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HYDRATION OF FERRITE Ca_2AlFeO_5 IN THE PRESENCE OF SULPHATES AND BASES

Anna Emanuelson[1], Eric Henderson[2] and Staffan Hansen[1]
[1]National Center for HREM, Inorganic Chemistry 2,
Center for Chemistry and Chemical Engineering, Lund University,
P.O. Box 124, S-221 00 Lund, Sweden
[2]Cementa AB, Ideon Lund, Sölvegatan 41, S-223 70 Lund, Sweden

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ABSTRACT

The reaction of synthetic Ca_2AlFeO_5 at 20 °C with (a) H_2O; (b) H_2O, $CaSO_4{\cdot}2H_2O$; (c) H_2O, $CaSO_4{\cdot}1/2H_2O$; (d) H_2O, $CaSO_4{\cdot}2H_2O$, Na_2SO_4; (e) H_2O, $CaSO_4{\cdot}2H_2O$, K_2SO_4; (f) H_2O, $CaSO_4{\cdot}2H_2O$, $Ca(OH)_2$; (g) H_2O, $CaSO_4{\cdot}2H_2O$, Ca_3SiO_5; (h) H_2O, $CaSO_4{\cdot}2H_2O$, KOH; was studied by differential scanning calorimetry and X-ray powder diffraction. Acetone dried samples were examined at hydration times between 2 min and 28 days, and 4 months in the instance of experiments (f) and (g). In (a) AFm forms immediately followed by hydrogarnet, while in (b-e) the formation of AFm is delayed, since the initial product is AFt, which then transforms into AFm. In the more basic samples (f-g), AFm formation is further delayed due to the introduction of a pronounced dormant period during AFt formation. The strongly basic sample (h) also exhibits this dormant period, but less AFt is formed and AFm appears as in (b-e). *Copyright © 1996 Elsevier Science Ltd*

Introduction

Large constructions in reinforced concrete suitable for dams or the marine environment, requires the use of a cement with low heat evolution and chemical resistance towards sea water. High-ferrite Portland cement will for example be utilised in the construction of the Öresund bridge. In this type of cement the ferrite phase has the ideal composition Ca_2AlFeO_5 (C_4AF), whilst ordinary Portland cement is richer in aluminate, ideally $Ca_3Al_2O_6$ (C_3A). The rapid hydration of these two compounds is important for the early rheological properties of concrete, while the mechanical strength is due to the reaction products of the silicates, ideally Ca_3SiO_5 (C_3S) and Ca_2SiO_4 (β-C_2S). Different forms of calcium sulphate is added to the cement, in order to retard the rapid hydration of Ca_2AlFeO_5 and $Ca_3Al_2O_6$. Alkali sulphates are also present in the cement clinker.

The hydration reactions of synthetic $Ca_3Al_2O_6$ and Ca_2AlFeO_5 in the absence or presence of additives have been reviewed (1,2) and further information on the hydration of Ca_2AlFeO_5 is to be found in references (3-7). There seems to be general agreement that: (i) both com pounds give analogous reaction products; (ii) synthetic aluminate reacts more quickly than ferrite; (iii) the hydration of aluminate is the more exothermic; (iv) the hydration of both compounds is retarded by the addition of calcium sulphate, or calcium hydroxide, to the water and the retardation is even stronger when both additives are present; and (v) the retardation is caused by the formation of a protective layer of reaction products covering the hydrating grains. Differing opinions exist concerning: (i) the nature of the phase forming the protective layer; (ii) the mechanism by which this layer is eventually destroyed; and (iii) the distribution of iron among the product phases in the case of Ca_2AlFeO_5. Though most studies have been performed on synthetic materials, it has been emphasized (1) that the hydration behaviour of the corresponding interstitial phases in a real cement can be different, since they are hydrated in the presence of other clinker phases and that all clinker phases contain varying amounts of substituting ions. The hydration reactions of Ca_2AlFeO_5 have been less investigated than those of $Ca_3Al_2O_6$ and most hydration studies of Ca_2AlFeO_5 seems to have been limited to calcium sulphate and calcium hydroxide as additives (1-7). Here we present a study of the hydration of a synthetic ferrite in the presence of an extended set of additives.

