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MORPHOLOGY AND MICROSTRUCTURE OF HYDRATING PORTLAND CEMENT AND ITS CONSTITUENTS

**I. CHANGES IN HYDRATION OF TRICALCIUM ALUMINATE
ALONE AND IN THE PRESENCE OF TRIETHANOLAMINE
OR CALCIUM LIGNOSULPHONATE**

by
T.D. Ciach and E.G. Swenson

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MORPHOLOGY AND MICROSTRUCTURE OF HYDRATING
PORTLAND CEMENT AND ITS CONSTITUENTS
I. CHANGES IN HYDRATION OF TRICALCIUM ALUMINATE
ALONE AND IN THE PRESENCE OF TRIETHANOLAMINE
OR CALCIUM LIGNOSULPHONATE

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(Communicated by G. M. Idorn)

ABSTRACT

Morphological changes which occur during the hydration of C_3A^* paste were observed by electron microscopy from the age of 5 minutes to 3 months. X-ray analyses were used to identify phases. The effects of the admixtures, triethanolamine and calcium lignosulphonate, were investigated with and without gypsum. The dosage of admixture was 0.5%; the water to C_3A ratio was 1.0. The results showed clearly the morphological changes that took place as hydration proceeded, and showed the specific influences of each of the two admixtures.

SOMMAIRE

Les changements morphologiques qui prennent place au cours de l'hydratation d'une pâte de C_3A ont été observés par microscopie électronique à partir de l'âge de 5 minutes jusqu'à l'âge de 3 mois. Les analyses aux rayons-X ont servi à identifier les phases. L'effet, avec et sans gypse, des adjuvants triéthanolamine et lignosulfonate de calcium a été examiné. Le dosage de l'adjuvant était de 0.5% et la fraction eau: C_3A était de 1.0. Les résultats ont clairement démontré les changements morphologiques qui ont pris place au cours de l'hydratation et ont aussi montré l'influence particulière de chacun des deux adjuvants.

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

This is the first of a series of papers reporting the results of long-term studies on the relationship between morphological changes in hydrating portland cement and its microstructure in the hardened state. The ultimate aim is to identify particular morphological changes and the corresponding changes in microstructure with changes in the physical and mechanical properties.

The method consisted of taking electron-micrographs on a sequential basis, being careful to select representative and characteristic structures and formations. X-ray was employed to identify phases where initial doubt existed. Where changes occur, the corresponding series of electron-micrographs are shown. Where no change occurs, one or two only may be shown. Although the formations given are representative, they constitute a qualitative picture.

Although many micrographs showing morphology changes in hydrating cement compounds, with and without admixtures, have been published, most have somewhat limited value in the practical sense for several reasons: hydration has usually been carried out in excess water; clear-cut crystalline formations were often selected in preference to indefinite, amorphous masses which may have been predominant; and hydration has often been largely completed when the electron micrographs were taken, thus earlier changes were missed. This systematic study is expected to provide a better understanding of the practical consequences of the presence of an admixture in concrete, and the methods followed are expected to form a better basis for studies of new systems.

The study of C_3A described in this paper is being followed by similar studies of the other pure compounds of portland cement, combinations of these, and portland cement itself. These first several papers will consist mainly of observations of morphological changes. Other studies attempt to show a correlation between microstructure and mechanical properties (1).

Introduction

Studies of the hydration process of C_3A indicate that the presence of small amounts of certain organic chemicals affects the rate of reactions,

but apparently not the basic nature of the hydration products (2-10). Such agents may, however, produce modifications of the crystal habits of these hydrates (2, 3, 7).

Some organic compounds appear to block the conversion of C_2AH_8 and C_4AH_{13} to C_3AH_6 while others facilitate the reaction (6). Ligno-sulphonates, for example, are shown to inhibit the change from the hexagonal hydroaluminates to C_3AH_6 under normal conditions (2). Addition of gypsum and lime does not apparently alter the course of the reaction (2, 4, 5, 9). Daugherty and Kowalewski review, in their 1968 Tokyo Symposium paper (6), the major researches in this area.

Any changes in the morphology of hydration products of portland cement compounds, of which C_3A is one, must necessarily affect both the nature of the plastic state and the microstructure and properties of the hardened state of cement paste.

The present paper is intended primarily to demonstrate the value of a systematic sequential study using the electron microscope for direct observation of the morphological changes. It is limited to two commercially used concrete admixtures, triethanolamine and calcium lignosulphonate, in the absence and in the presence of gypsum. In concrete technology, triethanolamine is used in formulations to reduce excessive retardation of other admixtures agents, and lignosulphonate is one of several basic components of set-retarders and water-reducers. In this first study, the hydration of C_3A was carried out in the absence of added lime.

