NRC Publications Archive Archives des publications du CNRC

Morphology and microstructure of hydrating Portland cement and its constituents. III. Changes in the hydration of a mixture of C3S, C3A and gypsum with and without triethanolamine and calcium lignosulphonate present

Ciach, T. D.; Swenson, E. G.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

[https://doi.org/10.1016/0008-8846\(71\)90002-0](https://doi.org/10.1016/0008-8846(71)90002-0)

Cement and Concrete Research, 1, 3, pp. 257-271, 1971-05

NRC Publications Archive Record / Notice des Archives des publications du CNRC :

<https://nrc-publications.canada.ca/eng/view/object/?id=b37f1f2d-d2d4-4e3f-8433-7bee67522141>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=b37f1f2d-d2d4-4e3f-8433-7bee67522141>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

Ser
TH1
N21r2
no. 474
c. 2
BLDG

INTERNATIONAL RESEARCH COUNCIL OF CANADA
CONSEIL NATIONAL DE RECHERCHES DU CANADA

MORPHOLOGY AND MICROSTRUCTURE OF HYDRATING PORTLAND CEMENT AND ITS CONSTITUENTS

III. CHANGES IN THE HYDRATION OF A MIXTURE OF C_3S ,
 C_3A AND GYPSUM WITH AND WITHOUT TRIETHANOLAMINE
AND CALCIUM LIGNOSULPHONATE PRESENT

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

Reprinted from

CEMENT AND CONCRETE RESEARCH

An International Journal

Vol. 1, No. 3, May 1971
p. 257

BUILDING RESEARCH
- LIBRARY -

MAY 25 1971

NATIONAL RESEARCH COUNCIL

45362

Research Paper No. 474
of the
Division of Building Research

OTTAWA
MAY 1971

Price 25 cents

NRCC 11858

This publication is being distributed by the Division of Building Research of the National Research Council of Canada. It should not be reproduced in whole or in part without permission of the original publisher. The Division would be glad to be of assistance in obtaining such permission.

Publications of the Division may be obtained by mailing the appropriate remittance, (a Bank, Express, or Post Office Money Order, or a cheque made payable at par in Ottawa, to the Receiver General of Canada, credit NRC) to the National Research Council of Canada, Ottawa. Stamps are not acceptable.

A list of all publications of the Division is available and may be obtained from the Publications Section, Division of Building Research, National Research Council of Canada, Ottawa 7, Canada.

CISTI / ICIST

3 1809 00211 3279

ANALYZED

MORPHOLOGY AND MICROSTRUCTURE OF HYDRATING
PORTLAND CEMENT AND ITS CONSTITUENTS
III. CHANGES IN THE HYDRATION OF A MIXTURE OF C_3S ,
 C_3A AND GYPSUM WITH AND WITHOUT TRIETHANOLAMINE
AND CALCIUM LIGNOSULPHONATE PRESENT

T. D. Ciach and E. G. Swenson
Division of Building Research, National Research Council of Canada
Ottawa, 7, Ontario, Canada

(Communicated by G. M. Idorn)

ABSTRACT

Systematic sequential observations with the electron microscope were made of the morphological changes which occurred during the hydration of a paste mixture of C_3S^* , C_3A and gypsum. It was found that this system produced hydration products similar in nature to those produced by the monomineral systems with gypsum present. The two organic admixtures studied had some effect on changes in morphology and microstructure of the hydrating mixture, but they showed a pronounced influence on the rate of the hydration processes.

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 composée de C_3S , C_3A et de gypse. Ce système a des produits d'hydratation semblables par leur nature à ceux produits par les systèmes monominéraux en présence de gypse. Les deux adjuvants organiques examinés ont un léger effet sur la morphologie et la microstructure du mélange au cours de l'hydratation, mais ont une influence prononcée sur la durée du processus d'hydratation.

