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MECHANISM OF HYDRATION OF
CALCIUM SILICATE BASED HYDRAULIC BINDERS

Final Report

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INTRODUCTION

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This report summarizes the findings of our work sponsored by the United States Army Research office through Contract No. DAAG 29-78-C-0041 over the period September 1978 - September 1981. The research proposal entitled "Mechanism of Hydration of Calcium Silicate-Based Hydraulic Binders" was aimed at obtaining a more complete understanding of the hydration mechanism and microstructure of calcium silicates, the major constituents of portland cement. The portland cement paste, at the microstructural level, has major influences on the strength, dimensional stability, durability and other properties of the concrete. Better prediction and control of these properties demand more complete knowledge than presently exists on both the structure of the hardened paste and the process by which this structure is attained.

During the past three years several aspects of these problems were investigated jointly at the Martin Marietta Laboratories (Principal Contractor) and the University of Aberdeen (Sub-Contractor). The work at the Martin Marietta Laboratories was concentrated on the early hydration reaction of tri- and di-calcium silicates (C_3S and β - C_2S) using the techniques of Electron Spectroscopy for Chemical Analysis (ESCA) complemented by high resolution scanning electron microscopy (SEM). Other techniques used included differential thermal and thermogravimetric analyses (DTA and DTG), X-ray diffraction (XRD), calorimetry, and liquid phase analysis by atomic absorption spectrophotometry. The work at the University of Aberdeen dealt with the hydration products formed at later ages from C_3S , β - C_2S and cement

using the technique of analytical transmission electron microscopy (ATEM) and studies of silicate anion structure by trimethylsilylation, infrared spectroscopy, mass spectrometry and various chromatography techniques. The final phase of the project included studies on the effect of fly ash additions on the hydration of calcium silicates and cement and on the composition of their hydration products.

The following scientific personnel actively participated in the research work performed under this program:

Martin Marietta Laboratories (Principal Contractor)

Dr. J. Skalny

Dr. I. Jawed

Dr. D. Ménétrier (visiting scientist, University of Dijon, France)

Dr. T. Sun

Mr. D. McNamara

University of Aberdeen (Sub-Contractor)

Dr. H.F.W. Taylor

Dr. K. Mohan

Dr. E. Lachowski

Dr. J. Gard

A fuller summary of the work performed by late 1980 is contained in a recent review paper entitled "Hydration Studies on Cement and Calcium Silicate" published in World Cement Technology Vol. 12, pp. 124-178 (1981). A list of papers with titles published during the course of this work is given at the end of this report.

Electron Spectroscopy for Chemical Analysis

The ESCA technique made it possible for the first time to characterize both qualitatively and quantitatively the surface of hydrating calcium silicates. This information is of great importance in formulating the hydration

mechanism of these systems. In ESCA an electron beam is directed at the surface which causes electrons to be emitted and their kinetic energies are determined. The resulting energy spectrum shows peaks each of which corresponds to a particular energy level of a single element. The position, shape and intensities of these peaks provide information on the chemical composition and environment of the atoms of each element. In addition, by sputtering the surface, the underlying areas can be characterized.

The ESCA results provided indications that for both C_3S and $\beta-C_2S$, protonation of oxygen atom at the solid surface begins within seconds and the condensation or polymerization of silicate ions within hours. The surface protonation is most likely the first step in the hydration process.

The surface analysis of both C_3S and $\beta-C_2S$ hydrated in water showed that the initial hydration product is of low C/S ratio. This ratio subsequently increases (within 30 sec) and then falls again to about 1.5 for C_3S after about 1 to 3 hours at 25°C. For $\beta-C_2S$ the ratio approaches a value of about 1.3 after 24 hours. The variation in the C/S ratios with time for $\beta-C_2S$ and C_3S is similar and implies that essentially the same type of mechanism for initial hydration of both calcium silicates is operating. The differences, only in time scale, can be attributed to the differences in the hydration rates of the two silicates. The induction period is seen to correspond to a period when very little change in C/S ratio with time is noticed.

In the presence of silicate or aluminate ions, the C/S (or C/S+A) ratios were much lower than in their absence; the ratio being lowest in presence of silicate ions. In the presence of aluminate ions significant

amounts of Al were found on the C_3S surface indicating formation of Al-containing hydration products in addition to calcium silicate hydrates.

The above ESCA studies were complemented with liquid phase analysis and conduction calorimetry studies. The liquid phase analysis showed highest Ca^{+2} ion concentration in water for C_3S , lowest in presence of silicate ions, and intermediate in presence of aluminate ions. The conduction calorimetry studies showed an acceleration of C_3S hydration by the silicate ions and a retardation by the aluminate ions. These results can be explained on a dissolution-precipitation mechanism for C_3S hydration.

