

THE DETECTION OF THE CARBOALUMINATE PHASE IN HYDRATED HIGH ALUMINA CEMENTS BY DIFFERENTIAL THERMAL ANALYSIS

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INTRODUCTION

Calcium aluminate cements include a family of cements varying from cement fondu with 40% Al_2O_3 up to refractory cements such as Alcoa CA-25 and Secar 80 with 80% Al_2O_3 . According to the temperature, time, and initial water:cement ratio, the products of hydration may vary, but will include some or all of the following phases: alumina gel, gibbsite (AH_3) CAH_{10} , C_2AH_8 and C_3AH_6 .^{*} If the calcium aluminate hydrates are exposed to air they are gradually attacked by atmospheric carbon dioxide with the formation of the carboaluminate, $\text{C}_3\text{A}\cdot\text{CaCO}_3\cdot 11\text{H}_2\text{O}$ or $\text{C}_4\text{ACH}_{11}$. When calcium aluminate cements are hydrated in the presence of calcium carbonate, e.g. limestone aggregate, the carboaluminate phase may be formed in substantial amounts.

Various authors [1-6] have reported DTA curves including evidence for the presence of $\text{C}_4\text{ACH}_{11}$. All report an endothermic peak due to dehydration somewhere in the range 160-230°C, dependent on the amount of the phase present and the procedural variables associated with the DTA experiment. In a recent paper, Madgley [6] reported the endotherm to be between 180 and 200°C. This temperature range is closely similar to that reported for the endothermic peak associated with the dehydration of C_2AH_8 , an important hydration product of calcium aluminate cements, especially in products from hydration at 30°C.

EXPERIMENTAL

Samples of cement powder (30 g) were weighed and mixed with boiled, distilled water (15 ml), the water already being at the appropriate temperature for the hydration. The paste was mixed using a spatula for two minutes. It was then poured into plastic tubes which were stoppered and sealed in plastic bags before placing in a water bath which was controlled to $\pm 1^\circ\text{C}$. After various periods of hydration samples were removed and ground. A.R. grade acetone was added, the cement was reground and allowed to dry at ambient temperature. The dried powder was sieved before examining by X-ray diffraction (XRD) and differential thermal analysis (DTA).

XRD curves were obtained using a Philips PW 1050/25 goniometer with a graphite monochromator. DTA curves were obtained using a Stanton-Redcroft 67-4 apparatus on 100 mg samples heated at $10^\circ\text{C}/\text{min}$ in air with $\alpha\text{-Al}_2\text{O}_3$ as the reference material.

RESULTS AND DISCUSSION

DTA curves are shown for Secar 71 hydrated at 22°C for 4 days and at 30°C for 7 days in Fig. 1. These traces are similar (except for the peak attributed to alumina gel at 107-120°C) and the peak in the 190-200°C region could readily be attributed to C_2AH_8 in both patterns. Reference to the XRD peak heights also shown in Fig. 1, however, shows that the first sample contains an appreciable amount of $\text{C}_4\text{ACH}_{11}$ and relatively little C_2AH_8 , whereas the second sample contains a large amount of C_2AH_8 and relatively little $\text{C}_4\text{ACH}_{11}$. It seems reasonable, therefore, to attribute the peak at 198°C in the first DTA curve to $\text{C}_4\text{ACH}_{11}$ and that at 192°C in the second DTA curve to C_2AH_8 . Careful examination of the DTA curves reveals the presence of a shoulder below the peak temperature in both cases, believed to be due to the presence of the minor phase.

These results indicate both the necessity to consult XRD data when labelling DTA traces and the confusion which may arise because of the similar

* C = CaO, A = Al_2O_3 , H = H_2O , \bar{C} = CO_2

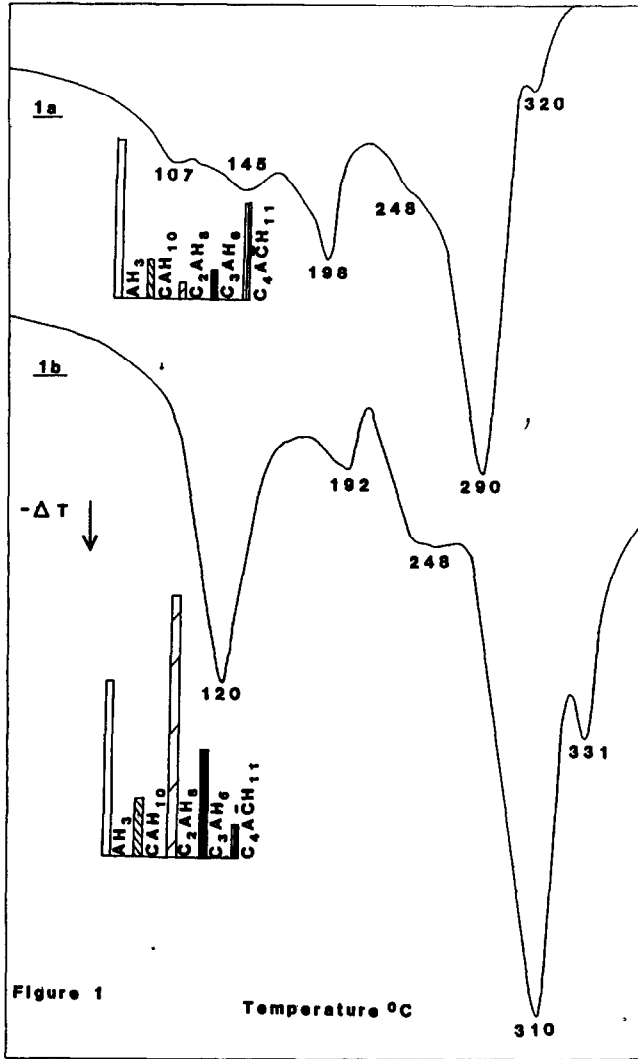


Figure 1 DTA curves and XRD peak heights of Secar 71 hydrated for a) 4 days at 22°C
b) 7 days at 30°C