*Standard cement nomenclature is used; e.g. $C_3S = 3CaO.SiO_2$;
 $C_3A = 3CaO.Al_2O_3$; $C_2S = 2CaO.SiO_2$; CSH = calcium silicate hydrate(s);
CAH = calcium aluminate hydrate(s); w/c = water:cement ratio by weight.

This is the third paper in a continuing series which studies the morphological changes occurring during the hydration of portland cement and its pure components in the absence and in the presence of admixtures. The first dealt with C_3A (1) and the second with C_3S and C_2S (2), and in each the changes with and without gypsum were observed.

The method used in the studies so far consists of taking electron micrographs of the hydrating pastes on a sequential basis, and reporting only those changes and structures which appear to be dominant. Electron micrographs are included to illustrate different forms of microstructure and changes in morphology which affect the main components. Proportions of phases are to be considered on a qualitative basis.

The object of these investigations is to improve the understanding of the nature of morphological changes occurring in the hydration of portland cement, and to relate microstructure of cement paste to physical and mechanical properties of paste and concrete.

The present paper deals with the morphological changes occurring during the hydration of a mixture of C_3S , C_3A and gypsum in the absence and in the presence of two organic admixtures.

Introduction

The morphological changes occurring during the hydration of C_3S and C_2S and the effects of gypsum and other admixtures have been briefly referenced in a previous paper in this series (2). Experiments with a mixture of C_3S , C_3A and gypsum appear to be extremely limited. From x-ray studies it has been found that the formation of ettringite appeared to be accelerated when C_3S was used in place of $Ca(OH)_2$ with C_3A (0.75 moles C_3S to 1 mole C_3A) (3). The second stage of formation of the low sulphoaluminate and the last reactions with the remaining C_3S were found to be affected: the rates of reaction decreased and the products were more poorly crystallized. At molar ratios of 3 to 1 of C_3S and C_3A , the second stage was retarded. In general it was concluded that the behaviour of this system closely resembled that of the corresponding components in the portland cement system.

Recent review papers indicate that there is general acceptance of the idea that the aluminum, or some compound of this element derived from C_3A , enters readily into the calcium silicate hydrate product of the hydration of C_3S (4, 5). Some researchers claim that this results in a change in the morphology of the CSH gel (6) and others that little or no change occurs (7). It is reported (8, 9) that the hydration of alite is increased by the presence of free C_3A . Gypsum also has this effect but in this case the sulphate concentration is an influencing factor. The same review paper (8) reports that in a different investigation up to 4 per cent gypsum had no effect on C_3S hydration.

It has been noted (3) that "the behaviour of lignosulphonate in more complex mixtures differs markedly from the effects on hydration of base mixtures or on C_3S alone."

The observations noted above were made on the basis of x-ray, calorimetric and DTA measurements, with some limited evidence from electron microscopic examination. Comparison is difficult because the various investigators used different proportions of mix water as well as different proportions of solid components.

Materials and Procedures

The C_3S and C_3A used in this series were supplied by the Portland Cement Association. The gypsum and the two organic admixtures, triethanolamine and calcium lignosulphonate, are the same as those used in the previous studies in this series and their properties are described therein (1, 2).

The dry mixture consisted of 76.9 per cent C_3S , 15.4 per cent C_3A and 7.7 per cent gypsum. These were ground together in a porcelain-alumina ball-mill.

Pastes were prepared with a proportion of water to dry powder of 0.5 by weight. Admixture dosages were 0.5 per cent by weight of the dry mixtures. Further characteristics of the materials and a description of the

methods and procedures used in preparing and examining the test specimens are given in the first two papers (1, 2).

At intervals of 5 minutes, 1, 4 and 8 hours, 1, 2, 3 and 7 days, and 1, 2 and 3 months, samples were taken and tested. To stop hydration, the samples were frozen by treating them with acetone at about -18°C and then drying them in vacuum.

Single stage replicas from 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.

