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A Mössbauer study of the high temperature reactions of iron oxides with tricalcium aluminate

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Mössbauer spectroscopy and X-ray diffraction techniques were used to study the solid state reactions between tricalcium aluminate and both Fe_2O_3 and FeO (0.5 to 5.0 wt % iron oxide) in both oxidizing and reducing atmospheres. The iron oxides interact with the aluminate both by forming solid solutions (as evidenced by changes in the aluminate lattice parameter) and by the formation of separate ferrite and/or aluminoferrite phases. Under oxidizing conditions, solid solution of Fe^{3+} increases the aluminate lattice parameter, whereas under reducing conditions, the lattice parameter is decreased, suggesting some solid solution of Fe^{2+}. The Mössbauer spectra of oxidized samples are typical of tetracalcium aluminoferrite and related ferrite phases, while under reducing conditions the spectra all show a pair of Fe^{3+} doublets characteristic of ferrite phases, and a pair of Fe^{2+} doublets suggesting four-fold co-ordination in distinctly different sites. Consideration of the possible ferrous sites in the aluminate and aluminoferrite systems suggests the ferrous ions might replace Al in the aluminate.

1. Introduction

The formation and stability relationships of oxide compounds of calcium, aluminium and iron (the so-called "ferrite" phases) are of considerable importance to the chemistry of Portland cement clinker formation. Of particular interest is the interaction between ferric iron and tricalcium aluminate, since there is evidence that, at low concentrations, Fe^{3+} can enter into solid solution with tricalcium aluminate [1–4]. Opinions differ as to the extent of this solid solution: Majumdar [1] determined it as 8.1 wt% "$Ca_3Fe_2O_6$" in tricalcium aluminate at 1325° C, whilst Schlaudt and Roy [2] obtained a value of 3.5 mol % "$Ca_3Fe_2O_6$" for the limit of solid solubility at 1389° C. On the basis of X-ray crystallographic measurements of the tricalcium aluminate unit cell dimension, Tarte [3] deduced that up to 10 mol % Fe_2O_3 can enter into solid solution with the aluminate at 1310° C. Subsequent X-ray measurements at 1350° C by Moore [4] on samples made both by dry mixing and co-precipitating the reactants (the so-called dry and acid preparations) indicated solid solution limits of about 4.3 and 3.6 mol % "$Ca_3Fe_2O_6$" respectively. Expressing all these values on a common basis of wt% Fe_2O_3 the results of Majumdar, Schlaudt and Roy and Tarte become 3.95, 2.05 and 5.9 wt% respectively, while those of Moore become 2.5 and 2.1 wt% for the "dry" and "acid" preparations respectively.

At between 1300 and 1350° C a small but significant amount of reduction of Fe^{3+} to Fe^{2+} occurs in iron-doped tricalcium aluminate, even in samples fired in air and oxygen [1]. Majumdar [1] suggests that the ferrite phase may tolerate a certain amount of replacement of Ca^{2+} by Fe^{2+}, but that additional phases may be precipitated simultaneously. Moore [4] quotes data which indicate that both monovalent Na and divalent Mg can be accommodated by tricalcium aluminate without the loss of its cubic structure, presumably by replacement of Ca^{2+}. The lattice parameter of such samples is *decreased*, by contrast with the effect of Fe^{3+} substitution, which *increases* the lattice parameter [4]. No indication could be found in the literature of the effect of Fe^{3+} on

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the lattice parameter of tricalcium aluminate, even though the location of ferrous ions in the aluminate system is of some interest in clinkers fired under reducing conditions [5] where the concentration of Fe^{2+} is considerably increased. Mössbauer spectroscopy of such materials [5] suggests that the ferrous ions are located in unusual sites, possibly of square planar symmetry, but does not indicate whether these are predominantly associated with the aluminate or silicate phases of the clinker.

