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THE EFFECT OF TEMPERATURE ON THE HYDRATION OF THE CALCIUM ALUMINATES AT HIGH WATER–SOLID RATIOS

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ABSTRACT

The hydration behavior of the calcium aluminates as a function of the curing temperature was investigated using a combination thermogravimetric analysis/differential thermal analysis (TGA/DTA) system. Samples were hydrated with a water–solid ratio of 10/1 for periods of 1 to 90 days. Three curing temperatures were studied: 2, 25 and 50°C. The percent combined water was used to approximate the degree of hydration. Changes in the curing temperature were accompanied by changes in the rate of hydration, as well as, in some cases, changes in the hydration products.

INTRODUCTION

It is generally accepted that there are five stable compounds occurring in the binary phase system, $CaO–Al_2O_3$. The compounds are tricalcium aluminate (C_3A) **, dodecacalcium hepta-aluminate ($C_{12}A_7$), monocalcium aluminate (CA), calcium dialuminate (CA_2), and calcium hexa-aluminate (CA_6). With the exception of CA_6, all of these compounds are found in either Portland cement or high-alumina cement [1]. Because, however, all calcium aluminates are known to take Fe^{3+} ions into their crystal lattices, they are rarely found in a substantially pure form in clinker [2].

The only stable calcium aluminate hydrate present in the system $CaO–Al_2O_3–H_2O$ at normal temperature and pressure is C_3AH_6 [3]. There are, however, a number of metastable hydrates also found in this system. The specific products obtained during the hydration of the anhydrous calcium aluminates are dependent upon a number of factors. At room temperature, all of the metastable compounds are known to eventually convert to C_3AH_6, although in some cases only after long periods of time.

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** Cement chemistry shorthand notation is used throughout this paper: C = CaO, A = Al_2O_3, H = H_2O.

The water–solid ratio is an important factor which must be considered when studying hydration reactions. Previous investigations [4–8] on the effect of the water–solid ratio on the hydration rate and reaction products of cementitious compounds, have used water–solid ratios of 2 : 1 or less (some as low as 0.25 : 1). It is not enough to provide a sample with sufficient water to theoretically form the predicted stable hydrates, since, in most cases, the sample will first form one or more metastable species. If there is not sufficient water to form these intermediates, the formation of the final hydrate could be delayed indefinitely.

According to Kondo and Ueda [4], the hydration rate is accelerated by an increase in the water–solid ratio if the slow step is dissolution, and is decelerated when the rate is controlled by nucleation. This, however, depends upon the hydration proceeding via a "through solution" mechanism, and there are instances when the observations indicate a "topochemical" or solid-state mechanism [9]. Some investigators [5,7] have found the hydration to depend little on the water–solid ratio.

This investigation examines the effects of temperature on the hydration behavior of the calcium aluminates at a water–solid ratio of 10 : 1. By using a large water–solid ratio, the influence of small errors in the amount of water added can be minimized, and the effect of temperature on the hydration reactions can be more precisely studied.

EXPERIMENTAL

Stoichiometric mixtures for the formation of each compound synthesized in this study were prepared from reagent grade calcium carbonate and aluminum hydroxide. In order to assure uniformity of results, the chemicals were always taken from bottles with the same lot number. In order to obtain homogeneous samples, each raw mix was blended for 24 h in a porcelain jar mill.

The samples were placed into 50-ml platinum crucibles and calcined for 2 h at 900°C. The furnace temperature was slowly raised to either the melting point of the desired compound or to 1500°C, whichever came first. The samples were allowed to equilibrate at the final temperature for several hours. They were then air-cooled and subsequently ground with an agate mortar and pestle. Samples were repeatedly fired until the presence of the desired compound was confirmed by X-ray diffraction, and the absence of free calcium oxide was confirmed by the ASTM standard method [10].

The glass content of each sample was measured using optical microscopy. The technique used was a modification of the "South African Procedure", previously described by Fulton [11]. In this procedure, a portion of each sample, having a particle size between 200 and 270 mesh, was placed on a glass slide and wetted with glycerol. The samples were then viewed under both plane and polarized light. The particles which were visible under polarized light were counted as crystalline, and subtracted from the total number of particles to calculate the percent glass. Allowances were made for particles which showed partial crystallinity.