Materials and Procedures

The tricalcium aluminate used in the experiments was made in the Materials Section Laboratory of the Division of Building Research (2): it contained 2 per cent free lime and has a specific surface area of about $3000 \text{ cm}^2/\text{gm}$ Blaine.

The C_3A pastes were prepared on the basis of water to C_3A by weight = 1.0, and admixture dosages of 0.5 per cent by weight of dry C_3A . The ratio of C_3A to gypsum was 2:1. The gypsum was prepared from large, clear, natural crystals which were ground to pass 200 DIN. As in the case

of portland cement, gypsum in these studies was considered as an additive, and is to be distinguished from the organic chemical admixtures added.

The triethanolamine used was a chemically pure reagent grade. The calcium lignosulphonate was a commercially prepared product chemically treated to destroy excess sugars. Total sugars averaged 0.08 per cent and total reducing bodies about 4 per cent.

The paste consisted of 5 grams C_3A , 5 grams water and 0.025 grams admixture, the latter always premixed with the water. The choice of dosage of admixture was made on the basis of probable availability to C_3A in the cement paste, rather than on the actual proportion of admixture to C_3A in the paste. The paste was kept at $23 \pm 1^\circ C$ in tightly stoppered plastic tubes which were rotated continuously to prevent segregation.

At intervals of 5 minutes, 1 and 4 hours, 1, 2, 3 and 7 days, and 1, 2 and 3 months, samples are taken out and tested. Hydration was stopped by treating with acetone at about $-18^\circ C$, then drying the frozen samples in a vacuum.

Single stage replicas of the broken surfaces of the C_3A paste were made using the platinum-carbon technique (11).

Electron microscopic examinations were done at different times during hydration from 5 minutes to 3 months, and at significant times X-ray examinations were made.

The electron micrographs shown are those that depict the general morphology. Exceptional forms and structures are not taken into account.

Observations and Discussion

1. Hydration of C_3A in Absence of Gypsum

(a) No Admixture Present

The first hydration products were hexagonal phases of CAH in the form of semicrystalline foils and plates (Fig. 1). Among these it was possible to distinguish by X-ray examination C_2AH_8 which was probably the main form present.

After 1 hour's hydration the cubic hydrogarnet phase, which has a crystal size of about 1 micron, made its appearance among the hexagonal phases of CAH, and after one day's hydration it was the dominant phase (Figs. 2 and 3). The crystals of hydrogarnet were twinned many times and displayed a very compact structure. Starting at about 3 days these hydrogarnet crystals became partly covered by some small particles which slowly transferred to the hexagonal plates (Fig. 4). X-ray examination showed these hexagonal or pseudo-hexagonal phases to be $\text{Al}(\text{OH})_3$ and $\text{Ca}(\text{OH})_2$, and also revealed the presence of very small quantities of the hexagonal CAH, mainly C_2AH_8 (Table I). This pseudo-hexagonal phase of $\text{Al}(\text{OH})_3$ and the hexagonal phase of $\text{Ca}(\text{OH})_2$ were formed probably by the decomposition of the cubic phase of C_3AH_6 under these conditions, but some may have resulted directly as hydration products of C_3A .

After 1 month's hydration there appeared more hexagonal-like plates of $\text{Al}(\text{OH})_3$ and $\text{Ca}(\text{OH})_2$ which covered the large hydrogarnet crystals (Fig. 5). After 3 months the stable products appeared to be the cubic phase of C_3AH_6 and the hexagonal or pseudo-hexagonal phases of $\text{Al}(\text{OH})_3$ and $\text{Ca}(\text{OH})_2$ (Table I).

(b) With Triethanolamine

For the first few days, the hydration process of C_3A paste with triethanolamine was similar to the paste without admixtures, but after 7 days of hydration the hydrogarnet crystals had the cube habit (Fig. 6).

After 7 days the size of these cubes was about 2 microns and they occurred as loose aggregations of individual single crystals, in contrast with those formed without admixture which were twinned and showed close structure. Some of these crystals were covered by a material appearing like hexagonal plates of calcium hydroxide and aluminum hydroxide. After about 1 month of hydration the cube form was transformed to the rich cubic form.

