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by

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ANALYZED

MICROSTRUCTURE OF CALCIUM SILICATE HYDRATES*

T. D. Ciach, J. E. Gillott, E. G. Swenson and P. J. Sereda
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(Communicated by D. M. Roy)

ABSTRACT

Morphological and microstructural changes with time of a hydrating C_3S paste** were studied by electron microscopy and x-ray diffraction. Products consisted of amorphous material, crumpled foils, fibrous particles and plates. The plates appear to have an underlying mesh structure of interlocking fibres, the space between these having been filled with a lime-rich calcium silicate hydrate or with calcium hydroxide. The platy morphology occurs for the silicate hydrates as well as for calcium hydroxide. This study included also portland cement paste to allow a comparison with the C_3S system. Conclusions are given regarding mechanical properties of these cementing systems.

SOMMAIRE

Les changements dans le temps de la morphologie et de la microstructure durant l'hydratation d'une pâte de C_3S ont été étudiés au microscope électronique et par diffraction X. Les produits comprenaient des matériaux amorphes, des feuilles froissées, des particules fibreuses et des paillettes. Ces paillettes avaient une structure de mailles de fibres enclenchées et l'espace entre les fibres paraît rempli d'une forme de silicate de calcium hydraté riche en chaux ou d'hydroxyde de calcium. La morphologie en paillettes a lieu aussi bien dans les silicates hydratés que dans l'hydroxyde de calcium. Cette étude comprend également la pâte de ciment portland afin de permettre une comparaison avec le système de C_3S . Les conclusions sont tirées concernant les propriétés mécaniques de ces systèmes de cimentation.

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

**Standard cement nomenclature is used; e.g. $C_3S = 3CaO \cdot SiO_2$;
W/C = water:cement ratio by weight.

Introduction

The object of the present work is to elucidate the microstructure and nature of the hydration products of portland cement, the chief component of which is calcium silicate hydrate. This microstructure is thought to be a key to a better understanding of the physical and mechanical properties of the cement.

Many authors (1 - 20) have studied the structure and morphology of CSH (calcium silicate hydrate). Some have presented evidence for the semicrystalline fibrous forms of the hydration products, and others (5 - 7) have discussed the fibrous particles which appear as bundles, aggregates, and sometimes as sheets having an interlocking structure oriented in three directions at an angle of about 60°. But neither the interrelation between the various observed shapes of particles, nor their role in the formation of the final microstructure of hardened paste, have been established. The final form of the microstructure of cement paste after long hydration time, appearing as cleaved tabular masses has often been identified as calcium hydroxide.

Recent work in the laboratories of DBR/NRC has involved the study of the changes in morphology of the hydration products of the various pure constituents, singly and in combinations, as well as of cement paste. As part of this study triethanolamine and other compounds were included to observe the effects of additives on portland cement. This paper is concerned with microstructure; a separate series of papers will deal with specific morphological changes occurring with different combinations of the constituents.

Experimental Methods

Changes with time in the morphology and nature of the hydration products of cement and C_3S paste, of 0.5 water to cement ratio, were studied by electron microscopy, x-ray and electron diffraction.

The microstructure was examined at different intervals of hydration from 5 minutes to 6 months. The hydration was stopped by treating the sample with acetone at -18°C and drying in vacuum. Single-stage replicas from the freshly broken surfaces of cement and C_3S paste were made using the

platinum-carbon technique (1 - 5). The microstructure of 6-month-old samples was more clearly revealed by etching the sample surface with ethylene glycol. The effect of etching on hydration products was also studied by x-ray diffraction.

Results

In portland cement paste the initial products of hydration are amorphous-looking thin foils and fibrous particles (Fig. 1). These products appear mainly on the surface of unhydrated grains, filling in void spaces as they grow. The fibres bridge unhydrated grains, often meeting at about 60° angles (Fig. 2), and creating an interlocking mesh. Space between fibres becomes filled in so that the final products are plates with marked cleavage (Fig. 3). Surfaces of the plates often reveal the underlying fibrous structure. This paper will attempt to establish the relation between the initial products, appearing as fibres and thin sheets, and the final, tabular, massive structure.

It was believed that the vital steps in the formation of the final microstructure of portland cement would be best revealed by studying the essential constituents individually. For this reason the formation of the microstruc-

FIG. 1

Cement paste, W/C = 0.5, 3 days hydration. Fibrous hydration products with interlocking arrangement.

