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The hydration of doped tricalcium aluminate

Part 1 *Hydration of $Ca_3(Al_{2-x}Fe_x)O_6$ in the presence of gypsum*

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The limit of solid solution of iron in tricalcium aluminate prepared in an oxygen atmosphere increases with increasing temperature to give a solid solution of composition $Ca_3Al_{1\cdot85}Fe_{0\cdot15}O_6$ at 1325° C. The lattice parameter of the cubic unit cell increases from 1.5263 to 1.5289 nm. Iron-doping causes a significant retardation in the reactivity of the Ca_3A_{ss} hydrated in the presence of gypsum. Not only does the rate of disappearance of the C_3A_{ss} decrease as the iron content increases, but also the setting time of the paste, the time taken for the gypsum to be totally consumed, and the time when rapid conversion of the AFt phase into the AFm phase takes place all increase. These observations apply even more to samples with iron contents greater than the solid solution limit, due to the presence of CaO and C_4AF_{ss} in addition to C_3A_{ss}.

1. Introduction

The early hydration of Portland cement clinker can lead to rapid evolution of heat and a flash set of the paste. This action is attributed to the hydration of tricalcium aluminate ($Ca_3Al_2O_6$ or CaA*), which is present in Portland cements in amounts up to 15 wt%. The nature of the flash set is to produce a body of low strength caused by inadequate hydration of the calcium silicates. It is, therefore, the universal practice to add a few per cent of gypsum to the clinker to control this reaction. Gypsum is effective as a retarder of the hydration of C_3A as it combines to form either of two calcium alumino-sulphate hydrates, ettringite, $C_6A\bar{S}_3H_{32}$, and monosulphate, $C_4A\bar{S}H_{12}$, better referred to as the AFt and AFm phases, respectively, when Fe(III) replaces some of the aluminium.

The hydration of pure C_3A in the presence of gypsum has been extensively studied [1–13 and references therein], but the C_3A phase present in Portland cements is a solid solution involving the replacement of calcium and aluminium by elements such as sodium, potassium, magnesium, iron and silicon. The incorporation of foreign ions into the structure of C_3A must influence its reactivity. The principal aims of this series of papers are to determine the limits of solid solution and to investigate the reactivity of the phases so formed relative to that of pure C_3A. In this paper the effect of replacement of some aluminium by Fe(III) on the reactivity of C_3A in the presence of gypsum is reported.

Most of the iron present in Portland cements enters the ferrite solid solution of approximate composition C_4AF. It is well known, however, that some iron enters into solid solution in C_3A to give a phase of composition $Ca_3Al_{2-x}Fe_xO_6$ [14–25]. Lea [26] reports that EPMA studies have shown that 4.4 to 6.0 wt% Fe_2O_3 (equivalent to 7.5 to 10.3 mol% "C_3F") may be found in the C_3A phase of cement clinker. There is, however, considerable disagreement concerning the maximum value of x and the way in which it varies with temperature. Some of the reasons for this have been discussed by Lee *et al.* [25]. Most workers prepared mixtures of C_3A with different amounts of the hypothetical compound "C_3F" and then measured the lattice parameter, a_0, of the cubic unit cell by X-ray diffraction. Although "C_3F" is unstable and decomposes into CaO and

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*Abbreviations: C = CaO, A = Al_2O_3, F = Fe_2O_3, $\bar{S}$ = SO_3, H = H_2O. ss = solid solution.

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C_2F [16], the substitution of aluminium by Fe(III) in C_3A is a straightforward replacement up to a solid solution limit. Tarte [15] reported this limit to be 10.0 mol% "C_3F" at 1310° C, Majumdar [16] 6.7 mol% at 1325° C, and Moore [18, 19] 4.5 mol% at 1350° C. These results suggest that the higher the temperature the lower the "C_3F" content needed to reach the solid solution limit, but this conclusion was contradicted by Schlaudt and Roy [17], who reported that the limiting concentration of "C_3F" in C_3A decreased as the temperature decreased below 1389° C. Moore [18, 19], in an attempt to resolve this difference, fired a high "C_3F" (18 mol%) mix at 1190° C and found less iron taken up into the C_3A than at 1350° C, thus supporting the conclusion of Schlaudt and Roy [17]. Recently, Varma *et al.* [24] have used low temperature infrared spectroscopy to determine the solid solution limit to be between 5 and 7 mol% "C_3F" for a mixture fired at 1350° C.

Beyond the solid solution limit, the phase diagram [16, 20, 22, 23] indicates that C_3A_{ss}, CaO and the ferrite phase coexist at sub-solidus temperature. Just as the composition of the C_3A_{ss} changes with temperature, so also does that of the ferrite phase. At 1325° C, Majumdar [16] found the composition of the ferrite phase to be close to that of C_4AF, but slightly on the C_2F-rich side, whereas Imlach and Glasser [22] found it to be slightly on the C_2A-rich side of C_4AF. Since these compositions are very close together, the quantitative phase estimation reported below is based on the composition of C_4AF.

The only previous study of the hydration of C_3A doped with controlled amount of iron is that by Fierens *et al.* [27], but they did not add gypsum.

2. Experimental procedure

Pure C_3A was made from Analar reagent grade $CaCO_3$ and α-Al_2O_3, which were ground and sieved before accurately weighing and mixing. The mixture was fired in a covered platinum dish at 1400° C in a Carbolite furnace for 24 h. The mix was removed, ground, and refired for a further 24 h. The resulting C_3A was ground in an agate mortar and pestle for 40 min, sieved and stored in a desiccator.

