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HYDRATION CHARACTERISTICS OF MONOCALCIUM ALUMINATE AT A LOW WATER/SOLID RATIO

ANALYZED

by
V. S. Ramachandran and R. F. Feldman

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HYDRATION CHARACTERISTICS OF MONOCALCIUM ALUMINATE AT A LOW WATER/SOLID RATIO

by

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(Communicated by F. D. Tamás)

ABSTRACT: The hydration characteristics of calcium monoaluminate were studied using an effective water/aluminate ratio of 0.15 at 20° or 80°C, from a few minutes to two months. The material hydrated at 80°C shows a large shrinkage while at the lower temperature a continuous expansion occurs. The product at 80°C shows a much higher strength than that hydrated at 20°C. The main initial hydration products are 2CaO , Al_2O_3 , $8\text{H}_2\text{O}$ and alumina gel. Microcracks are developed in the products hydrated at 20°C while at the higher temperature a very compact mass results. The data indicate that it is possible to obtain a durable high alumina cement by using a low water/cement ratio and hydrating at higher temperatures, and under these conditions C_3AH_6 - C_3AH_6 bond is favoured.

Les caractéristiques d'hydratation de l'aluminate monocalcique ont été étudiées à l'aide d'un rapport eau-aluminate effectif de 0.15 à 20° ou à 80°C sur une période variant de quelques minutes à deux mois. Le matériau hydraté à 80°C subit un retrait considérable tandis qu'à une température plus basse il se produit une dilatation continue. La résistance du produit hydraté à 80°C est beaucoup plus grande qu'à 20°C. Les principaux produits d'hydratation initiaux sont 2CaO , Al_2O_3 , $8\text{H}_2\text{O}$ et le gel d'alumine. Des microfissures apparaissent dans les produits hydratés à 20°C, tandis qu'à la température plus élevée le résultat est une masse très compacte. Les données indiquent qu'on peut obtenir un ciment alumineux durable en utilisant un faible rapport eau-ciment et en effectuant l'hydratation à des températures plus élevées, et que dans de telles conditions une liaison C_3AH_6 - C_3AH_6 est facilitée.

Introduction

High alumina cement, also known as aluminous cement or calcium aluminate cement develops a very high strength within 24 hr of curing in water. It has a good resistance to sulfate attack and can be used in refractory concrete. This cement is also used as an expanding or stressing cement in combination with gypsum and other constituents.

The high alumina cement comprises several phases viz., CA, CA₂, C₁₂A₇, C₂AS, C₂S, C₂F and C₄AF*, Much attention has been directed to a study of the hydration characteristics of CA. The hydration products of CA consist of CAH₁₀, C₂AH₈, C₃AH₆ and AH₃ (gel or crystalline), the relative proportions of which depend on the hydration conditions and curing period. At lower temperatures CAH₁₀, C₂AH₈ and AH₃ gel are preferentially formed and these are converted to C₃AH₆ and gibbsite at higher temperatures, according to the following scheme (1).

The 'conversion' or 'inversion' that occurs as a consequence of the transformation of the hexagonal phases, CAH₁₀ or C₂AH₈ into the cubic phase (C₃AH₆) is known to be accompanied by a loss in strength of the hardened alumina cement.

The conversion reactions may be described according to the following equations.

The conversion of CAH₁₀ to C₃AH₆ results in a volume decrease to about 50 per cent whereas that of C₂AH₈ results in a decrease to about 65 per cent of the original volume of the reactants.

*Cement chemistry nomenclature: C=CaO, A=Al₂O₃, S=SiO₂, F=Fe₂O₃, H=H₂O

Several theories have been proposed to explain the loss in strength in high alumina cement. They are summarized below.

As already stated the conversion of the hexagonal to the cubic phase results in a substantial decrease in the solid volume. In the hardened concrete this may be accompanied by the formation of pores and hence lower strength. This is essentially the explanation for strength loss advanced by Robson (2), Neville (3), Lafuma (4), Cottin (5), Midgley (6), and Mehta (7). The porosity may also increase due to the evaporation of water that is formed in the conversion reaction.

The earlier theory that the oxidation of ferrous iron in the high alumina cement is responsible for the retrogression in strengths has been conclusively disproved by Lea and others (8, 9, 10).