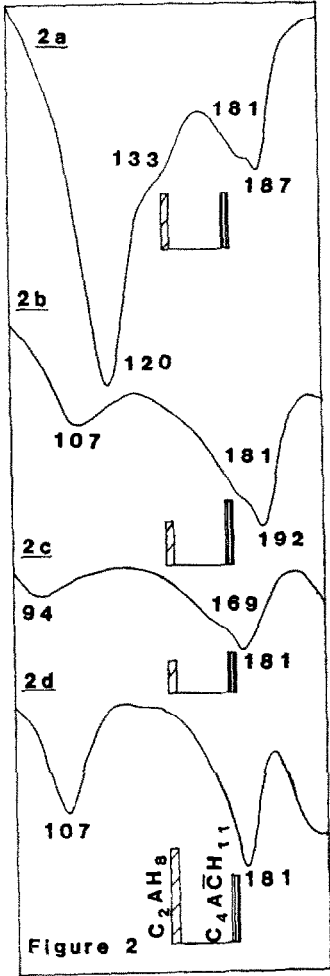


Figure 2 DTA curves of
 a) Secar 51 hydrated at 30°C for one day.
 b) Alcoa CA25, 40°C, 4 hrs + 24 hrs at room temperature.
 c) Secar 80; 40°C, 2 hrs.
 d) Secar 80; 40°C, 7 days.

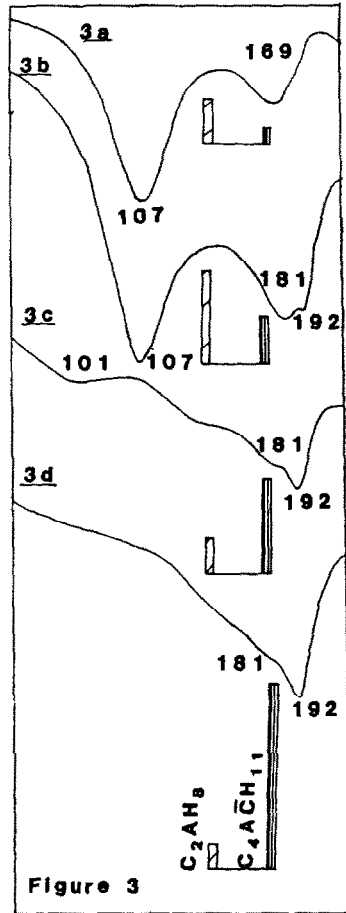


Figure 3 DTA curves of Secar 51 plus CaCO₃ hydrated at 40°C
 a) for 6 hrs.
 b) 1 day.
 c) 2 days.
 d) 5 days.

temperatures of the endothermic peaks given by these two phases.

Similar doublets can sometimes be seen when samples of cement with 50% Al_2O_3 (Fig. 2a) and with 80% Al_2O_3 (Fig. 2b and c) have been hydrated. When substantial amounts of the C_2AH_8 and $\text{C}_4\text{ACH}_{11}$ phases are present (Fig. 2d), the peak is more intense but tends to appear as a singlet. To promote the formation of the $\text{C}_4\text{ACH}_{11}$ phase, some pastes were prepared using CaCO_3 (5 g) incorporated in the cement (25 g) instead of the 30 g of cement used previously. DTA and XRD data from the resultant pastes are shown in Fig. 3. After hydration for 6 hours a single DTA peak at 169°C was detected, but XRD shows that very little $\text{C}_4\text{ACH}_{11}$ had been produced. After longer periods of hydration, clear doublets were observed with the peak due to the $\text{C}_4\text{ACH}_{11}$ phase at 192°C .

It is confirmed, therefore, that both C_2AH_8 and $\text{C}_4\text{ACH}_{11}$ give DTA endothermic peaks in the range $160\text{--}200^\circ\text{C}$ under the experimental conditions used here. If either phase is present in much greater amounts than the other, then only one, fairly sharp peak is observed. If the amounts of the two peaks present are comparable, then a doublet is sometimes observed, or at least a suggestion of a second peak from a broadening on the low temperature side of the peak. When both phases are present in substantial amounts, the peak is frequently observed as a singlet.

The temperature at which each phase gives a peak is strongly dependent on the amount present (and other procedural variables). In one hydration series in which C_2AH_8 was present in excess, its endothermic peak was observed at 192°C accompanied by an inflexion attributed to the presence of $\text{C}_4\text{ACH}_{11}$ at 169°C . When CaCO_3 was added to the cement to promote the formation of $\text{C}_4\text{ACH}_{11}$ in greater amounts, its endothermic peak was observed at 192°C , accompanied by a smaller peak attributed to C_2AH_8 at 181°C (Fig. 3).

CONCLUSIONS

It is concluded that $\text{C}_4\text{ACH}_{11}$ and C_2AH_8 do indeed give DTA peaks in the same temperature range. When a relatively large amount of either phase is present, an endothermic peak at $180\text{--}200^\circ\text{C}$ is observed. The minor phase may produce a shoulder on this peak at a lower temperature. Relatively small but approximately equal amounts of both phases sometimes produce a more obvious doublet. To avoid possible misinterpretation of an endothermic peak in the range $160\text{--}200^\circ\text{C}$, DTA should be backed up by XRD data.

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