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CHARACTER OF HYDRATION OF $3\text{CaO} \cdot \text{Al}_2\text{O}_3$

BY

R. F. FELDMAN AND V. S. RAMACHANDRAN

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CARACTERISTIQUES DE L'HYDRATATION DE $3\text{CaO} \cdot \text{Al}_2\text{O}_3$

SOMMAIRE

Les auteurs ont hydraté des masses compactes de C_3A (C symbolise CaO et A symbolise Al_2O_3) et ont étudié la réaction par analyse calorimétrique différentielle, par diffraction aux rayons X, par porosimétrie au mercure, et par analyse des variations volumiques. Les aluminates hydratés de système hexagonal, C_2AH_8 (H symbolise H_2O) et C_4AH_{19} , se sont formés à 2°, 12° et 23°C par une réaction directe entre C_3A et H_2O . La réaction d'hydratation à 52° et 80°C a été arrêtée par la formation de C_3AH_6 autour des grains de C_3A . La vitesse de recristallisation des hydrates de système hexagonal en C_3AH_6 de système cubique s'accélère avec l'accroissement de la température. L'analyse des variations volumiques a confirmé que C_3AH_6 s'accroît par épitaxie à la surface du grain de C_3A . La réaction à cette surface et le passage de l'eau au travers de la couche d'aluminates hydratés de système hexagonal déterminent la vitesse générale de la réaction. La recristallisation des hydrates de système hexagonal en C_3AH_6 accélère la réaction par l'enlèvement de la couche entourant le grain de C_3A par un mécanisme de solubilisation. A 52 et à 80°C, le C_3AH_6 peut se former directement, sans passer par le stade intermédiaire d'hydrate de système hexagonal.

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Character of Hydration of $3\text{CaO}\cdot\text{Al}_2\text{O}_3$

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The C_3A compacts were hydrated and the reaction was studied by DTA, X-ray diffraction, mercury porosimetry, and volume change analysis. The hexagonal hydroaluminates C_2AH_6 and C_4AH_{13} formed at 2°, 12°, and 23°C by a direct mechanism between C_3A and H_2O . The hydration reaction at 52° and 80°C was stopped by formation of C_3AH_6 around the C_3A grains. The rate of conversion of the hexagonal hydrates to cubic C_3AH_6 increased with temperature. Volume change analysis confirmed that C_3AH_6 grows epitaxially on the surface of the C_3A grain. The reaction at this surface and the passage of water through the layer of hexagonal hydroaluminates control the overall reaction rate. The conversion

of the hexagonal hydrates to C_3AH_6 accelerates the reaction by removing the layer of products from around the C_3A grain by a solution mechanism. At 52° and 80°C, C_3AH_6 may form without the intermediate formation of the hexagonal hydrate.

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At the time this work was done, the writers were, respectively, research officer and postdoctorate fellow (on deputation from the Central Building Research Institute, Roorkee, India), Inorganic Materials Section, Division of Building Research, National Research Council.

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I. Introduction

THE aluminate phase in portland cement, although of low proportions, is of great importance owing to its role in the early hydration reactions. Research on this phase has proceeded in several directions, one of these being a study of the equilibria in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$. Work by several investigators¹⁻⁴ has established that the only stable compounds in the system at normal temperatures are gibbsite, $\text{Ca}(\text{OH})_2$, and C_3AH_6 .*

The previous work provided some basis for predicting reactions which occur during hydration of C_3A . Reactions of this type, however, are complex because equilibrium is not attained for some time. The kinetics of these reactions are not only affected by the products formed, but also by the changing conditions of the reaction owing to the formation of products. These reactions occur in limited quantities of water so that metastable products may exist for long periods and may have profound influence on the mechanism and rate of the whole reaction.

During the hydration of portland cement, C_3A hydrates along with the other constituents in the presence of $\text{Ca}(\text{OH})_2$, $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$, and alkalis in solution, which will affect the reaction. The study of C_3A hydrating in a solution of $\text{Ca}(\text{OH})_2$ is aimed at determining rates and mechanisms in the hydration of C_3A in portland cement.