Results and Observations

1. Hydration of C_3A , C_3S and gypsum with no admixture present.

After 5 minutes of hydration, the microstructure of this three-mineral paste with no admixture present displayed a mixture of unhydrated grains with some very thin crumpled foils of hydration products around them. At 1 hour, ettringite-type rod-like particles appeared (Fig. 1). Between 4 and 8 hours some irregular particles were also present (Fig. 2); these and the ettringite-type phase were the major hydration products to 1 day of hydration.

At the age of 1 day, between the rods of ettringite (high sulpho-aluminate hydrate), some hexagonal plates of low sulpho-aluminate hydrate appeared (Fig. 3). Semi-amorphous fibres, which were probably CSH in a three-dimensional arrangement of plates, were also present (Fig. 4). Usually these interlocking structures of fibrous particles displayed ribbon-like aggregates at the edges of plates (Fig. 5). After 2 days of hydration, the paste had the quite close, partly unoriented microstructure made up of a variety of plate forms (Fig. 6).

During the whole period from 2 days to 6 weeks these platy hydration products were dominant. Sometimes they displayed striated or hexagonal forms, and sometimes three-dimensional cleavage. The most characteristic forms of the hydration products during the time from 3 days to 3 months are shown in the electron micrographs (Figs. 7-9).

FIG. 1

Microstructure of C_3S , C_3A and gypsum paste, $w/c = 0.5$. Age 1 hr. Large plate crystals of gypsum and irregular grains of C_3S and C_3A covered by small ettringite-type rod-like particles.

FIG. 2

Microstructure of C_3S , C_3A and gypsum paste, $w/c = 0.5$. Age 8 hr. Some small irregular particles of hydration products on the surfaces of unhydrated grains.

FIG. 3

Microstructure of C_3S , C_3A and gypsum paste, $w/c = 0.5$. Age 1 day. Ettringite-type rod-like particles and some plates of low calcium sulfo-aluminate hydrate.

FIG. 4

Microstructure of C_3S , C_3A and gypsum paste, $w/c = 0.5$. Age 1 day. Between the rods of ettringite and the plates of CSH and CAH there appear some semicrystalline fibrous particles of CSH forming basket-like fracture on the surfaces of plates of hydration products.

FIG. 5

Microstructure of C_3S , C_3A and gypsum paste, $w/c = 0.5$. Age 1 day. Hydration products of fibrous or rod-like habit form an interlocking structure of plates which display ribbon-like aggregates at the edges.

FIG. 6

Microstructure of C_3S , C_3A and gypsum paste, $w/c = 0.5$. Age 2 days. Various forms of hydration products with dense unoriented microstructure.

FIG. 7

Microstructure of C_3S , C_3A and gypsum paste etched with glycol for $\frac{1}{2}$ hr., $w/c = 0.5$. Age 6 weeks. Fibrous particles of rosette-like form are arranged on plate-like, striated forms.

FIG. 8

Microstructure of C_3S , C_3A and gypsum paste etched with glycol for $\frac{1}{2}$ hr., $w/c = 0.5$. Age 6 weeks. Unoriented plates of low calcium sulpho-aluminate hydrate and binders between pseudomorphous or partly hydrated grains of each component.

In this period it was very difficult to distinguish between some of the hydration products because of their very similar plate-like forms. For this reason, at the end of 6 weeks the paste was treated with glycol for 30 minutes and part of the rich calcium hydroxide phase was removed. Many plates then showed the three-dimensional interlocking or rosette-like arrangements of semicrystalline fibrous particles that are so characteristic of CSH (Fig. 7). The small hexagonal plates of low sulpho-aluminate hydrate of many different orientations were also present (Fig. 8). Pseudomorphs of individual mineral components can be observed where the hydration products were partly or almost entirely removed. The essentially amorphous binders can also be seen between each of these grains.

At the next times of observation, 2 and 3 months, the microstructure did not show any further clear changes (Fig. 9).

