

The Hydration Products of a Refractory Calcium Aluminate Cement at Intermediate Temperatures

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ABSTRACT: *The major hydraulic phase in all the calcium aluminate cements including cement fondué is CA (CaAl₂O₄). Once hydrated, it starts to form the hexagonal crystals of CAH₁₀ and C₂AH₈ that depending on the time and temperature of hydration convert to the cubic crystals of C₃AH₆ and AH₃. The nature, sequence, crystallinity and microstructure of hydrated phases of commercial refractory calcium aluminate cement were analyzed using differential scanning calorimetry (DSC), differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results showed that the formation of different hydrated phases was temperature dependent. At 28 °C, the hydration products at the beginning of hydration were a gel phase, C₂AH₈ and gibbsite, while CAH₁₀ also formed after four days of hydration, both C₂AH₈ and CAH₁₀ were converted to C₃AH₆ at latter ages. The rate of conversion of C₂AH₈ is dependent on the temperature and time of hydration at temperatures higher than 28 °C and accelerates with increasing temperature, but still takes several weeks for completion at 36 °C.*

KEY WORDS: *Calcium aluminate cement (CAC), Hydration reactions, CA (CaAl₂O₄), CA₂ (CaO.2Al₂O₃), CAH₁₀ (CaO.Al₂O₃.10H₂O), C₂AH₈ (2CaO.Al₂O₃.8H₂O), C₃AH₆ (3CaO. Al₂O₃. 6H₂O), AH₃ (Al₂O₃.3H₂O).*

INTRODUCTION

Calcium aluminate cements are a group of inter-related cementitious materials, with alumina contents varying from about 38% to 90%, which incorporate calcium monoaluminate (CaAl₂O₄ or CA) as the major constituent. Second phases are always present, but vary with the lime; alumina-ratio and with the level of impurities, especially silicon and iron. In all the calcium aluminate cements, CA is the major hydraulic. CA reacts with water to form a series of calcium aluminate hydrates, which vary with temperature and time [1-3].

At low temperatures (<20 °C), the only crystalline hydrate formed is CAH₁₀, although an amorphous phase is formed in considerable amounts [4,5]. This amorphous phase is usually taken to be alumina gel, but Payne and Sharp have argued that it must be C-A-H phase (i.e. one containing a calcium aluminate hydrate of unknown composition) since no CH or calcium rich aluminate hydrates are simultaneously formed to maintain a chemical balance [6]. At higher temperatures, and in cements containing C₁₂A₇, C₂AH₈ is formed as well as or

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instead of CAH_{10} . Both of these hydrates are hexagonal in morphology and thermodynamically metastable. Above 28 °C, they convert relatively rapidly into C_3AH_6 which has a cubic structure and gibbsite, AH_3 or $Al(OH)_3$. The reactions are schematically summarized in Fig. 1.

The conversion products are denser than hexagonal hydrates. Since these reactions take place after the cement has set and hardened, the overall dimensions of the concrete are fixed and so the change in density has to be accommodated by an increase in porosity. Although the presence of major hydrates, CAH_{10} , C_3AH_6 and AH_3 , can be detected by X-ray diffraction (XRD), the peaks are not readily suitable for quantitative determination. Preferred orientation can occur with hexagonal phases such as CAH_{10} and also the hydrates may not be entirely crystalline, especially at the early stages of hydration. Also there are certain phases, which are amorphous by nature, e. g. the gel phases, and the presence of these will not be detected by XRD. Therefore, the use of thermal analysis techniques is very important in the study of cements as it gives information as to the hydrate phases present in the early stages of hydration, when this may not be possible from XRD [7-9].

The morphology and mechanism of crystallization of the gel phase has previously been studied by TEM [10].

Although there have been some reports about conversion reactions products in high alumina and calcium aluminate cements, but there is lack of information about the exact microstructure and growth of these phases[11-13].

In present investigation, attempts have been taken to give a clear understanding from the conditions under which various hydration reaction products form by different techniques such as XRD, DSC, DTA and SEM.

EXPERIMENTAL

Hydration studies were carried out on Secar 71 which is a 70% Al_2O_3 supplied by Lafarge co. Pastes were prepared by mixing the cement powder with boiled, distilled water, at water cement ratio of 0.5, which had been equilibrated in the water bath at the appropriate temperature and maintained for required time intervals.

To prepare samples for various instruments, the ground powder was passed the appropriate sieve.