Experimental

Preparation of Samples. Ferrite Ca_2AlFeO_5 was prepared by firing stoichiometric amounts of $CaCO_3$ (Merck, p.a.), γ-Al_2O_3 (Merck, puriss), Fe_2O_3 (Merck, p.a.) in air at 1350 °C for 20 hours, with one intermediate grinding. After grinding and sieving (< 60 μm) the size distribution of the ferrite powder was determined using a granulometer HR 850 with ethanol as the suspension fluid. The median size was 6.9 μm, with 10 weight% of the particles smaller than 0.7 μm and 90 weight% less than 24.9 μm. The eight powder mixtures in Table 1 were prepared using ferrite and the following chemicals; $CaSO_4 \cdot 2H_2O$ (Merck, p.a.), $CaSO_4 \cdot 1/2H_2O$ (Kebo, LF), K_2SO_4 (Merck, puriss), Na_2SO_4 (puriss), $Ca(OH)_2$ (Merck, p.a.), KOH (Merck, titration solution), Ca_3SiO_5 (prepared from $CaCO_3$ and SiO_2 at 1450 °C) and quartz SiO_2. For all the sulphate containing samples (b-h), the molar ratio SO_4^{2-}/Ca_2AlFeO_5 was equal to 1/2.

0.5 g dry powder was mixed with 0.5 ml of distilled water for 30 s, using a spatula. In experiment (h), 0.5 ml 0.2 mol l^{-1} aqueous KOH was added instead of water. The samples were then allowed to hydrate at room temperature for 2, 5, 10, 60, 240 min, 1, 14, 28 days and in two cases (f, g) 4 months. The hydration was stopped by mixing with acetone (99.5%) for 30 s, followed by vacuum filtering, and washing with acetone 4 times with final drying by vacuum filtering for 8 min.

TABLE 1

Composition (in weight %) of Dry Powder Mixtures Used in the Hydration Experiments

Sample	a	b	c	d	e	f	g	h
ferrite	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0
gypsum	-	20.0	16.8[a]	16.0	16.0	20.0	20.0	20.0
additive	- -	- -	- -	Na_2SO_4 3.3	K_2SO_4 4.1	$Ca(OH)_2$ 10.0	Ca_3SiO_5 10.0	KOH[b] -
quartz	40.0	20.0	23.2	20.7	19.9	10.0	10.0	20.0

[a] hemihydrate; [b] added as aqueous solution, see text.

X-Ray Powder Diffraction. Three to five samples in each series were selected at times chosen to monitor the particular reaction sequence. The acetone dried sample was mounted on Scotch tape and X-ray powder diffraction films were recorded using a Guinier-Hägg camera with monochromatic CuKα1 radiation. Phases were identified by comparison with films recorded on reference samples of ferrite, gypsum, ettringite and quartz. In the case of AFm phases, hydrogarnet and hemihydrate, interplanar spacings were calculated and these were then compared with literature data in order to determine the phases present in the sample (2,8).

Differential Scanning Calorimetry. The acetone dried samples (35 mg) were enclosed in aluminium capsules fitted with a 0.05 mm diameter hole in order to create a suitable water vapour pressure during heating and thus allowing separation of dehydration peaks. Aluminium oxide was utilised as an inert reference material in the measurements. The temperature range covered was 25 to a maxi-mum of 400 °C and the samples were heated at a rate of 20 °C min^{-1}. A Perkin Elmer-DSC7 differ-ential scanning calorimeter was used. The measurements were made on duplicate samples and the average error was estimated to ±5%.

The following characteristic DSC peaks were observed in the temperature range investigated: gypsum (160, 195 °C), AFt (135 °C), sulphate-AFm (130, 225, 300 °C), nonsulphate-AFm (115, 200, 285 °C) and hydrogarnet (355 °C). The observed temperatures show a resonable correspondence with literature data for these phases (2). The peak observed at 115 °C for nonsulphate-AFm persists to the end of hydration experiment (a), while the peaks at 200 and 285 °C disappear with time. This indicates the presence of more than one type of sulphate-free AFm phase, or possibly the peak at 115 °C is due to $Fe_2O_3{\cdot}xH_2O$.

In cases of moderate overlap between peaks, e.g. between AFt (135 °C) and gypsum (160 °C), the area of overlap was simply divided in two halves, which were then added to the respective peak areas. Serious overlap problems occurred in samples containing AFt (135 °C) and AFm (130 °C). Since the proportions of the three AFm peaks were relatively constant, the heat of dehydration from AFm at 130 °C was first estimated using the peak at 225 and 300 °C and the heat from the AFt at 130 °C was then determined by subtraction.

