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SIGNIFICANCE OF LOW WATER/SOLID RATIO AND TEMPERATURE ON THE PHYSICO-MECHANICAL CHARACTERISTICS OF HYDRATES OF TRICALCIUM ALUMINATE

by

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L’IMPORTANCE D’UN FAIBLE RAPPORT EAU/SOLIDE ET DE LA TEMPERATURE POUR LES CARACTERISTIQUES PHYSICO-MECANIQUES DES HYDRATES DE L’ALUMINATE TRICALCIQUE

SOMMAIRE

Les auteurs présentent les caractéristiques d’hydratation de l’aluminate tricalcique étudié à 20 et à 80 °C pour des rapports eau/solide de 0.2 et de 1.0. Les produits d’hydratation sont soumis à l’analyse thermique différentielle, à l’analyse thermogravimétrique, à la microscopie électronique à grille et aux mesures de changement de longueur, de porosité, de répartition du diamètre des pores et de microdureté.

L’hydratation est plus rapide à 80 °C qu’à 20 °C et l’on observe la phase cubique de C₃AH₆ dès les premières secondes. À 20 °C l’hydratation accompagne la formation initiale des phases hexagonales et l’expansion est continue. À des températures plus élevées, après une légère expansion initiale, le changement de dimensions est faible. À 80 °C la valeur de dureté du produit est de plus de quatre fois celle qui se manifeste à 20 °C. Après deux jours d’hydratation, la porosité, le pourcentage de C₃AH₆ et la microdureté sont de 15.2%, 83% et 38.9 kg/mm²; les valeurs correspondantes pour le produit qu’on obtient à 20 °C sont 21.5%, 75% et 9.1 kg/mm². Un examen microstructural du matériau qui se forme à 80 °C révèle un réseau étroitement soudé et continu pour la phase cubique. Ces résultats indiquent qu’à un faible rapport eau/solide et des températures plus élevées la formation de la phase cubique à partir de C₃A entraîne un renforcement de la résistance, contrairement à la thèse répandue que le C₃AH₆ n’est pas un bon liant.
Significance of Low Water–Solid Ratio and Temperature on the Physico-mechanical Characteristics of Hydrates of Tricalcium Aluminate

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Hydration characteristics are reported of tricalcium aluminate studied at 20 and 80 °C using water–solid ratios of 0.2 and 1.0. Hydration products were subjected to differential thermal analysis, thermogravimetric analysis, scanning electron microscopy, length change, porosity and pore size distribution, and micro-hardness measurements.

Hydration proceeds faster at 80 °C than at 20 °C and the cubic C₃ÅH₆ phase is detected in the first few seconds. At 20 °C hydration occurs with the initial formation of the hexagonal phases and expansion is continuous. At higher temperatures and a water–solid ratio of 0.2, after an initial small expansion, the dimensional change is low. The product at 80 °C develops more than four-fold the hardness value developed at 20 °C. After 2 days of hydration, porosity, per cent C₃ÅH₆ and microhardness are 15.2%, 83% and 38.9 kg/mm²; corresponding values for the product obtained at 20 °C are 21.5%, 75% and 9.1 kg/mm². Microstructural examination of the material formed at 80 °C indicates a closely welded and continuous network of the cubic phase. These results reveal that at a low water–solid ratio and higher temperatures the formation of the cubic phase from C₃A results in an enhancement of strength.

1. Introduction

Although it is present in low proportions only, the tricalcium aluminate phase (C₃A) in portland cement has a great influence on early setting characteristics. As a result much attention has been directed to the hydration behaviour of C₃A and C₃A-gypsum systems. The main conclusions on these systems have been drawn from data obtained by hydrating at a water–solid ratio of 0.5 or higher and ambient or sub-ambient temperatures. Thus it has been accepted that C₃A hydrates to a mixture of metastable hydration products C₂ÅH₈ and C₃ÅH₁₉ before converting to the stable cubic hydrate C₃ÅH₆. It has also been thought that C₃A and CA lose strength on prolonged hydration owing to the formation of C₃ÅH₆.