The surface area of each sample was measured with a Blaine air permeability apparatus, using the ASTM standard method [12]. All of the samples, except CA_6, were ground to a surface area of 2500 $cm^2\ g^{-1}$. In the case of CA_6, even after 177 h at 1500°C, a sample with a surface area of 2500 $cm^2\ g^{-1}$ could not be produced, and a sample with a surface area of 3500 $cm^2\ g^{-1}$ was used instead.

Each sample was mixed with distilled, deionized water at a water–solid ratio of 10:1, and placed in a tightly covered polyethylene container. Samples were cured at three temperatures (2, 25 and 50°C), and maintained for intervals of 1 to 90 days. In order to stop the hydration, samples were placed in an excess of cold ethanol and ground with an agate mortar and pestle. They were then filtered using a 10–15-μm Hirsch funnel, and washed with cold acetone. The samples were dried at 105°C for 15 min to remove traces of acetone and ethanol.

The hydration behavior of the calcium aluminates was followed using a Mettler model TA-HE20 thermobalance. Samples were heated from 25 to 900°C in a flowing-air atmosphere. The conditions for this investigation included a heating rate of 10°C min^{-1}, a chart speed of 8 cm h^{-1}, and a 200 μV range for the DTA. Alumina was used as a reference material.

RESULTS AND DISCUSSION

Conditions for the preparation of each sample, and the characteristics of the final products are given in Table 1. X-ray powder diffraction patterns of the samples were in good agreement with data from the JCPDS powder

TABLE 1

The preparation and analysis of the calcium aluminates

	C_3A	$C_{12}A_7$	CA	CA_2	CA_6
Furnace temp. (°C)	1325	1350	1500	1500	1500
Firing time (h)	35	19	25	49	177
Free lime content (%)	0.2	0.0	0.0	0.1	0.1
Surface area ($cm^2\ g^{-1}$)	2500	2500	2500	2500	3500
Glass content (%)	4	–	1	0	3
TGA background (%)	0.99	0.45	0.84	0.52	1.16

diffraction file [13]. In general, a small weight loss was noted on the TGA patterns of the non-hydrated species. This weight loss could be attributed to the small amount of hydration which the samples undergo during their preparation and analysis. For further calculations, this weight loss was considered as a background, and was subtracted from the weight loss observed for each of the hydrated samples.

Because of the cubic symmetry of the compound $C_{12}A_7$, it was not possible to obtain a reasonable glass count using optical microscopy. Sam-

