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Morphology and microstructure of hydrating Portland cement and its constituents. IV. Changes in hydration of a C3S, C2S, C3A, C4AF and gypsum paste with and without the admixtures triethanolamine and calcium lignosulphonate

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MORPHOLOGY AND MICROSTRUCTURE OF HYDRATING PORTLAND CEMENT AND ITS CONSTITUENTS

IV. CHANGES IN HYDRATION OF A C_3S , C_2S , C_3A , C_4AF AND
GYPSUM PASTE WITH AND WITHOUT THE ADMIXTURES
TRIETHANOLAMINE AND CALCIUM LIGNOSULPHONATE

by
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AND GYPSUM PASTE WITH AND WITHOUT THE ADMIXTURES
TRIETHANOLAMINE AND CALCIUM LIGNOSULPHONATE*

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ABSTRACT

Systematic sequential observations with the electron microscope were made of morphological changes which occurred during hydration of a paste mixture of C_3S^{**} , C_2S , C_3A , C_4AF and gypsum. The pronounced effect on rate of hydration of each of two organic admixtures was clearly observed. Differences could be seen also in the stability and habit of hydration products and in the microstructure itself. The electron micrographs shown illustrate the forms of the products at different hydration times.

SOMMAIRE

Des observations au microscope électronique ont été faites en séquence systématique pour observer les changements morphologiques qui prenaient place au cours de l'hydratation d'une pâte de C_3S^{**} , C_2S , C_3A , C_4AF et de gypse. Les effets prononcés de deux adjuvants organiques sur la vitesse d'hydratation ont été nettement observés. On a pu constater des différences dans la stabilité et l'habitus des produits d'hydratation de même que dans la microstructure elle-même. Les résultats de la micrographie qui sont présentés illustrent la forme des produits à différents stades de l'hydratation.

*Presented at the Cement Symposium of the American Ceramic Society,
72 Annual Meeting, Philadelphia, May, 1970.

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

This is the fourth of a continuing series of papers which report the morphological changes occurring during the hydration of portland cement and its pure constituents in the absence and in the presence of admixtures. The first dealt with C_3A (1), the second with C_3S and C_2S (2), and the third with C_3S and C_3A (3); in each case the changes with and without gypsum were noted.

The present paper deals with the morphological changes that occur during the hydration of a synthetic cement: a mixture of C_3S , C_2S , C_3A , C_4AF and gypsum, in the absence and in the presence of two admixtures, triethanolamine and calcium lignosulphonate.

Introduction

Studies that describe the morphological changes occurring during the hydration of simple systems of cement minerals have been referred to in the previous papers in this series (1, 2, 3). Experiments with the multi-component mixture used in the present study, C_3S , C_2S , C_3A , C_4AF and gypsum, apparently have never been performed. Chatterji and Jeffery (4) used electron optical and x-ray diffraction techniques in a study of the hydration to three months of a mixture of alite, C_3A , C_4AF and gypsum. This and other simpler systems have been reviewed relatively recently by Copeland and Kantro (5), Taylor (6) and de Jong (7). These studies would lead one to expect considerable differences to occur in the rates of reaction and in the nature of products formed, as a result of varying the conditions or combining the components.

Certain forms of alumina, iron and sulphate, such as C_3A in C_3S systems, can enter the CSH lattice structure; such penetrations are reported to affect the rate of hydration of the silicates and possibly also the microstructure (5, 6, 7). Rather than being isomorphous, penetrations may be due to additions to the lattice (5); for example, $SO_4^{=}$ may be added by an extension of the CSH lattice.

The presence of gypsum appears to accelerate the hydration of alite but only during the first day or so of C_3S hydration (5). Water-to-solids

ratio in a C_3S component system affects the formation of lime and this is believed to effect changes in the rates of formation of silicate hydrates.

