A Review of the Chemistry, Structure and Formation Conditions of Silico-Ferrite of Calcium and Aluminum ('SFCA') Phases

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This paper critically reviews published research on silico-ferrite of calcium and aluminum ('SFCA') phases, the major bonding phases found in modern iron ore sinters. In particular, we focus on describing the different 'SFCA' phases formed in iron ore sinter and examining their phase chemistry, crystal structures, characteristic textures and microstructures, and formation conditions. Information for the two main bonding phases SFCA and SFCA-I are reviewed and, based on a critical analysis of the data, we suggest future research directions required to generate the information necessary to fully describe the properties of both phases.

KEY WORDS: iron ore sinter; SFCA; phase chemistry; crystal structure; microstructure; formation mechanisms.

1. Introduction

In the modern high basicity iron ore sinter-making process, complex calcium ferrites consisting of predominantly Fe, Ca, Al, Si, (Mg) and O are formed from high temperature reactions between the iron ore fines, coke breeze and flux (Fig. 1). The calcium ferrite phases are considered the dominant bonding phases in the sinter product and are usually grouped together under the acronym ‘SFCA’ (Silico-Ferrite of Calcium and Aluminium) phases. The properties and behaviour of ‘SFCA’ phases are of significant importance to iron and steelmakers as they impact on the physical properties of the sinter product (e.g. strength of the agglomerated fines) and also in the subsequent blast furnace ironmaking process where the reducibility and strength of the sinter during reduction are important sinter quality parameters. Extensive research involving high temperature phase equilibrium studies,1,2) empirical laboratory compact scale3–9) or pilot-scale sinter pot tests10) has been conducted to understand the composition range(s), stability, crystal structure, texture/morphology and formation mechanisms of ‘SFCA’ and their effect on sinter properties. Despite the large and seemingly comprehensive literature data available, there nevertheless remain uncertainties at both a practical and fundamental level in understanding many aspects of the ‘SFCA’ phases.

Two major types of literature studies on ‘SFCA’ are available; information generated from pilot-scale sinter pot tests (sinter pot grate test work), or more focussed results obtained under controlled laboratory experimental parameters. The conditions used in pilot scale test studies are more typically aligned to actual sintering practice (e.g. sample preparation, bulk composition, representative sintering times and temperature profiles) and these generally provide essential

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Fig. 1. Schematic of (a) a typical mixture of iron ore particles surrounded by ultra-fine ore, calcite flux, and coke breeze, and (b) a typical iron ore sinter product showing the development of a physically strong but porous ‘SFCA’ dominated matrix. The matrix also contains finer grained magnetite, hematite, larnite (dicalcium silicate) and glass (quench melt). Modified from Sasaki and Hida51) and Webster et al. 2012.31)
information regarding the effect of process conditions on sinter phase formation and overall sinter properties. The derivation of accurate fundamental information on ‘SFCA’ formation/properties from these studies however, is usually impractical due to multiple uncontrolled factors (e.g. variable heating and cooling profiles, and variations in atmosphere during heating and cooling). Laboratory experimental studies, on the other hand, are usually carried out under more tightly constrained conditions and typically investigate specific aspects of ‘SFCA’ formation. The focus of the present review is primarily on the well-constrained fundamental laboratory studies, but for areas of research where little or no laboratory studies are available in the literature, the results of pilot scale tests are also included. The review aims to summarise the key findings from previous studies examining the phase chemistry, crystal structures, textures/microstructures and formation mechanisms of ‘SFCA’ phases. At the end of each section we highlight any additional information we believe is required to complete the description of the properties of ‘SFCA’ in iron ore sinter. We anticipate that the review will provide a platform for further research.

2. Chemical Composition of ‘SFCA’ Phases

Phases formed during iron ore sintering generally occur at temperatures above 800–900°C and are characterised by an assortment of phases including complex calcium ferrites, the iron oxides hematite (Fe₂O₃) and magnetite (Fe₃O₄), minor silicates such as larnite (Ca₂SiO₄), and some melt/glass. Relict coarse-grained iron ore nuclei, unreacted flux and aluminosilicate gangue particles are also typically present. Within industrially prepared iron ore sinters, previous measurements have shown that ‘SFCA’ phases exhibit a wide variation in composition. In this section, the composition of ‘SFCA’ phases is reviewed using data from industrial, pot-grate and laboratory-based studies.