The very fast transformation to the cubic form (between the ages of 4 hours and 1 day), appears to have been responsible for delaying the setting of the C_3A paste with triethanolamine in the absence of gypsum. Actually the paste did

TABLE I

Results of Hydration of Tricalcium Aluminate Paste with
Admixtures as Determined by X-ray Examination

| Storage Time | C_3A Paste | C_3A Paste + Triethanolamine | C_3A Paste + Ca Lignosulphonate |
|--------------|--|--|---|
| 4 hours | C_3A C_2AH_8 C_3AH_6 | C_3A C_2AH_8 C_3AH_6 | C_3A C_2AH_8 C_4AH_{13} |
| 3 days | C_3A C_3AH_6 C_2AH_8 CH, AH | C_3A C_3AH_6 C_2AH_8 CH, AH | C_3A C_2AH_8 C_4AH_{19} CH |
| 3 months | C_3AH_6 CH AH C_3A | C_3AH_6 CH AH C_3A | C_3AH_6 CH, AH $C_3A \cdot CaCO_3 \cdot 12H_2O$ |



FIG. 1

C_3A paste. Age 5 min. Small particles of wrinkled foils and plates of hydration products.

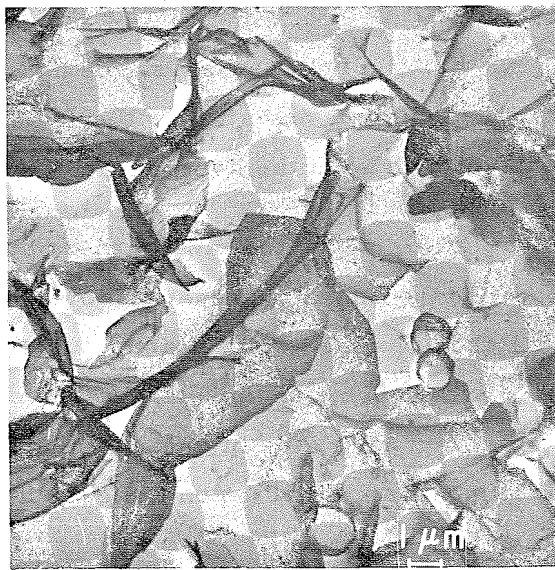


FIG. 2

C_3A paste. Age 1 hr. Large, loosely wrinkled plates of hexagonal CAH and small cubic hydrogarnet crystals.

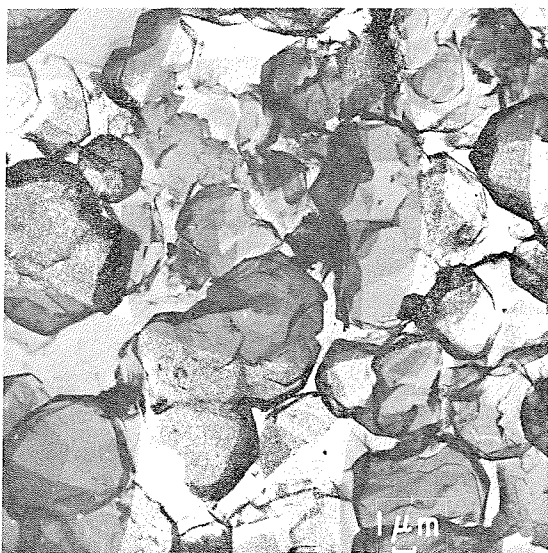


FIG. 3

C_3A paste. Age 1 day. The rich cubic habits of hydrogarnet crystals.

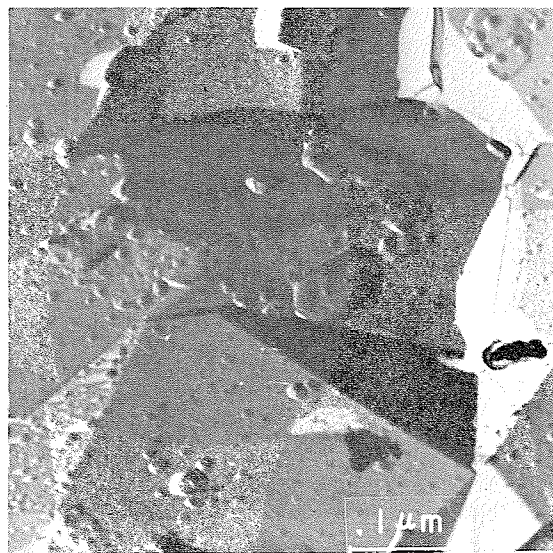


FIG. 4

C_3A paste. Age 3 days. Twinning hydrogarnet crystals covered by very small particles of other hydration products.