Earlier work at DBR/NRC on the hydration of C₃A at low water–solid ratio and different temperatures indicated that higher temperatures enhance the strength of the product,⁴ that contrary to general opinion the formation of C₃ÅH₆ by itself is not detrimental to strength development. In these investigations C₃A containing about

* In cement chemistry nomenclature, C = CaO, A = Al₂O₃ and H = H₂O.
2.2% free lime was used as a starting material and attention was focussed on the mechanism of hydration of C₃A. The present paper presents the effect of hydration of C₃A (containing almost no free lime) at a low water–solid ratio on microhardness, morphology, hydration, dimensional change and porosity characteristics and attempts to re-examine the relevance of some of the mechanisms proposed for strength development in cementitious materials. This study is mainly concerned with the products obtained after 48 h of hydration, when the major portion of C₃A is converted to the cubic phase.

A water–solid ratio of 0.2 was chosen to emphasise its significant effect on the mechanism of hydration and strength development. Results may be extended to practical mixes having a low water–solid ratio.

2. Experimental

2.1. Materials

Tricalcium aluminate of high purity was prepared by calcination of CaCO₃ and Al₂O₃. The sample was ground to pass a 200-mesh sieve and had a Blaine surface area of 4350 cm²/g. Free lime was scarcely detectable by the X-ray method.

Tricalcium aluminate powder was compacted at a load of 4000 lb b into discs of nominal diameter 0.5 in to achieve an effective water–solid ratio of 0.2 for hydration. The samples were hydrated in duplicate at temperatures of either 20 or 80 °C for two days. For hydration at 80 °C the samples were preheated to 80 °C before immersion in hot water. At the end of two days each sample was evacuated for 24 h, using liquid air trap. A set of samples was also obtained using a water–solid ratio of 1.0. All the samples were ground to approximately 100-mesh size for thermal analysis and fractured for microscopic examination and porosity determinations. Microhardness measurements were carried out on the uncut samples.

The specimens were examined by a scanning electron microscope supplied by Cambridge Instruments Co. A Leitz miniload hardness tester was used to determine Vickers hardness values. Each value represents an average of ten determinations carried out on both sides of the specimen. The Amino-Winslow porosimeter was used to evaluate the pore size distribution and porosity of both unhydrated and hydrated samples. This instrument measures pore size diameter down to 0.012 μm. Differential thermal analysis was carried out using a DuPont 900 thermal analyser, in each run heating 50 mg of sample in air at a rate of 20 °C/min. The reference material was ignited α-Al₂O₃. Thermogravimetric curves were obtained by means of a sensitive Cahn balance by heating the samples in a continuous vacuum. The experimental details have been published elsewhere.¹⁻⁴

3. Results and Discussion

The differential thermal curves of C₃A hydrated for 2 days at water–solid ratios of 0.2 and 1.0 are shown in Figure 1. All show two large endothermal effects, the very intense peak occurring at about 330 °C representing the dehydration of 4.5 molecules

b Throughout this paper 1 lb ≈ 0.45 kg; 1 in = 2.540 cm.
of water from C₃AH₆, and the second, of moderate intensity at about 510 °C, denoting the loss of the remaining 1.5 molecules of water. In all samples the hexagonal phases must have been present in minute amounts if at all.

Figure 1. Differential thermal analysis curves of C₃A hydrated as a compact or a paste at 20 or 80 °C (after 2 days).

The relative amounts of C₃AH₆ formed at 20 or 80 °C may be estimated by comparing the relative intensities of the endothermal effects of C₃AH₆. Measurements carried out on either the first or the second peak yield the same values. At 2 days at water–solid ratios of 0.2 and 1.0, C₃A hydrated at 80 °C contains about 8 to 10% more C₃AH₆ than that hydrated at 20 °C. The thermogravimetric method was also adopted for estimating the amounts of C₃AH₆ in the hydrated samples, by determining the total ignition loss. Thermogravimetric curves for two samples are shown in Figure 2. The sample hydrated at 20 °C contains about 75% C₃AH₆ and that at 80 °C contains 83% C₃AH₆. These values are in agreement with those obtained by the d.t.a. technique. In previous work at DBR/NRC the degree of hydration of C₃A was lower because the starting material contained free lime and hydration was carried out at a much lower water–solid ratio.