Iron-doped C_3A_{ss} was made from the same reagents and Jeweller's rouge (α-Fe_2O_3) which had a purity not less than 99.0%. Molar mixes of 3C+A and 3C+F were made from these constituents and the following weight proportions were then mixed together: 97.0:3.0, 94.0:6.0, 91.0:9.0, 88.0:12.0, 85.0:15.0, 80.0:20.0 and 75.0:25.0 C_3A:"C_3F". The pellets were fired in a horizontal platinum-wound furnace using an aluminous porcelain work-tube. Two batches of C_3A:"C_3F" mixtures were fired, one at 1180° C and the other at 1325° C, both in the presence of oxygen to prevent reduction of iron(III) to iron(II). Samples were fired for 24 h and then air quenched on removal from the furnace. The pellets were crushed and ground for 40 min, sieved and stored in a desiccator.

The lattice parameter of the $C_3(A,F)_{ss}$ was measured using an 11.46 cm Philips camera and nickel filtered Cu*Kα* radiation; it was calculated using the computer program of Cox and Steward [28]. The free lime content was measured using an ethylene glycol extraction method and was always less than 0.1% for samples within the solid solution limit. The grinding procedure was standardized to ensure that each sample had a similar mean particle size and surface area. This was confirmed by means of a Fisher sub-sieve sizer, which is an air permeability method, and gave an average particle size of 9.5 μm at a bed porosity of 0.6.

Analar gypsum was used and was checked for absence of hemihydrate and anhydrite by X-ray diffraction. The ratio of C_3A_{ss} to gypsum was 10:3, which is approximately that present in a typical OPC and corresponds to a molar ratio of 2.13:1. Distilled water was boiled to remove any dissolved CO_2 and stored in a stoppered flask connected to a KOH bubbler. The C_3A and gypsum were mixed in a shaker and after water was added, they were stirred for 2 min. The water:solid ratio was 0.8 and the hydration temperature was 21° C. The hydration was stopped after selected times by the use of acetone. Anatase (TiO_2) was added (33.3% by weight) to the dried powder as an internal standard for quantitative X-ray diffraction analysis (XRD). Hydration products were examined by means of a Philips PW1010 diffractometer using nickel filtered Cu*Kα* radiation. The reflections used for quantitative XRD were: C_3A (844 at 59.3° 2θ), gypsum (141 at 29.2°) and TiO_2 (at 25.3°). Infrared spectra were obtained in the range 4000 to 400 cm^{-1} using a Perkin-Elmer 337 grating spectrophotometer. The anhydrous compounds were analysed by the KBr disc method and the hydrated specimens by the nujol mull method, to avoid decomposition of the hydrates under vacuum. Differential thermal analysis (DTA) curves were obtained on 300 mg samples heated in a nichrome-wound furnace controlled by a Stanton Redcroft linear temperature, variable rate programmer. Samples were heated in air at either 5 or 10° C min^{-1}. Transmission electron micrographs were obtained by standard procedures using either a Philips EMB 100 or a Hitachi HU11A electron microscope.

3. Results

3.1. $Ca_3Al_{2-x}Fe_xO_6$ solid solutions

Analysis of the high 2θ angles in the X-ray powder photograph of C_3A confirmed that it has a cubic unit cell with $a_0 = 1.5263(1) \pm 0.0001$ nm, in good agreement with literature values. Incorporation of iron(III) ions into C_3A brought about an increase in the lattice parameter as shown in Fig. 1. When C_3A–"C_3F" mixes were fired at 1180° C, the solid solution limit occurred at approximately 3.5 wt% "C_3F", corresponding to $Ca_3Al_{1.942}Fe_{0.058}O_6$. The lattice parameter of the C_3A_{ss} increased markedly to 1.5272(5) nm at 3.0 wt% "C_3F", but with further increases in iron content it gradually increased up to 1.5277(8) nm at 25.0 wt% "C_3F". When the mixes were fired at 1325° C more iron entered the solid solution, resulting in a value of a_0 of 1.5288(6) nm at a limiting composition of 9.0 wt% "C_3F", corresponding to $Ca_3Al_{1.850}Fe_{0.150}O_6$. On further increasing the iron content of the mixes, the lattice parameter became constant and at 25.0 wt% "C_3F" was still 1.5288(6) nm.

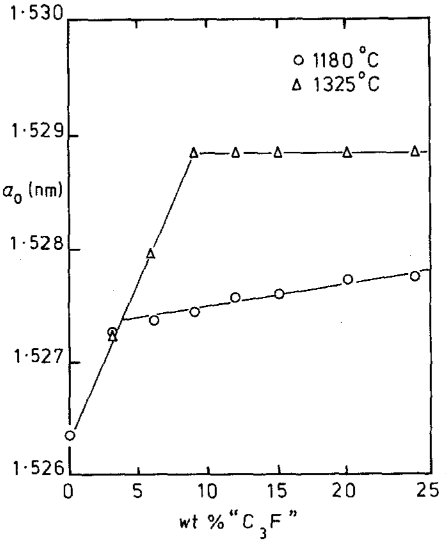

Figure 1 Variation of a_0 with wt % "C_3F".