FIG. 2

Cement paste, W/C = 0.5, 3 days hydration. Fibrous particles forming criss-cross connection between unhydrated grains of cement.

FIG. 3

Cement paste, $W/C = 0.5$, 28 days hydration. Close-textured, tabular, massive structure composed of plates which show cleavage and striated appearance

FIG. 4

C_3S paste, $W/C = 0.5$, 7 days hydration. Semicrystalline fibres of calcium silicate hydrate covering unhydrated grains.

FIG. 5

C_3S paste, $W/C = 0.5$, 1 month hydration. Hydration product showing cleavage and parallel cleavage face; the interlocking arrangement of fibres in this face is evident.

FIG. 6

C_3S paste, $W/C = 0.5$, 1 month hydration. Hydration products showing fibrous structure merging into plates made up of fibres intersecting at approximately 60° angles.

ture during the hydration in C_3S paste was studied in great detail and the essential observations are presented here.

During the first 7 days of hydration, the surface of the C_3S grains became covered by radiating fibrous particles of calcium silicate hydrate (Fig. 4). These formed an interlocking mesh in the space between grains. As time of hydration increased, the fibrous structure developed into a platy form (Figs. 5 and 6) similar in appearance to that observed in cement (Fig. 3), although the fibrous structure of the plates in C_3S paste was clearer than that seen in portland cement. The triangular disposition of the fibres is clearly seen in Figure 6.

After 6 months' hydration, the paste displayed a massive tabular structure with platy and occasionally fibrous hydration products between less well-defined masses which appeared like pseudomorphs of grains of C_3S (Fig. 7). Etching of this tabular material for $\frac{1}{2}$ hr with ethylene glycol revealed textural details. As shown in Figure 8 the appearance was strikingly similar to that of C_3S in early stages of hydration (Fig. 4). Platy hydration products corroded by glycol displayed a pseudo-hexagonal form resulting from their underlying fibrous structure (Figs 9 and 10). For comparison a study was made of an etched surface of natural tobermorite from Skye. It showed that the glycol also attacked the natural crystalline form of calcium silicate hydrate and revealed the pseudo-hexagonal platy structure (Fig. 11).

X-ray diffractograms showed that the glycol reacted with all the hydration products of C_3S although at different rates. Peaks attributed to both $Ca(OH)_2$ and C-S-H were markedly weakened; some of the peaks, particularly those at about $3.07\text{\AA}$, were broadened. This may have been the result of small crystallite size, or internal residual stress in the crystals, or of both. Etching appears to have decreased the crystallinity of the material which remained after glycol treatment (Fig. 12).

In a study concerned with the effect of triethanolamine additive on the morphology of C_3S hydration products, it was observed that the steps in the development of microstructure were more clearly defined; the essential

FIG. 7

C_3S paste, $W/C = 0.5$, 6 months hydration. Main hydration product is massive tabular structure showing strong parallel cleavage. The tabular masses connect together less defined masses appearing as pseudomorphs of unhydrated grains.

FIG. 8

C_3S paste, $W/C = 0.5$, 6 months hydration. Etched with glycol $\frac{1}{2}$ hour. Platy form of hydration product displays fibrous morphology.

FIG. 9

C_3S paste, $W/C = 0.5$, 6 months hydration. Etched with glycol $\frac{1}{2}$ hour. Pseudo-hexagonal plates composed of interlocking fibres meeting at about 60° .

FIG. 10

C_3S paste, $W/C = 0.5$, 6 months hydration. Etched with glycol $\frac{1}{2}$ hour. Intergrowing fibres of hydration product are seen forming the tabular masses.

FIG. 11

Natural tobermorite from Skye etched by glycol for $\frac{1}{2}$ hour. Mineral displays fibres with intersections forming pseudohexagonal angle.

FIG. 12

X-ray diffractograms of C_3S paste, $W/C = 0.5$, 180 days hydrated.

features are presented here to add to the understanding of the microstructure of cement paste. A full report on this study will be presented later.

The products during the early stages of hydration of C_3S with triethanolamine additive were radiating fibres and sheets of fibrous structure between unhydrated grains (Fig. 13). The morphology was very similar to that shown in Figure 10. The fibrous texture of the unoriented intergrowing plates is shown very clearly in Figure 14. After about 1 month of hydration the fibrous texture was still visible on the surface of plates, which sometimes displayed pseudohexagonal morphology (Figs. 15 and 16). Figure 17 shows most clearly how the fibrous hydration products formed the plates. The plates had parallel orientation and were stacked to form the tabular masses.