Lehman and Leers (11) ascribe the higher strengths in the alumina cement to CAH_{10} having a high surface area. Conversion, producing the cubic form with a lower surface area is thought to be responsible for low strengths. In a recent paper Mehta (12) has affirmed that a poor adhesive capacity of the cubic phase and low specific area are additional factors contributing to a loss in strength. It is also possible that the conversion of the flat plates with overlapping or interlocking system to icositetrahedron or cubic morphology dislocates the bonds.

Wells and Carlson (13a) failed to observe substantial decrease in the surface area during conversion and hence attribute the fall in strength to the formation of macrocrystalline alumina hydrate from the microcrystalline alumina hydrate. This is not in accord with the opinion of Lehman and Leers (11) who believe that crystalline alumina hydrate increases the strength in high alumina cements.

Révy found that during conversion reaction the surface area is actually increased due to the formation of alumina gel (13b).

Ueda (14a) did not find a direct relationship between the porosity and strength in high alumina cement. He has attributed the loss in strength to a decrease in the combined water in the converted product and also to the increase in the quantity of water filling the small pores.

The deteriorating influence of CO_2 , through the formation of $\text{CaCO}_3 + \text{AH}_3$ + H from C_3AH_6 has been proposed by Talaber for alumina cements (14b).

It has now been discovered that converted alumina cement can be strong and of low permeability if prepared at a low water/cement ratio. Robson and others (15, 16) maintain that at a low water/cement ratio the water released during the 'conversion' reacts with the anhydrous cement kernel not utilized in the initial hydration reaction, and fills the pores and thus prevents strength losses. Stiglitz (17) explains that the strength loss is mainly caused by increased porosity due to the evaporation of water released during conversion. At low water/cement ratios this water can bind with the unhydrated CA. According to Midgley (18) the major factor that prevents loss in strength is the grain size of the converted minerals viz., C_3AH_6 and AH_3 . At low water/cement ratios the low porosity is maintained by the packing of the small crystallites while at higher water/cement ratios the porosity is increased by the crystal size.

From the foregoing survey it can be concluded that the strength loss in a normally cured high alumina cement is ascribed to the conversion reaction; the exact mechanism however, is not clear. It is also implicit in the literature that the cubic hydrate (C_3AH_6) does not have a binding capacity. For example, the strengths of the aluminate hydrates are thought to be in the decreasing order, $\text{CAH}_{10} > \text{C}_2\text{AH}_6 > \text{C}_3\text{AH}_6$ (19). But this is not in consonance with the strength results obtained at low water/cement ratios even after conversion (16, 20).

Earlier work (21) on the hydration of C_3A indicated that the conversion of C_3A to C_3AH_6 under certain conditions, in fact, enhances the strength. It appears that the formation of C_3AH_6 per se should not be construed as detrimental to strength. In order to examine the applicability of the above findings to the hydration and strength development in high alumina cements, CA was hydrated at a low water/cement ratio at 20°C and 80°C for different periods. The water/solid ratio was chosen at 0.15 to emphasize its significant effect on the mechanism of hydration and strength development. The results may be advantageously extended to practical mixes having low water/solid ratios.

Attempts were made to find a possible correlation between the hydration

characteristics and other properties such as microhardness, porosity, morphology and dimensional changes.

Experimental

Materials

The calcium monoaluminate used for this investigation was supplied by Tetrattech International, San Diego. The sample contained 35.2 per cent, CaO, 64.3 per cent Al_2O_3 with free lime less than 0.2 per cent. The x-ray analysis of this material showed all the lines typical of CA. The surface area was $0.62m^2/g$. No thermal effects were observed in the differential scanning calorimeter (DSC) or thermogravimetric analysis (TGA).

Calcium monoaluminate powder was compacted at a load of 75,000 lb into discs 1.25 in. in nominal diameter and 0.05 in. thick. The effective water: aluminate ratio for hydration was calculated to be 0.15. The compacts were hydrated in duplicates at a temperature of $20^\circ C$ or at $80^\circ C$ for 10 min, 30 min, 1 hr, 2 hr, 5 hr, 10 hr, 1 day, 2 days, 5 days, 10 days, 21 days and 60 days. At the end of each period the sample was washed with alcohol and evacuated for 24 hr using liquid air trap. The sample was ground to approximately 100 mesh size for thermal and x-ray analysis, fractured for microscopic examination and cut to a rectangular shape for length change measurements.