FIG. 5

C_3A paste. Age 1 month. Large cubic crystals of hydrogarnet often covered by precipitations of hexagonal form.

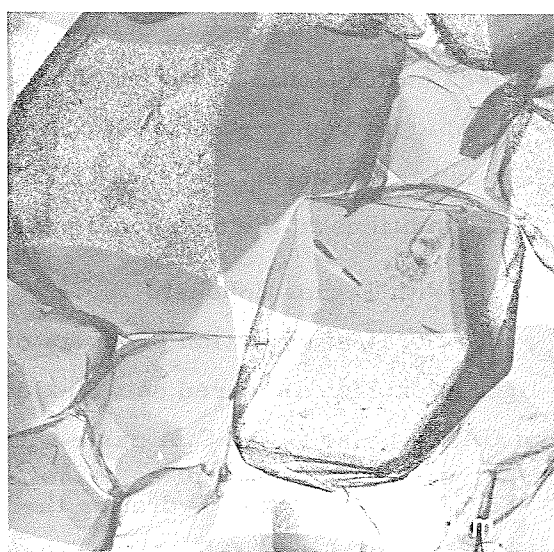


FIG. 6

C_3A paste with triethanolamine. Age 7 days. Large hydrogarnet crystals of cube habit with some hexagonal-like particles.

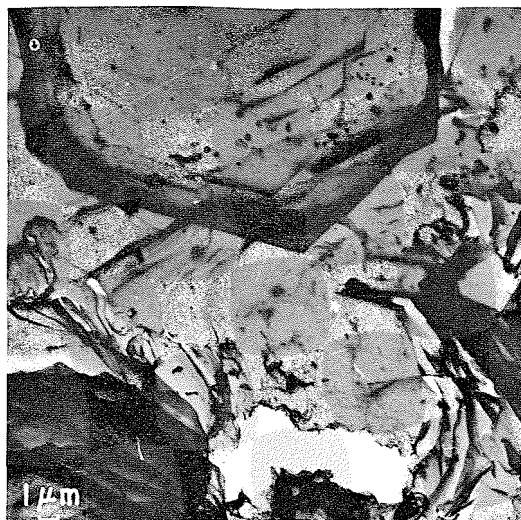


FIG. 7



FIG. 8

C_3A paste with calcium lignosulphonate. Age 4 hrs. The large aggregates of very thin plates of hexagonal CAH. The clustering of their edges can be likened to bundled ribbons.

not begin to harden significantly until after about 2 months, at which time it was observed that the twinning, rich cubic form of hydrogarnet, as well as hexagonal plates of CH and AH, appeared. Thus, with water only and with triethanolamine, the first hydration products of C_3A paste without gypsum were metastable phases of hexagonal CAH, which were then very quickly transformed to the cubic hydrogarnet phase which is more stable at room temperature. The latter, however, appeared then to be partly transformed under these test conditions to the hexagonal phases of $Al(OH)_3$ and $Ca(OH)_2$.

(c) With Lignosulphonate

The first hydration products of C_3A with 0.5 per cent calcium lignosulphonate appeared as wrinkled foils or plates of hexagonal phases of CAH similar to the C_3A paste without admixtures (Fig. 1).

After 4 hours of hydration there appeared large aggregates (of about 11 microns) of very thin plates; after 2 days of hydration these displayed an edge-fracture surface (Figs. 7 and 8). The X-ray examination showed that between these hexagonal forms of CAH one can distinguish only C_2AH_8 and C_4AH_{13} . The edges of these plates were cluster-like bundled plates (Fig. 9). The hexagonal phase of CAH remained stable for about 7 days.

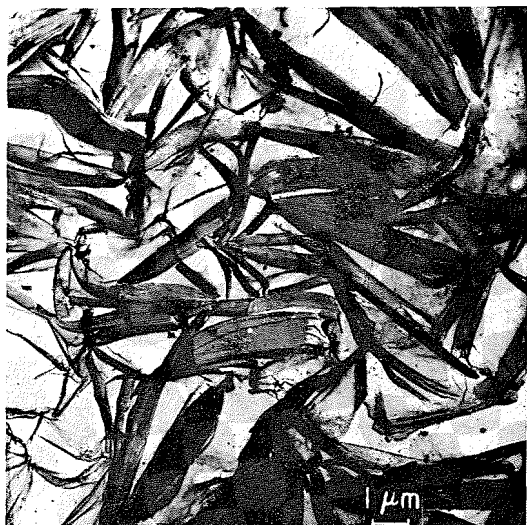


FIG. 9

C_3A paste with calcium lignosulphonate. Age 2 days. The clusters of edges of thin hexagonal plates are displayed in the interlocking structure.