2. Hydration of C_3A , C_3S , gypsum and triethanolamine.

At 5 minutes' hydration, the microstructure of a paste of C_3A , C_3S , gypsum and 0.5 per cent triethanolamine ($w/c = 0.5$) displayed a mixture of unhydrated grains of mineral components. There were some amorphous, crumpled foils around these components and also unoriented hexagonal plates of hydration products on their surfaces. The small, rod-like particles of ettringite were also visible. Up to 1 hour's hydration there was no significant change in the microstructure (Fig. 10). During the next few hours small rounded particles appeared mainly on the surfaces of C_3S grains. These new hydration products were probably the result of nucleations of calcium silicate hydrate, which was also present in the fibrous form. During the next period until 1 day of hydration, more hydration products of this form, and also large thin hexagonal plates developed (Fig. 11). At 3 days, the microstructure had a more closed structure of plate-like forms, but rosette-like aggregates of ettringite rods were present as well (Fig. 12). Very often large plates of hydration products displayed the three-dimensional, interlocking structure of fibrous particles that is so significant of CSH. These products also appeared as loose bundles. Between them one could distinguish the small, single hexagonal rods of ettringite.

FIG. 9

Microstructure of C_3S , C_3A and gypsum paste, $w/c = 0.5$. Age 2 months. Close, unoriented, partly striated microstructure of hydration products.

FIG. 10

Microstructure of C_3S and C_3A paste with gypsum and triethanolamine, $w/c = 0.5$. Age 1 hr. Unhydrated grains of cement minerals with plates or rods of ettringite-type hydration products and some very small rounded particles.

FIG. 11

Microstructure of C_3S and C_3A paste with gypsum and triethanolamine, $w/c = 0.5$. Age 17 hr. Large plates of hydration products and some small fibrous particles.

FIG. 12

Microstructure of C_3S and C_3A paste with gypsum and triethanolamine, $w/c = 0.5$. Age 3 days. Fracture of interlocking fibrous structure on the surfaces of plates.

From 3 to 7 days, ribbons of aggregate radiated out from the edges of many plates that had an interlocking fibrous structure (Fig. 13). The three-dimensional arrangement of the fibrous particles on the surfaces could also be observed.

During the time of hydration from 7 days to 1 month, no clear changes in microstructure appeared. Occasionally one could see the partly parallel orientation of the plates of hydration products and their interlocking three-dimensional fibrous structure (Fig. 14). Smaller hexagonal plates of low sulpho-aluminate hydrate were also discernable.

After 6 weeks' hydration the paste with triethanolamine was also treated with glycol in the same way that the paste with no admixture had been treated. The rich calcium hydroxide phases were removed by this treatment but to a lesser extent than had been removed from the paste with no admixture. A large proportion of the radially-arranged fibrous particles of CSH and of the plate-like forms arranged in a three-dimensional interlocking fibrous structure was still present. Sometimes the plate-like forms were also pseudo-hexagonal in shape.

Between 6 weeks and 3 months of hydration no clear changes in microstructure were observed (Fig. 15). The densely packed microstructure was built up from different forms of hydration products; among them one could distinguish plates or fibres of CSH, plates of low sulpho-aluminate hydrate, and larger single hexagonal rods of ettringite.

3. Hydration of C_3A , C_3S , gypsum and calcium lignosulphonate.

During the first 4 hours of hydration, the microstructure of a paste of C_3A , C_3S and gypsum with 0.5 per cent calcium lignosulphonate, displayed a mixture of unhydrated grains with thin crumpled foils around them (Fig. 16). Rod-like particles had also begun to appear.

At 8 hours of hydration, unoriented particles of ettringite-type rods appeared on the surfaces of grains, but between the rods the large crystals of gypsum were still present. At 1 day hydration more hydration products developed and the surfaces of some large crystals of gypsum became partly eroded.