Methods

Differential thermograms of the samples were obtained by a Differential Scanning Calorimeter (DSC) supplied as a module to Du Pont 900 thermal analyser. This unit utilizes chromal-constantan for differential temperature measurement. The reference material was ignited $\alpha - Al_2O_3$ and the heating rate was maintained at $10^\circ C/min$. The differential temperature was registered at a sensitivity of 0.02 mv/in. Thermograms were obtained in air. Both the sample and the reference material were contained in aluminum foil cups. In each experiment 40 mg of the sample was weighed into the aluminum cup.

Thermogravimetric analysis (TGA) of the samples was carried out using a sensitive Cahn Balance at a heating rate of $10^\circ C/min$. All the runs were carried out in a continuous vacuum.

The x-ray powder photographs were obtained with Philips Camera using Cu K_α source. The relative intensities of the lines were obtained by densitometer traces of the powder photographs.

The fractured surfaces of the specimens were examined by a scanning electron microscope supplied by Cambridge Co.

Samples cut to a rectangular shape approximately 1 in. by 0.25 in. were exposed to water at 20°C or 80°C continuously for periods of up to 7 days in a cell and the length change was measured periodically by a modified Tuckerman gauge extensometer. The details of this method are described elsewhere (22).

The Vickers hardness value of the unhydrated and the hydrated compacts was determined with a Leitz miniload hardness tester. Each value represents an average of 10 determinations carried out on both sides of the compact.

The Aminco-Winslaw porosimeter was used to determine the pore size distribution and porosity of both the unhydrated and hydrated samples. The instrument measures pore size diameter in the range 0.1 mm to 0.012 μ . The total porosity was also determined by vacuum-saturating the specimens with methanol.

A conduction calorimeter with six chambers was used to follow the rate of heat development during the hydration of CA. The sensitivity of the calorimeter was 20 mV/W.

Surface area was obtained with N_2 as the adsorbate by a Numinco-Orr surface area - pore volume analyser.

Results and Discussion

Differential Scanning Calorimeter

Representative differential scanning curves of CA hydrated at 20° or 80°C for different periods of up to 60 days are shown in Figures 1 and 2. At 20°C hydration proceeds slowly in the first few hours. At 10 hr hydration is indicated by an endothermal valley with a peak at about 100°C. A small endothermal doublet in the range of 175° to 225°C is also registered. At 1 day a

FIG. 1

Thermograms of CA Hydrated to Different Periods at 20°C at a Water/Solid Ratio of 0.15

FIG. 2

Thermograms of CA Hydrated at 80°C to Different Periods at a Water/Solid Ratio of 0.15

sharp endothermal peak appears at about 175°C and increases in intensity as the hydration progresses. Also an endotherm of small magnitude appearing at about 260°C at 1 day grows in intensity. An additional endothermal peak appears at about 300°C at 5 days and this also increases in intensity up to 60 days. The large endotherm appearing from the very early period with a peak around 100°C may be attributed to removal of water from the alumina gel. This endotherm is followed by another at about 125°C (not apparent in some instances) and may be ascribed to the presence of C_2AH_6 . An unmistakable endotherm appearing at about 175°C is due to the presence of CAH_{10} . The dual peaks occurring in the temperature range 200° to 325°C represent dehydration reactions in gibbsite and C_3AH_6 . Gibbsite is formed from the crystallization of alumina gel and C_3AH_6 is the conversion product of CAH_{10} and C_2AH_6 .

The thermal behaviour of CA hydrated at 80°C is significantly different from that hydrated at 20°C (Figure 2). A detectable amount of hydration is evident even at 10 min. By 30 min large endothermal effects appear at about 100°, 145°, 210°, and 280°C. The first effect is caused by alumina gel and is practically absent after 2 days of hydration. The endotherm effect at about 150°C is present in all samples up to 1 day and is attributable to the presence of C_2AH_6 . The endothermal effect at 280°C which increases in intensity with hydration is mainly caused by C_3AH_6 and gibbsite. The initial downward slope of this curve suggests the possibility of an additional endotherm. In fact at 2 days a clear endotherm emerges at about 225°C which may be due to CAH_{10} ; a maximum rate of formation of this compound seems to occur between 2 and 5 days. Possibly gibbsite also contributes to this endothermal effect. The resolution of the large endothermal effect into two effects at about 300° and 340°C at 5 days confirms the formation of gibbsite and C_3AH_6 . The endothermal peak at about 500°C represents the typical stepwise dehydration effect of C_3AH_6 .