X-ray diffraction of the mixtures beyond the solid solution limits showed the presence of CaO and C_4AF_{ss}, although the reflections due to C_4AF_{ss} (at $d = 0.724$, 0.277, 0.267 and 0.263 nm) were relatively weak compared with those from C_3A_{ss} and CaO. The phase assemblage has been calculated (Table I), taking the compositions for the C_3A_{ss} given above and for the C_4AF_{ss} as C_4AF. The free lime existing in some of the mixes was also determined chemically and found to be in good agreement with the calculations (Table I).

The infrared spectra of the iron-doped C_3A compounds were similar to the spectrum of C_3A itself. An extra absorption peak appeared at 655 cm^{-1}, several of the major C_3A absorption peaks became less sharp and some of the small overtones and combinations disappeared. The curves are not reproduced since they are in good agreement with those shown elsewhere [24, 27, 29–31].

3.2. The hydration of pure C_3A in the presence of gypsum

On mixing C_3A and gypsum with water, the paste had the consistency of a thin slurry. It had set after about 6 h and had become hard after 24 h. The hydration products detected by XRD and DTA after various periods of hydration are summarized in Table II. The formation of ettringite after hydration for 15 min was indicated by XRD peaks at $d = 0.973$ and 0.561 nm and from the presence of a DTA endotherm whose peak temperature varied with the amount of ettringite present between 106 and 136° C. The amount of ettringite present reached a maximum (as indicated by DTA) between 3 and 7 h hydration. Electron micrographs (such as that shown in Fig. 2a) showed the presence of substantial quantities of needles during this period. Gypsum was consumed steadily throughout the formation of ettringite, but was still visible in the DTA curve after 3 h by the presence of a doublet at 144 and 153° C. It had completely disappeared from the XRD and DTA patterns obtained after hydration for 7 h. Monosulphate was detected after 7 h and, in increased amount, after 24 h through its XRD peaks at 0.892 and 0.446 nm, and a DTA endotherm with a peak temperature of 200° C. Another endotherm was observed at about 250° C, which is attributed to the presence of monosulphate–

TABLE I Calculated phase assemblage in ternary phase field C_3A_{ss}–C_4AF_{ss}–CaO

Weight ratio C_3A:'C_3F'	% C_3A_{ss}	% C_4AF_{ss}	% CaO calculated	CaO chemical analysis
(a) solid solutions prepared at 1180° C with $C_3A_{ss} = C_3A_{0.971}F_{0.029}$				
97:3	100	0	0	< 0.1
94:6	95.7	3.9	0.4	
91:9	89.7	8.7	1.6	
88:12	83.7	13.6	2.7	2.5
85:15	77.6	18.5	3.9	
80:20	68.2	26.2	5.6	
75:25	58.7	33.8	7.5	7.3
(b) solid solutions prepared at 1325° C with $C_3A_{ss} = C_3A_{0.925}F_{0.075}$				
97:3	100	0	0	
94:6	100	0	0	
91:9	100	0	0	< 0.1
88:12	93.8	5.3	0.9	1.0
85:15	86.9	11.1	2.0	
80:20	76.0	19.9	4.1	
75:25	65.8	28.1	6.1	6.0

C_4AH_nss. There was no evidence from XRD or DTA for the presence of ettringite after hydration for 24 h.

The reaction of C_3A and gypsum was also followed by infrared spectroscopy. The contours of the SO_4^{2-} peak were observed to change substantially as reaction proceeded. Gypsum showed three separate bands at 1160, 1148 and 1115 cm^{-1}, but when ettringite became the major sulphate-bearing compound present only a single peak was apparent at 1112 cm^{-1}. On conversion of ettringite into monosulphate the peak was split again, becoming a doublet with peaks at 1162 and 1090 cm^{-1}. These values for ettringite and monosulphate correspond closely with those reported by Bensted and Varma [32]. Changes in the absorption

TABLE II Phases detected* by XRD, DTA and IR spectroscopy after hydration for various periods of time

System	15 min	1 h	3 h	7 h	24 h	7 days
$C_3A + C\bar{S}H_2 + H$	gypsum AFt	gypsum AFt	gypsum AFt	AFt AFm	AFm C_4AH_{13}	AFm C_4AH_{13}
$C_3A + C\bar{S}H_2 + C + H$	gypsum CH C_4AH_{13}	gypsum CH AFt C_4AH_{13}	gypsum CH AFt C_4AH_{13}	gypsum CH AFt C_4AH_{13}	CH AFm C_4AH_{13}	CH AFm C_4AH_{13}
C_3A:"C_3F" 91:9 (1180° C) + $C\bar{S}H_2 + H$	gypsum CH AFt	gypsum CH AFt	gypsum CH AFt	gypsum CH AFt C_4AH_{13}	CH AFt C_4AH_{13}	C_4AH_{13}
C_3A:"C_3F" 91:9 (1325° C) + $C\bar{S}H_2 + H$	gypsum AFt	gypsum AFt	gypsum AFt	gypsum AFt	AFm C_4AH_{13}	AFm C_4AH_{13}
C_3A:"C_3F" 75:25 (1325° C) + $C\bar{S}H_2 + H$	gypsum AFt CH	gypsum AFt CH	gypsum AFt CH	gypsum AFt CH	gypsum AFt CH	gypsum AFt CH

*In addition to the phases shown, C_3A_{ss} was always detected.