Another interesting aspect concerns the effect of Fe^{2+} on the composition of the aluminoferrite phases occurring at the low-iron end of the alumina–lime–iron oxide system. Ponomarev *et al.* [6] report that in clinkers fired under reducing conditions, higher-iron aluminoferrites such as $Ca_6Al_2Fe_4O_{15}$ are favoured, whereas under oxidizing conditions further reaction with "free" calcium aluminates can occur, resulting in compositions approaching $Ca_6Al_4Fe_2O_{15}$. These authors also consider [7] that reducing atmospheres suppress reactions between aluminates and aluminoferrites by some unspecified mechanism; although ferrous ions are stated to be present in the reduced clinkers, their influence either on the composition of the ferrite phases or on their reactivity with other aluminates is not considered [7].

A further aim of the present work was to investigate aspects of the reactions of tricalcium aluminate with both Fe_2O_3 and FeO, under oxidizing and reducing conditions. The behaviour of the iron during the reaction was studied by Mössbauer spectroscopy, and X-ray diffraction was used to determine the nature of the reaction products.

In the discussion which follows, the oxide compounds will be referred to using the standard abbreviations of cement chemistry, where $C = CaO$, $A = Al_2O_3$ and $F = Fe_2O_3$.

2. Experimental procedure

The tricalcium aluminate (C_3A) used in this work was prepared from a mixture of analytical grade $CaCO_3$ and Al_2O_3 by firing at a temperature of 1300° C, re-grinding and re-firing until the X-ray trace indicated crystalline C_3A with no reactant oxides. Mixtures containing 0.5 wt%, 2 wt% and 5 wt% of hematite (Fe_2O_3) and wustite (nominally FeO) were ground together and reacted in platinum-lined ceramic boats for 2.0 h in an electric tube furnace accurately controlled at 1310° C, air-quenched, ground and examined by X-ray diffraction. Firings were made both in static laboratory air and flowing reducing atmospheres (5 vol% H_2, 95 vol% N_2 at 80 ml min^{-1}). After examination, the air-fired samples were refired in the H_2/N_2 atmosphere for a further 2.0 h and re-examined. The lattice parameter of C_3A was estimated by measuring the a_1 component of the (12,4,0) reflection. The room-temperature Mössbauer spectra were obtained using a Co/Pd source, the isomer shifts being calibrated with respect to natural iron. The spectra were fitted to Lorentzian line shapes using a computer program developed by L. P. Aldridge of this laboratory.

3. Results and discussion

3.1. Mössbauer studies

Typical room-temperature Mössbauer spectra of samples both before and after firing are shown in Figs. 1 and 2.

The spectra of unfired samples containing Fe_2O_3 showed the inner four peaks of the 6-line magnetic spectrum of hematite (Fig. 1a); the outer pair were not observed due to the limited velocity range chosen for this work. Unfired samples containing wustite (FeO) showed spectra (Fig. 1b) which could be resolved into two pairs of doublets, one pair having a chemical isomer shift (IS) of 1.02 mm sec^{-1} and a quadrupole splitting (QS) of 0.90 mm sec^{-1}. The parameters of the other doublet are IS = 1.06 mm sec^{-1} and QS = 0.37 mm sec^{-1}. These spectra are very similar to those previously published for wustite [8] and although disagreement exists in the literature over the interpretation of these spectra [8], the important result here is that the identity of the starting phase is confirmed; precise assignment of the spectrum is not important, since the wustite features do not survive the heating process.

All the oxidized samples, irrespective of the initial valency of the added iron oxide, gave spectra as in Fig. 2a. Computer analysis of these spectra showed them to be composed of two pairs of overlapping doublets, one pair having the parameters IS = 0.30 to 0.46 mm sec^{-1}, QS = 1.68 to 1.74 mm sec^{-1}, and the other pair having the parameters IS = 0.13 to 0.27 mm sec^{-1}, QS = 1.52 to 1.68 mm sec^{-1}. These values are characteristic of those previously reported for the octahedral and tetrahedral Fe^{3+} sites, respectively, of the ferrite phase in laboratory-fired Portland cement