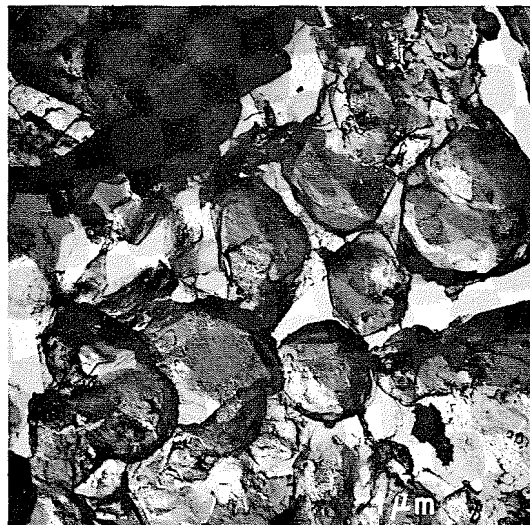


FIG. 10

C_3A paste with calcium lignosulphonate. Age 7 days. The large hydrogarnet crystals of the cubic form among aggregates of hexagonal phases.

After 7 days a transformation to a close-packed tabular structure occurred, and also the cubic form of hydrogarnet phase was observed (Fig. 10). The calcium lignosulphonate is thus shown to retard the transformation of the hexagonal phase of the calcium aluminate hydrate to the cubic phase of C_3AH_6 ; this phase remained stable for the next several days.

After hydration for 1 month, and up to 3 months, the major hydration product was the rich cubic form of hydrogarnet. This form was partly transformed to calcium hydroxide and aluminum hydroxide, and these products covered the hydrogarnet crystals.

2. Hydration of C_3A in Presence of Gypsum

(a) No Admixture Present

The first hydration products of C_3A paste with gypsum and no other admixture appeared after a few minutes of hydration; they displayed partly rolled, semicrystalline foils and rods which formed flower-like aggregates on the surfaces of the gypsum crystals (Fig. 11).



FIG. 11

C_3A paste with gypsum. Age 5 min. Rounded plates and rods of first hydration products on surface grains of C_3A and gypsum.

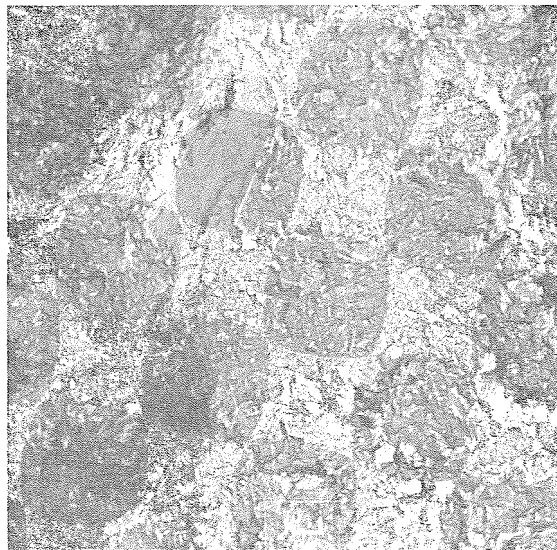


FIG. 12

C_3A paste with gypsum. Age 1 day. Unoriented rods of ettringite and a large crystal of gypsum.

After 1 day's hydration this flower-like form disappeared and the main hydration products were seen to be short, rod-like particles of the high sulphate form of CAH (ettringite); large crystals of gypsum were also present (Fig. 12). X-ray diffraction patterns show that there was a large proportion of high sulphate CAH, some amount of the low sulphate CAH, gypsum and unhydrated C_3A (Fig. 13, curve I).

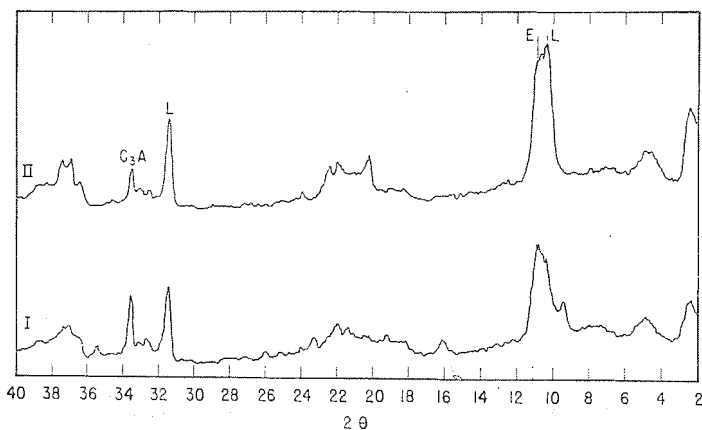


FIG. 13

X-ray diffraction pattern of C_3A paste with gypsum after different times of hydration. E = high sulphate CAH, L = low sulphate CAH, Curve I = 1 day, and Curve II = 8 days.