With admixtures like sucrose and calcium lignosulphonate, no new solid phases appear to occur (8) but the rates of hydration of the major components are sharply affected. The retardation of C_3S by such admixtures is believed to be due to the inhibition of the release of lime. The presence of C_3A , however, accelerates the hydration of C_3S due to a preferential adsorption of calcium lignosulphonate into the former (8, 9, 10, 11). A lignosulphonate is also able to delay the precipitation of gypsum. Some question exists as to the effect of calcium lignosulphonate in retarding the change of C_2AH_8 and C_4AH_{13} to the C_3AH_6 form (12, 13).

The various effects reported above were kept in mind when examining the systems in this study.

Materials and Procedure

The sample materials used, C_3S , C_2S , C_3A , gypsum, triethanolamine and calcium lignosulphonate, are the same as those described in previous papers (1, 2) dealing with the monomineral pastes. The C_4AF had been prepared some years ago at the University of Saskatchewan by Dr. T. Thorvaldson.

The dry mixture of the synthetic cement used consisted of 44 per cent C_3S , 34 per cent C_2S , 12 per cent C_3A , 5 per cent C_4AF and 5 per cent gypsum. These proportions were considered reasonably in line with those occurring in normal portland cement. They were ground together in a porcelain-alumina ball-mill.

Pastes were prepared based on a ratio of 0.5 per cent by weight water-to-dry powder. Admixture dosages were 0.5 per cent by weight of the dry mixtures.

At intervals of 5 minutes, 1 and 6 hours, 1, 2, 3, 7 and 14 days and 1, 2 and 3 months, samples were taken. Hydration was stopped by treating the paste with acetone at about -18°C , and then drying the frozen samples in vacuum.

Single stage replicas from broken surfaces of the paste were made using the platinum-carbon technique. Only those electron micrographs which depict the average and general morphology are presented in this paper.

Results and Observations

1. Hydration of synthetic cement paste with no admixture present

The microstructure of synthetic cement (w/c ratio 0.5) after 5 minutes of hydration displayed a mixture of unhydrated grains of cement minerals and amorphous films of hydration products. Also present were the rod-like particles of ettringite and some irregular plates on the surfaces of grains (Fig. 1).

By 6 hours the amorphous films and the ettringite particles were the main hydration products, but small rounded particles on the surfaces of grains appeared as well (Fig. 2).

At the end of 1 day of hydration, large thin plates of hydration products and small fibrous particles of CSH had formed between unhydrated grains of cement minerals (Fig. 3).

At 3 days hydration the microstructure displayed a closely knit structural form, with needles of ettringite, plates of hexagonal CAH and some small fibres of CSH radiating from calcium silicate grains (Fig. 4).

During the next 2 weeks, many different types of hydration products were formed, the dominant being platelet aggregations (Fig. 5). Fibrous particles of CSH were present between them, and sometimes a fibrous structure developed on the surface of plates (Fig. 6).

At 1 month of hydration the synthetic cement paste had a dense microstructure in which pseudomorphs of calcium silicate grains surrounded by fibrous particles or irregular forms of parallel cleavage could be distinguished (Fig. 7). Some of the plate-like forms of the hydration products displayed fibrous fracture on the surfaces.

During the second and third months of hydration the microstructure is very dense, although no new forms of hydration products appeared.

FIG. 1

Microstructure of synthetic cement paste, $w/c = 0.5$. Age 5 min. Mixture of unhydrated grains of cement constituents cemented by amorphous hydration products. Note rod-like ettringite particles and some irregular, plate-like products on the surfaces of grains.

FIG. 2

Microstructure of synthetic cement paste, $w/c = 0.5$. Age 6 hr. Rod-like ettringite and small rounded particles of hydration products.

FIG. 3

Microstructure of synthetic cement paste, $w/c = 0.5$. Age 1 day. Large thin plates of hydration products and small fibrous particles of CSH.

FIG. 4

Microstructure of synthetic cement paste, $w/c = 0.5$. Age 3 days. Dense structure of needles and plates of CAH and some small fibrous particles of CSH radiating from calcium silicate grains.