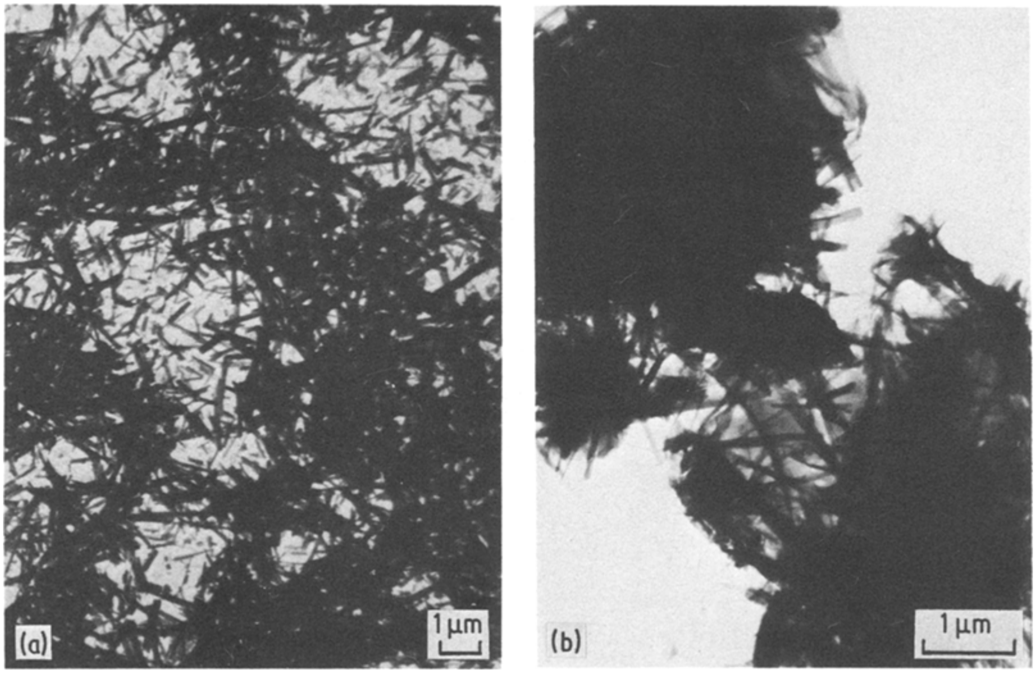

Figure 2 TEM of (a) C_3A + gypsum + H_2O:hydration product after 3 h, (b) 88.12 C_3A:"C_3F" sample + gypsum.

peak positions of the water molecule vibrations were also noticed and found to be reproducible. The infrared spectra yielded results that agreed closely with those from XRD and DTA.

Since the iron-doped C_3A samples were to be compared with this system, it was repeated three times and found to give almost identical XRD, DTA and IR patterns for the various hydration periods.

When a mixture of C_3A:gypsym:lime in the proportions 10:3:1 by weight and hydrated with a water:solid ratio of 0.8 at 21° C, the retardation of the hydration of C_3A was more pronounced than in the presence of gypsum alone. The amount of unreacted C_3A at any given time as indicated by quantitative XRD was always greater than in the presence of gypsum alone, and gypsum remained in the system for a longer time (~ 11 h). Although the paste had hardened after 24 h, the state of the paste during the first 7 h hydration was always more fluid.

The first reaction product to be detected by XRD was CH ($d = 0.490$ and 0.263 nm), followed by the formation of ettringite within the first hour. DTA curves confirmed the presence of these phases and a small peak at 220° C indicated the formation of a small amount of monosulphate—C_4AH_nss even after 15 min. A large amount of ettringite and some gypsum were present after hydration for 7 h, but neither was detected after 24 h. Instead the presence of monosulphate and its solid solution with C_4AH_n was indicated by peaks at 182 and 244° C, respectively. C_3AH_6 was never detected, even after hydration for 7 days. TEM of the product hydrated for 3 h showed the presence of both needles and small hexagonal plates. The sequence of hydration products is summarized in Table II.

3.3. The hydration of iron-doped C_3A (fired at 1180° C) in the presence of gypsum

Seven compositions of doped C_3A made at 1180° C were hydrated in the presence of gypsum and compared with one another and with the system containing pure C_3A. Only the 97.0:3.0 wt% C_3A:"C_3F" (subsequently referred to as the 97:3) sample was within the solid solution limit, so that all the other samples contained additional phases as shown in Table I.

The amount of unreacted C_3A_{ss} in the 97:3 sample was greater after all periods of hydration than in the pure C_3A-gypsum system. Moreover, gypsum was still present after 7 h in the 97:3 system, whereas none was evident in the undoped mix after hydration for this period. No conversion

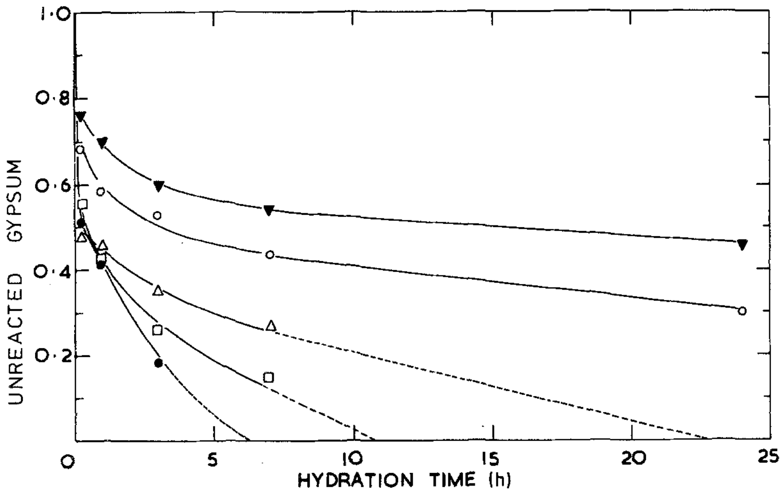

Figure 3 Plots of fraction of unreacted gypsum against time for the hydration of $C_3(A, F)_{ss}$ + gypsum.