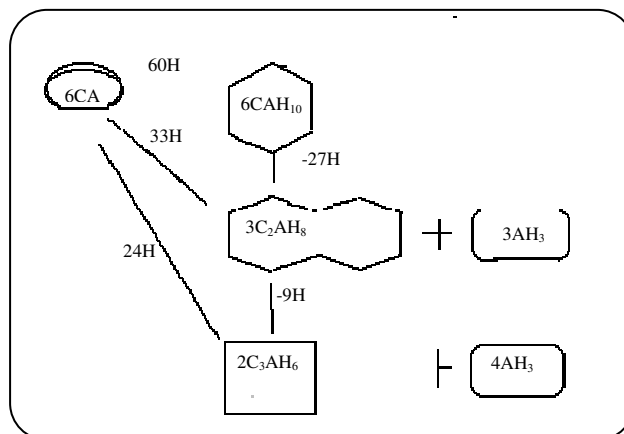


Fig.1: Reaction schemes for hydration of CA and its converted phases.

Freshly fractured and polished surface samples were used. The latter was mounted in araldite resin and polished with different meshes, and the former was mounted on stubs using electrode silver paint and coated with carbon and gold. The prepared samples were examined on a Cambridge cam scan microscope, operating at 20 Kv and a spot size of 320 °A.

The differential scanning calorimeter (DSC) was a Dupont 2000 instrument. This was linked to a PC computer. A heating rate of 10 °C/min was used from 25 °C to 500 °C. All samples were run in an atmosphere of dry nitrogen flowing at 120ml/min.

A Stanton-Redcroft 67-3 differential thermal analysis (DTA) was used in this study with platinum crucibles in which a sample weight {ground powder} of 100 mg was used in each run. Alumina reference of the same weight was also used. Analysis was carried out in argon flow 15 ml/min at a heating rate of 10°C /min. Mineralogical analysis was done by X-ray diffraction Esto-Stadi-P adjusted with copper tube.

RESULTS AND DISCUSSIONS

The hydration product of calcium aluminate cement varies with time and temperature. Different temperatures at various times were used based on the nature of hydration product forms at these temperatures. The hydration products forms at relatively low temperatures such as 12 and 20 °C were deeply discussed at previous paper [14]. In this part, the hydration products at intermediate temperatures such as 28 and 36 °C are considered.

Hydration at 28 °C

At 28 °C the story was different, the hydration products were very complicated. CAH_{10} no longer crystallizes while C_2AH_8 starts to form from beginning of hydration. The SEM micrographs taken at this temperature are very complicated. The crystals in micrograph shown in Fig. 2, from the paste hydrated for 9 days reveals the formation of AH_3 in bulk and plates of C_2AH_8 in various areas, but there are some crystals that seem to be CAH_{10} . This was confirmed by DTA thermograph, which shows evidence of formation of little amount of CAH_{10} after 7 days of hydration by the peak around 120 °C, the thermographs are shown in Fig. 4.

Samples of Secar 71 hydrated at 28 °C were quenched with acetone to stop further hydration. Traces of the resulting powder were examined by X-ray diffraction. Results of X-ray diffraction pattern peak height measurements are graphically shown in Fig. 3.

Referring to figure, the amount of CA and CA_2 detected were decreased as the time of hydration increased, but the consumption of CA was higher than that of CA_2 , which is related to the reactivity of this phase. Some CAH_{10} was detected after 4 days of hydration. Some C_2AH_8 was formed after 2 hours of hydration and the formation of this phase increased by increasing the time of hydration up to 8 hours, but subsequently this phase converted to C_3AH_6 . Some gibbsite was formed and the extent of crystallization of this phase increased with increasing the time of hydration.

Some other parts of the powder prepared for X-ray diffraction were used to investigate the hydration products by DTA. The results are shown in Fig. 4. These peaks are from the paste hydrated for 2 hours up to 7 days. The peak of the paste hydrated for 2 hrs reveals an endotherm at 273 °C that is attributed to the formation of gibbsite AH_3 as a result of hydration of CA_2 . The intensity of the peak increased and became very strong which is due to the formation of more gibbsite. Another peak started to appear as a shoulder at 310 °C, which is attributed to C_3AH_6 . When hydration continues for longer times, two other endotherms start to appear after 2 days, which were due to the formation of small amounts of CAH_{10} , and C_2AH_8 , these endotherms are around 140 and 180 °C respectively. The formation of CAH_{10} was also detected by X-ray diffraction, after four days of hydration.



Fig. 2: SEM micrograph of Secar71 hydrated for 9 days at 28 °C ----- 3um.