FIG. 5

Microstructure of synthetic cement paste, $w/c = 0.5$. Age 14 days. Many different types of hydration products with the dominant forms being platelet aggregations.

FIG. 6

Microstructure of synthetic cement paste, $w/c = 0.5$. Age 14 days. Some plates of hydration products display an oriented two-dimensional fibrous structure.

FIG. 7

Microstructure of synthetic cement paste, $w/c = 0.5$. Age 1 month. Various types of hydration products with closely packed structure.

Plates are the predominant form, with pseudomorphs of cement minerals also appearing plentifully (Fig. 8).

X-ray diffraction studies done on this synthetic cement paste after 1, 3 and 7 days of hydration, showed that the $4.9\text{\AA}$ peak for CH appeared after one day of hydration. Later the peaks of the cement minerals disappeared but none of the diffractograms showed much change due to the poor crystalline habits of the hydration products.

2. Hydration of synthetic cement paste with 0.5% triethanolamine present

The first hydration products developed between 5 minutes and 1 hour of hydration as short rod-like particles of ettringite type, and rounded, unoriented plates on the surfaces of unhydrated grains of cement minerals (Fig. 9).

At 6 hours' the main hydration products were plates and single rod-like particles (Fig. 10). After 1 day of hydration the microstructure was a closely knit structure consisting mainly of plates (Fig. 11). During the next period up to 3 days, the amorphous, fibrous particles of CSH were radiating grains of calcium silicates and in some places were in the form of plates (Fig. 12).

The dominant forms of hydration products at 7 days' hydration were large fibres of CSH, radiating grains of calcium silicates, and aggregates of plates, some of which displayed a fibrous structure (Fig. 13).

The microstructure at 14 days consisted of irregularly shaped hydration products which were forming an unoriented structure (Fig. 14). Fibrous particles of CSH were gradually changing to plates having a three-directional fibrous fracture or cleavage.

Many different forms of hydration products were present after 1 month of hydration. Among them the pseudomorphous grains of cement minerals, fibres and plates could be distinguished. Some of the plates also displayed fibrous fracture (Fig. 15).

FIG. 8

Microstructure of synthetic cement paste, $w/c = 0.5$. Age 2 months. Several forms of hydration products among which one can distinguish many platelets and fibrous forms.

FIG. 9

Microstructure of synthetic cement paste with 0.5% triethanolamine, $w/c = 0.5$. Age 1 hr. Hydration products appear as plates, amorphous films and short rods between the unhydrated grains of cement minerals.

FIG. 10

Microstructure of synthetic cement paste with 0.5% triethanolamine, $w/c = 0.5$. Age 6 hr. Main hydration products are plates and single rods or needle-like particles.

FIG. 11

Microstructure of synthetic cement paste with 0.5% triethanolamine, $w/c = 0.5$. Age 1 day. Various forms of hydration products displaying a somewhat dense structure, mainly of platelets.

FIG. 12

Microstructure of synthetic cement paste with 0.5% triethanolamine, $w/c = 0.5$. Age 3 days. Semi-amorphous fibrous particles of CSH in some cases assume a plate-like form.

FIG. 13

Microstructure of synthetic cement paste with 0.5% triethanolamine, $w/c = 0.5$. Age 7 days. Dominant forms are fibres, large radiating aggregates and plates which sometimes display fibrous fracture.

FIG. 14

Microstructure of synthetic cement paste with 0.5% triethanolamine, $w/c = 0.5$. Age 14 days. Irregular forms of hydration products display an unoriented structure.

FIG. 15

Microstructure of synthetic cement paste with 0.5% triethanolamine, $w/c = 0.5$. Age 1 month. Between the various forms of hydration products are pseudomorphs of cement minerals, fibres and plates. Some plates display three-directional fibrous fracture.

At 2 and also at 3 months the microstructure was very dense, with the main forms of the hydration products being plates and fibres (Fig. 16). In some instances small rounded platelets appeared to be growing on the larger plates.