Results and Discussion

The results are summarized in Fig. 1, where for simplicity the AFm phases have been represented by the dehydration peak around 200 or 225 °C. The amount of a certain phase is proportional to the heat of dehydration per total mass of sample given in the figure. But since the heats of dehydration vary in the literature, we prefer not to recalculate the values to mass of phase per mass of sample.

Hydration without additives (Fig. 1a) first produces X-ray amorphous AFm phases (and possibly $Fe_2O_3{\cdot}xH_2O$), which is then followed by crystalline hydrogarnet $Ca_3[(Al,Fe)(OH)_6]_2$, when the ferrite has been consumed. Hydration of ferrite in the presence of sulphate (Figs 1b-h) starts with the formation of sulphate-AFt or ettringite $[Ca_3(Al,Fe)(OH)_6(H_2O)_{12}]_2(SO_4)_3{\cdot}2H_2O$, while gypsum is being consumed. In the run with calcium sulphate hemihydrate instead of dihydrate (Fig. 1c), hemihydrate (DSC peak at 195 °C) is consumed, but some dihydrate (peak at 160 °C) was found to be detectable after 2 hours. When the calcium sulphate has been consumed, unreacted ferrite remains and AFm phases start to form, while AFt disappears (Figs 1b-h). In several of the hydrated and acetone dried samples, two AFm phases were detected in the powder X-ray diffraction experiments.

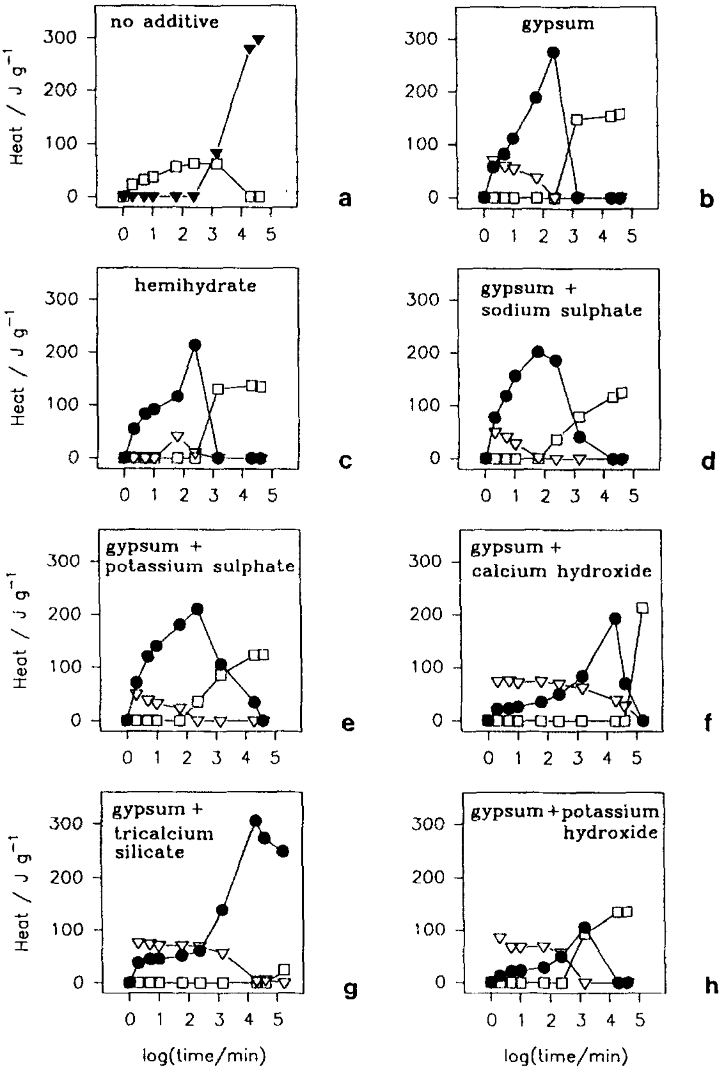

FIG. 1.

Hydration of ferrite samples a-h as a function of time studied by DSC. (a) Sulphate-free AFm phase is denoted by squares and hydrogarnet by filled triangles. (b)-(h) Gypsum (unfilled triangles), AFt (circles) and sulphate-containing AFm (squares).