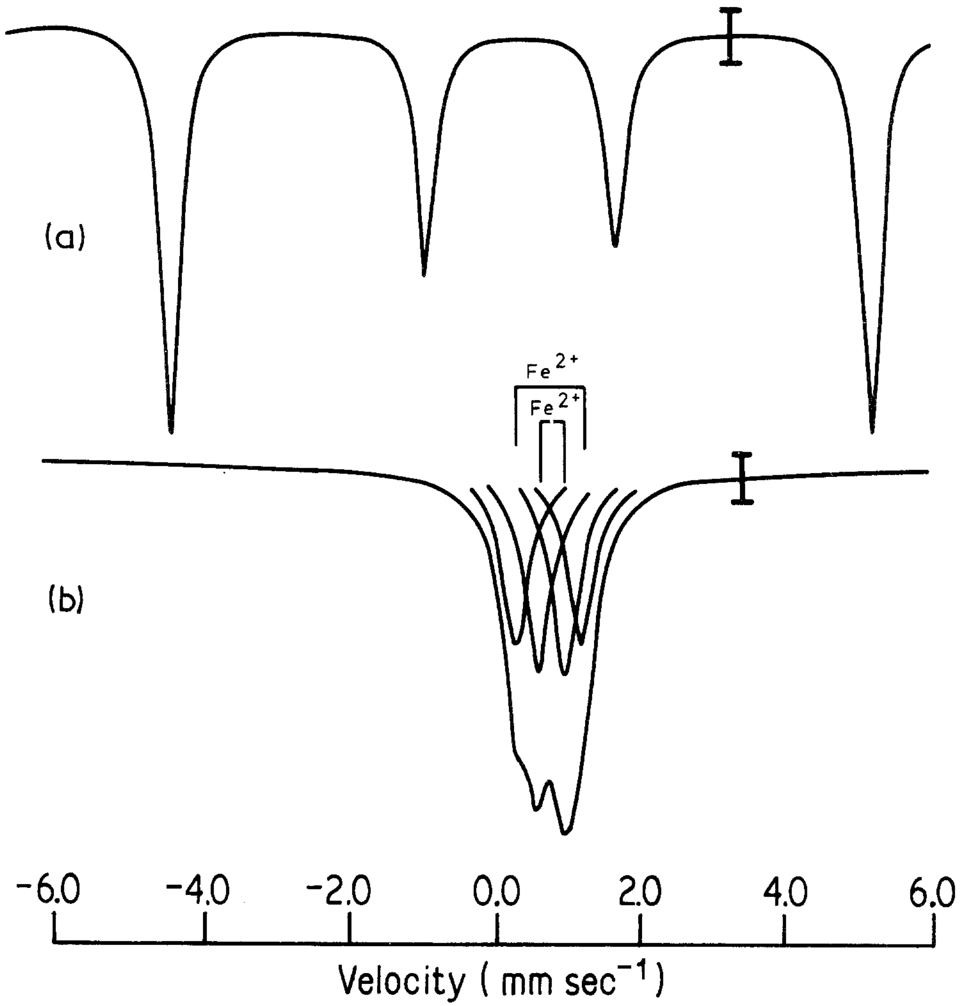

Figure 1 Typical Mössbauer spectra of unreacted C_3A–iron oxide mixtures (a) C_3A + Fe_2O_3, unheated; (b) C_3A + FeO, unheated.

clinker [5], which also compare well with the parameters for synthetic $Ca_4Al_2Fe_2O_{10}$ [5]. The Mössbauer parameters of the fired and unfired samples are collected in Table I.

As previously discussed [5] doublet spectra are only observed in aluminoferrites when the sample is above the critical temperature, which for pure synthetic C_4AF is 60° C [9]; the presence of impurities can however lower the critical temperature to less than 77 K [5]. The mechanism by which the critical temperature must have been lowered in the present samples is not clear, since considerable care was taken to exclude impurities from these samples; the most likely explanation of this effect is that the C_3A phase intimately associated with the aluminoferrite is playing the same role as an impurity. The assignment of the doublets to octahedral and tetrahedral Fe^{3+} sites was made by analogy with previous interpretations of the aluminoferrite spectra [10]. The occupancy of octahedral and tetrahedral sites can be deduced from the area ratios of the octahedral and tetrahedral peak, and indicates in all cases a markedly higher octahedral site occupancy in the samples in which the iron was initially in the ferrous form. From crystal field considerations, the site preference energy of Fe^{2+} is slightly greater for octahedral sites than for tetrahedral sites, whereas Fe^{3+} has no particular site preference. This suggests that if Fe^{2+} ions enter the C_4AF lattice prior to oxidation, they will preferentially occupy octahedral sites, where they will remain after being oxidized to Fe^{3+}. The area ratios also indicate that tetrahedral site occupancy in the C_4AF increases with increasing iron oxide concentration, suggesting that when some upper limit of octahedral