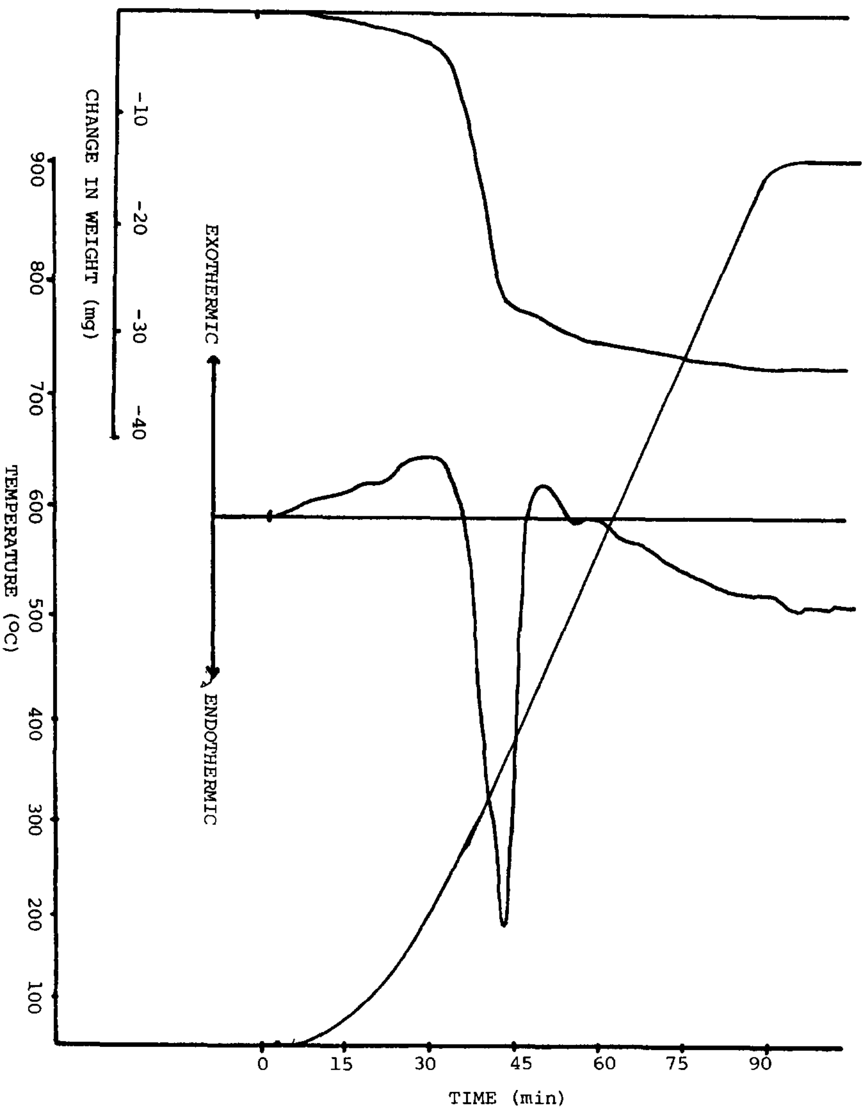

Fig. 1. Thermal analysis pattern of $C_{12}A_7$ hydrated for 90 days at 50°C.

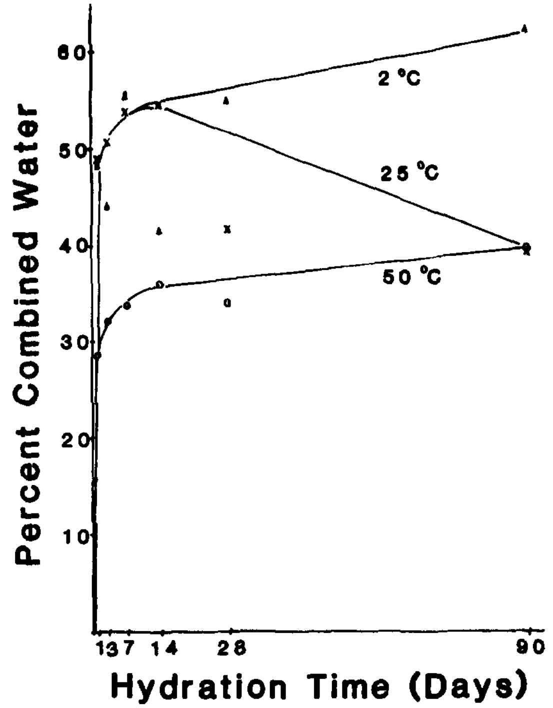

Fig. 2. The effect of temperature on the hydration of C_3A.

ples belonging to the cubic space group do not exhibit birefringence and, thus, are not visible under polarized light. Even though X-ray diffraction indicated a well-crystallized sample, optical microscopy showed an essentially pure glass. Although Table 1 does not give a value for the glass content of $C_{12}A_7$, it should be considered very small.

Figure 1 shows the thermal analysis pattern for the compound $C_{12}A_7$ which had been hydrated for 90 days at 50°C. The three plots, described from top to bottom, refer to the weight of the sample (TGA), the change in the temperature of the sample with respect to the alumina reference (DTA), and the temperature of the furnace. The dehydration process can essentially be described by the characteristic peaks observed on the DTA pattern. The large endothermic peak observed at approximately 43 min (340°C) corresponds to the dehydration of C_3AH_6 into $C_{12}A_7$ and $Ca(OH)_2$. The shoulder seen to the left of this peak (300°C) corresponds to the dehydration of $Al(OH_3)$. Finally, the $Ca(OH)_2$ produced in the dehydration of C_3AH_6 is dehydrated itself at 580°C, and can be seen as a small peak to the right of the others.