Thermograms suggest that compared with hydration at 20°C that at 80°C proceeds at a much faster rate. The degree and rate of conversion of the hexagonal phases and alumina gel to the cubic and gibbsite phases respectively are also enhanced at higher temperature. In addition it is possible that conversion to C_3AH_6 and gibbsite phases occurs directly on the surface of CA

particles. After an initial fast reaction, further hydration, especially after about 5 days, tends to be slow at 80°C. There is still a large amount of unhydrated CA even at 60 days. The rate of formation and the conversion effect are not only dependent on the temperature of hydration but also on the initial water/solid ratio. At room temperature a higher water/solid ratio of 0.5 promotes faster conversion and crystallization reactions compared with CA hydrated at a lower/solid ratio (Figure 3).

X-ray diffraction

Rates of hydration were compared using densitometer tracings of the x-ray films for CA compacts hydrated to different periods. The tracings were not intended for evaluating, quantitatively, the hydration reaction but were a guide to

the new products that are formed. As the peaks were less distinct at higher d values, the films were used for comparison purposes. Table I shows some of the more prominent lines by which various phases were recognized.

The unhydrated CA shows all the standard d values. At 20°C up to 10 hr there is no indication of any hydrated product though DSC shows formation of some hydration product. At 1 day faint lines appear at 10.5 and 5.20 due to C_2AH_8 . At 5 days the existence of CAH_{10} is indicated. The CAH_{10} lines become more intense at 60 days and there is also a small amount of C_3AH_6 . Gibbsite could not be detected with certainty. At 60 days considerable amounts of unhydrated CA are still present.

FIG. 3
Thermograms of CA Hydrated at
20°C at a Water/Solid Ratio of 0.5

TABLE I

<u>Phase</u>	<u>d values (Å)</u>
CA	4.66-4.70, 2.95-2.98, 2.50-2.53, 2.39-2.42, 2.19-2.20, 1.92.
CAH ₁₀	14.3, 7.16
C ₂ AH ₈	10.5, 5.24
C ₃ AH ₆	5.13, 2.81, 2.30, 2.04
Gibbsite	4.85, 4.32-4.37, 2.42-2.45, 2.39.

The characteristics of hydration of CA at 80°C are different from those of CA hydrated at 20°C. CA is consumed more rapidly at early times. At 60 minutes there is an indication of the formation of C₂AH₈ but no evidence of CAH₁₀. C₃AH₆ is possibly formed at this stage. At 5 days lines due to C₃AH₆ become clearer and CAH₁₀ begins to form. Gibbsite is also detected at this period. At 10 days increased amounts of CAH₁₀ are formed. At 21 days and 60 days the phases present are CA, CAH₁₀, C₂AH₈, C₃AH₆ and gibbsite. The results are generally in accord with those of DSC. Compared with x-ray DSC appears to be a more sensitive method for identification and estimation of hydration products of CA.

Thermogravimetric analysis

TGA was carried out in a continuous vacuum and the temperature was measured by a thermocouple placed near the sample. TGA showed inflections corresponding to the differential curves obtained by DSC but the temperatures were displaced.

CA hydrated for 5 min at 80°C showed a total weight loss of about 1.8 per cent at 500°C and is associated with a broad endothermal valley in the DSC curve of this sample (Figure 2). At 10 min the hydration seems to have proceeded to a greater extent as indicated by a weight loss of 9.98 per cent. At 30 min TGA clearly shows two inflections and DSC also exhibits two endotherms at this period. The first inflection corresponds to a weight loss of 6.97 per cent and the second, to about 6.6 per cent. At 5 hrs TGA exhibits four steps in weight losses corresponding to four endothermal effects. At this period the total weight loss is 20.76 per cent. At 1 day the total weight

loss is 18.84 per cent. At 2 days only very little loss in weight occurs up to 200°C and DSC also shows a much reduced peak below 200°C. At 5 days the total weight loss is 28.22 per cent, an increase of 7.86 per cent from 2 days. Most of this increase arises from the first inflection corresponding to CAH_{10} . Between 2 and 5 days the weight loss curve indicates that the amount of C_3AH_6 has not increased.