FIG. 13

Microstructure of C_3S and C_3A paste with gypsum and triethanolamine, $w/c = 0.5$. Age 7 days. Radial arrangement at edges of plates in fibrous interlocking structure of CSH.

FIG. 14

Microstructure of C_3S and C_3A paste with gypsum and triethanolamine, $w/c = 0.5$. Age 1 month. Plates of hydration products with fibrous fractures, sometimes of parallel orientation, around grains of unhydrated cement minerals with rough fracture.

FIG. 15

Microstructure of C_3S and C_3A paste with gypsum and triethanolamine, $w/c = 0.5$. Age 3 months. Platelets and fibrous unoriented microstructure of hydration products display many different forms.

FIG. 16

Microstructure of C_3S and C_3A paste with gypsum and calcium lignosulphonate, $w/c = 0.5$. Age 4 hours. Semicrystalline foils and rod-like particles of hydration products.

FIG. 17

Microstructure of C_3S and C_3A paste with gypsum and calcium lignosulphonate, $w/c = 0.5$. Age 1 day. Fibrous particles of CSH form plates with interlocking structure.

FIG. 18

Microstructure of C_3S and C_3A paste with gypsum and calcium lignosulphonate, $w/c = 0.5$. Age 2 days. Loose, unoriented structure of fibrous particles.

FIG. 19

Microstructure of C_3S and C_3A paste with gypsum and calcium lignosulphonate, $w/c = 0.5$. Age 7 days. Massive striated structure displayed between many of the various forms of hydration.

FIG. 20

Microstructure of C_3S and C_3A paste with gypsum and calcium lignosulphonate, $w/c = 0.5$. Etched with glycol for $\frac{1}{2}$ hour. Age 6 weeks. Plates of CSH and clear binder between partly hydrated grains of cement components. Some of the grains display clear zonal structure.

After 1 day of hydration, the fibrous particles of CSH were formed, usually with an interlocking structure (Fig. 17). Sometimes some large hexagonal plates were also visible. Some of the plates had a fibrous interlocking structure with a ribbon-like parallel arrangement at their edges. At 2 days, more fibrous hydration products appeared (Fig. 18), and during the period from 3 to 7 days they displayed mainly a platy or fibrous habit (Fig. 19).

After 14 days of hydration, the paste had developed a dense microstructure of particles of both platy and fibrous habit. Definite changes of microstructure during this period of hydration were not observed.

After treatment with glycol at 6 weeks of hydration, one could observe plates of low sulpho-aluminate hydrate, single hexagonal rods of ettringite type, and clear binders between the individual grains of the hydrated mineral components. Some of these grains displayed clear zonal structure (Fig. 20). The CSH appeared as fibres or cigar-shaped particles which formed a completely unoriented mass.

At 3 months' hydration there were still no clear changes of microstructure to be observed.

Discussion and Conclusions

1. Under the conditions of these experiments and with the proportions of compounds used, it was found that the system C_3S , C_3A and gypsum produced CSH products of similar nature and at about the same rates as had been produced by the C_3S and gypsum system (2). Differences that did occur were therefore either of a nature difficult to observe or of minor importance.

2. With no admixture present the first hydration products appeared after the first few minutes of hydration as thin, crumpled foils and small, rod-like ettringite-type particles. Between 8 and 17 hours some small irregular grains also developed. After 1 day of hydration the microstructure was made up of semicrystalline fibrous particles of CSH which had an interlocking arrangement of plates, plates of low sulpho-aluminate hydrate and rods of ettringite. During the next period of hydration the microstructure

became more close-knit and more hydration products appeared. After the treatment with glycol and removed the rich lime phases, the predominant structure was then the fibrous rosettes; the interlocking arrangement of CSH and the unoriented plates of low sulpho CAH were also evident. No new forms of hydration products appeared after 2 days of hydration.

3. The influence of each of triethanolamine and calcium lignosulphonate on the hydration process of a mixture of C_3A , C_3S and gypsum was very pronounced, but similar to their effects on the simpler systems of C_3S plus gypsum or C_3A plus gypsum (1, 2).