These results show that at two days temperature does not affect the degree of hydration of C₃A significantly. This does not necessarily mean that the rate of
Figure 2. Thermogravimetric curves of C₃A hydrated at 20 or 80 °C for 2 days (water-solid ratio = 0.2).

Figure 3. Thermograms of C₃A hydrated at 20 or 80 °C (water-solid ratio = 0.12).
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hydration is the same at earlier periods. D.t.a. curves of C\textsubscript{3}A hydrated in the first few minutes make this clear (Figure 3). Whereas it takes \(6\) h before C\textsubscript{3}AH\textsubscript{6} forms in considerable amounts at \(20 \, ^\circ\text{C}\), at \(80 \, ^\circ\text{C}\) it is evident at \(15\) s. A similar trend is obvious at higher water–solid ratios.\textsuperscript{5} The results indicate that at \(80 \, ^\circ\text{C}\) the cubic phase forms almost immediately on contact with water; hexagonal phases could not be detected at this temperature. At \(20 \, ^\circ\text{C}\) the rate of hydration is much slower; the hexagonal phases form initially and gradually convert to the cubic phase.

Measurement of length changes during the hydration of cementitious materials provides important information on the mechanism of hydration.\textsuperscript{1,3,6–9} Figure 4 shows length changes in C\textsubscript{3}A samples hydrated at 23 and 75 °C. The curves illustrate the significant differences in the effect of temperature of hydration on length changes. At 75 °C an initial expansion of 0.3% occurs in the first few minutes and further expansion continues at a greatly reduced level. The sample hydrated at 23 °C expands at a rapid rate and reaches a value of about 2.2% at 6 h. The initial expansion at higher temperatures represents the formation of a large amount of C\textsubscript{3}AH\textsubscript{6} at the original sites of C\textsubscript{3}A. This may form directly from C\textsubscript{3}A since the hexagonal phases are not detected at any time from a few seconds to several days. At 23 °C the hexagonal phases form first and are converted to the cubic phase gradually. Hexagonal phases, having a higher molar volume than the cubic phase, produce expansive forces continuously. Once bonds have been formed subsequent conversion to the cubic phase may not result in proportionately large expansion.

![Figure 4. Length changes of C\textsubscript{3}A hydrated at 23 or 75 °C.](image)

One of the important physical parameters that changes during the hydration of a cementitious material is porosity and pore size distribution. Figure 5 gives histograms of the pore size distribution in an unhydrated sample and in samples hydrated for two days at 20 and 80 °C. The unhydrated sample has a total porosity of 38.0%, with most of the pores distributed over a diameter in the range 0.2 to 2 \(\mu\text{m}\). The C\textsubscript{3}A sample, at a water–solid ratio of 0.2 and hydrated at 20 °C, exhibits a reduced porosity of only 21.5%; that hydrated at 80 °C shows a further decrease to 15.2%. The higher

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porosity in the sample hydrated at 20 °C, in relation to that hydrated at 80 °C, may be due to a combination of factors. At 20 °C the sample expands considerably more than at 80 °C, creating more pores. Also, the degree of hydration at 20 °C is slightly less than that at 80 °C. At 80 °C the main decrease in porosity (with respect to the unhydrated material) occurs in the range 0.5 to 2 μm, whereas at 20 °C pores of diameter 0.015 to 0.5 μm are formed. The creation of these small pores at 20 °C is probably due to recrystallisation and conversion of the hexagonal phases in the pores. At 80 °C the hydrated products are mainly formed at the original sites of C₃A and the conversion and growth of the cubic phases into the pores may not involve formation of small pores.