TGA curves for CA hydrated at 20°C show inflections that could be correlated with the endothermal peaks in DSC. The ignition losses for samples hydrated for 1 hr, 10 hr, 24 hr, and 5 days are respectively 1.34, 2.49, 18.96 and 22.83 per cent and the corresponding values for samples hydrated at 80°C are 17.38, 21.13, 18.84 and 28.22 per cent. The magnitude of these values does not represent the degree of hydration but it does show that the hydration sequence at 20°C is different from that at 80°C.

Conduction calorimetry

The rates of heat development of the compacts exposed to water were determined at 25°C or 72°C by the conduction calorimetric curves (Figure 4). Though the curves indicate the relative rates of heat development for hydration they are not directly comparable to the differential thermograms. At

FIG. 4
Conduction Calorimetric Curves of
CA Hydrated at 25°C or 72°C

25°C an initial peak results immediately on contact with water due to heat of wetting and possibly some surface hydration. At about 1 day hydration seems to commence at a fast rate with maximum intensity in the interval between 28 and 31 hr. The rate of heat evolution decreases steadily thereafter and hydration proceeds slowly after 2 days. DSC curves show that considerable hydration takes place at 1 day, further hydration and conversion progressing slowly (Figure 1). The hydration at 72°C seems to proceed faster, as evidenced by an intense heat effect with a peak appearing earlier than 10 min. The major heat development occurs within 30 min. In the differential thermograms considerable reaction seems to occur between 10 and 30 min (Figure 2).

As already shown hydration in compacts is carried out at an effective water/solid ratio of about 0.15 and it is expected that hydration and conversion reactions should occur at a more rapid rate at a higher water/solid ratio. This can be demonstrated by comparing the calorimetric curves of CA at a water/solid ratio of 0.15 or 0.5 (Figure 4). The maximum rate of hydration is found to proceed earlier (12 and 20 hr) and the total heat developed is also of greater magnitude at a higher water/solid ratio in the first few days. The total heat developed is also more than that registered for the compact hydrated at 72°C (Figure 4). The total amount of heat evolved for compacts hydrated at 72°C (for the first 30 min), 25°C (in about 2 days) and at 25°C at a water/solid ratio of 0.5 (1 day) are, respectively, 56.0, 39.0 and 72.6 cal/gm.

Microstructure

The unhydrated CA consists of particles of indefinite morphology of various sizes (Figure 5A). Practically no hydration products are detected up to 10 hr (Figure 5B). At 1 day there is evidence of hydration on the surface of the particles (Figure 5C). The hydrated sample is also characterized by extensive microcracking. The cracks may have either developed during hydration or during the preparation for the microscopic examination. It is more likely that they would have developed during hydration as the cracks seem to pass through the unhydrated CA particles; the micrograph of unhydrated CA does not show any cracks. In some instances hydrated products seem to have filled the cracks. The compacts formed at 20°C show a con-

FIG. 5A: Unhydrated CA
x3.5K

FIG. 5B: CA hydrated for 10 hr
at 20°C x6.0K

FIG. 5C: CA hydrated for 1 day
at 20°C x6.8K

FIG. 5D: CA hydrated for 21
days at 20°C x3.1K

tinuous expansion as the hydration progresses and this may have caused crack development. A large amount of fibrous material is seen in the sample hydrated for 21 days (Figure 5D) indicating the existence of CAH_{10} . At 60 days the sample shows some unhydrated amorphous, platy and fibrous material with no evidence of cubic C_3AH_6 as typified by the two micrographs (Figures 5E and F).

