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A Mössbauer study of the high-temperature reactions of iron oxides with calcium silicates

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The reactions of tricalcium silicate, beta-dicalcium silicate (larnite), and alpha-monocalcium silicate (pseudo-wollastonite) with 10 wt% Fe_2O_3 and FeO have been studied at 1300° C under both oxidizing and reducing atmospheres by Mössbauer spectroscopy and X-ray powder diffraction analysis. In air, tricalcium silicate forms γ-Ca_2SiO_4 and $Ca_2Fe_2O_5$ with both Fe_2O_3 and FeO but no Mössbauer or X-ray evidence was found for the formation of solid solutions of iron in tricalcium silicate. Under reducing conditions, metallic iron is formed, possibly via FeO. Neither β-dicalcium silicate nor α-monocalcium silicate form new phases with iron oxides under oxidizing or reducing conditions but, although the lattice parameters of the dicalcium silicate show little significant change after reaction, those of monocalcium silicate, particularly the a, b, α and β values, show greater variations. In all three silicates, but particularly in β-dicalcium silicate, oxidation followed by reduction results in the appearance of an unusual Mössbauer peak corresponding to a highly symmetrical iron site. The possible valence and location of this site is discussed.

1. Introduction

The incorporation of iron into cement mineral phases at high temperatures is of practical interest in studies of cement kiln chemistry, since such reactions, when they occur in clinkering, can influence the nature and relative proportions of the clinker phases formed, thereby influencing the practical properties of the product. Although the reactions of calcium aluminate phases with iron oxides to form alumino-ferrites have been the subject of several investigations (see for example the studies cited in [1]), less has been reported about the reactions of Fe_2O_3 and FeO with calcium silicate phases. At 1400 to 1500° C, Fe_2O_3 is said [2] to be soluble in tricalcium silicate to the extent of 1 wt%; in cement terminology, where $C = CaO$, $S = SiO_2$ and $F = Fe_2O_3$, the iron in solid solution is thought to exist as the hypothetical C_3F-phase [2]. The limit of solubility of Fe_2O_3 in tricalcium silicate has been confirmed as 1.1% at 1550° C by Woermann *et al.* [3], who suggest, however, that the Fe^{3+} substitutes for both Ca^{2+} and Si^{4+}. On the other hand, another study of the influence of Fe^{3+} on the structure of tricalcium silicate [4] has led to the slightly different conclusion that iron can either replace Ca or enter the structure interstitially.

Less is known about the effect of FeO on tricalcium silicate at high temperatures, although it has been suggested [5] that the presence of Fe^{2+} promotes decomposition to dicalcium silicate, in which it is soluble.

The solubility of Fe_2O_3 in α-dicalcium silicate is said to be 1.5 wt% at 1400° C, increasing to 2.5 wt% at 1500° C [6]. A different effect has been reported in β-dicalcium silicate which, on heating with > 2 wt% Fe_2O_3 for 5 h at 1450° C, was converted to the α'-form [7]. The interaction of FeO with dicalcium silicate is stated to stabilize the γ-form [8]. A Mössbauer examination [9] of γ-dicalcium silicate heated in air with 0.5 wt% FeO suggested that the iron had been oxidized to Fe(III); some conversion to Fe(IV) was also reported [9], but no spectra or Mössbauer parameters were presented to support this interesting contention. The *in situ* oxidation of Fe(II) is thought to encourage by some unspecified mechanism the complete inversion of the β- to γ-form

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on cooling [9]. Dicalcium silicate has also been reported to form a solid solution with FeO up to a limit of 4.6% FeO [7].

The interactions of iron oxides with the various monocalcium silicate polymorphs are less well documented, possibly because the latter do not commonly occur in cement clinkers. Hematite (Fe_2O_3) has been found to react with β-monocalcium silicate (wollastonite) below 1140° C to form an iron garnet [10], but no such reaction was found with the α-polymorph (pseudo-wollanstonite), which, being a higher-temperature form, occurs above the decomposition temperature of the iron garnet [10].

The aim of the present work was to investigate the reactions of Fe_2O_3 and FeO with tricalcium, dicalcium and monocalcium silicates under both oxidizing and reducing conditions, using X-ray powder diffraction analysis to identify the phases formed and to detect the formation of solid solution, the behaviour of the iron being monitored by Mössbauer spectroscopy. The present work was carried out at one temperature only, chosen to be below the melting temperature of the system in order to avoid the additional complication of a liquid phase.