The hydration of C_3A has been studied by many methods; X-ray and microscopic examination at several temperatures led to the conclusion that the development of the cubic hexahydrate was preceded by formation of the hexagonal hydroaluminates C_2AH_7-9 and $\text{C}_4\text{AH}_{12-14}$.^{3,5,6} It was not clear whether C_3AH_6 could form directly at higher temperatures and lime concentrations, although Lafuma⁷ and Assarsson⁵ suggested this. The metastable hexagonal hydrates converted to the stable cubic hexahydrate more rapidly at the higher temperatures, but a more specific knowledge of the reaction was lacking. Conflicting results have been obtained and even identical preparations did not yield completely similar results.³ The analysis by Brocard⁸ of the supernatant liquid of dilute suspensions of C_3A as a function of time showed that the rate of solubility increased with temperature although the solubility itself did not change much. Electrical conductometric work by Solov'eva and Segalova⁹ confirmed this. Stein¹⁰ and others¹¹ followed the conversion of the hexagonal hydrate to the cubic by calorimetric measurements. The DTA, although applied to some of these systems and used for kinetic studies to some extent in the hydration of C_3A by Segalova *et al.*¹² and by Young¹³ was not used to full advantage. This technique, although not completely quantitative, makes it possible to detect minute quantities of hydrates which might be very poorly crystalline as is often the case in the reaction in question.

A method for stopping the hydration reaction was developed in this work. A volume change method and porosimetry were used in conjunction with DTA for analysis, and X-ray diffraction was used in some cases as confirmation.

II. Experimental Procedure

C_3A was prepared from reagent grade CaCO_3 and $\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$. A stoichiometric mixture containing 2% excess CaO was fired three times at 1375° to 1390°C . X-ray diffraction showed no aluminate other than C_3A . Free lime, determined by the alcohol-glycerol method,¹⁴ was 2.2%; CO_2 and $\text{Ca}(\text{OH})_2$, determined by thermogravimetry, were 0.16 and 0.5%, respectively.

The C_3A compacts were hydrated at 2° , 12° , 23° , 52° , and 80°C . Calculating from the porosity (Fig. 1(A)), the water/solid ratio within the specimen was 0.12. Compaction pro-

Fig. 1. Pore-size distribution for compacts hydrated at various conditions.

cedures, length change measurements, and hydration techniques have been discussed previously.^{13,16}

The reaction was stopped by placing the compact in liquid air. The specimen was ground, washed, and filtered in cold absolute alcohol and degassed in a desiccator for 6 hr. Throughout the operations great care was taken to avoid contamination by CO_2 .

The DTA on all specimens was performed in the absence of air; the heating rate was $10^\circ\text{C}/\text{min}$.

Pore volume and pore size distribution were determined with a mercury porosimeter. The minimum pore size in which mercury could be injected was 0.012μ in diameter.

III. Results and Discussion

The unhydrated C_3A for all phases of this work was in compact form. This technique has some distinct advantages, as discussed previously,^{15,16} and facilitates studying very early reactions. Only low water/solid ratios, however, can be studied.

Stopping the reaction in liquid air has no effect on the hydrates formed; this was tested on specimens where hydration was very slow. Use of absolute alcohol or acetone for partial drying is well established³; it was verified in the present work by DTA that it had no effect on either the unhydrated or hydrated materials. The degree of drying achieved by the degassing procedures is open to question. It is possible that some hydrate water is removed from the hexagonal hydroaluminates C_2AH_8 and C_4AH_x . Roberts¹⁷ reported C_4AH_{19} as the reaction product but Stein¹⁰ suggested that C_4AH_{13} may occur at spots with local water shortage.

The consistency of the results at any one temperature and from temperature to temperature gives confidence in the assumption that if these procedures are used throughout, valid interpretations can be made.

* Throughout the text, the following cement chemistry nomenclature is used: C = CaO , A = Al_2O_3 , and H = H_2O .

Fig. 2. Thermograms for C_3A hydrated at (A) $2^\circ C$, (B) $12^\circ C$, (C) $23^\circ C$, and (D) $52^\circ C$.