High Resolution Scanning Electron Microscopy

Results of the morphological studies using high resolution SEM complemented the results obtained by ESCA. Changes on the calcium silicate surface were noticed within seconds of hydration; minute specks of hydration products were formed and the surface appeared "corroded". The process did not seem to occur evenly on the grain surface and a continuous protection layer of hydration product was not observed. During the induction period the surface gradually becomes covered with sheets or fossil-like material, which develops into honeycomb. From the end of the induction period, the sheets split and crumble and so develop into fibrous bundles. Both calcium silicate hydrates (C-S-H) and microcrystalline calcium hydroxide (CH) begin to form even before the bulk solution is saturated with respect to CH. The CH crystals do not grow until after the induction period. Subsequently large masses of CH are formed and overgrow C-S-H.

In lime solution the C_3S hydration appeared very similar to that in water; the sequence of formation of hydration products was the same, differing

only in the timing of their formation. Sheets of C-S-H were visible as early as 1 minute of hydration but in contrast to hydration in water, the hydrate formation was slow. Transformation of C-S-H sheets into fibers was seen much later compared to water. Liquid phase analysis also indicated that the rate of dissolution of C_3S in lime was slower than in water.

In presence of gypsum, the morphology of hydration products (C-S-H) shows less developed honeycomb structure in the early minutes of hydration (very similar to that observed in lime solution). However, the morphology developed at later stages is similar to that usually observed for C_3S hydrated in water. Energy dispersive spectroscopic analyses show that C-S-H formed contained substantial amounts of sulfate ions in the structure. The liquid phase analyses indicated an increased dissolution rate in presence of gypsum.

The morphology of hydrated β - C_2S is similar to that of C_3S . The formation of hydration products seems to be more localized on the β - C_2S surface than that of C_3S . The slow hydration of β - C_2S was also shown by the easier detectability of various morphological changes on the surface during hydration.

The results of ESCA and SEM studies complemented with liquid phase analysis and calorimetric studies suggest that the hydration calcium silicates is essentially a dissolution-precipitation process. Upon contact with water, the Ca and Si from C_3S (a less) surface are released into the liquid phase and are reprecipitated as less soluble C-S-H. The variations of surface Ca/Si ratio with time indicates that in the early seconds a Si-rich layer is formed on the C_3S (or C_2S) surface on which Ca^{+2} ions chemisorb. The rate of

calcium silicate dissolution and the chemical composition of the precipitated C-S-H is greatly influenced by the ionic composition of the liquid phase, resulting in the change in C/S ratio and the incorporation of various solution species in the C-S-H. The presence of various ionic species in the liquid phase also affects the nucleation and growth of various hydration products as shown by morphological studies.

Analytical Transmission Electron Microscopy

The technique of analytical electron microscopy (ATEM) allows determination of atom ratios in particles of dispersed materials. We considered it especially useful for the analysis of single phase in cement because it analyzes a much smaller volume compared to conventional microprobe or SEM analytical techniques.

About 300 particles of C-S-H from C_3S and C_2S hydrated at different water to solid ratios (W/C) and temperatures from one day to 30 years were analyzed by ATEM. The C/S ratios were found to be 1.43 to 1.66, with no variation with curing time (up to 30 years). No apparent compositional difference between the different morphological types of C-S-H was noticed. Also, there was no evidence to show that temperature and W/C ratio had any significant effect on the C/S ratios. For β - C_2S pastes, the mean C/S ratios, again independent of curing time, were 1.34 to 1.42.

Over 500 particles from normal portland cement pastes, mostly characterized as C-S-H, CH, AFm and AFt phases, were analyzed. The mean C/S ratio of C-S-H found by ATEM decreased from about 1.9 at one day to 1.4 to 1.6 after 2 to 3 years. The C-S-H took up significant amounts of Al, Fe and S. For typical, mature paste, 30 to 40% of total Al and Fe and at least

80% of the total SO_4^{-2} were present in the C-S-H. Pastes of very finely ground cements gave C-S-H with high C/S ratios.

The AFm phase of the cement pastes was not found to be monosulfate but had a complex composition which varied with time and was roughly intermediate between those of monosulfate, C_4AH_x and C_2AH_x . It also contained Fe and Si. In a 7-day old paste the interlayer anion sites were found to be occupied mainly by SO_4^{-2} and OH^- ions but at 28 days Si- and Al-containing anions, especially $\text{Al}(\text{OH})_4^-$, were relatively more important. Analysis of the AFt phase indicated that the composition of this phase also differs appreciably from that of ettringite.