2. Experimental procedure

The calcium silicates were synthesized from analytical-grade $CaCO_3$ and silicic acid mixed in the correct stoichiometric proportions, ground together, pressed into pellets and fired at 1300° C in platinum dishes. The grinding, pressing and firing steps were repeated several times, until the mixtures were found by X-ray powder diffraction analysis to be fully reacted. The C_3S thus prepared was found to occur in the triclinic form, but, contrary to expectations, the C_2S occurred in the monoclinic β-form. Although β-C_2S is metastable, resulting from the inversion of the higher-temperature α'-form and itself inverting to the γ-form when cooled below about 500° C [11], it can be stabilized by the presence of small amounts of impurities such as B_2O_3, Al_2O_3, or even residual CaO. Despite the strict precautions taken to exclude impurities from the synthesis, semiquantitative arc spectrographic analysis indicated the presence in this phase of up to 0.15 wt% boron, which may be sufficient to account for the stabilization of the β-form; alternatively, stabilization by CaO could well be occurring. The CS, as synthesized at 1300° C, was in the α-form (pseudo-wollastonite).

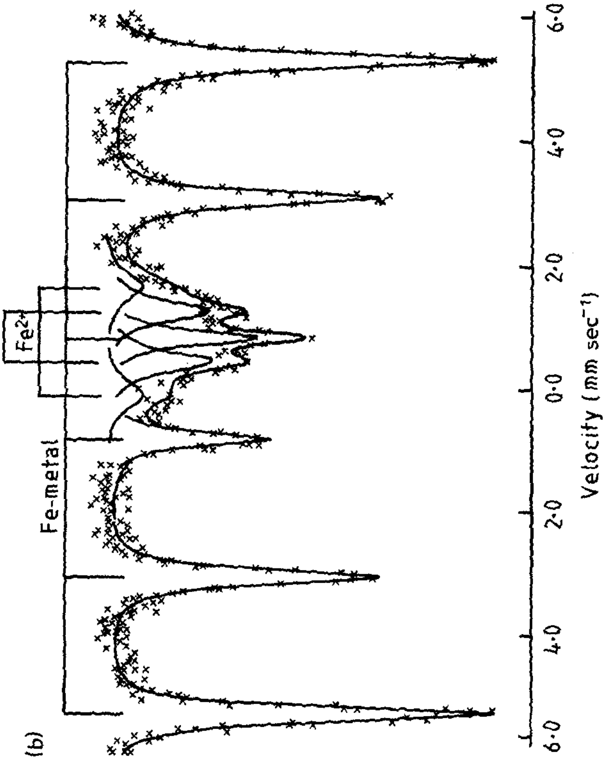
Additions of 10 wt% Fe_2O_3 and 10 wt% FeO were made to the calcium silicates and aliquots of the resulting well-blended mixtures were heated at 1300° C for 2.0 h in platinum-lined ceramic boats in an electric tube furnace both in ambient air and in a mixture of H_2/N_2 (5/95 V/V) flowing at $0.5\,l\,min^{-1}$. A set of experiments was also made in which samples heated in air for 2.0 h at 1300° C were then heated in the flowing H_2/N_2 for a further 2.0 h at 1300° C.

After reaction, the samples were examined by X-ray powder diffraction and Mössbauer spectroscopy techniques, as previously described [1]. All isomer shift values are relative to soft iron. The lattice parameters of the silicate phases were also determined from careful measurements of the angular positions of seven or more higher-angle X-ray reflections, using 10 wt% silicon powder as an internal standard. The parameters were computed using a programme by Evans *et al.* [12] in which the indexed observed reflections are compared with those computed from a set of assumed cell parameters, which are then progressively refined until a specified level of agreement is achieved between the observed and calculated data. The C_3S data were indexed on the basis of the triclinic structure of Yamaguchi and Miyabe [13], the β-C_2S data were indexed on the monoclinic cell of Midgley [14] (using J.C.P.D.S. card number 24–37) and the α-CS data were indexed on the basis of the triclinic cell of Heller and Taylor [15] (using J.C.P.D.S. card number 19–248). Samples for examination by scanning electron microscopy (SEM) were mounted on double-sided adhesive cellulose tape and coated with gold–palladium.