X-ray diffraction patterns of the synthetic cement paste with triethanolamine were taken after 4 hours, 1 day, 3 days and 90 days hydration time, and the results are presented in Figure 17. It is very significant that peaks of calcium hydroxide appeared after 3 days of hydration and that after this time, there was very little change.

3. Hydration of synthetic cement paste with 0.5% calcium lignosulphonate

The first hydration products at 5 minutes were amorphous foils and small rod-like ettringite-type particles between unhydrated grains of cement minerals. These were the main hydration products also during the next 6 hours of hydration (Fig. 18). In some cases these rod-like particles appeared as a sort of irregular plate.

At 1 day hydration the products appeared as unoriented platelets and fibres located around the grains of the calcium silicates (Fig. 19). After 3 days of hydration, the spaces between the unhydrated grains of cement minerals were nearly filled by these platelets and fibres (Fig. 20).

At 7 days of hydration the microstructure had become a closely knit structure with many different forms of hydration products. From this period up to 14 days the main hydration products were fibrous particles (Fig. 21).

At 1, 2 and 3 months the microstructure looked dense and un-oriented. Pseudomorphs of cement minerals appeared to be cemented together by platy and fibrous forms of the hydration products. Some of these platy forms had a striated cleavage and sometimes a fibrous fracture as well (Fig. 22).

X-ray diffraction patterns of the synthetic cement paste with calcium lignosulphonate were obtained at 4 hours, 1, 3 and 90 days of hydration. It

FIG. 16

Microstructure of synthetic cement paste with 0.5% triethanolamine, w/c = 0.5. Age 3 months. Fibres and platelets forming a dense structure.

FIG. 18.

Microstructure of synthetic cement paste with 0.5% calcium ligno-sulphonate, w/c = 0.5. Age 6 hr. Rod-like particles of ettringite are the dominant form of hydration products.

FIG. 17

X-ray diffractograms at various times of hydration of synthetic cement paste with 0.5% triethanolamine, w/c = 0.5. (Cu/Ni, 45KV, 25mA.)

FIG. 19

Microstructure of synthetic cement paste with 0.5% calcium ligno-sulphonate, w/c = 0.5. Age 1 day. Unoriented platelets and a fibrous structure of hydration products.

FIG. 20

Microstructure of synthetic cement paste with 0.5% calcium ligno-sulphonate, w/c = 0.5. Age 3 days. Fibrous particles of hydration products fill spaces between grains of cement minerals.

FIG. 21

Microstructure of synthetic cement paste with 0.5% calcium ligno-sulphonate, w/c = 0.5. Age 14 days. Different forms of hydration products, mainly of fibrous habit.

FIG. 22

Microstructure of synthetic cement paste with 0.5% calcium ligno-sulphonate, w/c = 0.5. Age 1 month. Dense microstructure with many platy forms of hydration products.

was observed that the major change occurred in the peaks representing calcium hydroxide; this peak appeared after 1 day of hydration (Fig. 23) instead of after 3 days as had been the case when triethanolamine had been present.

FIG. 23

X-ray diffractograms at various times of hydration of synthetic cement paste with 0.5% calcium lignosulphonate, w/c = 0.5. (Cu/Ni, 45KV, 25mA.)

Discussion

The products formed by this multicomponent system with no organic admixture present, and the times at which these products formed, when it was hydrated over a period of 3 months, were very similar to those formed by the simpler system, C_3S , C_3A and gypsum, described in the preceding paper of this series (3). Again the early product after a few minutes of hydration was an amorphous film, possibly corresponding in C/S ratio to the original C_3S . The irregular, fibrous material probably corresponded to the lower C/S stage, and the plate-like forms to the later, higher C/S product reported by others (6, 7). The failure to positively identify $Ca(OH)_2$ suggests that the lime liberated in the early reaction, in very finely divided form, is taken into the CSH lattice in some manner (2, 3, 7). It is clear

from these studies and the previous investigations (1-3) that both the CAH and CSH hydrates can and do take on crystal habits very like those of well-crystallized lime, and that all such crystallites have in the past been mistakenly believed to be Ca(OH)_2 . The free lime can occur more readily, of course, in suspensions than in pastes (5). Other work has indicated that similarly oriented lattices of foils of CSH link readily to the three-dimensional network of Ca(OH)_2 (14).