	C_3A : "C_3F"	
●	100	0
□	97	3
△	91	9
○	85	15
▼	75	25

of AFt into AFm was apparent in the 97 :3 sample after 7 h, whereas partial conversion was evident in the undoped sample. All of these observations indicate that the 97:3 system is more retarded than the undoped system.

The rate of consumption of gypsum against time is plotted for several of the iron-doped systems in Fig. 3. As the amount of iron in the sample increased, the system became more retarded. The same conclusion is drawn from XRD estimates of the amount of unreacted C_3A_{ss} remaining after different hydration periods. By extrapolation of the curves shown in Fig. 3, it is possible to estimate the time at which all the gypsum is consumed (Table III). Although these times are only approximate, in every case no gypsum was observed by XRD or DTA at the next sampling after the estimated time, e.g. no gypsum was detected after 24 h during the hydration of the 91:9 sample.

TABLE III Approximate time at which all the gypsum is consumed during the hydration of $C_3A_{ss} + C\bar{S}H_2$

Weight ratio C_3A:'C_3F'	Time for samples fired at 1180° C	Time for samples fired at 1325° C
100:0	6 h	
97:3	11 h	9 h
94:6	20 h	14 h
91:9	22 h	16 h
88:12	30 h	> 30 h
88:15	> 30 h	60 h
80:20	7 days	< 7 days
75:25	> 7 days	> 7 days

As the amount of iron present in the system increased, the rate of consumption of both C_3A and gypsum became very slow. Furthermore, the formation of AFt and its subsequent conversion into AFm, as shown by DTA, became very retarded. The areas under the DTA peaks due to the AFt phase are given in Table IV, from which it can be seen that as C_3A and gypsum reacted together, the area of the AFt peak increased steadily, before decreasing rapidly as AFt was converted into AFm. The time at which the rapid conversion of AFt into AFm occurred coincided with the time at which the gypsum content approached zero.

The 91 :9 sample was found to hydrate more slowly than the 97 :3 sample as can be seen from Fig. 3 and Tables III and IV. Both gypsum and AFt were present for longer times of hydration in the 91 :9 sample than in the 97 :3 sample. The AFt phase was still observed in the 91 :9 sample after hydration for 24 h, although extensive conversion into monosulphate had taken place. Since the 91 :9 composition is beyond the solid solution limit, some C_4AF_{ss} and CaO were present in the paste (see Table I). The free lime was immediately converted into calcium hydroxide, which was detected by its XRD peak at $d = 0.263$ nm. This peak remained almost constant in magnitude

TABLE IV Area of the DTA endotherm due to AFt after hydration of $C_3(A, F)_{ss}$–$C\bar{S}H_2$ mixtures for various times

Hydration time	Weight ratio C_3A: "C_3F"							
	100:0	97:3	94:6	91:9	88:12	85:15	80:20	75:25
(a) Solid solutions prepared at 1180° C								
15 min	8.5	2.2	3.6	2.3	2.8	0.0	0.0	0.0
1 h	17.1	3.0	7.1	4.7	6.3	1.7	4.2	2.4
3 h	28.7	14.8	13.7	10.2	10.8	3.3	5.9	3.9
7 h	15.2	23.9	15.3	15.2	19.8	6.6	9.6	5.5
24 h	0	0	4.8	7.4	28.6	13.1	13.3	8.4
7 days	0	0	0	0	0	0	6.3	25.9
(b) Solid solutions prepared at 1325° C								
15 min	8.5	4.8	5.3	2.2	3.9	4.5	3.5	2.9
1 h	17.1	11.0	6.8	10.2	6.4	5.3	4.9	3.5
3 h	28.7	17.1	16.8	19.4	10.0	7.9	5.8	3.8
7 h	15.2	26.2	24.9	23.6	14.2	11.7	6.7	4.3
24 h	0	0	0	0	24.5	17.2	17.3	7.2
7 days	0	0	0	0	0	0	0	30.3

between 15 min and 7 h hydration, then decreased and had disappeared after 7 days.

When samples with still higher "C_3F" contents were hydrated, the added gypsum could be detected in the paste for much longer periods; in the 85:15, 80:20 and 75:25 samples considerable amounts of gypsum were still observed after hydration for 24 h, and in the 75:25 sample some gypsum was still present after hydration for 7 days. The reactivity of the C_3A_{ss} was correspondingly decreased and the presence of the AFt phase was stabilized for longer periods as the amounts of C_4AF_{ss} and CaO in the original sample increased. The 75:25 paste was still soft after hydration for 7 days and contained both gypsum and AFt, but the samples with lower iron contents had all formed AFm and the pastes were hard. The AFt phase was still observed in the 80:20 sample after hydration for 7 days, but extensive conversion into AFm had taken place. An additional endotherm at ~ 255° C was always observed in the DTA curves whenever AFm had formed. This is probably due to the formation of the AFm phase as a solid solution equivalent to the monosulphate–C_4AH_nss observed during the hydration of pure C_3A. In spite of the presence of $Ca(OH)_2$ in these samples, no C_4AH_n was observed in the DTA curves except in the presence of AFm.