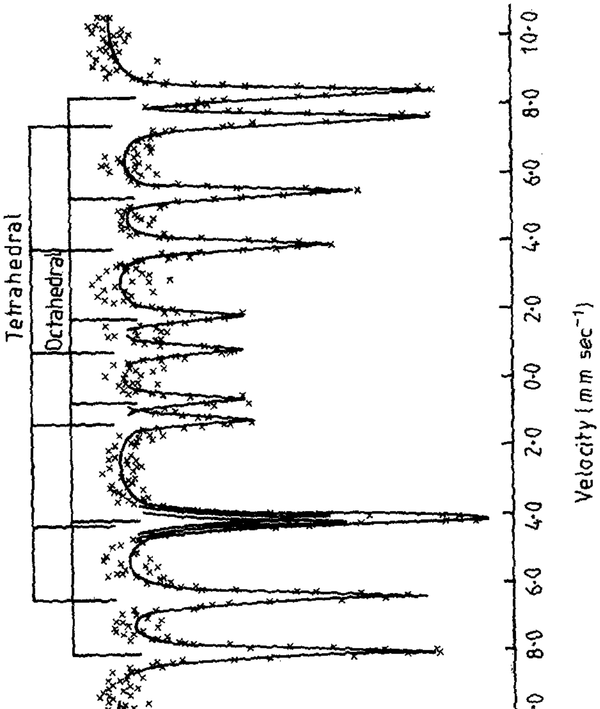
3. Results and discussion

3.1. Tricalcium silicate

X-ray diffraction shows that, in air, mixtures of C_3S with both Fe_2O_3 and FeO behave similarly, forming dicalcium ferrite (C_2F) and a little γ-C_2S. No evidence of residual Fe_2O_3 or FeO was detectable by X-ray diffraction analysis, indicating complete reaction with the large excess of C_3S, the diffraction pattern of which was strongly present in all samples. The Mössbauer spectra of the air-fired samples containing FeO and Fe_2O_3 were identical, showing two distinctive, partially-overlapping 6-line spectra (see Fig. 1a) which are identical with the spectrum of pure C_2F



(b)
Fe-metal
Fe2+
Fe2+
6·0
4·0
2·0
0·0
2·0
4·0
6·0
Velocity (mm sec-1)



(a)
Tetrahedral
Octahedral
10·0
8·0
6·0
4·0
2·0
0·0
2·0
4·0
6·0
8·0
10·0
Velocity (mm sec-1)