The microstructure features of the hydrated product at 80°C are different from that formed at 20°C (Figure 6). Even at 1 hr there is an indication of the hydration products covering the CA particles (Figures 6A and B). By

FIG. 5E: CA hydrated for 60 days at 20°C x3.2K

FIG. 5F: CA hydrated for 60 days at 20°C x3.2K

FIG. 6A: CA hydrated for 1 hr at 80°C x60

FIG. 6B: CA hydrated for 1 hr at 80°C x6.5K

2 days large amounts of hydration products are evident as curled sheets and plates of C_2AH_8 and CAH_{10} (Figures 6C and D). By 5 days the sheets and plates have disappeared and a dense structure is formed (Figure 6E). At 60 days the surface presents a 'vitrified' appearance with occasional masses, probably of C_3AH_6 (Figures 6F and G). There was no indication of crack development in any of the samples hydrated at 80°C.

Length changes

Length change measurements in compacted bodies have been shown to provide important data on the mechanism of hydration (21 to 26). In this study

FIG. 6C: CA hydrated for 2 days
at 80°C x1.4K

FIG. 6D: CA hydrated for 2 days
at 80°C x3.5K

FIG. 6E: CA hydrated for 5 days
at 80°C x3.3K

FIG. 6F: CA hydrated for 60 days
at 80°C x0.7K

FIG. 6G: CA hydrated for 60 days
at 80°C x1.5K

an attempt has been made to understand the hydration characteristics of CA based on the length changes occurring at 20°C or 80°C, up to a period of 5 days. The results are plotted in Figures 7 and 8. At 20°C considerable expansion occurs within an hour and it continues at a slower rate thereafter. At 4hr, during which about 50 per cent of the total expansion occurs, hydration has not progressed to any significant extent (Figure 1). Since the particles are in intimate contact with each other the initial products formed at the interparticle surfaces tend to push each other. The expansion may also be contributed to initially by a decrease in the surface energy. As the hydration progresses the hexagonal aluminate hydrates formed create some expansion and the alumina gel is accommodated in the pores. At 5 days very slight conversion has taken place (Figure 1).

At 80°C an almost immediate expansion is followed by large shrinkage (Figures 7 and 8). This type of behaviour has not been observed before during hydration of compacted bodies. The small initial expansion is similar to that observed for the sample cured at 20°C. The large amount of shrinkage occurring within the first 30 min is also reflected in the considerable hy-

FIG. 7

Length Changes in Compacts of Monocalcium Aluminate
Hydrated at 20°C or 80°C in the First Few Hours

dration and interconversion that has occurred at this period (Figures 2, 4, 6). The contraction may be attributed to the formation of hexagonal phases that bridge between particles; their very rapid conversion to the more dense C_3AH_6 phase at the original sites provides motive force for this effect. It is possible, however, that a direct formation of C_3AH_6 and AH_3 occurring at early periods on the surface of CA also involves a bridging effect of the interfaces. The contracting force may be caused by transportation of AH_3 into the pores. After a day the amount of C_3AH_6 formed does not increase very much but there is a gradual increase in the formation of CAH_{10} ; this is followed by a slow continuous expansion.

Porosity and microhardness

Attempts were made to study the effect of hydration on the physical and mechanical behaviour of CA. The pore size distribution may be evaluated for the unhydrated and hydrated CA from Figure 9. The unhydrated CA has a total porosity of about 28 per cent of which the major portion has a diameter in the range of 0.35 to 0.1 μ . After 5 days of hydration porosity decreases

FIG. 8

Length Changes in Compacts of Monocalcium Aluminate
Hydrated at 20°C or 80°C up to 5 Days

FIG. 9
Pore Size Distribution Curves of CA
Hydrated at 20°C or 80°C

to about 1 to 2 per cent whether CA is hydrated at 20°C or 80°C. The decrease in porosity cannot be easily explained just in terms of the absolute volume changes in the hydrated products. The hydration of CA to CAH_{10} involves an enormous increase in the volume, whereas a decrease in volume is expected in the conversion of CAH_{10} and C_2AH_3 to the cubic phase. In addition, the degree of hydration and interconversion, the morphology, the possibility of clogging of micropores by alumina gel and other products, are other factors that cannot be easily subjected to quantitative evaluation. It is, however, obvious that this is mainly due to the pores being filled up with the hydration products. The total porosity was also determined by vacuum saturation using methanol to check if mercury had penetrated all the pores. The methanol method gave a total porosity of 29.5 per cent for unhydrated CA and 2.0 per cent for products obtained at 5 days. This indicated that mercury penetrates practically all the pores intruded by methanol.