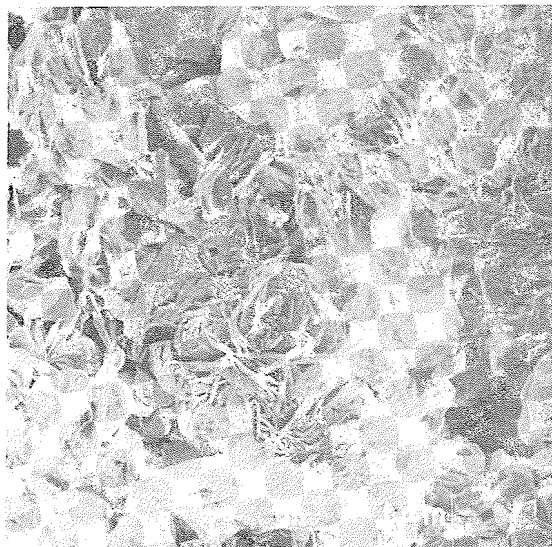


FIG. 14

C_3A paste with gypsum. Age 8 days. Plates of the low sulphate form of CAH.

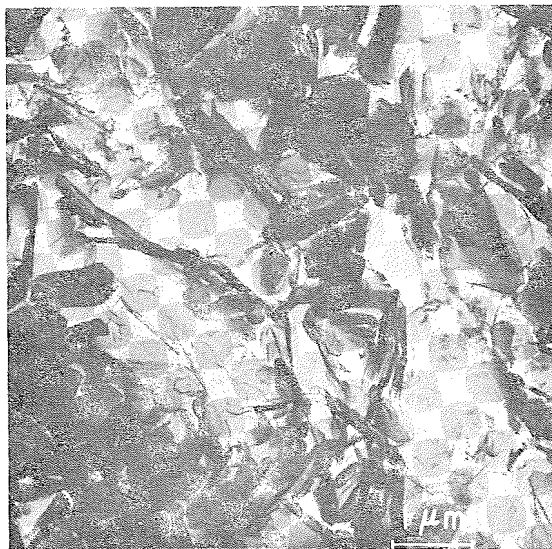


FIG. 15

C_3A paste with gypsum. Age 1 month. Unoriented plates of the low sulphoaluminate of CAH.

At 3 days of hydration the paste showed signs of setting and the hydration products appeared as a loose mass of unknown morphology partly covered by rod-like particles of ettringite of the "coin-in-coin" type.

After 8 days of hydration the paste had set, and the microstructure appeared as a loose structure of unoriented, thin hexagonal plates (Fig. 14). X-ray diffraction patterns showed that these plates, which comprised the dominant form, were low sulphate CAH crystals of apparently different types. Some ettringite was also present (Fig. 13, curve II).

For the first 3 months, the microstructure of the C_3A paste with gypsum was seen to be plates and a partly striated structure, which had been formed from the plates of the low-sulphate products, and also rods of ettringite (Fig. 15).

(b) With Triethanolamine

The hydration processes that occurred in the paste of C_3A with gypsum and triethanolamine were very similar to those that took place in the paste of C_3A with gypsum only. Thus, in pastes of C_3A with gypsum without admixture, and with both gypsum and triethanolamine, the hydration

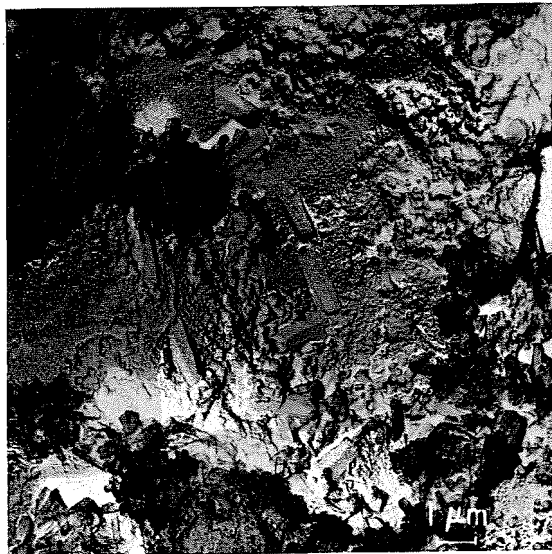


FIG. 16

C_3A paste with gypsum and calcium lignosulphonate. Age 1 day. Between the small rods of ettringite are large crystals of secondary gypsum of very good habit.