‘SFCA’ phases form within the four-component Fe₂O₃–FeO–CaO–Al₂O₃–SiO₂ pseudo-quaternary system. They are dominated by high levels of Fe₂O₃ and CaO and arise through high temperature reactions between early formed, low temperature calcium ferrite phases and minerals containing Al₂O₃ and SiO₂ gangue element impurities. A number of binary/pseudo-binary calcium ferrite phases are known and Hidayat et al. comprehensively reviewed their thermochemistry and stability. Examples are: CaFe₂O₄ (generally shortened to CF), Ca₃Fe₂O₆ (C₃F) and CaFe₂O₅ (CF₂). In iron ore sinter however, these simple binary/pseudo binary calcium ferrite phases are rarely observed due to the process conditions extending beyond their thermal stability limits and also because of the presence of SiO₂ and Al₂O₃ impurities which upon reaction with the calcium ferrites, generate more complex phases. Hancart et al. first identified these more complex phases and referred to them by the acronym ‘SFCA’.

2.1. SFCA

Within industrially and synthetically prepared iron ore sinters there are significant discrepancies with respect to the composition of ‘SFCA’ (Table 1). Although subject to considerable compositional variation (Fig. 2), there is in general a consensus regarding composition with most data plotting in the range: 60–76 wt% Fe₂O₃; 13–17 wt% CaO; 3–10 wt% SiO₂; 3–11 wt% Al₂O₃; and 0–3 wt% MgO. Variation in composition is likely a result of differences in feed composition, differences in operating conditions during the heating and cooling stages of sintering and likely uncertainties in the identity of the phase being measured.

Attempts by Hancart et al. to derive a formula for ‘SFCA’ from the compositions of ‘SFCA’ measured in industrially-prepared sinter samples suggested a composition between 7Fe₂O₃·2SiO₂·3Al₂O₃·5CaO and 5Fe₂O₃·2SiO₂·3Al₂O₃·2CaO + MgO.

Table 1. Electron Probe Microanalysis (EPMA) derived compositions of ‘SFCA’ measured in industrially prepared iron ore sinters according to different literature sources. All data in wt%.

| Oxide  | Hancart et al. | Ahsan et al. | Hsieh and Whiteman | Yang and Loo | Stenlake et al. 1981 | Ostwald 1981 | Dawson et al. 1985 |
|--------|---------------|--------------|--------------------|-------------|----------------------|-------------|-------------------|
| Fe₂O₃  | 60–74         | 63–76        | 77                 | 70–76       | 66–76                | 66–76       | 72–85             |
| CaO    | 14–16         | 13–16        | 14                 | 13–15       | 14–17                | 12–16       | 12–18             |
| SiO₂   | 3–10          | 7–9          | 5                  | 6–8         | 4–8                  | 3–10        | 0.5–11            |
| Al₂O₃  | 5–11          | 4–10         | 4                  | 3–8         | 5–10                 | 3–10        | –                 |
| MgO    | 0.7–1.5       | –            | 0.3–1.5            | 0.1–0.8     | 0–3                  | –           | –                 |

2 The Fe concentration in ‘SFCA’ phases has been typically reported as Fe₂O₃ in the literature, despite the presence of both Fe²⁺ and Fe³⁺. Hereafter, in the present paper, unless Fe²⁺ information is available, total Fe including both Fe²⁺ and Fe³⁺ is presented as Fe₂O₃.
9Fe₂O₃·2SiO₂·0.5Al₂O₃·5CaO. In their formula, the CaO content remained constant at 5 moles, while the remaining oxides substituted for each other and added up to approximately 12 moles. The compositional plane defined by ‘SFCA’ was along a plane beginning at C(F,A)₃ and extending towards (C,M)S (i.e. CF₃–CA₃–CS in Fig. 2). Further work by Dawson et al. and Whiteman et al. suggested that the structure was derived from that of hemicalcium ferrite (CF₃), in which Si³⁺ and Al³⁺ replace some Fe³⁺. Based on their results Dawson et al. suggested the alternative substitution plane CF₂–CA₂–CS₃ (Fig. 2).