The change in the hydration behavior of C_3A as a function of temperature is graphically represented in Fig. 2. The changes in the hydration curves reflect the changes in the hydration behavior. At 50°C, no metastable species are observed. The hydration curve reflects this by rising rapidly to a value

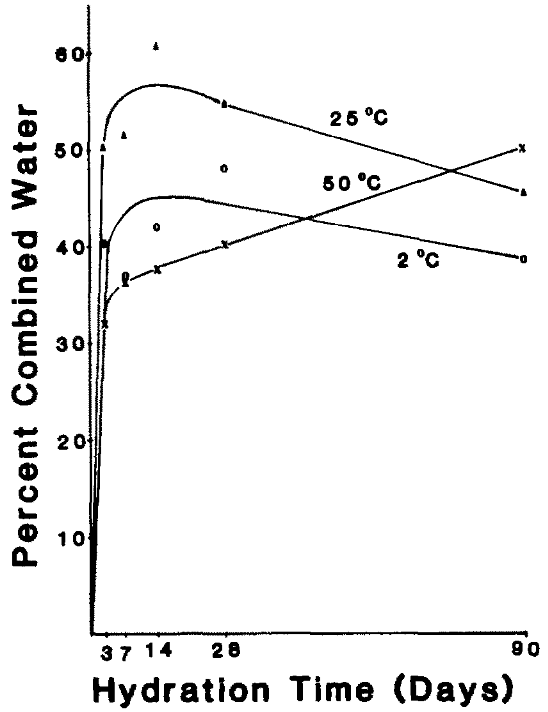

Fig. 3. The effect of temperature on the hydration of $C_{12}A_7$.

corresponding approximately to the water content of C_3AH_6, and then remaining relatively constant. A similar behavior is noted in the curve of C_3A hydrated at 2°C, with the exception that the metastable species, C_3AH_{8-12}, is now preferentially produced, and C_3AH_6 is not detected. The hydration curve for C_3A hydrated at 25°C starts out much like the 2°C curve with the formation of C_3AH_{8-12}. However, for longer curing periods, the C_3AH_{8-12} is slowly converted to the more stable C_3AH_6, and the hydration curve approaches the 50°C curve.

Figure 3 shows the change in the hydration behavior of $C_{12}A_7$ as a function of temperature. The difference in the height of the curves representing the hydration at 2 and 25°C is attributed to the difference in the rate of hydration. Similar to the behavior of C_3A, the hydration curve of $C_{12}A_7$ at 50°C shows a smaller amount of combined water, not because the hydration proceeds at a slower rate, but rather because the intermediate, C_3AH_{8-12}, is not formed, and the $C_{12}A_7$ hydrates directly to the more stable C_3AH_6 and AH_3. The larger value for the percent combined water, after 90 days of hydration, is simply due to a more complete hydration.

The change in the hydration behavior of CA as a function of temperature is shown in Fig. 4. The curves representing the hydration at 2 and 25°C are very similar. The small differences are due to changes in the hydration rate. The behavior of the CA hydrated at 50°C, however, is quite different from

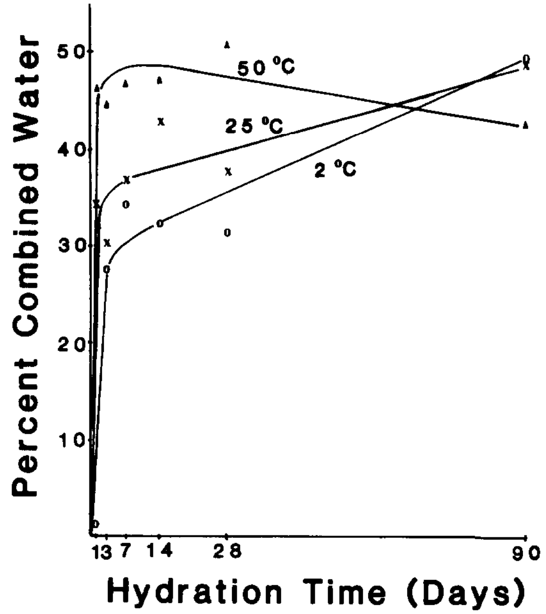

Fig. 4. The effect of temperature on the hydration of CA.