3.4. The hydration of iron-doped C_3A (fired at 1325° C) in the presence of gypsum

The solid solution limit of "C_3F" in C_3A had increased at 1325° C, so that the 97:3, 94:6 and 91:9 samples all contained only C_3A_{ss}. These three samples behaved quite similarly in that the XRD and DTA patterns indicated that they were retarded with respect of the pure C_3A in terms of rate of decrease of C_3A_{ss}, decrease of gypsum (Table III), and formation of AFt (Table IV). Gypsum was present for longer periods as the amount of iron in the solid solution increased, similarly the formation of AFt was stabilized over a longer period and the paste took longer to harden. After hydration for 7 h the amount of AFt in the undoped C_3A had decreased, whereas the amount in the three doped samples was still increasing, although no AFt was detected in any of the four samples after hydration for 24 h.

The hydration products of samples beyond the solid solution limit contained CH and C_4AF_{ss}. The XRD reflections due to C_4AF_{ss} were weak and little change was seen in their intensities during hydration. DTA curves of the products of hydration of the 85:15 sample are shown in Fig. 4 and are typical. The first peak (112 to 130° C) is that due to the AFt phase and gradually increased in magnitude as the time of hydration increased from 15 min to 24 h, but had disappeared after 7 days. The gypsum doublet (~ 145 and 155° C) decreased in magnitude with increasing hydration time and had disappeared after 7 days, when AFm and C_4AH_n were present.

The reactivity of the C_3A_{ss} decreased markedly as the amounts of C_4AF_{ss} and CH in the paste increased. The samples all contained gypsum after 24 h, but only the 75:25 sample still contained it after 7 days. Likewise, the amount of AFt

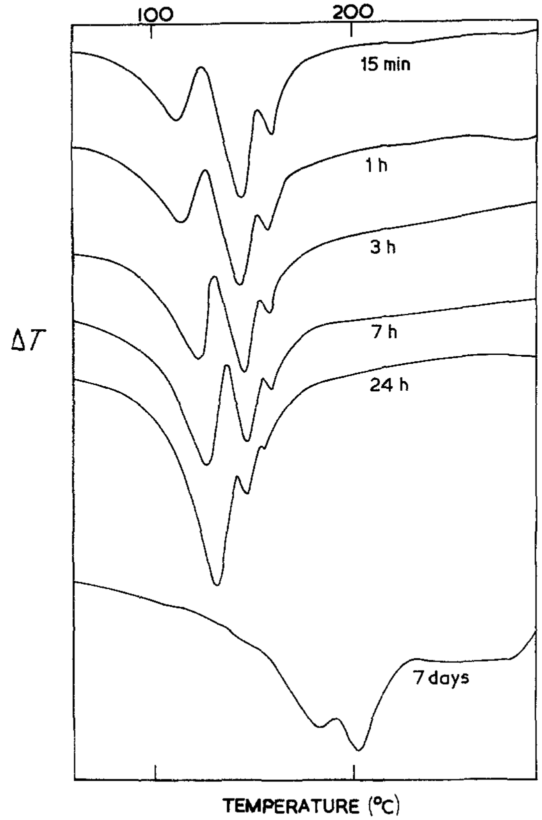

Figure 4 DTA curves of the reaction products from the 85:15 sample (made at 1325° C) hydrated for various periods.

detected (Table IV) increased up to 24 h for all these samples, but it had disappeared after 7 days, except for the 75:25 sample. In the 80:20 system, the AFm phase alone was present after hydration for 7 days, in contrast to the sample prepared at 1180° C when AFt was still detected as well as AFm.

Plots of unreacted C_3A_{ss} against hydration time have not been shown hitherto because of the inevitable uncertainty of the measurements from quantitative XRD. However, it was found that in many cases, especially for the samples with low iron contents, it was not possible to draw a smooth curve through the points. Hence, three systems, namely, pure C_3A, the 97:3 sample fired at 1325° C, and the 85:15 sample fired at 1325° C, were repeated in greater detail, not only to test the reproducibility of the points but also to provide extra points where the apparent discontinuities appeared. The curves for the first two of these systems, which are shown in Fig. 5, show a definite step in the curve corresponding closely with the time of hydration when the supply of gypsum was totally consumed. The curve for the 97:3 sample includes data from one run on the sample fired at 1180° C and two runs on the sample fired at 1325° C, which show good reproducibility. The discontinuity occurs after hydration for about 8 h. Gypsum was still present in small amounts after 7 h, but not after 9 h, and although some AFt was evident after 9 h, AFm was the dominant hydrate.

The more detailed analysis of the pure C_3A system indicated that the discontinuity in the curve occurred after hydration for about 6 h (Fig. 5). These curves confirm the retardation caused by the incorporation of iron in solid solution in C_3A.