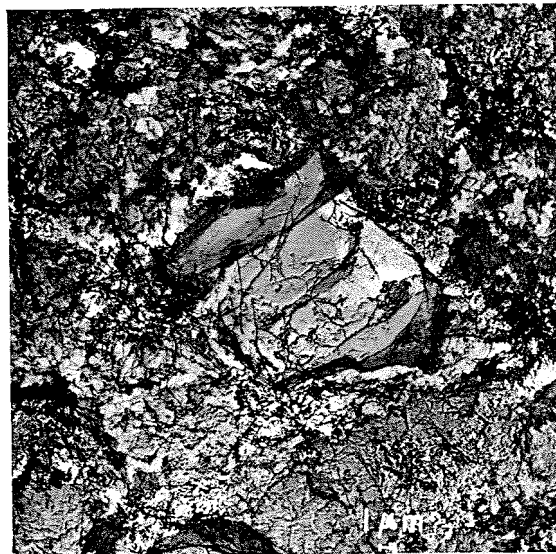


FIG. 17

C_3A paste with gypsum and calcium lignosulphonate. Age 3 days. Small, rod-like particles are sometimes formed in long fibres.

product at early stages of hydration was the high-sulphate CAH which appeared as rod-like ettringite-type particles. It was the dominant phase during the first 3 days of hydration. At this time the pastes showed signs of setting, and plate-like particles of low-sulphate CAH appeared. The pastes had set after 7 days, at which time the major hydration products were hexagonal phases of low-sulphate CAH.

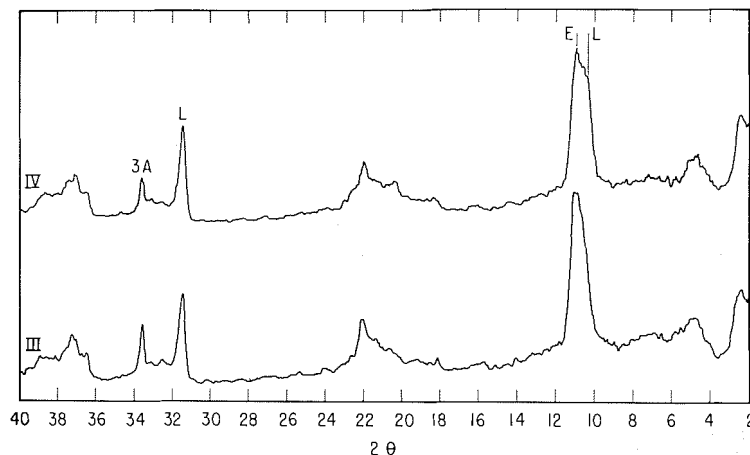
(c) With Lignosulphonate

Quite different results were obtained for the paste of C_3A with gypsum and calcium lignosulphonate. The first hydration products appeared after a few minutes as small rod-like particles on the crystal surfaces of the gypsum. Up to 1 day's hydration there appeared larger crystals of very good habit (Fig. 16). X-ray diffraction showed that these crystals were different forms of the ettringite type, i. e., the high-sulphate CAH; this was the main hydration product up to 14 days of hydration (Fig. 17, Fig. 18, curves III and IV).

After 14 days the paste showed signs of setting, and thin, unoriented

FIG. 18

X-ray diffraction pattern of C_3A paste with gypsum and calcium lignosulphonate after different times of hydration. E = high sulphate CAH, L = low sulphate CAH, Curve III = 8 days and Curve IV = 14 days.



hexagonal plates of low-sulphate CAH were observed as well (Figs. 19 and 20). During the next period up to 3 months, both forms of calcium sulphoaluminate were observed in the microstructure; the paste was only partly set during this time.

3. General Observations

The initial presence of a comparatively large amount of lime as in the samples studied by Seligmann and Greening (9) would undoubtedly have some different effects on the rates of changes found in the present experiments where only a small amount of lime was initially present. Since these investigations were intended to develop a procedure and technique that would enable one to follow morphological changes clearly, it was considered preferable to start with the simplest systems. Furthermore, the initial presence of a large amount of lime, with its relatively high degree of crystallinity, is not comparable to the normal gradual formation of extremely fine and active lime during the hydration of the silicate phases in portland cement.