Inoue and Ikeda studied the composition of ‘SFCA’ by sintering synthetic chemical mixtures of CaO, Fe₂O₃, Al₂O₃, and SiO₂ in air, followed by Electron Probe Microanalysis (EPMA) and X-Ray Diffraction (XRD) analysis. They proposed that the substitution trend followed a plane defined by the end-members CaO·3Fe₂O₃–CaO·3Al₂O₃–CaO·SiO₂ (CF₃–CA₃–CS₃) with the ‘SFCA’ solid solution spanning compositions from 2 to >20 mole% CA₃ and 0 to 12.5 mole% SiO₂ (Fig. 3). They recognised the phase as having M₂₀O₃₆ stoichiometry and being stable throughout the temperature interval of 1 100–1 250°C. In comparison, Hamilton et al. used synthetically prepared samples to determine that the solid solution followed the CF₃–CA₃–CS₃ pseudobinary for the alumina-free system and that Fe³⁺ substituted for Al³⁺ in the pseudounary system. In contrast with Inoue and Ikeda, Hamilton et al. reported that ‘SFCA’ had M₁₄O₂₀ stoichiometry and determined through single crystal diffraction studies that SFCA was a single phase (see section 3). Hereafter this phase, with M₁₄O₂₀ stoichiometry, is referred to as SFCA, sensu stricto.

Patrick and Pownceby systematically investigated the solid solution range and thermal stability of SFCA within the four-component Fe₂O₃–CaO–Al₂O₃–SiO₂ system using a high temperature equilibrium quenching method. They showed SFCA was stable within a plane connecting the end-members CF₃ (CaO·3Fe₂O₃), CA₃ (CaO·3Al₂O₃), and CS₃ (4CaO·3SiO₂), consistent with the proposed compositional plane by Hamilton et al. Chemical substitution in the four-component system followed the coupled substitution mechanism 2(Fe³⁺,Al³⁺) ↔ (Ca³⁺,Fe²⁺)+Si⁴⁺ with the greatest range in chemical substitution occurring in the direction of Al³⁺→Fe⁴⁺ exchange (ranging from 0 wt% Al₂O₃ to ~31.5 wt% Al₂O₃). The extent of Al³⁺→Fe⁴⁺ substitution decreased with increasing temperature and it was estimated that SFCA completely decomposes at temperatures above ~1 480°C in air.

Dolomite, (Ca,Mg)CO₃, and other MgO-bearing materials such as olivine, (Fe,Mg)SiO₄, and serpentine, (Mg,Fe)SiO₃(OH)₄, are increasingly being used as basic flux components for the production of fluxed iron ore sinter. The Mg-containing fluxes are useful as they provide the MgO required to give blast furnace slag good fluidity and desulphurisation properties. The incorporation of MgO flux materials in the sinter feed has the potential to significantly influence the mineralogy, microstructure and physical properties of the resultant sinter however studies examining the mineralogy of MgO-bearing iron ore sinters are limited. Mg²⁺ is able to be incorporated into the SFCA crystal structure, up to 3 wt% via cationic exchange. The exchange mechanism is still to be determined, but Mg²⁺ is considered likely to substitute for Fe³⁺ and/or Ca²⁺. Despite the ability to include Mg²⁺ in the SFCA crystal structure, these studies suggest that the most important influence of MgO being the suppression of SFCA formation and an increase in the amount of magnetite phase due to stabilisation of a mixed spinel phase of type (Fe,Mg)O.Fe₂O₃.

2.2. SFCA-I and SFCA-II

Despite SFCA having been defined as a separate and unique phase in iron ore sinter it was noted by many workers that many other SFCA-like phases were also present and that these phases typically had a different morphology (see section 4) and a different chemistry. Mumme et al. reported that another SFCA-like phase with composition 84.39 wt% Fe₂O₃, 12.77 wt% CaO, 0.93 wt% SiO₂, 2.19 wt% Al₂O₃, and minor MgO and TiO₂ (total 0.26 wt%). XRD analysis showed the sample had a distinctly different diffraction pattern from the reported XRD data for SFCA indicating it was a separate phase. Mumme et al. prepared a SiO₂-free composition of this phase, Ca₃.15Fe₁.82O₂₈, Al₃.10Fe₁.46Al₁₄.₆₆AI₃.₁₄Fe₂.₆₂0₂₈, and determined its crystal structure. This phase is related to SFCA but with a different crystal structure and is known as SFCA-I. Mumme et al. also reported that another composition – 82.6 wt% Fe₂O₃, 13.6 wt% CaO, 1.7 wt% SiO₂ and 2.1 wt% Al₂O₃ – had the SFCA-I structure when reacted at 1 250°C. The research to date has not defined the solid solution series for this phase and the solid solution limits with respect to both temperature and composition for SFCA-I are yet to be fully established.