From these results it is clear that the pseudohexagonal morphology resulted from the triangular disposition of the felted fibres of calcium silicate hydrate. The platy morphology would seem to have been the result of infilling between fibres.

FIG. 13

C_3S paste, with 0.5% triethanolamine, $W/C = 0.5$, 1 day hydration. Main hydration product appears as radiating fibres and unoriented irregular sheets (which sometimes display fibrous texture) between unhydrated grains.

FIG. 14

C_3S paste with 0.5% triethanolamine, $W/C = 0.5$, 2 days hydration. Hydration products appear as intergrowing plates or sheets composed of interlocking fibrous structure.

FIG. 15

C_3S paste with 0.5% triethanolamine, $W/C = 0.5$, 2 months hydration. Fibrous hydration products form the underlying structure of plates which in turn are stacked as parallel layers forming the tabular structure.

FIG. 16

C_3S paste with 0.5% triethanolamine, $W/C = 0.5$, 2 months hydration. Hydration products show fibrous texture and pseudo-hexagonal morphology.

FIG. 17

C₃S paste with 0.5% triethanolamine, W/C = 0.5, 3 months hydration. Hydration products display an interlocking mesh of fibres giving a pseudo-hexagonal plate morphology to the calcium silicate hydrate.

Triethanolamine accelerated the hydration of C₃S. Present work showed that when this additive is used it also caused the morphology of the hydration products to be more clearly defined.

Discussion

Many other workers have observed and reported the various forms of hydration products of portland cement and C_3S , described as crumpled foils, fibrous particles and plates, but no evidence has been presented to show the interrelation between them and the steps involved in the formation of the final microstructure. This study takes evidence from the hydration of portland cement paste, C_3S , and C_3S with triethanolamine paste to provide this missing link. The initial hydration products of C_3S formed in this condition were very poorly crystallized calcium silicate hydrates in the form of crumpled foils, fibrous particles and plates. These forms were most often observed and reported when portland cement and C_3S grains were allowed to hydrate in excess water (1-10).

In the early stages of hydration the unhydrated grains of cement or C_3S are readily identified. When hydration is nearly completed the space occupied by unhydrated grains seems to be replaced by pseudomorphs (Fig. 7) of no particular distinguishable morphology; they may well be composed of the same material that fills the space between the interlocking fibrous particles.

Cementitious material between pseudomorphs and grains of partly hydrated cement or C_3S consists of tabular masses composed of platy hydration products (Figs. 3, 7, 15 and 16). Because of its morphology and cleavage this has commonly been regarded as $Ca(OH)_2$. As shown by the present work (Fig. 17), however, these plates appear to have an underlying pseudo-hexagonal mesh structure of interlocking or felted fibres. These fibres frequently intersect one another with an approximate isosceles-triangle type of arrangement. The space between fibres becomes filled with an apparently amorphous material composed of either a lime-rich form of calcium silicate hydrate or calcium hydroxide. The infilling material was generally more susceptible to etching by glycol than were the fibres. The above evidence that the C-S-H material has varying forms and morphology and even different response to etching by glycol, leads to the conclusion that the hydration products cannot be regarded as separate crystalline phases of fixed stoichiometric chemical composition, but rather, are solid solutions of calcium silicate hydrates and calcium hydroxide. This is completely in agreement with the

ideas presented by Taylor (12) and the evidence of D. M. Roy (13) showing that the Ca/Si ratio varies within the hydrated product.

Morphological evidence that the hydration products are of poor crystallinity is supported by x-ray and electron diffraction data. Only ab-plane reflections were detected from the calcium silicate hydrates. The absence of a definite c-axis spacing for the calcium silicate hydrates suggests that Ca, OH and H₂O may be held in sheets of CSH of variable thickness and poor crystallinity. Analogous situations are known in some of the clay minerals where monoclinic and triclinic structures of pseudohexagonal symmetry exist.

The same morphological form of calcium silicate hydrate as found in the products of C₃S hydration was also found in hydrated cement. This system is, however, much more complex because of the more variable composition.