For a particular material, if all the conditions are the same, then strength is known to be a function of porosity. It follows that the reduced porosity due to hydration of CA must result in an increase in the hardness values for CA

at 20°C or 80°C. Compared with a value of 19.9 kg/mm² for the unhydrated compact of CA sample, those hydrated at 20° or 80°C show hardness of 109.5 and 160.5 kg/mm² respectively. It is generally believed that higher temperatures are detrimental to strength development in high alumina cement, as these conditions favour the formation of the cubic phase. These results demonstrate that neither the high temperature nor the formation of the cubic phase is detrimental to strength development. On the other hand, although the sample hydrated at 20°C has about the same porosity as that hydrated at 80°C, the latter has a much higher hardness value. At 80°C the reaction proceeds very fast and enhances hydration of CA to the C₃AH₆ and AH₃ phases. As the particles of CA in the compact lie very close to each other, direct bond formation between C₃AH₆ products is enhanced. At 20°C however, direct bond formation due to C₃AH₆ may not be favoured as C₃AH₆ and AH₃ products are transported and recrystallized in the pores. This is evident from the microscopic examination in which only dense structuration is evident at 80°C (Figure 6).

At 60 days the hardness of the hydrated product formed at 20° and 80°C are 73.9 and 152.4 kg/mm² respectively. The fall in strength for the sample hydrated at 20°C is mainly due to the conversion of CAH₁₀ and C₂AH₈ to alumina gel and C₃AH₆. This process involves a slower conversion of CA to C₃AH₆ and hence C₃AH₆ - C₃AH₆ bonds are not promoted to the same extent. It is very likely that at ambient conditions and at a water/cement ratio higher than that used in this investigation a still poorer system would result. The samples continuously exposed at 80°C up to 60 days do not significantly change in strength due to strong bonds developed by C₃AH₆ at early stages. It is expected that for higher strengths, CA may be hydrated at higher temperatures at a sufficiently low water/solid ratio for a few hours only and then exposed to normal temperatures.

These results suggest that the present theories on strength deterioration in high alumina cements should take into account the important contribution of the strength promoting properties of the cubic and gibbsite phases, especially when formed at low water/solid ratios. It has also been observed that the increase in the surface area per se need not necessarily mean that strengths

increase. For example, the unhydrated CA has a surface area of $0.62\text{m}^2/\text{g}$, the samples hydrated for 5 days at 20°C or 80°C yield a surface area of $1.88\text{m}^2/\text{g}$ and $1.52\text{m}^2/\text{g}$ respectively but the strength of the product formed at 80°C is much higher than other samples.

Conclusions

This study has thrown new light on the hydration characteristics of CA and suggests reassessment of the popular concepts in the field of high alumina cements. At a low water/solid ratio some of the characteristics of the hydrated product formed at 80°C are different from that prepared at 20°C . At 80°C a direct bond formation of C_3AH_6 may occur on the surface of CA even within 30 min due to rapid conversion of the hexagonal phase; curing at 20°C involves a continuous expansion that at 80°C results in a substantial shrinkage. Strength development occurring at 80°C in the first few days does not change during further hydration over several months. A deterioration in strength occurs in the sample hydrated at 20°C as the hydration and interconversions occur over longer periods.

Both at 20°C and 80°C , C_2AH_8 and alumina gel and not CAH_{10} seem to be the main initial hydration products. At 80°C the hydration products do not show any definite morphological characteristics of CAH_{10} , C_2AH_8 or C_3AH_6 . Contrary to general opinion enhanced temperature actually results in the development of strength provided the water/solid ratio is low. Also the formation of C_3AH_6 by itself should not necessarily be construed as detrimental to strength development; in fact C_3AH_6 enhances strength. An increase in the surface area need not necessarily result in an increase in strength. Similarly in hydrated CA, identical strengths need not result for products of equal porosity. The present theories seeking to explain strength retentions in high alumina cement produced at low water/solid ratio should also take into account the possible contribution of C_3AH_6 phase for strength development.

It appears possible that a durable high alumina concrete can be produced within minutes of curing using a low water/cement ratio and higher temperatures.

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