Although reported to contain Fe²⁺ based on charge balance considerations in the crystal structure refinement, no chemical analysis was conducted in the Mumme et al. study to determine the presence of Fe²⁺ in the SFCA-I phase. However, in the work of Webster et al. an SFCA-I sample with composition 83.5 wt% Fe₂O₃, 12.9 wt% CaO and 5 wt% Al₂O₃ was found to contain 1.38 wt% Fe²⁺. In the same study the Fe²⁺ content of an SFCA (bulk composition 80.0 wt% Fe₂O₃, 13.5 wt% CaO, 3.0 wt% SiO₂ and 4.7 wt% Al₂O₃) was 0.46 wt% and so based on these limited

Fig. 3. Previously proposed compositional planes for SFCA and SFCA in the Fe₂O₃–Al₂O₃–CaO–SiO₂ system. The shaded area shows the region where most ‘SFCA’ compositions formed in industrial iron ore sinter.
data it appears SFCA-I can accommodate more Fe\textsuperscript{2+} than SFCA. A more comprehensive testing program is required to confirm this.

Figure 4(a) shows the location of the Ca\textsubscript{1.18}Fe\textsuperscript{3+}\textsubscript{14.66}Al\textsubscript{1.34}Fe\textsuperscript{2+}\textsubscript{0.82}O\textsubscript{28} SFCA-I in the Fe\textsubscript{2}O\textsubscript{3}(Al\textsubscript{2}O\textsubscript{3})–FeO–CaO system, in relation to SFCA and other relevant CAF-type phases.\textsuperscript{22} SFCA-I has also been observed as a product phase in laboratory-based compact sinter testing.\textsuperscript{25}

Based on the presence of Mg impurities in SFCA-I (and SFCA), phase-equilibria experiments by Pownceby et al.\textsuperscript{26} showed that MgO is also able to be incorporated at low levels into the SFCA-I structure. The addition of MgO was observed to stabilise SFCA-I at the expense of SFCA.\textsuperscript{22} Beyond 2 wt\%, a magnesioferrite phase became stabilised. SFCA-I appears to be able to accommodate more Mg in its crystal structure than SFCA. Given the sizes of the Mg\textsuperscript{2+} and Fe\textsuperscript{2+} cations (0.86 and 0.92 Å for Mg\textsuperscript{2+} and Fe\textsuperscript{2+} in octahedral coordination, respectively\textsuperscript{27}), and the significantly larger size of the Ca\textsuperscript{2+} cation (1.16 Å), it may be that Mg substitutes for Fe\textsuperscript{2+} in the SFCA-I and SFCA structures. A greater solubility of Mg in SFCA-I would be consistent with this phase incorporating a higher proportion of Fe\textsuperscript{2+}. Based on the results of another recent, but limited, set of experiments, Webster et al.\textsuperscript{29} report that SFCA can incorporate more TiO\textsubscript{2} (up to 1.2 wt\%) than SFCA-I (0.6 wt\%).

Mumme et al.\textsuperscript{23} further synthesised and performed XRD on a third ‘SFCA’-type phase, denoted SFCA-II. One of the studied compositions of this phase has the formula Ca\textsubscript{5.1}Al\textsubscript{9.3}Fe\textsuperscript{3+}\textsubscript{18.7}Fe\textsuperscript{2+}\textsubscript{0.9}O\textsubscript{48. SFCA-II is believed to be an intergrowth-type phase of SFCA and SFCA-I.\textsuperscript{23} Figure 5(b) shows the representation given by Mumme\textsuperscript{23} of the compositional relationships of SFCA, SFCA-I and SFCA-II (note the mol\%, rather than wt\%, used on the axis scales in 5b). It is worthwhile to note, however, that in Fig. 5(b) the solid solution range of the “ternary phase” of Lister and Glasser\textsuperscript{29} appears not to extend from SFCA to SFCA-I. Recently, Mumme and Gable reported a second SFCA-II containing significant Fe\textsuperscript{2+}. This variant of the previously determined SFCA-II has a different crystal structure.\textsuperscript{30} To date, SFCA-II has not been reported as occurring in industrial sinter and does not feature prominently in laboratory-scale testing. SFCA-II is therefore not considered any further in this review.