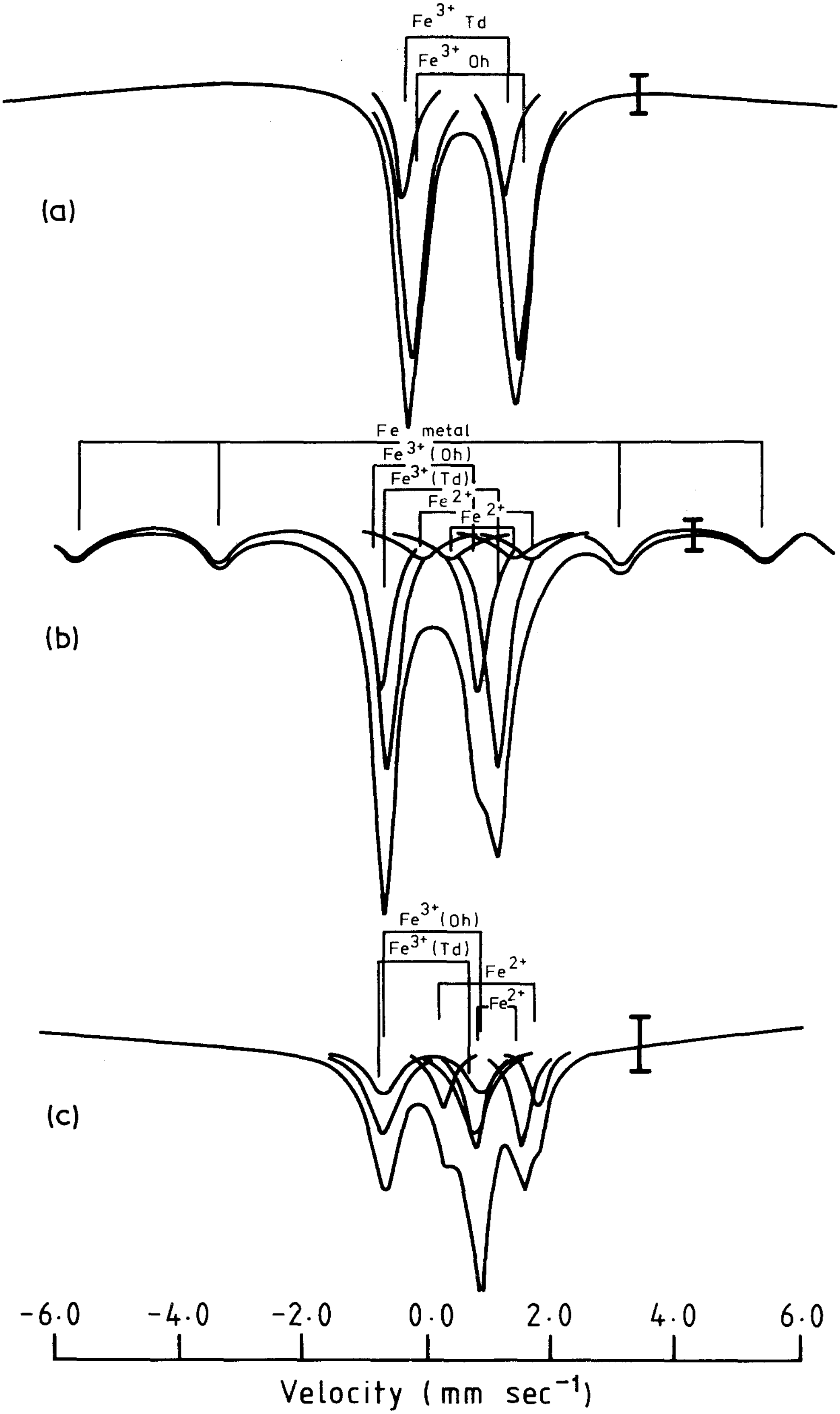

Figure 2 Typical Mössbauer spectra of reacted C_3A–iron oxide mixtures (a) C_3A + Fe_2O_3 or FeO, heated in air; (b) C_3A + Fe_2O_3 or FeO heated in H_2/N_2; (c) as for b except less heavily reduced. Oh = octahedral; Td = tetrahedral.