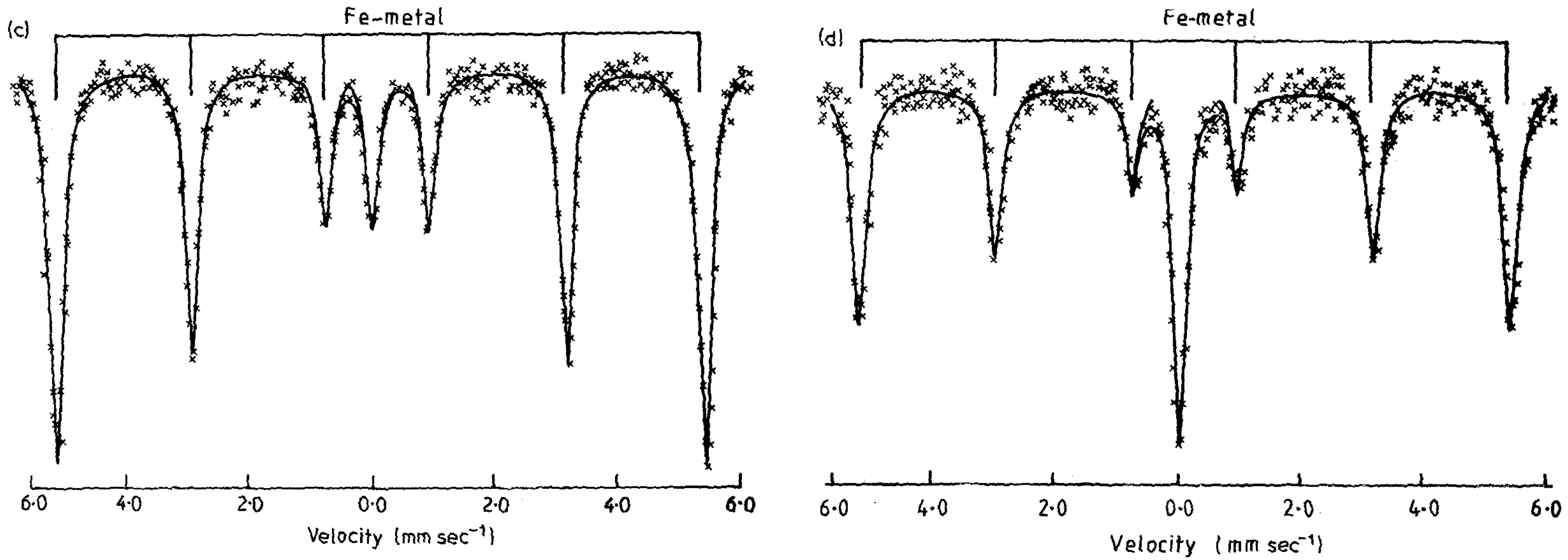


Figure 1 Typical room-temperature Mössbauer spectra of calcium silicates reacted with iron oxides at 1300° C for 2 h. Source: Co/Rh. (a) *C_3S* + 10 wt% Fe$_2$O, heated in air; (b) *C_3S* + 10 wt% FeO, heated in 5/95 (V/V) H_2/N_2, showing incomplete reduction; (c) *C_3S* + 10 wt% FeO, heated in air and then in 5/95 (V/V) H_2/N_2; and (d) *β-C_2S* + 10 wt% FeO, heated in air and then in 5/95 (V/V) H_2/N_2, showing strong development of symmetrical site.

synthesized from the oxides and shown by X-ray diffraction analysis to contain no detectable Fe_2O_3, CaO or other ferrite phases. An identical spectrum for C_2F has also been reported by Geller *et al.* [16], who assign the more widely-spread 6-line component to Fe^{3+} in the octahedral ferrite sites, the closer-spaced 6-line component being assigned to Fe^{3+} in the tetrahedral sites.

The crystal structure of C_3S contains Ca ions in 6-fold co-ordination [13], which is, however rather irregular. The silicon ions are in their usual tetrahedral configuration. If Fe^{3+} enters the C_3S structure in the manner proposed by previous workers, it may either substitute for both Ca^{2+} and Si^{4+} [3], or it may substitute only for Ca^{2+}, the charge balance being maintained by adjustments in interstitial site occupancy [4]. If either of these situations occurs, the resulting octahedral Fe^{3+}-sites should be distinguishable from the ferrite octahedral sites by Mössbauer spectroscopy, and, in the event of Si^{4+} substitution, an additional tetrahedral Fe^{3+} resonance should also be observed. The third possibility which has been suggested, the formation of hypothetical "C_3F" [2], should be apparent both from X-ray diffraction analysis and Mössbauer spectroscopy; if, as expected, its structure was similar to that of C_3A, the iron should occur in two types of distorted tetrahedral sites [1]. There is no evidence in the Mössbauer spectra of the present air-fired samples for the occupancy of any iron sites other than those of the well-defined C_2F phase, and attempts to fit additional peaks to these spectra completely failed. It therefore appears that, under the present experimental conditions, Fe^{3+} is not incorporated into the C_3S structure (although substitution by any or all of the previously proposed mechanisms at higher temperatures or under more rigorous conditions is clearly not ruled out by these results). The present conclusion that iron has not entered the C_3S lattice is further supported by the absence of significant changes in the measured cell parameters, discussed more fully in Section 3.4.