Silicate Anion Structure

The process of anion polymerization is believed to run parallel with changes in mechanical properties. One view suggests that Si-O-Si links formed between C-S-H particles during polymerization should produce a stronger, less deformed material. Another view suggests that changes in mechanical properties are associated with replacement of one morphological variety of C-S-H by another, and these variations could contain different distributions of silicate ions. Whichever view is correct, anion polymerization is of great interest in relation to mechanical properties.

The silicate anion polymerization was studied by trimetry silylation technique on C_3S and cement pastes hydrated from 1 day to 30 years. For C_3S pastes, the C-S-H formed during the first few days contained solely the dimer (Si_2O_7). During the next 6 to 9 months, the contents of dimer and more highly condensed species increased. Subsequently, the polymer content continues to increase and that of dimer decreases. After 20 to 30 years, about 40% of Si occurs as dimer and 60% as polymer.

In C_3S pastes the distribution of anion size within the polymer fraction changes very little during the first 6 to 12 months, but polymerization advances more rapidly thereafter. At all ages the most important single species is linear pentamer (Si_5O_{16}); species with 3 or 4 Si are of very minor importance or absent. For the 1-year old paste the number and weight mean anion sizes are respectively about 7 and 11 Si; for the 22-year old paste, the corresponding values are about 11 and 33 Si. The nature of the species higher than pentamers is not yet settled, but there are indications that anions with 8 to 9 Si atoms are relatively abundant, and that these are more highly connected than single chains. Results for cement pastes are, in general, very similar to those for C_3S pastes.

The results for C_3S pastes suggest that polymerization of silicate anions within C-S-H is an extremely slow process, and occur on a time scale of years. We suspect that it is associated with reconstitution of C-S-H particles and thus with microstructural change. If this view is correct, polymerization is not the cause of changes in mechanical properties, though study of it is still useful because it serves to monitor the microstructural changes which are the cause of these changes.

Introduction of Fly Ash with C_3S

The final phase of the project included studies on the interaction of fly ash with C_3S . The early hydration of C_3S (up to 1 day) was found to be retarded by the presence of fly ash. Two fly ashes of similar chemical and mineralogical composition showed a difference in their effect on C_3S hydration. The results were attributed to the differences in the dissolution behavior of the two fly ashes. The retardation of C_3S hydration in the early stages was

interpreted in terms of delayed nucleation and growth of CH and C-S-H in the presence of fly ash. This study also emphasized the need for a better and more reliable method for evaluating the quality of fly ash for use in concrete.

Results of analytical transmission electron microscopy indicated on acceleration of C_3S hydration after 1 day. At times up to 9 months, the main chemical effect of adding fly ash was reduction in CH content. About 35% of fly ash was found to have reacted in 9 months. The mean C/S ratio (1.4 to 1.5) of C-S-H was only slightly affected. Small amounts of Al, Fe, and SO_4^{2-} were found in the C-S-H. Silicate polymerization studies using trimethylsilylation method on C_3S -fly ash pastes gave results similar to those for C_3S alone but the mean anion size in C-S-H was found to be greater.

PRESENTATIONS

Numerous presentations on topics related to and based on the contract subject were made by H.F.W. Taylor, J.P. Skalny and I. Jawed. These include presentations at the annual meetings of The American Ceramic Society, Materials Research Society, and Cement Association of Jpana. In addition, lectures and seminars were presented at two Engineering Foundation Conferences, University of S. Pacific (Fiji), University of Minnesota, National Bureau of Standards, Chinese Silicate Society and other institutions in China, Conference on Mineralogy and Microstructure of Ceramics (U.K.), Portland Cement Association of Brazil, and Mexican Institute for Cement and Concrete.

OTHER ITEMS

H.F.W. Taylor and J.P. Skalny (together with D.M. Roy and J.F. Young) were invited to be the Principal Reviewers of two of the topics, relevant to this contract, covered at the 7th International Conference on Chemistry of Cements, Paris, 1980.

H.F.W. Taylor has received The Society of Chemical Industry (U.K.) Medal 1981. The invited lecture was published (see ref. 18).

D. Ménétrier was awarded a bronze medal by CNRS, 1981 (France) for her contributions to silicate chemistry.

H.F.W. Taylor was invited to give the 1981 Mellor Memorial Lecture to the Institute of Ceramics (U.K.).

The paper by Jawed et al (ref. 19) has been submitted as a candidate for R.G. Lye Award (awarded yearly for the best scientific paper published by Martin Marietta Laboratories employees).

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