TABLE I Room-temperature Mössbauer parameters for fired and unfired C_3A–iron oxide mixtures. Isomer shifts quoted with respect to natural iron.

Sample		IS (mm sec^{-1})	QS (mm sec^{-1})	Assignment	
C_3A/Fe$_2$O$_3$, unfired		0.57	–	Fe^{3+}, hematite	
C_3A/FeO, unfired		1.02 1.06	0.90 0.37	Fe^{2+}, wustite	
C_3A/Fe$_2$O$_3$	fired in air	0.39–0.46	1.68–1.74	Fe^{3+}, octahedral	ferrite
C_3A/FeO		0.13–0.27	1.52–1.68	Fe^{3+}, tetrahedral	
C_4AF, lab-fired		0.35–0.50	1.61–1.78	Fe^{3+}, octahedral	ferrite
Portland cement clinker [5]		0.14–0.27	1.59–1.80	Fe^{3+}, tetrahedral	
Synthetic		0.41	1.56	Fe^{3+}, octahedral	ferrite
C_4AF [5]		0.20	1.51	Fe^{3+}, tetrahedral	
C_3A/Fe$_2$O$_3$	fired in H$_2$/N$_2$	0.12–0.65	1.57–1.82	Fe^{3+}, octahedral	ferrite
C_3A/FeO		0.04–0.26	1.27–1.69	Fe^{3+}, tetrahedral	
		0.93–1.22	1.50–1.85	Fe^{2+}, tetrahedral	
		1.04–1.28	0.67–0.93	Fe^{2+}, square planar (?)	
Portland cement clinker		0.71–0.89	1.57–1.98	Fe^{2+}	
Lab-fired in H$_2$/N$_2$ [5]		1.07–1.16	0.24–0.54	Fe^{2+}	

site occupancy is reached, the excess iron proceeds into the remaining tetrahedral sites. These remarks on site occupancy refer only to the initial stages of aluminoferrite formation, and there is no suggestion that site occupancy changes once the aluminoferrite phase is established; indeed, the evidence indicates that initial site configurations are retained, surviving even oxidation and reduction processes.

The Mössbauer spectra of samples fired under oxidizing conditions show only well-defined aluminoferrite peaks and give no indication of other peaks attributable to Fe^{3+} in solid solution in C_3A. The absence of additional peaks could be due either to the concentration of Fe^{3+} in solid solution being insufficient to give a Mössbauer spectrum, or because the spectrum of the iron in solid solution is very similar to, and obscured by, the stronger aluminoferrite spectrum. In an attempt to obtain a spectrum of C_3A/Fe^{3+} solid solution without the complication of aluminoferrite, a very dilute sample containing 0.1 wt% Fe$_2$O$_3$ was prepared, using ^{57}Fe-enriched Fe$_2$O$_3$ to secure a Mössbauer resonance at this low iron content. Although X-ray diffraction showed that aluminoferrite formation was below the limits of X-ray diffraction detection (about 3%), the Mössbauer spectrum, whilst being not well defined, again coincided with an alumino-ferrite spectrum. Lattice parameter measurements of this sample showed a very small expansion, suggesting that again too little of the available iron had entered into solid solution to give a Mössbauer spectrum characteristic of that phase.

The Mössbauer spectra of samples fired under reducing conditions are more complex (Figs. 2b and c), but can all be resolved by computer into a pair of doublets with parameters identical to the aluminoferrite phase, and a pair of doublets with parameters similar to those of Fe^{2+} (Fig. 2c). In some spectra a pair of doublets corresponding to the outer peaks of a 6-line metallic iron spectrum were also seen (Fig. 2b). The associated low-intensity innermost iron doublet was not fitted, since iron was a minor phase in most of the reduced samples. The parameters of the doublets tentatively assigned to Fe^{2+} were reasonably consistent in all the reduced samples, irrespective of their pre-oxidation history. By analogy with known assignments of silicate spectra [11], the doublet with the larger QS could be associated with Fe^{2+} in tetrahedral co-ordination, and the doublet with smaller QS was more like that of Fe^{2+} in square-planar configuration. The parameters of these doublets are not sufficiently similar to those of FeO (Table I) to suggest that they arise from a wustite-type phase, but they bear some resemblance to the two Fe^{2+} doublets observed in Portland cement raw mixes fired under reducing conditions [5] (Table I).