X-ray diffraction analysis again showed no differences between Fe_2O_3- and FeO-containing C_3S samples fired under reducing conditions; no Fe_2O_3, FeO or ferrite phases were detectable but in all samples metallic iron was found, in addition to C_3S. The Mössbauer spectra indicated metallic iron, with a possible very small trace of C_2F, which was, however, too weak to be satisfactorily computer-fitted. In one of the FeO-containing samples examined, reduction appeared to be less complete than in the others, and two additional doublets could be distinguished (see Fig. 1b). The more intense of these has an isomer shift, v_{IS}, of $1.05\,mm\,sec^{-1}$ and a quadrupole splitting, v_{QS}, of $0.84\,mm\,sec^{-1}$, and is thus rather similar to one of the doublets present in the FeO starting material ($v_{IS} = 1.02\,mm\,sec^{-1}$, $v_{QS} = 0.90\,mm\,sec^{-1}$ [1]). The less intense, broader doublet ($v_{IS} = 0.97$, $v_{QS} = 1.73\,mm\,sec^{-1}$) has parameters typical of tetrahedral Fe^{2+} and could therefore represent ferrous iron dissolved in a glassy phase, since such sites typically have rather broad spectra. Mössbauer parameters reported for Fe^{2+} in $CaO{-}SiO_2$ glass [17] fall in the range, $v_{QS} = 1.3$ to $2.0\,mm\,sec^{-1}$, $v_{IS} = 0.86\,mm\,sec^{-1}$ (recalculated with respect to soft iron). This agreement with the present parameters strengthens the possibility that the broader Fe^{2+} doublet may be identified with a glassy phase. Further, X-ray diffraction showed a broad, featureless band centred at a d-spacing of about $d = 0.45\,nm$, suggesting the presence of amorphous material in the reduced samples. This feature was absent from the X-ray traces of the oxidized samples and appears to be a consequence of reducing conditions. The absence of C_2S in the present reduced samples is contrary to a previous suggestion that Fe^{2+} promotes the formation of this phase from C_3S [5].

As discussed in more detail in Section 3.4, reduction does not significantly change the cell parameters of C_3S containing iron oxides and, by contrast with previous results for C_3A [1], heating pure C_3S in H_2/N_2 also has no effect on the cell parameters.

X-ray diffraction showed that oxidized samples subsequently heated under reducing conditions contain a little γ-C_2S and considerable amounts of CaO and Fe-metal, probably resulting from the decomposition of the C_2F formed in the oxidation stage, but of which no trace remained after subsequent reduction. No Fe_2O_3 or FeO was detected by X-ray diffraction. The Mössbauer spectra of these samples (shown in Fig. 1c) indicated the presence of Fe-metal, but contained an additional single peak with v_{IS} values in the range 0.10 to $0.12\,mm\,sec^{-1}$. This peak was approximately three times more intense in the FeO-containing samples (Table I) and is also observed in the Mössbauer spectra of both C_2S and CS, fired under similar conditions, the peak being particularly strong in the C_2S samples (see Sections 3.2 and 3.3 and Table I).

TABLE I Room-temperature Mössbauer results for calcium silicates plus 10 wt% iron oxides heated at 1300° C in air for 2.0 h, then at 1300° C in 5/95 (V/V) H_2/N_2 for 2.0 h. Six-line Fe-metal spectra omitted. Isomer shifts relative to Fe-metal

Silicate phase	Iron oxide	v_{IS}* ($mm\ sec^{-1}$)	Area ratio Fe(II)?/Fe metal
C_3S	Fe_2O_3	0.12	0.04
C_3S	FeO	0.10	0.10
β-C_2S	Fe_2O_3	0.10	0.16
β-C_2S	FeO	0.11	0.34
α-CS	Fe_2O_3	0.10	0.05
α-CS	FeO	0.11	0.06

*Isomer shift values derived from single-peak fits of the resonance assigned to the symmetrical site.

In all the spectra containing this peak, its linewidth was comparable with the Fe-metal calibration peaks, giving no reason to suspect the presence of a doublet; furthermore, in no case did the fitting of a doublet to this peak significantly improve the fit. This site apparently does not result from the oxidation of C_3S during the initial firing in air, since it does not appear in the Mössbauer spectra at that stage. It must therefore occur during the reduction step, but only in samples previously modified by oxidation.

The nature of this unusual peak requires comment; typically the species which have such small v_{IS} values are low-spin Fe(II) and Fe(III), Fe(IV), where spin, $s = 2$, and diamagnetic covalent species. Further, the absence of a quadrupole splitting suggests that the site is very symmetrical. Two other factors must also be taken into account when assigning this peak:

(i) the reducing conditions under which it is formed (militating against Fe(IV) or even Fe(III)); and

(ii) the fact that it is a site common to all three calcium silicates or their associated amorphous phases.