The large initial acceleration of C_3A hydration observed by Seligmann and Greening may have been caused, according to their own speculations, by the inhibition of lime release (9). This effect was also observed in the present experiments.

Although no attempt was made to determine and relate the time when

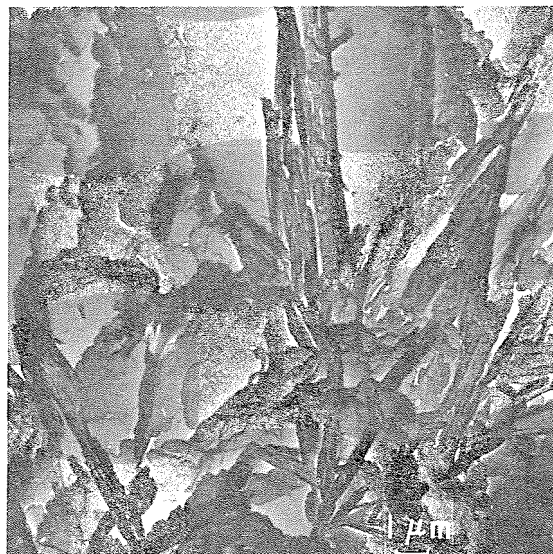


FIG. 19

C_3A paste with gypsum and calcium lignosulphonate. Age 14 days. The short rods of ettringite are formed in large aggregations between some small rounded plates of the low sulphate form of CAH.

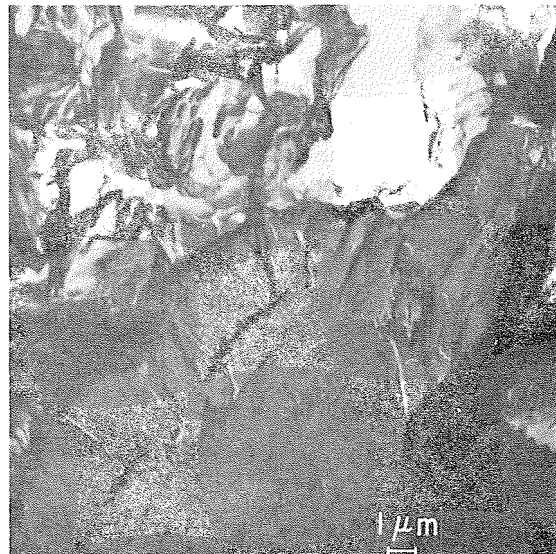


FIG. 20

C_3A paste with gypsum and calcium lignosulphonate. Age 3 months. Grain of hydrated C_3A with very clear spherical structure of hydration products.

the pastes used in these studies set, one observation was of interest. The triethanolamine in the absence of gypsum appeared to delay stiffening until the rich cubic form of the hydrogarnet appeared. The hydrogarnet crystals have habits of different forms of the cubic system: as icositetrahedra and rhombicdodeahedra (Fig. 3). It was observed by Sersale (3) that these forms occur at an early stage in the transformation of the hydration product of C_3A to the cubic phase of C_3AH_6 , and that the last form is, in fact, the cube.

It is recognized that the comparatively small dosages of the organic chemical used may have different effects on rates of change than would larger dosages. These are, of course, subjects for separate study.

Considered in the light of previously published researches, these experiments made it clear that acceleration and retardation in rates of reaction having to do with morphological changes, are not necessarily related to acceleration and retardation pertaining to setting and hardening.

It is the latter criterion that has established the accepted classification of admixtures used in concrete.

Summary

Systematic sequential observations with the electron microscope were made of the morphological changes occurring during the hydration of C_3A in the absence and in the presence of selected admixtures. X-ray analyses were made to identify some phases.

The effects of small dosages of the organic chemicals, triethanolamine and calcium lignosulphonate, were studied in the absence and in the presence of gypsum.

The method used showed clearly the manner in which hydration proceeded and the accelerating or retarding effects of the presence of each admixture. Changes in crystal habit were observed.

Similar procedures are being used to study other compounds and mixtures of compounds of portland cement with the ultimate aim of determining which factors of microstructure influence mechanical properties, dimensional change and durability of portland cement paste.

Acknowledgements

We acknowledge gratefully the invaluable contribution of Mr. E. Quinn in preparing replicas from the samples for electron microscopic examination. To Portland Cement Association for supplying the pure constituents of cement we are also most grateful.

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