The two phases in which Fe^{2+} ions could be located are the aluminoferrite or a C_3A solid solution. Structural studies of aluminoferrites [12] indicate that ferric iron is located in both

TABLE II Distribution of iron in the various phases of reduced samples, estimated from Mössbauer peak areas

wt % of added oxide	Sample pre-oxidized	Fe % in various phases						
		Ferrite						
		Fe^{3+} (octahedral)	Fe^{3+} (tetrahedral)	Fe^{3+} (total)	Fe^{2+} (tetrahedral)	Fe^{2+} (square planar)	Fe^{2+} (total)	Fe metal
2% Fe_2O_3	No	25.0	36.9	61.9	11.3	26.8	38.1	0
2% Fe_2O_3	Yes	19.5	37.3	56.8	16.2	27.0	43.2	0
5% Fe_2O_3	No	12.6	22.8	35.4	2.6	8.3	10.9	53.6
5% Fe_2O_3	Yes	40.2	27.0	67.2	7.2	7.1	14.3	18.4
2% FeO	No	13.4	35.6	49.0	11.5	17.0	28.5	22.5
2% FeO	Yes	16.4	44.6	61.0	13.2	25.9	39.1	0
5% FeO	No	49.2	21.6	70.8	3.7	4.5	8.2	20.9
5% FeO	Yes	56.1	21.9	78.0	3.4	2.8	6.2	15.7

octahedral and tetrahedral sites, which on reduction might lead to octahedral and tetrahedral Fe^{2+}. On the other hand, if the iron is initially in the ferrous state, and not subjected to pre-oxidation, its site preference might tend towards an octahedral environment; differences would therefore be expected in the Mössbauer spectra of C_3A containing FeO, depending on the pre-oxidation history of the sample. The existence of two distinctly different sites of four-fold co-ordination does not seem very likely in aluminoferrite, even if Fe^{2+} entered into the Ca^{2+} sites, since the Ca in C_4AF is in a site surrounded by an irregular array of seven O sites [12].

The most recent structural determination of C_3A [13] indicates that Al is present in two types of distorted tetrahedral sites, which are also the sites in which isomorphous replacement by Fe^{3+} should occur. On reduction, this would give rise to two types of four-co-ordinate Fe^{2+}. There is no indication, in the initial C_3A structure, of sites approaching a square-planar configuration, but bond lengths and angles could be modified by reduction, giving rise to the observed spectra. This interpretation has some interesting implications for the substitution of Fe^{2+} in the lattice, since by analogy with Mg^{2+} (or even Na^{+}) [4], it might be expected that Fe^{2+} isomorphously replaces Ca^{2+}. There are six types of Ca site in the C_3A structure [13], five of which are 6-co-ordinate to oxygen, and the sixth position irregularly co-ordinated to five near-neighbouring oxygens with three more distant oxygen neighbours. None of these sites appears likely to approximate to a four-fold site, and the similarity in the results for samples in which the iron is originally Fe^{2+} with those containing Fe^{3+} which was subsequently reduced suggests that Fe^{2+} might be isomorphously replacing tetrahedral Al rather than octahedral Ca.

Information on the distribution of the available iron in the various phases in reduced samples can be obtained from the areas under the various Mössbauer peaks, as fitted by the computer program. These data are shown in Table II. The following trends can be seen from Table II:

(a) For samples with identical starting concentrations of the same valency iron oxide, pre-oxidation tends to result in a higher ferrite concentration. Where metallic iron is formed in the reduction, its concentration is less in the pre-oxidized samples, suggesting that pre-oxidation gives rise to compounds which are less prone to reduction.