4. The hydration process with triethanolamine present was similar to that without an admixture, but faster. Semicrystalline foils and ettringite-type hydration products were the dominant forms up to 4 hours of hydration. After this time nucleation of CSH became visible, and by 8 hours' hydration CSH particles were present in the form of interlocking fibrous plates. CSH and large thin plates of CAH were the dominant forms for the first 3 days of hydration. At 3 days, more ettringite-type rods appeared in a rosette arrangement. After this time the microstructure was quite dense, and no further significant change in morphology took place. The treatment with glycol removed smaller amounts of the rich lime phases of the hydration products than it had when no admixture was present. After treatment the microstructure displayed a three-dimensional fibrous arrangement of CSH, and also some rosette formations.

5. The hydration process began more slowly when calcium lignosulphonate was present than when no admixture was present. The thin crumpled foils which appeared in the first few minutes of hydration were dominant up to 8 hours. At this time more hydration products, with mostly ettringite-type rods between them, appeared. By the end of one day of hydration, CSH fibres formed an interlocking structure. The microstructure then became more dense as more hydration products developed. The treatment with glycol removed larger amounts of hydration products, with the result that the remaining products exhibited an unoriented fibrous structure. Comparing these results with those previously reported (2) for the system

C_3S , C_2S plus gypsum with added lignosulphonate, one concludes that the presence of C_3A does, to some extent at least, reduce the retarding action of the lignosulphonate on the hydration process of C_3S . This is essentially in agreement with others, and has been most recently substantiated by Young (9).

6. From this and the previous studies in this series (1, 2) a preliminary picture of the formation of the ultimate microstructure of such silicate-aluminate systems begins to emerge. The early, thin, amorphous films convert more or less rapidly to very thin crumpled foils and to needle shapes or fibres. These arrange themselves between the pseudomorphs of the original minerals in bundles or aggregations which gradually fill in with hydration products to form plates. The plates in turn arrange themselves into tabular masses which then constitute the microstructure. The two organic admixtures used, while they strongly affect the rates of reactions, do not appear to significantly influence this form of the final structure. Separate experiments carried out in this laboratory have confirmed that the mechanical properties of cement pastes at advanced ages of hydration are not greatly affected by the presence of these and other admixtures.

7. The etching experiments performed in this and the previous study (2) prove rather conclusively that the plates constituting the tablets had evolved from a fibrous form. More work is required to throw light on precisely what takes place in this filling-in process (10).

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.

This is a contribution from the Division of Building Research, National Research Council of Canada, and is published with the approval of the Director of the Division.

References

1. T. D. Ciach and E. G. Swenson, Submitted to J. Cement and Concr. Res.
2. T. D. Ciach and E. G. Swenson, Submitted to J. Cement and Concr. Res.
3. P. Seligmann and N. R. Greening, Highw. Res. Rec. No. 62, 80(1964).
4. H. F. W. Taylor, Fifth Int. Symp. on the Chem. of Cement, Tokyo, II, 1(1968).
5. J. G. M. de Jong, The Interaction of Tricalcium Silicate and Tricalcium Aluminate during their Hydration. Ph.D. Thesis, Technische Högskola, Eindhoven (1968).
6. L. E. Copeland, E. Bodor, T. N. Chang and C. H. Weise, J. Res. Dev. Labs Portld Cem. Ass., 9, 61(1967).
7. S. Diamond, J. L. White and W. L. Dolch, Am. Mineral. 51, 388(1966).
8. L. E. Copeland and D. L. Kantro, Fifth Int. Symp. on the Chem. of Cement, Tokyo, II, 387(1968).
9. J. F. Young, J. Am. Ceram. Soc., 52, 44(1969).
10. T. D. Ciach, J. E. Gillott, E. G. Swenson and P. J. Sereda, J. Cement and Concr. Res. 1, (1970).