Exploring the Composition and Structure of Triclinic SFCA-I

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The synthesis and characterisation of SFCA-I compounds has been performed. SFCA-I is one of the key bonding phases in iron ore sinter, influencing physical properties such as strength, reducibility, and strength degradation during reduction. The results reported herein extend the understanding of the solid solution limits of the SFCA-I phase, with the synthesis of single-phase SFCA-I materials containing 2.71, 3.23 and 3.73 mass% Al₂O₃. These materials contain less Al₂O₃ than any previously reported SFCA-I compounds. The results also confirm the low tolerance of the SFCA-I structure for SiO₂, and a low tolerance for the variation of the CaO concentration. Finally, the results confirm that the SFCA-I structure accommodates more FeO than the related sinter phase SFCA.

KEY WORDS: iron ore sinter; SFCA-I; FeO content; unit cell volume.

1. Introduction

‘SFCA’ (Silico-Ferrite of Calcium and Aluminium) phases are key bonding materials within industrial iron ore sinter. Sinter is utilised extensively worldwide in the production of steel from iron ore and typically constitutes more than 60% of the ferrous burden in modern blast furnaces in Japan and most of the blast furnaces in Europe. The compositional, structural and/or textural characteristics of the ‘SFCA’ phases described in the literature – SFCA (triclinic crystal structure), SFCA-I (triclinic), SFCA-II (triclinic) and Fe-rich SFCA – have been reviewed recently. Mumme and Gable have also recently reported the crystal structures of the monoclinic variants of SFCA-I and SFCA-II, and Kahlenberg et al. has reported the structural elucidation of triclinic and monoclinic SFCA-III. This paper focusses on the triclinic variant of SFCA-I, which, along with triclinic SFCA, is one of the two ‘SFCA’ phases commonly observed in industrial iron ore sinter.

Mumme et al. reported that a triclinic SFCA-I (M₂₀O₂₈) phase in industrial sinter contained 84 mass% Fe₂O₃, 13 mass% CaO, 1 mass% SiO₂ and 2 mass% Al₂O₃, and also synthesised Si-free triclinic SFCA-I which had the composition Ca₃₂Fe²⁺₀.₉Fe³⁺₁₄.₇Al₁₃O₂₈. They also reported that another synthetic composition – 82.6 mass% Fe₂O₃, 13.6 mass% CaO, 1.7 mass% SiO₂ and 2.1 mass% Al₂O₃ – had the triclinic SFCA-I structure when reacted at 1 523 K. Other synthetic triclinic SFCA-I compounds reported in the literature are all Si-free and their compositions are reported in Table 1. The SFCA-I structure appears to accommodate a significant amount of substitution of Al₂O₃ for Fe₂O₃, with a corresponding decrease in unit cell volume.

Interestingly, the evidence available to date suggests that triclinic SFCA-I contains more FeO in its structure than triclinic SFCA. Studies involving chemical methods (i.e., titration) indicate that SFCA-I contains ~1.8 mass% FeO, compared to ~0.4–1.0 mass% for SFCA. This may be considered counter-intuitive given that SFCA-I is stable at lower temperature (i.e., more oxidising) conditions during sintering, compared to SFCA. Indeed, SFCA-I is consistently observed as the lower-temperature phase, relative to SFCA, during in-situ X-ray diffraction (XRD)-based studies of SFCA and SFCA-I phase formation mechanisms and the effect of various sinter parameters (e.g., basicity, alumina source, titanium concentration) on them. In addition, whilst triclinic SFCA-I appears to accommodate a significant amount of substitution of Al₂O₃ for Fe₂O₃, it is unclear what the effect of variation of Ca and Si content would be on the equilibrium phase assemblages. A series of phase equilibria experiments with ex-situ XRD phase characterisation have been performed here to improve the understanding of SFCA-I in terms of its FeO, Si and Ca content.