In view of (i), low-spin Fe(II) in a very symmetrical site is a possibility, although such a situation has not previously been identified in an oxide or silicate system; in all reported oxide systems, Fe^{2+} is high-spin. Comparison of the present spectrum with those of other oxide systems shows that Fe(II) occupying the tetrahedral sites of a normal $A^{II}B_2^{III}O_4$ spinel, such as FeV_2O_4 or $FeCr_2O_4$, has no resolvable quadrupole splitting, but shows a room-temperature v_{IS} value of $0.82\ mm\ sec^{-1}$ with respect to natural iron [18], a value rather larger than the present v_{IS} values. A closer similarity to the present spectrum is shown by the room-temperature spectrum of Fe(IV) in $SrFeO_3$, which consists of a single peak of $v_{IS} = 0.055\ mm\ sec^{-1}$ relative to Fe-metal [19]. The reported formation of Fe(IV) from γ-C_2S when heated in air with 0.5 wt% FeO has already been mentioned [9], but a similar result is difficult to envisage under reducing conditions.

Factor (ii) above, is significant when considering the possible location of this unusual iron site; since X-ray diffraction analysis does not indicate the presence of any detectable new phase common to all three calcium silicates, the site must occur either in the silicates themselves or in the amorphous phase which is particularly apparent under reducing conditions. Both C_3S and β-C_2S contain 6-co-ordinate Ca sites, which probably also occur in α-CS, although the details of this structure have not been worked out. Although these sites would seem the most appropriate for Fe^{2+} substitution, they are too distorted in the pure phases (particularly C_3S) to give rise to the observed singlet peak, unless the substitution of the slightly smaller Fe^{2+} enables the site to become more regular. If such an effect occurs, it has virtually no influence on the cell parameters of C_3S, and only a slight influence on those of β-C_2S (see Section 3.4).

The alternative possibility, that the site is a tetrahedral one occurring in the amorphous phase is not attractive; if the peak is fitted to a doublet, its parameters ($v_{IS} = 0.10$ to $0.12\ mm\ sec^{-1}$, $v_{QS} = 0.09\ mm\ sec^{-1}$) are small, even for tetrahedral Fe(III). Further, the reported line-widths of Mössbauer iron resonances in glasses [20] are characteristically broader than the present peak. Thus, although the present results do not allow an unambiguous interpretation, the tentative identification of this Mössbauer peak with Fe(II) in a highly symmetrical site in the crystalline silicate phase may have slightly greater merit.

Examination of the various samples by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX) microprobe provides some further information on the nature of the phase in which this unusual site occurs; in all three silicates heated in air, there is evidence of closer association of the iron and silicate phases than the discrete silicate/ferrite or silicate/iron oxide assemblages indicated by the X-ray and Mössbauer results. Subsequent reduction of these oxidized samples produces no common Ca–Si–Fe phase of distinctive composition, although all three silicates show evidence of regions in which Ca, Si and Fe coexist. The elemental proportions of these regions differ widely in the three silicates, however, being extremely Ca-rich in C_3S, Fe-rich in β-C_2S and both Ca- and Fe-rich in α-CS. The occurrence of these regions of mixed composition appears to carry over from the oxidation step since, in samples reduced directly without pre-oxidation, no such mixed regions could be found; moreover, these directly-reduced samples do not show the single-line Mössbauer resonance. However, if, as the SEM/EDAX results might suggest, this resonance is associated with crystalline regions containing Ca, Si and Fe^{2+}, the sharpness of the resonance is surprising in view of the variations in the composition of these regions and the apparent absence of a diagnostic crystalline phase.

3.2. β-dicalcium silicate (larnite)

X-ray diffraction of the pure silicate phase, heated in air at 1300° C for 2.0 h, showed it to contain predominantly the β-polymorph, with a small amount of γ-C_2S, and a little cristobalite also detectable. Heating the pure silicate phase in the H_2/N_2 mixture at 1300° C resulted in a slight decrease in the amounts of γ-C_2S and cristobalite.

When fired in air at 1300° C, samples containing either Fe_2O_3 or FeO melted, the melting being more complete in the former. X-ray diffraction showed no γ-C_2S or cristobalite present, the only identifiable phases being β-C_2S and Fe_2O_3, with evidence of a small amount of amorphous material. A previous finding [8] that FeO stabilizes the γ-form of C_2S is not confirmed by these results. The Mössbauer spectra showed only the 6-line features of Fe_2O_3, with no evidence for either the Fe(III) or Fe(IV) sites previously reported [9] to develop in γ-C_2S heated in air with FeO. As discussed later (see Section 3.4), significant changes in the cell parameters were not found either in oxidized or reduced samples, although slightly more significant changes were recorded in the samples which were oxidized and subsequently reduced.

