that only about 7 days are required to determine the effects of any given variable, and that subsequent changes can be predicted. This, at least, appears to apply to the organic admixtures used in this study.

The main constituents of hydrated cement paste that were observed were the pseudomorphs of cement grains, the platy or amorphous CSH hydration products largely filling the spaces between them, and the hexagonal or cubic forms of CAH interspersed in the system. Also present was the ettringite or the low sulphate form of calcium sulphoaluminate.

Except for the cases mentioned above, crystals of CH were relatively rare in occurrence. The glycol etching treatment of the massive, tabular structure, which developed during hydration, clearly exposed the basic fibrous structure of the original plate-like slabs, and showed that a "filling-in" process, presumably with both amorphous CSH and CH, produced the changes from fibres to plates to tabular masses (16). This underlying three-dimensional fibrous structure of platy forms of CSH began to develop early, and continued to make the ultimate, dense, massive tabular units which developed between the pseudomorphs of CSH (4). In addition to these, at any given time of hydration, even at later ages, bundles or rosettes of fibres of CSH appear, which eventually develop into plates and slabs.

In general, the portland cement system apparently developed more amorphous forms of the CSH products than did the simpler systems.

The sequential method of study by the electron microscope has shown clearly the changes in morphology and microstructure occurring during the hydration of cement. The results demonstrate the value of the method in improving the understanding of first the nature of morphological changes occurring in the hydration of portland cement paste, and, secondly, the influence of an admixture at different stages of hydration, and thus

finally helping to relate the physical and mechanical properties of cement paste to its microstructure.

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