In addition to monosulphate $[Ca_2(Al,Fe)(OH)_6]_2(SO_4)\cdot nH_2O$; n = 6, another AFm phase is often present. This could be the lower hydrate with n = 4, formed during drying of the samples, but could also correspond to AFm(hydroxide) or AFm(carbonate/hydroxide). The last remains of the ferrite disappear during the formation of Afm.

All the reactions observed in the experiments, Figs 1a-h, can be rationalised using a sequence of phases with falling sulphate content, as can be seen from the molar ratio in parenthesis:

gypsum (S/Ca = 1)→AFt (S/Ca = 0.5-0.33)→AFm (S/Ca = 0.25-0)→hydrogarnet (S/Ca = 0).

In pure water (Fig. 1a), the first products are sulphate-free AFm phases, which then transform to hydrogarnet. The first half of the sequence is thus omitted. In the presence of gypsum (Figs 1b-h), one starts from the beginning of the sequence, but the final transformation of AFm to hydrogarnet was not observed in the present experiments. When the ferrite is nearly depleted, hydroxide AFm probably starts to form, either as a separate phase or as a solid solution AFm(sulphate-hydroxide).

At some stage the AFm phase occurs in all these experiments and is thus suitable as a starting point for discussion of the ferrite hydration reactions. This phase is also of critical interest, since it is known from the hydration of cement that quick set does not occur when AFm formation is delayed until after the time of rapid tricalcium silicate hydration, which typically occurs after around 1000 min, i.e. between 10 and 24 hours (2, 9). In pure water AFm phases start to form immediately, cf. Fig 2a. Formation of AFm before hydrogarnet suggests that the temperature of the sample does not rise much above room temperature, otherwise hydrogarnet would have formed directly (10). In water, with sulphates added, the formation of AFm commences after approximately 2 hours, when all the gypsum has been consumed. The retardation is due to formation of AFt, which introduces a new reaction step prior to AFm, see Fig. 2b. The results are similar for the various sulphates, i.e. gypsum, hemihydrate, gypsum plus sodium sulphate, or gypsum plus potassium sulphate. The presence of alkali ions accelerates the initial crystallisation of AFt (Figs 1b-e and 2b) and formation of AFm starts somewhat earlier, compared to when only calcium sulphate is present.

When the hydration is carried out in the presence of tricalcium silicate (Figs 1g and 2a) or calcium hydroxide (Fig. 1f) and added gypsum, the formation of AFm is delayed by up to a month. The extra delay is caused by the pronounced dormant period, which is introduced into the formation of AFt, see Fig. 2b. It appears that a high concentration of hydroxide is necessary for the creation of this extended induction period. An induction period is also observed when ferrite is hydrated in the presence of potassium hydroxide, Fig. 1h. Although the amount of AFt formed is reduced, the forma-tion of AFm starts at a time similar to that observed in the systems with sulphate, but without added base (Figs 1b-e). A less pronounced retardation is observed when the sulphate addition consists of calcium sulphate hemihydrate, see Fig. 1c. Here the retardation in the formation of AFt is associated with the

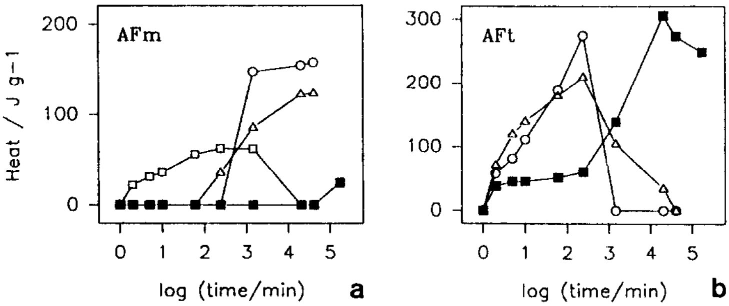

FIG. 2.

Formation of AFm (a) and AFt (b) as a function of time. Ferrite hydrated with: water only (empty squares); water and gypsum (circles); water, gypsum and potassium sulphate (triangles); and water, gypsum and tricalcium silicate (filled squares).

hemihydrate to dihydrate side-reaction, which perhaps competes for the calcium and sulphate ions in solution. The formation of calcium sulphate dihydrate, in this instance, peaks after around 2 hours. In cement, this type of gypsum formation can cause false set (9).

Conclusion

It appears that the presence of calcium hydroxide or tricalcium silicate in addition to calcium sulphate, is necessary in order to retard the formation of AFm for more than one day during the hydration of synthetic Ca_2AlFeO_5.

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