The repeat experiment on the 85:15 sample gave additional points between 24 h and 7 days. Good reproducibility was observed and the discon-

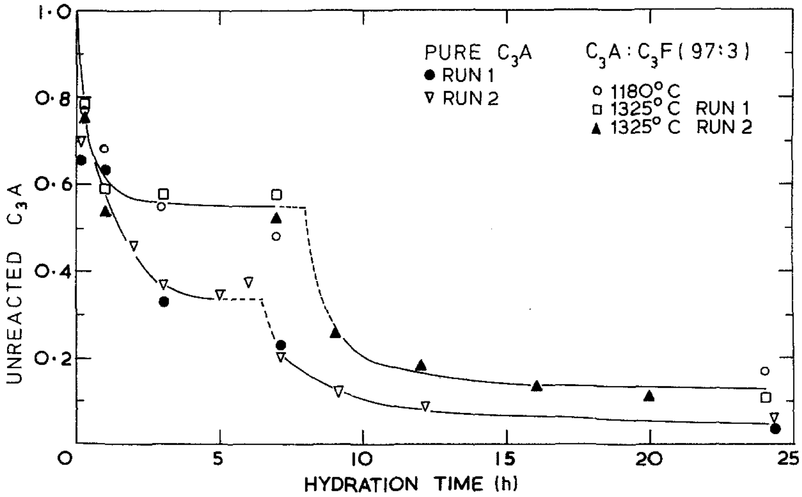

Figure 5 Plots of fraction of unreacted C_3A against time for the hydration of (a) pure C_3A + gypsum, and (b) 97:3 C_3A:"C_3F" + gypsum.

TABLE V Estimate of the average length (μm) of AFt needles from TEM of hydration products of $C_3(A, F)_{ss}$–$C\bar{S}H_2$

Hydration time	Weight ratio C_3A:"C_3F" 100:0	97:3	94:6	91:9	88:12
15 min	1.14	0.61	0.66	0.66	0.63
3 h	1.43	0.78	0.73	0.79	0.72
24 h	0	0	0	0	0.44

tinuity appeared between 2 and 3 days when the rapid conversion of AFt into AFm also occurred.

TEM of samples containing AFt in the hydrated samples of C_3A_{ss} showed the presence of needles (Fig. 2b) and measurements of the needle size at various C_3A:"C_3F" ratios from many photomicrographs are summarized in Table V. The incorporation of iron into C_3A caused a decrease in length of the needles when iron was present in small amounts, but as this increased the length of the needles remained approximately constant.

4. Discussion

4.1. The C_3A–"C_3F" solid solution series

Widely differing solid solution limits have been reported for the incorporation of iron in $Ca_3Al_2O_6$. It was found in the present investigation that this limit increases with increasing firing temperature from approximately 3.5 wt% "C_3F" (2.9 mol%) at 1180° C to 9.0 wt% "C_3F" (7.5 mol%) at 1325° C. The value at 1180° C is less reliable than that at 1325° C, since the value of the lattice parameter drifts upwards slightly beyond the solid solution limit, which indicates that some additional iron is entering the C_3A structure in the mixes of higher iron content, i.e. equilibrium has not been reached. The increase in the lattice parameter is approximately 0.000 36 nm per mol% "C_3F" incorporated, which leads to an estimate of 4.1 mol% "C_3F" in the 75:25 sample fired at 1180° C.

Our value of 7.5 mol% "C_3F" for the limiting solid solution at 1325° C agrees closely with that determined by Majumdar [16] and is slightly higher than that of Varma *et al.* [24], but is very different from that reported by other workers. Although it is not known why there should be so much variation between different investigations, it is clearly important to maintain all the iron in the +III oxidation state and to work along the C_3A–"C_3F" join [25]. It may be significant, therefore, that in the present study and in that by Majumdar, the samples were fired in an atmosphere of oxygen rather than air.

Our observation that the magnitude of the solid solution limit increases with increased firing temperature is in agreement with the conclusions of Schlaudt and Roy [17] and Moore [18, 19].

The less dramatic changes observed in the infrared spectra of the $C_3(A, F)_{ss}$ showed only the introduction of a peak at 655 cm^{-1} and a weakening of some of the minor peaks of pure C_3A as the iron content of the solid solution increased. This additional peak was attributed by Fierens *et al.* [27] to the presence of tetrahedral $(FeO_4)^{5-}$ groups in C_3A_{ss}. Although C_4AF_{ss} is known to contain octahedral $(FeO_6)^{9-}$ groups, no further evidence of peaks was observed in the compounds of higher iron content, but the infrared spectrum of a pure C_2F sample showed only two weak peaks, at 580 and 437 cm^{-1}.

4.2. The hydration of pure C_3A in the presence of gypsum

The first hydrate to be detected was ettringite, which gradually increased in amount as the rate of decrease of C_3A more or less levelled off after about 3 h (Fig. 5). A sudden increase in the reactivity of C_3A was observed after about 6 h, which was also approximately the time that the paste set and the concentration of gypsum approached zero (Fig. 3). Furthermore, the amount of ettringite present reached a maximum and subsequently converted rapidly into monosulphate. After 7 h, no gypsum could be detected and the amount of ettringite present was much less than after 3 h (Table IV). These reactions may be summarized by the equations:

$$C_3A + 3C\bar{S}H_2 + 26H \rightarrow C_6A\bar{S}_3H_{32}$$

$$C_6A\bar{S}_3H_{32} + 2C_3A + 4H \rightarrow 3C_4A\bar{S}H_{12}$$

These observations are essentially similar to those in the literature [1–13] with one notable exception [8], when monosulphate rather than ettringite was observed as the major early hydrate, but relatively large crystals of gypsum were used. Bensted [32] concluded from DTA studies of the hydration of Portland cements that the sequence of reactions, gypsum → ettringite → monosulphate → C_4AH_{13}, does not proceed to completion at any one stage before the next stage becomes significant. While we confirm this observation, it was apparent in this system and several of those involving iron-doped C_3A_{ss} that as the concentration of gypsum approached zero, the paste set and the amount of

AFt present reached a maximum before decreasing suddenly to be replaced by a rapid increase in the amount of AFm present over a relatively short interval of time.