2. Experimental

2.1. Phase Equilibria Experiments

Table 2 shows the nominal composition of each mixture (in terms of weighed mass% of oxides). The compositions of Samples 1 and 2 were designed to replicate the Si-free, and Si-containing SFCA-I compositions reported by Mumme et al. The compositions of Samples 3 to 5 were designed...
The mixtures were prepared from fine grained synthetic hematite, Fe₂O₃ (Acros Organics, 99.999%); calcite, CaCO₃ (Thermo Fisher, 99.95%); quartz, SiO₂ (Sigma Aldrich, 99.995%); and gibbsite, Al(OH)₃ (Alcan OP25 Super White, 99.9%). Weighed powders were mixed by hand in acetone using a mortar and pestle to ensure homogeneity. Mixed powders were pelletised and heated for 24 hr in a platinum crucible in a vertical tube furnace in air at 1513 K. Based on in-situ XRD work performed in air, this temperature was considered to be close to the maximum achievable before melting of SFCA-I occurred. Samples were air quenched and then crushed, ground, repelletised, heated at 1513 K for an additional 24 hr and then air quenched to produce the final sample. A small piece of each sample was collected and prepared as a resin-impregnated polished microscope mount for ex-situ characterisation using scanning electron microscopy (SEM) and electron probe micro-analysis (EPMA). The remainder was crushed and ground for XRD and titrimetric analyses. It should be noted that XRD analysis was also performed for each sample after the initial 24 hr heating, and each sample was confirmed to be at equilibrium after the additional 24 hr heating because the XRD patterns collected after 24 hr and 48 hr heating were identical. In addition, the compositions of all samples were uniform (i.e., low standard deviation) when probed using EPMA which also confirms that equilibrium had been reached.

### 2.2. Characterisation

XRD data were collected in Bragg-Brentano geometry over the range 5° ≤ 2θ ≤ 140° using a Panalytical Empyrean instrument fitted with a cobalt long-focus X-ray tube operated at 40 kV and 40 mA, a BBHD incident beam optic, and a PIXcel Si strip detector used in scanning line (1D) mode with an active length of 3.3482° 2θ. Rietveld refinement-based quantitative phase analysis (QPA) of the XRD data was performed using Topas (Version 6, Bruker AXS). The crystal structure data of Mumme et al., Liles et al. and Blake et al. were used as starting parameters in the refinement for SFCA-I, SFCA and hematite, respectively. For unit cell parameter refinement of single-phase SFCA-I materials, samples were mixed with NIST 640c silicon internal standard. SEM was performed using a FEI Quanta 400 field emiss-
sion environmental SEM (FEI Corporation, Hillsboro, OR) operated at an accelerating voltage of 20 kV and a working distance of 10 mm. EPMA was performed using a JEOL JXA-8500F Hyperprobe (JEOL Ltd., Tokyo, Japan). Hematite (Fe₂O₃), wollastonite (CaSiO₃), and “Magalox” (a synthetic spinel, composition MgAl₂O₄) were used as standards for the microprobe analyses that were conducted in wavelength dispersive mode using an accelerating voltage of 15 kV, a beam current of 20 nA, a beam diameter of 5 μm, and peak and background counting times of 15 sec. Due to possible differing Fe²⁺/Fe³⁺ ratios in the samples, oxygen was directly measured in all samples using hematite as the standard for oxygen.

For determination of FeO content, the materials were dissolved with hydrofluoric and hydrochloric acids. The resulting solutions were then titrated to the electrochemical equivalence point against a standard dichromate solution using a 798 Metrohm MPT Titriuto autotitrator. The FeO content was calculated from the titre volumes.

3. Results and Discussion

Figure 1 shows the final Rietveld fits to the XRD data collected for Samples 1 (Si-free composition) and 5 (1.50 mass% SiO₂), and Fig. 2 shows the results of the XRD-based QPA for all samples. Based on the outcomes of the work of Harano et al., we consider the QPA results of multiphase samples to be accurate to within ± 3 mass%. Here we found that Samples 1 and 2 did not form pure triclinic SFCA-I when equilibrated in air at 1 513 K, although...
Sample 1 only contained a minor amount of hematite (3 mass%) in addition to SFCA-I. Sample 2, in contrast, contained a significant amount of SFCA (61 mass%). Samples 3-5 demonstrate that with progressively higher SiO\textsubscript{2} additions, a progressively higher amount of SFCA is formed at the expense of SFCA-I. Even at only 0.5 mass% addition of SiO\textsubscript{2} (i.e., Sample 3) a significant amount of SFCA is formed (21 mass%). The triclinic SFCA-I structure, therefore, has little tolerance for the incorporation of Si. The effect of varying CaO concentration below ~13 mass% was to form progressively higher amounts of hematite, in addition to the SFCA-I, due to an excess of FeO. The effect of increasing CaO concentration above ~14.5 mass% requires additional work, although Kahlenberg et al. suggest that incorporation of more than about 7 atoms per formula unit of the large Ca\textsuperscript{2+} into the octahedrally coordinated positions is probably not compatible with the short M-O bond distances.\textsuperscript{10}