Melting did not occur in samples fired in the H_2/N_2 gas mixture, in which the only phases detectable by X-ray diffraction analysis were β-C_2S and Fe-metal. The presence of the latter was confirmed by the Mössbauer spectra, which showed no other features. Similar phase compositions were also found in oxidized samples which had subsequently been reduced; the X-ray traces also indicated a certain amount of amorphous material in these samples and minor intensity changes in the β-C_2S lines were noted. The Mössbauer spectra of these samples contained, in addition to the metallic iron spectrum, the unusual single peak noted in C_3S (see Fig. 1c). As with C_3S, this peak was particularly strong in the FeO-containing specimens (see Fig. 1d) and in both FeO and Fe_2O_3-containing specimens (see Fig. 1d); in both FeO- and Fe_2O_3-containing samples the peak was at least four times as strong as it was in C_3S (see Table I). As with C_3S, this peak was not significantly better fitted by a doublet. The increased strength of this peak compared with that in C_3S suggests that the structure of larnite, which contains, in addition to octahedral Ca, irregular 8-co-ordinate Ca-sites, might facilitate the formation of the unusually symmetrical iron site; this observation however yields little further insight on the nature of this species or its formation mechanism.

3.3. Alpha-monocalcium silicate (pseudo-wollastonite)

X-ray diffraction showed that samples heated in air contained only α-CS and Fe_2O_3, irrespective of the initial valency of the iron oxide. The Mössbauer spectra showed only the characteristic hematite spectrum. Samples heated in the H_2/N_2 gas mixture contained only Fe-metal, in addition to α-CS, while in samples reduced after prior oxidation, similar results were found as for β-C_2S, the intensity of the central singlet peak of the Mössbauer spectra being, however, more similar to those found in C_3S (see Table I). Again, this peak was slightly stronger in samples originally containing FeO.

Although the Mössbauer spectroscopy and X-ray diffraction analysis results suggest that α-CS containing Fe_2O_3 or FeO behaves very similarly to β-C_2S, the measured cell parameters. indicate larger changes in α-CS. The cell parameter measurements are now discussed in more detail.

3.4. Changes in the cell parameters of the silicate phases

For the triclinic cells, C_3S and α-CS, the computer program [12] calculates from each measured data set values of the cell lengths a, b and c, the cell angles, α, β and γ and the cell volume. For monoclinic β-C_2S, the program computes all the para-

TABLE II Percentage changes in the cell volumes of C_3S, β-C_2S and α-CS resulting from reaction with 10 wt% iron oxides at 1300° C for 2.0 h. A positive change indicates cell expansion

Iron oxide	Firing atmosphere	Change in cell volume (%)		
		C_3S	β-C_2S	α-CS
None	air	–	–	–
None	5/95 (V/V) H_2/N_2	0.05*	0.14*	−0.01*
Fe_2O_3	air	0.05*	−0.13*	−1.10*
FeO	air	−0.05*	−0.02*	−0.31*
Fe_2O_3	5/95 (V/V) H_2/N_2	−0.05†	−0.01†	1.36†
FeO	5/95 (V/V) H_2/N_2	−0.06†	0.01†	−1.22†
Fe_2O_3	air, then 5/95 (V/V) H_2/N_2	−0.04†	−0.44†	0.63†
FeO	air, then 5/95 (V/V) H_2/N_2	−0.14†	−0.26†	6.09†
Fe_2O_3	air, then 5/95 (V/V) H_2/N_2	0.01*	−0.31*	0.61*
FeO	air, then 5/95 (V/V) H_2/N_2	−0.09*	−0.13*	6.08*

*Referred to pure phase heated in air.

†Referred to pure phase heated in H_2/N_2.

meters except α and γ, which are set at 90°. Although it is possible to directly compare the measured cell constants with the literature values which were used as a starting point in the calculations [13–15], a more meaningful comparison can be made between the parameters of the iron-containing material and those of the pure phases heat-treated under the same conditions. Since all the measured parameters vary differently, an overall impression of the changes can be obtained from the percentage changes in the cell volumes. These changes in all volumes are shown in Table II for all three silicates.