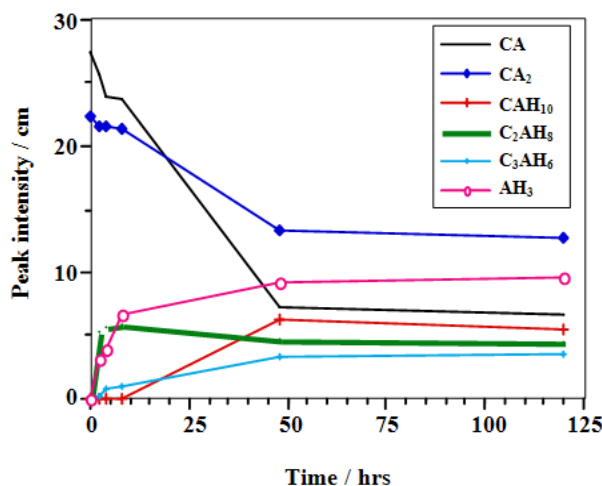


Fig. 3: Effect of time on the hydration of Secar 71 (CAC) at 28 °C.

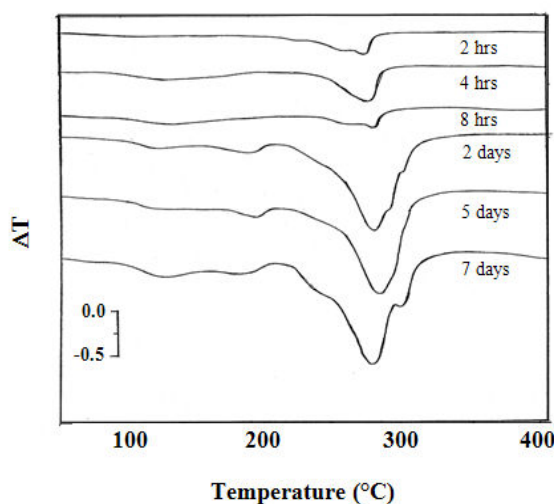


Fig. 4: DTA thermographs of the pastes hydrated at 28 °C.

Table 1: X-ray peak heights of Secar 71 hydrated at 36 °C.

n	Hydration time	CA (cm)	CA ₂ (cm)	CAH ₁₀ (cm)	C ₂ AH ₈ (cm)	C ₃ AH ₆ (cm)	AH ₃ (cm)
1	--	27.4	18.5	--	--	--	--
2	2 hrs	18.2	17.8	ND	ND	ND	3.1
3	4 hrs	15.6	17.2	ND	6.0	1.2	4.5
4	6 hrs	8.0	17.9	ND	8.3	1.7	5.6
5	8 hrs	5.9	15.8	ND	9.3	2.2	5.8
6	1 day	4.2	15.3	ND	9.3	4.5	7.9
7	2 days	2.9	10.6	ND	10.3	5.5	9.2
8	4 days	2.8	8.9	ND	7.2	7.8	10.6
9	6 days	2.6	8.8	ND	9.8	7.3	11.4
10	15 days	2.3	7.8	ND	8.6	7.1	12.5
11	50 days	2.1	7.2	ND	9.0	8.9	13.5

Hydration at 36 °C

The pastes hydrated at 36°C were removed from water bath and quenched with acetone at certain time intervals; traces of the resulted powder were examined by X-ray diffraction. Results of peak height measurements are summarized in table 1. Referred to the table, the intensity of the peaks of CA and CA₂ decreased as the time of hydration increased. There was no sign of formation of CAH₁₀. The intensity of the characteristic peak of C₂AH₈ increased up to 2 days of hydration and it seems that traces of this phase were converted after 4 days of hydration.

The amount of this phase detected was fairly constant in the case of 6, 15 and 50 days hydration. It seems from the table that the formation of C₃AH₆ started after only 4 hours, and increased with increasing time of hydration, which might be related to the conversion of C₂AH₈. The formation of AH₃ also increased with increasing the time of hydration. The overlays of four X-ray diffraction patterns of these samples are also shown in Fig. 5.

Traces of the paste hydrated after different time intervals were also, examined by DSC. The curve of the paste hydrated for 2 hours showed the formation of the following phases. A weak endotherm at around 107 °C can be attributed to the formation of a gel phase. The other endotherm appeared at around 279 °C with a shoulder at 290 °C, which should be attributed to the formation of gibbsite and C₃AH₆, respectively. After

hydration for 4 hours, an endotherm at 180 °C appeared which is attributed to the formation of traces of C₂AH₈ and the intensity of the other peaks increased compared to the one hydrated after two hours. Not very much difference was observed in the DSC curves of the paste hydrated for 6 hours compared to the previously mentioned curves, except for increasing intensity of the peaks of the gel phase and C₂AH₈, but the major difference was splitting of the intense endotherm attributed to the formation of gibbsite, to an intense peak and 2 shoulders at 279, 295 and 315 °C, respectively. This effect is more clearly shown in the DSC curve of the paste hydrated 8 hours. There is also a shoulder starting to appear at 226 °C, which should also be attributed to the formation of gibbsite and another at 180 °C to C₂AH₈. Overlays of the above mentioned endotherms are graphically shown in Fig. 6.