Figures 2 and 3 show DTA thermograms for C_3A hydrated at 2° , 12° , 23° , 52° , and $80^\circ C$, each for several times. The interpretation of these thermograms was based in part on the results of several workers. The dehydration of C_3AH_6 was shown to take place in two stages by Schneider and Thorvaldson¹⁸ at $\sim 275^\circ$ and at 400° to $500^\circ C$. Other workers¹⁹⁻²² suggested, however, that the thermogram of C_3AH_6 has only one endotherm, at 315° to $330^\circ C$. Work by Young¹³ and by Majumdar and Roy²³ confirmed that endotherms exist at 330° and $500^\circ C$ whereas Segalova *et al.*¹² suggested that the thermogram includes a small endotherm near $150^\circ C$.

Kalousek *et al.*²⁰ have shown that the thermogram for C_4AH_{13} consists mainly of a large endotherm at $240^\circ C$ whereas Young¹³ assigns three endothermic peaks at 120° , 215° , and $310^\circ C$ to a mixture of C_4AH_{13} and C_2AH_8 . Segalova *et al.*¹² showed large endothermic peaks at 190° , 260° , and $290^\circ C$, with small peaks at 410° and $490^\circ C$ representing the hexagonal aluminates. Rey²² suggested that C_2AH_8 is represented mainly by peaks at 140° and $310^\circ C$. In the present study, the C_2AH_8 hydrate is considered to be represented mainly by an endothermic peak varying from 140° to $190^\circ C$, and C_4AH_{13} is represented by an endothermic peak varying from 230° to $260^\circ C$.

The DTA thermograms show formation of the hexagonal aluminates at all temperatures at the earliest times. Associated with these peaks representing these compounds is an exothermic peak between 800° and $900^\circ C$ which has been attributed to the formation of CaO and Al_2O_3 from the dehydrated C_2AH_8 ,²⁴ but it is not clear from this work that the exothermic effect is associated with both C_2AH_8 and C_4AH_{13} . This effect is absent for C_3AH_6 and is useful in confirming the presence of the hexagonal hydroaluminates. From a study of the thermograms, it is clear that the reactions involved are very temperature dependent; the rate of hexagonal hydrate formation increases as the temperature increases; at 6 min for 52° and $80^\circ C$, only a small amount of hexagonal hydroaluminate is present, C_3AH_6 being present at the earliest times examined (30 sec at 52° and 5 sec at $80^\circ C$). There is evidence of a small amount of C_3AH_6 after 10 days at $2^\circ C$, after 6 hr at $12^\circ C$, and after 30 min at $23^\circ C$. At 12° and

Fig. 3. Thermograms for C_3A hydrated at $80^\circ C$.

$23^\circ C$, at certain times of hydration, both the hexagonal hydrates and C_3AH_6 were increasing in quantity, but in general the disappearance of the hexagonal hydrates indicated that they were converting to C_3AH_6 , and at a faster rate as the temperature increased. The probability of C_3AH_6 forming directly, especially at the higher temperatures, is very real and will be discussed later. There is no evidence that the C_2AH_8 converts to C_4AH_{13} as an intermediate phase in the conversion to C_3AH_6 .³

The DTA shows that at $52^\circ C$ little hydration occurs after 30 min whereas at $80^\circ C$, considering the rapid rate of hydration in the first 15 sec, the rate has been greatly reduced at 6 min; for $23^\circ C$ hydration the product forms steadily up to 25 hr and slowly beyond that. The degree of hydration determined by TGA after 25 hr at $23^\circ C$ is 52.5%, whereas after 4 days at $52^\circ C$ it is 17.5%.

The endothermic peak at 500° to 530°C that developed with the other peaks at $\sim 150^\circ$ and 240°C when hydration occurred at 2° and 12°C , was absent at the higher temperatures and thus does not seem to be characteristic of the hexagonal or cubic hydrates. This endotherm may be due to a small amount of $\text{Ca}(\text{OH})_2$ formed during the hydration of C_3A at low temperatures even though the temperature of the endotherm is somewhat higher than the $\text{Ca}(\text{OH})_2$ with endotherm at 450°C , in the original C_3A preparation. The latter endotherm was probably formed, however, by vapor phase hydration of CaO at more accessible regions, whereas the former endotherm may be the result of $\text{Ca}(\text{OH})_2$ embedded in the hydroaluminate. Alternatively, the hydration of CaO in the C_3A can explain the endotherm but it should produce a thermogram for the 23°C hydrated specimen similar to that at 2° and 12°C .