Based on the XRD results, several of the samples – 12–15, 20, and 27–28 – produced single-phase triclinic SFCA-I after equilibration in air at 1513 K, and the EPMA and titration-determined compositions of the SFCA-I materials are shown in Table 3. Several of the compositions approximate those in Table 1, however the compositions of Samples 20, 27 and 28 indicate that the SFCA-I structure is stable at Al\textsubscript{2}O\textsubscript{3} concentrations below the 4.7 mass% level of the Mumme et al. specimen shown in Table 1.\textsuperscript{4} The measured Al\textsubscript{2}O\textsubscript{3} concentrations of Samples 20, 27 and 28 were 3.73, 3.23 and 2.71 mass%, respectively (Table 3). Additional work could involve further probing the low, and high, Al\textsubscript{2}O\textsubscript{3} concentration limits of SFCA-I. However, Kahlenberg et al. observed that a mixture with nominal composition Ca\textsubscript{8}Al\textsubscript{0.8}Fe\textsubscript{31.2}O\textsubscript{56} (i.e., 1.4 mass% Al\textsubscript{2}O\textsubscript{3}) contained the α-CFF phase (nominal composition Ca\textsubscript{3.4}Fe\textsubscript{14.3}O\textsubscript{25})\textsuperscript{19} in addition to SFCA-I,\textsuperscript{10} and so the lower limit for Al\textsubscript{2}O\textsubscript{3} concentration appears to be in the range 1.4–2.7 mass%.

Kahlenberg et al. also speculated on whether there exists an upper limit of the Al\textsubscript{2}O\textsubscript{3} solubility in SFCA-I, and recently demonstrated that the alumina-rich starting composition Ca\textsubscript{8}Al\textsubscript{16}Fe\textsubscript{16}O\textsubscript{56} (32 mass% Al\textsubscript{2}O\textsubscript{3}) formed the SFCA-II-type phase rather than SFCA-I.\textsuperscript{20} Therefore, the upper limit for Al\textsubscript{2}O\textsubscript{3} concentration in the SFCA-I structure is likely to be in the range 23–32 mass%.

The SFCA-I material does accommodate minor amounts of SiO\textsubscript{2} (~0.10–0.15 mass%) which, along with MgO, is contamination from the high-temperature synthesis. The Zoll et al. compound in Table 1 indicates that the SFCA-I structure accommodates a reasonable amount of MgO, which probably substitutes for FeO based on charge balance and cation size considerations. An affinity of the SFCA-I structure for MgO has been noted previously,\textsuperscript{21} whereas one of the other common impurity cations, Ti\textsuperscript{4+}, appears to be more readily accommodated by SFCA.\textsuperscript{14} A minor amount of hematite was detected during SEM examination of Sample 16 (Fig. 3). It should be noted the morphology of the SFCA-I phase in Fig. 3 did not match that reported for SFCA-I (i.e., platy); this may be due to the pellets being compacted using a die press before heating and the material

![Fig. 3. Backscattered scanning electron micrographs of the products of the heat/quench experiments performed for Samples (a) 16 and (b) 28. A very small grain of hematite is observed as a region of white in (a).](image)