When the concentration of SO_4^{2-} ions in solution decreases, because the gypsum content approaches zero, it has been suggested [1, 33] that the transformation of AFt into AFm produces a slight expansion, sufficient to rupture the ettringite layer and reopen the surface of the C_3A to further reaction. More recently, various workers [34, 35] have proposed that hydration occurs within a membrane surrounding the grains of clinker compounds, which rupture periodically due to build-up of osmotic pressure. Whatever their cause, the quantitative results shown in Fig. 5 indicate a gradual retardation of the rate of hydration of C_3A, followed by a sudden increase in reactivity consistent with spalling of a surface layer. Similar observations were made during the hydration of many of the iron-doped C_3A_{ss} samples.

When both gypsum and lime were present, calcium hydroxide was formed immediately, followed by C_4AH_{13} and subsequently by ettringite. These reactions can be summarized as follows:

$$C + H \rightarrow CH$$

$$C_3A + CH + 12H \rightarrow C_4AH_{13}$$

$$C_4AH_{13} + 3C\bar{S}H_2 + 14H \rightarrow C_6A\bar{S}_3H_{32} + CH$$

The calcium hydroxide liberated is then a further source of Ca^{2+} ions for the formation of C_4AH_{13} and hence of ettringite [7]. The reaction was observed to be more retarded than that in the presence of either gypsum alone or lime alone.

4.3. The effect of iron-doping on the hydration of C_3A_{ss} in the presence of gypsum

The introduction of iron(III) into the structure of C_3A has a significant retarding effect on the reactivity of C_3A when it is hydrated in the presence of gypsum. The setting time of the paste, the time taken for the gypsum to be totally consumed, and the time at which rapid conversion of AFt into AFm takes place all increased as the iron content of the C_3A:"C_3F" samples increased. Furthermore, the rate of disappearance of the C_3A_{ss} decreased, as the iron content increased. These observations apply not only to those samples which contain CaO and C_4AF_{ss} as well as C_3A_{ss} (group II), but also to those which are within the C_3A_{ss} limit (group I).

The behaviour of the 97:3 samples (Fig. 5) is typical of that of a group I sample. The discontinuity in the amount of C_3A_{ss} reacted against hydration time curve, which was after about 8 h, is virtually the same as the setting time, and similar to the time taken to consume all the gypsum (Table III), and the time that the AFt phase reaches a maximum (> 7 h, see Table IV) before its rapid conversion into AFm. Since the 97:3 samples are within the solid solution limit at both firing temperatures, their hydration behaviour is very similar, but clearly retarded when compared with that of the pure C_3A system. The hydration of other samples in group I with higher iron contents is slightly more retarded than that of the 97:3 sample.

This effect is still more pronounced when group II samples are considered, so much so that the 75:25 samples had not set after hydration for 7 days and both gypsum and AFt were still present. There are three factors influencing the increased retardation of samples within group II:

1. since the amount of C_3A_{ss} present decreases as the iron content increases (Table I), the gypsum : C_3A_{ss} ratio increases from 0.3 to approximately 0.5 in the 75:25 sample prepared at 1180° C. It is well known that the greater this ratio, the greater the stability of AFt and the more retarded the hydration of C_3A;
2. the presence of free lime causes further retardation even in the presence of gypsum;
3. the presence of C_4AF_{ss}, which has a higher $Fe_2O_3:Al_2O_3$ ratio than that of C_3A_{ss}, has been reported [37, 38] to be much less reactive than C_3A.

Little change was detected in the XRD intensities of the C_4AF_{ss} peaks during hydration in the present study, and no new product phases were observed.

Although the data listed in Table III show that, in general, the time taken to consume all the gypsum is greater for the 1180° C series of samples than for the 1325° C series, this is somewhat misleading. It can be seen from Table I that the actual composition of the 94:6 sample fired at 1180° C is similar to that of the 88:12 sample fired at 1325° C, assuming that the composition of the C_4AF_{ss} is unchanged. Likewise, the 80:20 sample fired at 1180° C is similar to the 75:25 sample fired at 1325° C. The hydration of these pairs of systems proceeded in a similar manner for the first 7 h, but subsequently the systems containing the C_3A_{ss} with the higher iron contents (i.e. those samples prepared at 1325° C) became the more retarded. This provides further confirmation that the incorporation of iron(III) into the structure makes the C_3A_{ss} inherently less reactive. A similar conclusion was reached by Fierens *et al.* [27] who investigated the hydration of $C_3(A, F)_{ss}$ in the absence of gypsum.

5. Conclusions

The limits of solid solution of iron(III) in C_3A are 3.5 wt % (or 2.9 mol %) "C_3F" at 1180° C and 9.0 wt % (or 7.5 mol %) "C_3F" at 1325° C. The lattice parameter of the cubic unit cell increases by approximately 0.000 36 nm per mol % "C_3F" up to a maximum value of 1.5289 nm at 7.5 mol %.

The hydration of $C_3(A, F)_{ss}$ in the presence of gypsum is retarded compared with that of pure C_3A. As the iron content is increased, the hydration becomes more retarded, especially beyond the solid solution limit when C_4AF_{ss} and CaO are present as well as C_3A_{ss}. The first hydration product was AFt (related to ettringite), which eventually transformed into AFm (related to monosulphate) when the concentration of unreacted gypsum approached zero. This transformation took place rapidly at the same time as a discontinuity was observed in the plot of C_3A_{ss} reacted against hydration time, indicating an acceleration in the consumption of C_3A.

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