The complete disappearance of the peak at 140°C for hydration at 52° and 80°C and almost complete at 23°C indicates that the thermogram for C_3AH_6 has only two endotherms, at about 320° and 500°C . It is evident that for systems that may produce several compounds, and where transformations of various types may occur, DTA thermograms must be interpreted from series obtained at different stages as the reaction progresses. Also, in these reactions, where products may form on the surface of an unhydrated grain and progress inward, and where the crystal size or habit may change, the peak temperatures will shift with an increase in degree of hydration as was observed in these thermograms.

Formation of a hydration product causes a decrease in the rate of hydration, but the subsequent rate is still temperature dependent. Although this may be partly due to the difference in rate of moisture flow to the unhydrated C_3A , the reaction rate between C_3A and H_2O at the surface of the unhydrated C_3A grain must be considered as is illustrated by the great increase with temperature of the reaction rate very early when little product was formed. Thus it is considered that the reaction rate is controlled by both the reaction between C_3A and H_2O at the surface of the unhydrated C_3A grain and the rate of permeation of water through the hydrate product formed close to the surface of the C_3A grain. The effect of this second factor is well illustrated by the results of Stein¹⁰; he observed (through calorimetric measurements) a marked increase in hydration rate due to the conversion of the hexagonal hydroaluminates to C_3AH_6 , thus removing the barrier close to the grain surface.

Specimens used for X-ray diffraction patterns were those in which larger amounts of product were formed. In general the lines for C_4AH_{13} and C_2AH_8 were diffuse and not clear, in contrast to those for C_3A and C_3AH_6 . Consequently the results are useful only in a general sense and show the advantage of using DTA for this system.

Length changes, measured at four temperatures, are shown in Fig. 4. These results are reproducible to $\pm 5\%$ except at 23°C where the rate and degree of hydration and expansion were very great, with the result that in some cases the specimens broke. These results are used for qualitative and semi-quantitative analysis of the system. At each temperature, expansion began as soon as water contacted the specimen. The results corresponded to those obtained from the DTA.

The expansion rate at 52°C at short times is very high relative to the other temperatures but after 5 min it decreases rapidly. After 1 day the expansion ceases completely at 0.66% , even though it was kept for 3 days at 52°C and for 3 more days at 23°C . This specimen, autoclaved at 214°C and 300 psi, expanded by 21% and was completely hydrated. In results not shown here, C_3A after hydrating for 92 days at 12°C , had expanded 14.4% and the rate of expansion was slow.

The pore size distribution and total pore volume results are shown in Fig. 1. Specimen A is the unhydrated compact of C_3A . Specimen B is a C_3A compact hydrated at 52°C for 4

Fig. 4. Length change of C_3A compacts hydrated at 2° , 12° , 23° , and 52°C .

days (17.5% hydrated); the volume of larger pores above 0.5μ is still about half the original. Thus hydration of C_3A at 52° and 80°C involves formation of C_3AH_6 which acts as a very impermeable barrier localized around the C_3A grain, despite the fact that adequate space is available and the reaction has a high potential for expansion. The C_3AH_6 formed at a different region than that from the reaction at 23°C , the mechanisms of the respective reactions probably differing.

Specimen C in Fig. 1, a compact of C_3A hydrated at 23°C for 25 hr (52.5% hydrated), shows a large reduction in volume of large pores and an increase in volume of smaller pores relative to specimens A and B. Specimen D hydrated at 2°C for 1 week (26.6% hydrated by estimate) gave a total pore volume of 10.9% . By calculation, assuming the average composition of the hexagonal hydroaluminates as $\text{C}_3\text{AH}_{10.5}$ with a density of 2.04 ,²⁵ the pore volume is 9.13% . Errors in the degree of hydration determination and use of $\text{C}_3\text{AH}_{10.5}$ as the formula for the mixed product may account for this difference. These results show that the increase in solid volume of 1 g of the solid, to be accommodated in the body, is 0.1190 cm^3 for specimen C and 0.1345 cm^3 for specimen D. The approximate expansions would be 6 to 8% and 4% , respectively, suggesting that under the conditions of the reactions the hexagonal hydroaluminates can be accommodated in the voids with the development of less stress than the C_3AH_6 . The rate of the respective reactions may also have an influence. It is significant, however, that although the formation of the hexagonal hydroaluminates is the more accommodative, considerable hydration pressures are exerted as shown by the 4% expansion. Mikhailov²⁶ stated that formation of plate-structured compounds like the hexagonal hydroaluminates does not lead to expansion, but it is clear now that this is not the case. It is indicated that the stresses created by the rapid formation of C_3AH_6 at 23°C and subsequent rupture of bonds weaken the structure under these conditions. This is in contrast to the views of Segalova *et al.*,¹² who consider that the conversion to the cubic form occurs by a solution mechanism resulting in dissolution of the bonds. It is not likely that all the bonds would break simultaneously; during the conversion more bonds can form because of the crystallization of C_3AH_6 and further hydration of the C_3A .