Significant amounts of the plate-like CSH products apparently do not develop as early in this system as in somewhat similar systems with alite in place of C_3S (4). This may be due to the claimed higher activity of the alite (5) or to the differences in conditions, materials or proportions.

A relative abundance of pseudomorphs of original C_3S particles in later stages of hydration, and apparently forming an integral part of the final microstructure of the paste, was observed in this study. Such pseudomorphs do not appear to be mentioned by other researchers as a major component. Their occurrence might be interpreted as indicating that hydration does not occur as a through-solution process.

In this multicomponent system the cubic form of CAH did not appear as it does in a hydrating portland cement system. It has been observed (7) that the presence of large amounts of C_3S retards the formation of C_3AH_6 ; this may be the explanation. Chatterji and Jeffery (4) did not report the cubic form in their system of alite, C_3A , C_4AF and gypsum, but did report it in the same system with no gypsum present, with or without the presence of alkali. It is concluded that in their systems the gypsum has taken up so large a proportion of the C_3A hydrate in producing the sulpho-aluminates that not enough CAH is left to produce significant or noticeable quantities of the cubic C_3AH_6 . The system in the present study appears to support this.

The present study did not reveal the rather extensive variations in morphology and rates one might have expected from the literature on simpler systems. It is believed that the low diffusion rates in such a low water-cement ratio system may have been a contributory factor. Also, the various interactions reported may tend to dampen out in a multicompo-

nent system such as was used in this study. It should be recalled that only the predominant products were studied in this series, and also that the proportions of original constituents of mixtures in this system, as well as in the previously reported systems, were in the same order as normally found in portland cement.

There were definite differences between the pastes with the two different organic admixtures, triethanolamine and calcium lignosulphonate, in their rates of reaction, and in the products they formed, but no significant difference could be detected in the final morphology of the pastes.

The pastes, with and without the admixtures, ultimately take on a close-packed microstructure; the filling-in process occurs in much the same way in both pastes although the timing varies. A characteristic of this dense structure is the cleaved, tabular mass made up of the combined hydration products, CH, CSH and CAH and pseudomorphs of original constituents. Further interpretation of the apparently pseudo-hexagonal plates that form the tabular masses is provided in a separate publication (15) which is based on the present and previous studies (1-3).

Conclusions

1. The effect of each of the admixtures, triethanolamine and calcium lignosulphonate, on the hydration processes of the synthetic cement was very pronounced, but not as definite as the effects which were apparent during the hydration of the monomineral pastes. This was probably due to the different action of each admixture on each of the mineral components as well as to the influence of one mineral on the other.

2. The hydration processes with no admixtures present appeared to be very similar to those occurring with triethanolamine and calcium lignosulphonate present.

3. With calcium lignosulphonate it was noted that during the entire time of hydration there was considerably less hydration of the cement minerals than when either no admixture or triethanolamine had been used. These hydration products, however, displayed better crystal habit. With

triethanolamine more hydration products appeared, but at a lower level of crystallinity.

X-ray diffraction examinations showed that the presence of calcium lignosulphonate produced peaks of crystalline CH at 1 day of hydration, compared with 3 days for the triethanolamine paste. Peaks of CH were smaller with triethanolamine than those which occurred with calcium lignosulphonate (Figs. 17 and 23).

4. The morphology of the hydration products, and the sequence in which they formed during the hydration process, did not differ significantly from the products of the simpler systems, but the times of their appearance were dependent upon the admixture present.

5. Almost all changes occurred within the first 7 days of hydration, and during this time differences in microstructure of synthetic cement paste as compared with the monomineral pastes were most significant.

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