(b) There appears to be no systematic difference in the reduction behaviour of samples containing Fe_2O_3 and those containing FeO, but increasing the initial concentration of added oxide results in an increase of ferrite and in some cases iron metal content and a decrease in Fe^{2+} content. This suggests that the iron metal results from further reduction of the phase containing Fe^{2+}, i.e. the reduction proceeds in steps.

(c) The octahedral/tetrahedral ratio of the aluminoferrite phase is between about 0.4 and 0.7 for all samples except those in which reduction to metallic iron has occurred where the ratio assumes much higher values (between 2.5 and 3.5). This suggests that where extensive reduction has affected even the ferrite phase, the tetrahedral ferrite sites are the most readily reduced.

(d) The ratio (total Fe^{3+} in ferrite)/(Fe^{2+}) is about 1.3 to 1.7 in all samples except those reduced to metallic iron, where the ratio increases to between 4.7 and 12.6, supporting the conclusion of (b) that the metallic iron results principally from reduction of the phase containing Fe^{2+}.

(e) The ratio of the Fe^{2+} doublets varies in a random manner, although in pre-oxidized samples, the intensity of the tetrahedral component is in all cases higher than in unpre-oxidized samples. Both doublets appear to be equally affected by reduction.

3.2. X-ray examination of the fired samples

In addition to the X-ray peaks of C_3A, all the samples were found to contain minor amounts of aluminoferrite phases of differing crystallinity. Because of the low concentrations of these phases considerable difficulty was experienced in some cases in distinguishing precisely which ferrites were present, especially in the poorly crystalline samples. The phase compositions, determined by X-ray analysis, of samples containing 2 wt% and 5 wt% oxide additions (typical of the behaviour of the lower and higher additive levels) are shown in Table III, from which the following general points may be concluded:

(a) Under oxidizing conditions, C_4AF is predominantly formed in the samples containing FeO in contrast with the samples containing Fe_2O_3 in which one of the lower-iron aluminoferrite phases is formed.

(b) Under reducing conditions (including the cases where pre-oxidation has occurred before reduction) the tendency in samples containing both FeO and Fe_2O_3 appears to be towards the formation of ferrites as opposed to aluminoferrites. In some cases the presence of metallic iron was also noted under reducing atmospheres.

(c) The X-ray line half-widths of the ferrites and aluminoferrites appear to be independent of the firing atmosphere but dependant on the iron oxide used; the X-ray peaks of the phases resulting from the addition of FeO were all noticeably sharper than those occurring in the samples containing Fe_2O_3, in which ferrite phase development was so poor as to preclude positive identification in the samples of lower-iron concentration.

Estimates of the C_3A lattice parameter from measurements on the (12, 4, 0) reflection showed that in all samples containing iron, fired in air, irrespective of the initial valency of the added iron oxide, the undoped lattice parameter of 15.261 Å was slightly increased, reaching a maximum value of 15.265 Å between 0.5 wt% and 2.0 wt% of added oxide. The lattice expansion is consistent with the presence of Fe^{3+} in solid solution [4], but the measurements suggest that the concentration of solid solution is small (about 1.25 mol% Al^{3+} replaced, on the basis of a lattice parameter change of 0.0032 Å per mol% Al^{3+} replaced [4]). The upper limit of Al^{3+} replacement, reported previously, calculated on a similar basis, ranges from 5.3 mol% [4] to 10.3 mol% [3]. Clearly, in the present case, not all of the added iron is incorporated in the C_3A lattice, as is demonstrated by the concomitant appearance of ferrite and aluminoferrite phases. One difference between these experiments and those previously described is that in this work the iron was added as the oxide, without the addition of a compensating amount of CaO (either free or combined as ferrite). This apparently imposes constraints on the system, since direct replacement of Al^{3+} by Fe^{3+} should result in the expulsion of Al_2O_3 or the formation of aluminium-rich phases.

On the basis of the X-ray data, the reaction with Fe_2O_3 in air can be represented as

$$\begin{aligned} &3Ca_3Al_2O_6 + Fe_2O_3 \\ &\rightarrow Ca_6Al_4Fe_2O_{15} + Ca_3Al_2O_6^* , \end{aligned} \qquad (1)$$

where the asterisk denotes iron (III) in solid solution. The reaction with FeO in air can be

TABLE III X-ray identification of the phases present in C_3A samples fired with iron oxide additions at 1310° C for 2.0 h, under oxidizing and reducing conditions.