From the standpoint of mechanical properties of hydrated cement, the microstructure of the cementing system is really a composite material in which a fibrous network is imbedded in an amorphous material. Such a structure should provide a material having very good mechanical properties; the high compressive strength of the dense (low porosity) hydrated cement may well be a reflection of this. It would be expected that the tensile strength of such a composite would be high also, but such is not the case and generally the tensile strength is only 1/10 that of the compressive strength. To account for this, the work presented here shows that the masses of the cementing material appearing as tabular structures are not usually interconnected with each other but rather are joined to areas representing the original unhydrated grains (pseudomorphs, etc.), so that what might be considered as interparticle connections must be defined as material that apparently lacks the reinforcement of the fibres.

Conclusions

The most important conclusions from the present work are as follows:

1. The main products of C₃S hydrated under these conditions cannot be regarded as crystalline components of stoichiometric chemical composition; rather, they are solid solutions of calcium silicate hydrates and calcium hydroxide.

2. A platy morphology is not a reliable criterion for the identification of $\text{Ca}(\text{OH})_2$ as a hydration product because the final morphology of calcium silicate hydrates is also plate-like.
3. The plates of calcium silicate hydrate are based upon a skeletal structure of fibres which have a pseudo-hexagonal arrangement.
4. The same platy morphology of calcium silicate hydrate is also found in hydrated cement paste.
5. The hydration products, assembled into tabular structures, act as cementing agents, first between adjacent unhydrated grains and subsequently between pseudomorphs where unhydrated grains had been.
6. The pseudomorphs seem to have no definite morphological structure; they are suspected to have a composition similar to that of the infilling material.
7. The cementing system consists of a composite material in which a fibrous network is embedded in an amorphous matrix (infilling material). This material itself is expected to have excellent mechanical properties; the interparticle connections, however, seem to be made up of the pseudomorphs of the infilling material (matrix) and do not have the reinforcement of the fibres.

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References

1. J. J. Comer and J. W. Turley. J. appl. Phys. 26, 346 (1955).
2. S. Brunauer, D. L. Kantro and L. E. Copeland. J. Am. chem. Soc., 80, 761 (1958).

3. S. Brunauer and S. A. Greenberg. Chem. of Cement, Proc. Fourth Int. Symp., Washington, D.C., 1960 (NBC Monograph 43, p. 135, 1962).
4. A. Grudemo. Chem. of Cement, Proc. Fourth Int. Symp., Washington, D.C., 1960 (NBC Monograph 43, p. 615, 1962).
5. L. E. Copeland and E. G. Shulk. J. Res. Dev. Labs Portld Cem. Ass. 4, 2 (1962).
6. H. F. W. Taylor. The Chemistry of Cements. Academic Press, London, New York (1964).
7. A. Grudemo. K. tek. Högsk. Handl., Trans. Royal Inst. of Techn., Stockholm, Sweden, 242 (1965).
8. S. Brunauer. Proc. Eighth Conf. Silicates Industry, Budapest (1966).
9. L. E. Copeland, E. Bodor, T. N. Chang and C. H. Weise, J. Res. Dev. Labs Portld Cem. Ass., 9, 61 (1967).
10. J. G. M. de Jong. The Interaction of Tricalcium Silicate and Tricalcium Aluminate during their Hydration. Ph.D. Thesis, Technische Högskool, Eindhoven (1968).
11. L. E. Copeland and D. L. Kantro. Fifth Int. Symp. on the Chem. of Cement, Tokyo, II, 387 (1968).
12. H. F. W. Taylor. Fifth Int. Symp. on the Chem. of Cement, Tokyo, II, 1 (1968).
13. M. W. Grutzeck and D. M. Roy. Nature, Lond., 223, 492 (1969).
14. R. B. Williamson. J. Crystal Growth, 3, 787 (1968).
15. R. B. Williamson. Science, N.Y., 164, 549 (1969).
16. S. Chatterji and J. W. Jeffery. Nature, Lond., 209, 1233 (1967).
17. H. E. Schwiete and U. Ludwig. Proc. Eighth Conf. Silicates Industry, Budapest, p. 285 (1966).
18. Ch. W. Lentz. Symp. Struct. of Port. Cement Paste and Concrete, Washington, D.C., Spec. Rep. High. Res. Bd., 90, p. 269 (1966).
19. T. D. Ciach and E. G. Swenson, Submitted to J. of Cem. and Concr. Res.
20. S. Diamond. Proc. Third Annual Conf. on Scanning Electron Microscopy, Symp. IIT Research Inst., Chicago, Illinois, p. 385 (1970).