A distinct difference in the microstructure of the C₃A samples hydrated at either 20 or 80 °C at a water–solid ratio of 0.2 or 1.0 is evident in Figure 6. At 20 °C the hydrated product prepared at a lower water–solid ratio consists of irregular as well as spherically shaped particles in the form of disconnected chunks [Figure 6(a) and (b)]. Large voids that may have resulted from expansion of the sample may also be observed. The product formed at 80 °C shows spherical particles connected or welded into a continuous network [Figure 6(c) and (d)]. These probably result from a direct bonding of the C₃AH₆ products formed mainly on the original sites of C₃A.
Figure 6. Electron micrographs of C_3A hydrated at 20 or 80 °C for 2 days (a) to (d) at a water–solid ratio of 0.2, and (e) to (f) at a water–solid ratio of 1.0: (a) C_3A sample hydrated at 20 °C; (b) C_3A sample hydrated at 80 °C; (c) C_3A sample hydrated at 20 °C; (d) C_3A sample hydrated at 80 °C; (e) C_3A sample hydrated at 20 °C; (f) C_3A sample hydrated at 80 °C.
Properties of tricalcium aluminate hydrates

Micrographs indicate that material hydrated at 80°C should be stronger than material formed at 20°C. The paste (water-solid ratio 1.0) formed at 20 or 80°C shows clearly the formation of particles of spherical shape [Figure 6(e) and (f)]. In comparison with products formed at a lower water-solid ratio, paste formed at a water-solid ratio of 1.0 does not exhibit intimate contact between hydrated particles and should be weak. At 80°C the paste formed at the higher water-solid ratio shows agglomerated spherical regions without adequate interconnections.

Microhardness measurements generally support the conclusions drawn from investigation of porosity, length change, and microstructure. As microhardness is a measure of strength, microhardness and strength are used interchangeably in the present paper. Hardness values of the unhydrated C₃A sample, that hydrated at 20°C, and that hydrated at 80°C are, respectively, 2.8, 9.1 and 38.9 kg/mm². It is widely believed that the formation of C₃AH₆ is not conducive to strength development though Robson¹¹ and our recent work¹² has shown that high strengths can be obtained in high alumina cement pastes containing C₃AH₆ provided the water-solid ratio is low. In the present work the product formed at 80°C yields a hardness value about 14 times that of unhydrated C₃A. The product formed at a lower water-solid ratio at 20°C yields a hardness value greater than that of unhydrated material or paste formed at a water-solid ratio of 1.0 and far less than that of material hydrated at 80°C. This difference cannot be explained in terms of the degree of hydration because the difference in the amount of C₃AH₆ formed in the two samples is only about 8%.

The small difference in porosity values cannot explain the appreciable difference in microhardness values. Soroka and Sereda¹⁰ have shown that in cementitious systems porosity is exponentially related to microhardness. In a more recent work Sereda found that for gypsum preparations obtained by different methods the microhardness versus porosity curve is distinct for each preparation.¹¹ It appears that the crystal habit and interparticle bonding may be responsible for the differences in strength. The wide variation in strength of samples hydrated at 20 or 80°C may be due to the greater area and number of bonds formed as a result of direct formation of C₃AH₆ at 80°C (Figure 6). At 20°C C₃AH₆ has to go through the metastable hexagonal phases that involve conversion and transportation phenomena and thus less probability of direct C₃AH₆-C₃AH₆ bonding. The pastes obtained at 20 or 80°C were not amenable to microhardness measurements because they had either not set or showed extensive cracks during hydration.

4. Conclusions

Tricalcium aluminate hydrated at a low water-solid ratio shows a higher microhardness value when hydrated at 80°C than at 20°C. At 20°C the rate of hydration to the cubic hydrate proceeds more slowly, involving initial formation of the hexagonal hydrates, and is accompanied by continuous expansion. At 80°C the formation of C₃AH₆ seems to occur by direct conversion from C₃A; the hydrated product forms and grows at the original sites of C₃A. This results in a closely welded and continuous network with enhanced mechanical strength, and initially involves a small rapid expansion followed by a lower rate. These results show that the formation of C₃AH₆
is conducive to strength development. Hydration at 20 °C results in lower final strength development, probably due to the formation of the hexagonal phases which undergo subsequent conversion to the cubic phase and may involve the breaking of initial bonds and transportation of the product. This interferes with the formation of direct C₃AH₆-C₃AH₆ bonding.

The development of strength in hydrated cementitious products is generally explained in terms of one or more of the following: degree of hydration, chemical composition of the product, porosity, morphology, surface area. The present study reveals that conditions of formation of the cementitious product may be so adjusted as to demonstrate that either a weak or a strong system may be produced. It also shows that not just one factor per se is operative in the development of strength.

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