the others, due to the fact that not only does it hydrate at a faster rate, but it also hydrates directly to the stable hydrates, C_3AH_6 and AH_3. The samples hydrated at the lower temperatures, on the other hand, hydrate to the

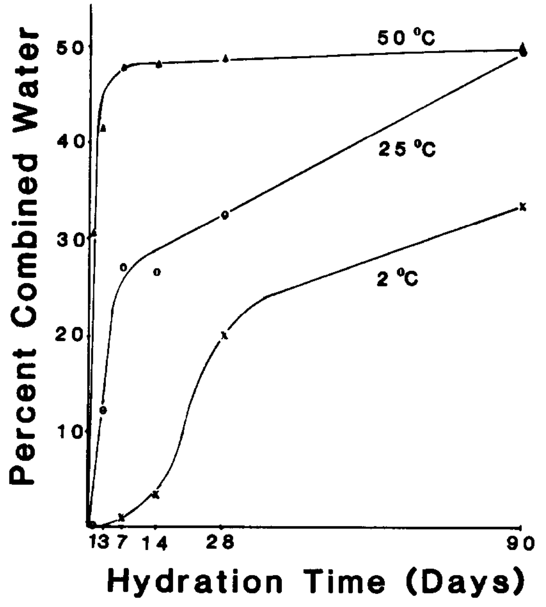

Fig. 5. The effect of temperature on the hydration of CA_2.

metastable intermediate, C_3AH_{8-12}, with the C_3AH_6 appearing only in the 25°C sample hydrated for 90 days.

Figure 5 graphically represents the hydration behavior of CA_2 as a function of temperature. The curve representing the hydration at 2°C starts out very slowly, indicating that the hydration proceeds through a dormant stage. This stage may also be present in the hydration at higher temperatures, although for a much shorter duration. The curves representing the samples hydrated at 25 and 50°C differ only in the fact that the hydration rate increases with increasing temperature. The metastable species, C_3AH_{8-12}, was found in all hydrated CA_2 samples, unlike the more basic aluminates (C_3A, $C_{12}A_7$, and CA).

The compound CA_6 showed no hydration at any temperature.

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REFERENCES

1 F.M. Lea, The Chemistry of Cement and Concrete, 3rd edn., Chemical Publishing Company, New York, 1971, pp. 50, 51, 498.
2 T.D. Robson, Proc. 5th Symp. on the Chemistry of Cement, Part II, Tokyo, 1968, pp. 349–365.
3 H.E. Schiete and U. Ludwig, Proc. 5th Int. Symp. on the Chemistry of Cement, Part II, Tokyo, 1968, pp. 37–67.
4 R. Kondo and S. Ueda, Proc. 5th Int. Symp. on the Chemistry of Cement, Part II, Tokyo, 1968, pp. 203–248.
5 D.L. Kantro, C.H. Weise and S. Brunauer, Proc. Symp. on the Structure of Portland Cement Paste and Concrete, Washington, DC, 1966, pp. 309–327.
6 F.W. Locher, Proc. Symp. on the Structure of Portland Cement Paste and Concrete, Washington, DC, 1966, pp. 300–308.
7 R. Kondon, S. Ueda and M. Kodama, Semento Gijutsu Nempo, 21 (1967) 83.
8 P. Seligmann and N.R. Greening, Highw. Res. Rec., 62 (1964) 80.
9 W.C. Hansen, Proc. 3rd Int. Symp. on the Chemistry of Cement, London, 1952, pp. 318–321.
10 ASTM Designation: C114-58, 1958 ASTM Book of Standards, Part IV, pp. 82–85.
11 F.S. Fulton, Portland Cement Institute Monograph, Johannesburg, 1974, pp. 6, 7.
12 ASTM Designation: C204-55, 1958 ASTM Book of Standards, Part IV, pp. 140–146.
13 JCPDS, International Centre for Diffraction Data, Powder Diffraction File, Cards No. 1-888, 7-82, 7-85, 8-5, 9-413.