**Table 3.** Average composition in mass% oxides, determined by EMPA and by titration (FeO), of the SFCA-I in Samples 12, 14, 15, 20, 27 and 28. The numbers in parenthesis are the standard deviation of the 40 point analyses performed for each sample. Also shown are the refined unit cell parameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>FeO\textsubscript{2}</th>
<th>FeO</th>
<th>CaO</th>
<th>SiO\textsubscript{2}</th>
<th>Al\textsubscript{2}O\textsubscript{3}</th>
<th>MgO</th>
<th>Total</th>
<th>S.G.</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
<th>Vol. (Å\textsuperscript{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>79.61 (25)</td>
<td>1.89</td>
<td>12.76 (11)</td>
<td>0.13 (2)</td>
<td>4.73 (11)</td>
<td>0.07 (2)</td>
<td>99.83 (27)</td>
<td>P-1</td>
<td>10.4241</td>
<td>10.6060</td>
<td>11.8329</td>
<td>94.151</td>
<td>111.322</td>
<td>110.259</td>
<td>113.5</td>
</tr>
<tr>
<td>14</td>
<td>78.69 (24)</td>
<td>1.83</td>
<td>13.15 (10)</td>
<td>0.11 (2)</td>
<td>5.25 (10)</td>
<td>0.07 (2)</td>
<td>99.08 (29)</td>
<td>P-1</td>
<td>10.4254</td>
<td>10.6100</td>
<td>11.8432</td>
<td>94.158</td>
<td>111.289</td>
<td>110.278</td>
<td>115.1</td>
</tr>
<tr>
<td>15</td>
<td>77.43 (23)</td>
<td>1.98</td>
<td>13.33 (16)</td>
<td>0.10 (1)</td>
<td>6.18 (10)</td>
<td>0.08 (2)</td>
<td>99.12 (24)</td>
<td>P-1</td>
<td>10.4228</td>
<td>10.6063</td>
<td>11.8347</td>
<td>94.176</td>
<td>111.305</td>
<td>110.240</td>
<td>113.7</td>
</tr>
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<td>20</td>
<td>80.38 (32)</td>
<td>1.83</td>
<td>12.92 (32)</td>
<td>0.14 (2)</td>
<td>3.73 (08)</td>
<td>0.07 (2)</td>
<td>99.03 (24)</td>
<td>P-1</td>
<td>10.4261</td>
<td>10.6119</td>
<td>11.8421</td>
<td>94.140</td>
<td>111.304</td>
<td>110.298</td>
<td>115.0</td>
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<tr>
<td>27</td>
<td>80.79 (21)</td>
<td>2.17</td>
<td>12.65 (7)</td>
<td>0.13 (2)</td>
<td>3.23 (7)</td>
<td>0.06 (3)</td>
<td>99.06 (23)</td>
<td>P-1</td>
<td>10.4345</td>
<td>10.6150</td>
<td>11.8485</td>
<td>94.139</td>
<td>111.305</td>
<td>110.296</td>
<td>116.9</td>
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<tr>
<td>28</td>
<td>81.16 (22)</td>
<td>2.07</td>
<td>12.87 (10)</td>
<td>0.13 (2)</td>
<td>2.71 (10)</td>
<td>0.06 (2)</td>
<td>99.04 (21)</td>
<td>P-1</td>
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<td>10.6223</td>
<td>11.8652</td>
<td>94.132</td>
<td>111.251</td>
<td>110.343</td>
<td>119.5</td>
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</table>

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which formed was a dense sintered mass.

The likely lower limit of Al₂O₃ concentration in SFCA-I (i.e., 1.4–2.7 mass%), and the low level of SiO₂ solubility (~0.15 mass%), is worthy of discussion in the context of the in-situ XRD analysis of Scarlett et al.²²,²³ There, in an alumina-free mixture designated Al0 by the authors and designed to form the Al₂O₃-free form of triclinic SFCA, SFC, SFCA-I was identified as forming, along with SFC, above ~1 400 K and through reaction of Fe₂O₃ with calcium ferrite (i.e., CaO·Fe₂O₃, or CF). The compositional limits of SFC were probed by Pownceby and Patrick²⁴ and more recently by Cheng et al.,²⁵ and the crystal structure by Ding and Guo.²⁶ Upon annealing of this SFCA-I at 1 488 K for more than 15 min it had completely converted to SFC.