Many factors operate in structure formation by a hydrate product and in the resultant length changes during hydration; these factors include the initial particle size and degree of dispersion of the product and its crystal form and habit. The rate and mechanism of the reaction, involving the degree of supersaturation that may be attained, are also important. For this complex system the length change reflects only the degree and rate of hydration and does not give a quantitative evaluation.

(1) Mechanism of the Reaction

The apparent solubility of a hydrating material and the solubility of its products have long been considered the important criteria governing the reaction rate; approaches to the hydration mechanism have not considered the reactivity of the solid. Workers^{8,9} have shown, however, that solubilities of C_3A and its hydrates do not increase much with temperature although the rate of dissolution increases.

Defects in solids are now recognized as being closely connected to their chemical behavior.^{27,28} Experimental evidence has indicated that dislocations intersecting a surface have a significant influence on reaction rates.²⁷ Gilman²⁹ has shown how dislocation density contributes to the rate of dissolution and dislocations intersecting the surface may also be the starting points for the hydration process.

Environmental factors affect the operation of the various types of surface sources of dislocations and the emergence of dislocations through the surface of the material. It has been suggested³⁰ that adsorbed polar molecules on these sites can hinder the operation of these sources. It is suggested here that certain ions in solution decrease the rate of reaction of C_3A with water or its dissolution rate by a process similar to the foregoing. The hydration of C_3A is retarded in the presence of $Ca(OH)_2$ in solution.³

The exact mechanism of the C_3A and water reaction is difficult to prove conclusively, but the following explains most of the experimental evidence: water at 2°, 12°, and 23°C reacts immediately, forming poorly crystalline hexagonal hydroaluminates by direct reaction on the surface of the C_3A grain. These soluble products are a source of ions in the solution and also contribute to retardation of the reaction by limiting the supply of water to the C_3A . This stage of the reaction is consistent with the immediate expansion observed on first wetting. As the hydration of C_3A continues, the crystals of the hexagonal aluminates may become bigger. At a certain stage in the reaction the conversion to C_3AH_6 occurs, probably by a "through-solution mechanism." This conversion removes the hexagonal hydroaluminates from the surface of the grain and the reaction accelerates. It is significant that for a time at these three temperatures the quantity of both C_3AH_6 and the hexagonal hydroaluminates increases. The conversion begins earlier at the higher temperature because the energy conditions at this temperature permit earlier nucleation. The rate of conversion is governed also by the rate of dissolution.

Energy conditions at 52° and 80°C permit C_3AH_6 to form not only by direct reaction of C_3A with water, but without going through the intermediate stage of the hexagonal hydroaluminate. This may account for the complete elimination of reaction between C_3A and H_2O ; the C_3AH_6 grows epitaxially on the C_3A grain completely sealing it off. A small amount of hexagonal hydroaluminate may be evidence, however, for a very rapid conversion of most of it to the C_3AH_6 but the possibility exists of C_3AH_6 forming by both mechanisms.

IV. Conclusion

The hexagonal hydroaluminate forms at 2°, 12°, and 23°C by a direct mechanism between C_3A and H_2O . The rate of the reaction at the surface and the passage of water through the layer of hexagonal hydroaluminates control the overall rate of the reaction. Polar ions in solution can retard the rate of hydration by adsorbing on the sites of defects and

dislocations, hindering their operation. The conversion of the hexagonal hydrates to C_3AH_6 accelerates the reaction by removing this layer from around the C_3A grains by the through-solution mechanism. At 52° and 80°C, C_3AH_6 forms immediately. This reaction may also occur by a direct mechanism and it forms a layer of C_3AH_6 on the surface of the C_3A grain.

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