Some other portions of the paste were removed after longer periods than those previously discussed. The first was hydrated for 2 days. The DSC curves of this paste had endothermic peaks at 107°C and 169°C, which should be attributed to the formation of a gel phase, a shoulder at 240 °C showed formation of C₂AH₈ and a very intense peak at 290 °C respectively attributed to the formation of gibbsite, while a peak at 310 °C revealed C₃AH₆ too.

Increasing the hydration time to 4 days did not have much effect; only the extent of hydration was increased. This is shown by broadening of the endotherms compared

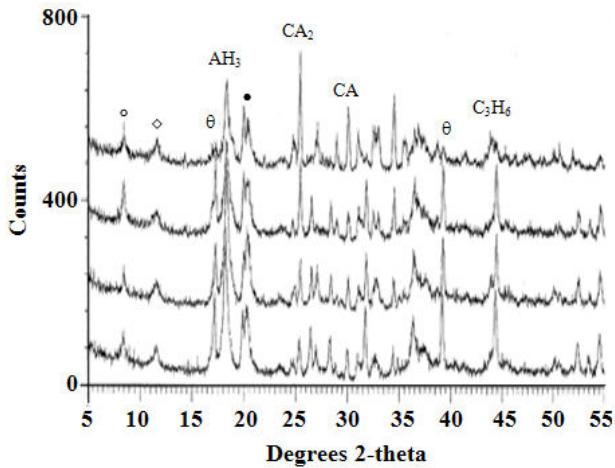


Fig. 5: X-ray diffraction patterns of Secar 71 hydrated at 36 °C.

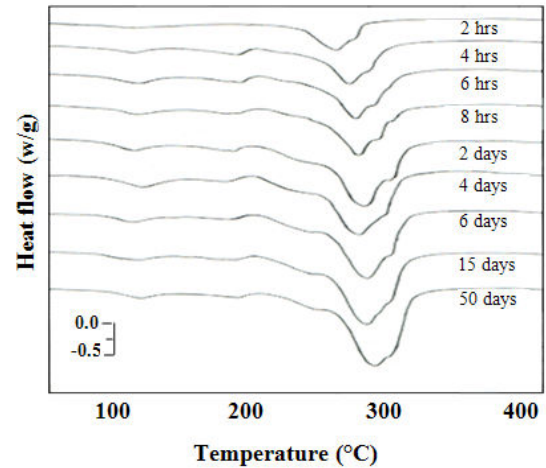


Fig. 6: The DSC peaks of cement hydrated at 36 °C.



Fig. 7: SEM micrograph of Secar71 hydrated for 7 days at 36 °C ----- 3um.



Fig. 8: SEM micrograph of Secar71 hydrated for 90 days at 36 °C ----- 30um

to the paste hydrated for 2 days. The same effect was observed after 6 days of hydration. The paste hydrated for 15 days revealed the formation of an increased amount of gibbsite and C_3AH_6 . This was the evidence of progress in the extent of hydration and conversion of metastable hydrates to the more stable form. It seems from the DTA curve of the paste hydrated for 50 days that C_2AH_8 was still present, but the major part of this phase had been converted into AH_3 and C_3AH_6 . A very intense peak at 290 °C and an intense shoulder at 310 °C show this. There is still evidence of traces of the gel phase at 107 °C too.

The morphological changes that occurred during the hydration of Secar 71 at 36 °C were also investigated by SEM. The microstructure of cement paste hydrated for 7 days consists of hexagonal plates embedded in a matrix of amorphous looking material plus cubic crystals of

C_3AH_6 . The electron micrograph of the fractured surface of the paste hydrated for seven days is shown in Fig. 7. The microstructural investigation of the paste hydrated after 90 days of hydration also reveals that the paste is fully converted to the ill cubic crystals of C_3AH_6 . This electron micrograph sample is shown in Fig. 8.

CONCLUSIONS

1- The present investigation reveals that curing conditions, time and temperature, are key parameters in the processing of calcium aluminate cements, since they affect the specimens hydration rate and the type of hydrates formed.

2- At 28 °C the hydration products were very complicated. CAH_{10} no longer crystallizes easily at early stage of hydration, less than 7 days, while C_2AH_8 starts to form from beginning of hydration reactions.

3- At 28 °C C_2AH_8 is formed in the first 24 hours and then conversion to C_3AH_6 takes place after several days of hydration.

4- The rate of conversion of C_2AH_8 is dependent on the temperature and time of hydration at temperatures higher than 28 °C and accelerates with increasing temperature, but still takes several weeks for completion at 36 °C.

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