It may be that Al₂O₃-free SFCA-I is a metastable phase. Another possibility is that in the experiment performed for the Al0 mixture, the peaks assigned to SFCA-I were, instead, due to the formation of α-CFF. We note that in their investigation of the formation process of SFC from calcium ferrite, Ding and Guo observed α-CFF in addition to SFC after reaction of Fe₂O₃, SiO₂ and CF in air at 1 473 K.²⁶ XRD data collected during in-situ experimentation are, generally, of lower quality in terms of peak resolution and signal-to-noise ratio when compared with ex-situ data collected using conventional diffractometer configurations. In addition, the available 2θ range is, generally, smaller during in-situ experimentation due to geometric constraints imposed by using a reaction cell. Therefore, it is not inconceivable that the SFCA-I phase was misidentified, and it should be noted that SFCA-I and α-CFF have overlapping peaks at d-spacings of 3.23, 3.16 and 2.89 Å. These are within the d-spacing/2θ range most useful for characterising phase decomposition, formation and transformation throughout the whole iron ore sintering reaction between 298 and ~1 623 K. Additional in-situ XRD analysis of Al₂O₃-free materials to confirm either the formation of Al₂O₃-free SFCA-I, or α-CFF, under dynamic conditions should be carried out in future. Synchrotron-based experimentation, which affords greater peak resolution and peak-to-background ratio than laboratory-based instrumentation, may be necessary.

The FeO-content results shown in Table 3 confirm that SFCA-I synthesised in air at 1 513 K contains between 1.7 and 2.2 mass% FeO. Patrick and Pownceby, in their phase equilibria study of the stability of SFCA in air in the range 1 513–1 663 K, determined that for single-phase SFCA materials equilibrated at 1 513 K the FeO content was 0.4 to 0.8 mass%. For single-phase SFCA materials equilibrated at higher temperatures (1 573–1 633 K) the FeO content was 0.8 to 1.0 mass%.²⁷ Pownceby and Patrick, in their phase equilibria study of the stability of SFC, determined that for single-phase SFC materials synthesised at 1 523 K the FeO content was 0.5 to 0.8 mass%.²⁸ These results, therefore, appear to confirm that SFCA-I accommodates more FeO in its structure than SFCA (and SFC), even though SFCA-I is the lower temperature phase.

Finally, in addition to the EPMA and FeO results, Table 3 shows the refined unit cell parameters for each of the single-phase SFCA-I materials synthesised as part of this study. Figure 4 shows the evolution of the unit cell volumes of these six SFCA-I materials as a function of Al/Fe Tot ratio. Also included in the plot are the unit cell volume vs Al/Fe Tot ratio for the nine SFCA-I materials in Table 1. The plot for the Kahlenberg et al.,³ samples is essentially linear \( (R^2 = 0.98) \). The plot for the samples synthesised as part of the current study deviates further from linearity \( (R^2 = 0.65) \), and the trendline is at lower unit cell volumes than the trendline for the Kahlenberg et al. samples. What should also be considered, however, is i) the positions of the points for the Zoll et al., Mumme et al. and Arakcheeva et al. samples in Fig. 4, relative to the trends observed for the current, and the Kahlenberg et al., samples (lower, lower, and higher, respectively), and ii) the knowledge that Ca²⁺ is a larger cation than Fe³⁺, Fe²⁺, Al³⁺ and Si⁴⁺.²⁷ The Mumme et al. and Zoll et al. samples both had lower CaO content (12.47 and 12.38 mass%), respectively, relative to the current (12.65–13.33 mass%) and Kahlenberg et al. (13.11–14.17 mass%), samples. In contrast, the Arakcheeva et al. sample had a higher CaO content (14.58 mass%).

4. Concluding Remarks

The results reported in this study sit alongside other recent investigations into the compositional and structural characteristics of the triclinic SFCA-I phase, which between
the years 1998 and 2017 had not attracted significant research attention despite its status as a key component of iron ore sinter. They also raise several additional questions, and future work could involve further probing the lower and upper limits of Al$_2$O$_3$ concentration, as well as investigating the effect of more reducing atmosphere on compositional limits given the ability of SFCA-I to accommodate FeO. The moderately reducing conditions of pO$_2$ = $5 \times 10^{-3}$ atm have been utilised previously in several fundamental investigations of sinter bonding phases and would be a valid starting point. Finally, we have noted that the results of a previous in-situ XRD investigation appear inconsistent with the current knowledge of SFCA-I stability. Therefore, additional in-situ XRD work is required to verify the phase formation mechanisms in Al$_2$O$_3$-free mixtures.

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