The following points emerge from the results given in Table II:

(1) A negligible change is produced in the cell volume of C_3S by heating with iron oxides under oxidizing or reducing conditions. Slightly larger changes are found in β-C_2S, but the largest changes are found in α-CS.

(2) For all three silicates, some of the largest changes are found in the reduced samples which had first been oxidized; these are also the samples which contain the unusual Mössbauer peak. However, no relationship appears to exist between the intensity of this peak and the degree of change in the cell volume, since α-CS, which shows the greatest volume change has a weak Mössbauer peak, while β-C_2S, with only a small volume change, shows a very strong Mössbauer peak.

(3) There is no clear relationship between the initial valence of the iron oxide or the reaction atmosphere and the tendency of the cell to expand or contract. This may be due to the fact that the cell volume reflects the mean of changes in all parameters.

(4) Heating the pure silicate under reducing conditions has little effect on the cell constants in any case, unlike the effect noted when pure C_3A is reduced [1].

A further question is the degree to which the changes noted in Table II are significant. Although a rigorous treatment of the effect of measurement errors on the calculated cell constants has not been made, examination of the individual parameters for C_3S indicates differences of typically 0.004 to 0.04%. As stated in Section 3.1, these changes are considered too small to be significant, but they also suggest that the reproducibility of the measurements must be at least as good as this, since determinations on many different samples gave constants which were in agreement to this extent. The individual parameters for the β-C_2S samples indicate a similar agreement except those for samples which were oxidized and then subsequently reduced; the cell dimension changes in these samples could possibly be significant. In the case of α-CS, the greatest differences are found in the a, b, α and β parameters, the changes in c and γ being much smaller, and probably not significant. These results suggest that iron probably does not enter C_3S or β-C_2S under the present reaction conditions (or alternatively, enters in such a way as not to distort the structure). This latter possibility is not supported by the Mössbauer results. By contrast, α-CS is comparatively more modified by reaction with iron oxides, but a detailed atomistic or mechanistic discussion awaits a full determination of the crystal structure of α-CS.

4. Conclusions

(a) Under oxidizing conditions, C_3S reacts with either FeO or Fe_2O_3 at 1300° C, forming C_2F and γ-C_2S by a reaction of the type

$$2Ca_3SiO_5 + Fe_2O_3 \rightarrow Ca_2Fe_2O_5 + 2Ca_2SiO_4. \quad (1)$$

Neither the Mössbauer spectra nor the cell parameters of the remaining C_3S show any evidence of significant iron substitution in C_3S under these conditions. In reducing atmospheres, the iron oxides are reduced to the metal, possibly *via* FeO. In incompletely reduced samples there is also Mössbauer evidence for the entry of some Fe^{2+} into the glassy phase which forms under these conditions. Again, there is no evidence of the entry of iron into the C_3S. In samples which are first oxidized and then reduced, the C_2F formed in the initial oxidation (see Equation 1) is reduced to iron metal and CaO, with the γ-C_2S formed by Equation 1 remaining unchanged. The cell parameters of the C_3S are again virtually unchanged by this heat treatment.

(b) Under oxidizing conditions, no new phases are formed by reaction between iron oxides and either β-C_2S or α-CS. Under reducing conditions, iron metal is formed, but no other phases are observed. A similar result is found for samples initially oxidized, then subsequently reduced. These heat treatments produce little change in the β-C_2S cell parameters, but changes in the parameters of α-CS are more marked, particularly in the a, b, α and β parameters.

(c) In all three silicates, but particularly in β-C_2S, oxidation followed by reduction results in the appearance of an unusual Mössbauer peak with $v_{IS} = 0.10$ to $0.12\,\text{mm sec}^{-1}$ and no resolvable quadrupole splitting. In all three silicates, this peak was stronger in samples where the iron oxide was originally FeO. Although an unambiguous assignment of this peak cannot be made, its parameters and the circumstances of its formation suggest that it may represent Fe(II) in an extremely symmetrical site, which, from the narrow linewidth, probably occurs in a crystalline silicate phase rather than in the amorphous phase found in all the reduced samples.

SEM and EDAX microprobe investigations suggest that this unusual site might be associated with crystalline regions containing Ca, Si and Fe^{2+}, rather than with a discrete crystalline phase of fixed composition.

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