Wt %* of added oxide	Phases detected†		Pre-oxidized, then reduced.
	Oxidizing conditions	Reducing conditions	
2% Fe_2O_3	Aluminoferrite (tr, diff)	Aluminoferrite (tr, very diff)	Aluminoferrite (tr)
5% Fe_2O_3	C_6A_2F (?)	C_2F (tr) + Fe (s)	C_6A_2F (s) + C_4AF (tr, s) + Fe (tr)
2% FeO	C_4AF (s)	C_2F + Fe	C_2F (tr) + Fe (tr) (?)
5% FeO	C_4AF + C_2F (tr)	C_4AF (s) + Fe (tr)	C_4AF (s)

*In samples of lower added oxide concentration the ferrite phases were too weak and diffuse for identification.
†Key: s = sharp X-ray pattern; diff = diffuse X-ray pattern; tr = trace.

represented as

$$5Ca_3Al_2O_6 + 6FeO + \tfrac{3}{2}O_2 \rightarrow 3Ca_4Al_2Fe_2O_{10} + Ca_3Al_2O_6^* + Al_2O_3 . \quad (2)$$

Insufficient free alumina is formed to be detectable by X-ray diffraction methods and it may well be accommodated in the C_4AF phase.

Under reducing conditions, the lattice parameter of C_3A containing iron oxide contracted to 15.245 Å, a change that was again irrespective of the initial valency of the iron oxide. This contraction is consistent with the reported effect of divalent ion substitution in C_3A [4] (or, indeed, the substitution of ions of any valency other than Fe^{3+} [4]). An unexpected observation was that *pure* C_3A, heated under similar reducing conditions, underwent a lattice contraction from 15.216 Å to 15.254 Å, which would account for part but not all of the contraction in Fe^{2+}-doped C_3A. The nature of the changes induced in the undoped aluminate lattice by reducing conditions is not clear at present.

The lattice parameter behaviour of iron-containing C_3A under reducing conditions suggests that the ease with which the iron solid solution is reduced is independent of its initial valency. However, the appearance of various ferrites and aluminoferrites in the X-ray patterns of these samples (Table III) indicates that by no means all of the iron was reduced under these conditions, and, further, reduction of the iron in aluminoferrite is apparently more difficult than reduction of iron in solid solution in C_3A (a conclusion which supports the previous Mössbauer evidence). The presence of iron metal could result in some cases from partial reduction of the ferrite phases, since iron metal is known to be one of the reduction products [14].

4. Conclusions

(a) Under oxidizing conditions, mixtures of C_3A with FeO form predominantly C_4AF, by contrast with samples containing Fe_2O_3 which form less crystalline phases which are poorer in iron. Some ferric iron is also incorporated in the C_3A lattice under these conditions, as shown by an increase in the lattice parameter, irrespective of the initial valency state of the iron. The Mössbauer spectra of all the air-fired samples show only Fe^{3+} doublets characteristic of aluminoferrite phases, the octahedral site occupancy being greater in samples in which the iron was initially in the ferrous state.

(b) Under reducing conditions, ferrites are formed in preference to aluminoferrites, and a contraction in the C_3A lattice parameter is also observed which is due partly to an interaction of the C_3A itself with the firing atmosphere, and partly to replacement by Fe^{2+} of lattice Ca^{2+} or Al^{3+} (probably the latter). In some cases metallic iron is also formed, in the first instance from the Fe^{2+} in solid solution in C_3A, but more extensive reduction can also affect the ferrite phase, particularly in the tetrahedral sites. Prior oxidation of samples results in increased resistance to subsequent reduction. The Mössbauer spectra of the reduced samples can all be interpreted in terms of a pair of characteristic Fe^{3+} ferrite doublets and a pair of Fe^{2+} doublets, one of which corresponds to a tetrahedral site and the other to a distinctly different 4-co-ordinate site, possibly approaching a square-planar configuration.

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