2.3. Fe-rich (Ca-deficient) ‘SFCA’

Based on the results of an in-situ XRD investigation of SFCA and SFCA-I formation mechanisms and stability, Webster et al.\textsuperscript{31} determined that a phase, structurally and chemically distinct from SFCA and SFCA-I and designated as Fe-rich ‘SFCA’, was the first phase to form from a melt during cooling of an artificial sinter mixture. EPMA analysis of a synthetic sample gave a composition of 84.2(6) wt\% Fe\textsubscript{2}O\textsubscript{3}; 9.6(3) wt\% CaO; 3.12 wt\% SiO\textsubscript{2}; and 5.00 wt\% Al\textsubscript{2}O\textsubscript{3} for this phase (the numbers in parentheses are the standard deviation of the ~30 point analyses for this phase). The CaO content was lower than that for both SFCA and SFCA-I, and a more appropriate name is probably “Ca-deficient SFCA”. At a lower temperature (~20–30°C lower depending on the composition studied), this Fe-rich
phase reacted with the melt to form SFCA.\textsuperscript{31)}

In unpublished work, this phase has also been identified in sinter produced in pilot-scale pot grate testing (Fig. 6). The average composition of the Fe-rich ‘SFCA’ phase analysed in the sample was 84.8(10) wt% Fe\textsubscript{2}O\textsubscript{3}; 9.4(6) wt% CaO; 2.2(2) wt% SiO\textsubscript{2}; 2.8(1) wt% Al\textsubscript{2}O\textsubscript{3} and 1.8(1) wt% MgO, similar to that of the synthetic study with the exception of the MgO content. The Fe-rich ‘SFCA’ phase labelled in Fig.6 encases a grain of Fe\textsubscript{3}O\textsubscript{4} (magnetite), and is itself surrounded by SFCA, which is consistent with the results of the fundamental study of Webster et al.\textsuperscript{31)}

2.4. Summary and Directions for ‘SFCA’ Composition

Further Research

‘SFCA’ phases in iron ore sinter have been divided on the basis of composition into two main types. One is a low-Fe form that is simply referred to as SFCA that in industrial, plant sinter typically contains 60 to 76 wt% Fe\textsubscript{2}O\textsubscript{3}; 13 to 16 wt% CaO; 3 to 10 wt% SiO\textsubscript{2}; 4 to 10 wt% Al\textsubscript{2}O\textsubscript{3}, and 0.7 to 1.5 wt% MgO that is stabilised in the pseudoternary CF\textsubscript{3}–CA\textsubscript{3}–C\textsubscript{4}S\textsubscript{3} plane. The chemical substitution in the quaternary system follows the substitution mechanism 2(Fe\textsuperscript{3+}, Al\textsuperscript{3+}) = Ca\textsuperscript{2+} + Si\textsuperscript{4+} with the greatest range of substitution occurring between Fe\textsuperscript{2+} and Al\textsuperscript{3+}. The second ‘SFCA’ type is a high-Fe, low-Si form called SFCA-I. Mumme et al.\textsuperscript{22)} reported that an SFCA-I found in plant sinter contained 84.39 wt% Fe\textsubscript{2}O\textsubscript{3}; 12.77 wt% CaO; 0.93 wt% SiO\textsubscript{2}; and 2.19 wt% Al\textsubscript{2}O\textsubscript{3}. A rigorous investigation of the solid-solution limits and thermal stability has not been performed for SFCA-I. However, based on the work of Mumme et al.\textsuperscript{22)} it is expected that the solid-solution range would be narrower in comparison with SFCA. A third and now recently a fourth ‘SFCA’ sub-type was identified by Mumme et al.\textsuperscript{23)} and Mumme and Gabler\textsuperscript{30)} and denoted SFCA-II. The two SFCA-II sub-types are chemically similar but differ only in terms of their crystal structure. This phase has not been reported as occurring either laboratory testwork or industrial processes. Recently, Webster et al.\textsuperscript{31)} described a fourth ‘SFCA’ phase, denoted as Fe-rich (or Ca-rich deficient) and observed in both laboratory and pot-grate sinters. The existence of this phase in industrial plant sinters is yet to be confirmed.

Despite over 50 years of research on the phase chemistry of ‘SFCA’ bonding phases in iron ore sinter, there remains considerable avenues for potential research to resolve remaining uncertainties. These include:

- limited or no results have been reported on the effect of sinter variables such as gas atmosphere, impurities (e.g. MgO, P\textsubscript{2}O\textsubscript{5}, TiO\textsubscript{2}) and cooling rates on the stability of SFCA and SFCA-I phases.
- phase relations between SFCA, SFCA-I and liquid under sintering conditions have not been fully described (e.g. see Pownceby et al.\textsuperscript{32}). This information is crucial for predicting the proportion as well as the chemistry of the liquid formed that serves as the primary binding agent in sinter-making at high temperatures.
- for SFCA-I, no extensive study has been carried out to investigate its solid solution series, solid solution limits and stability in air and/or under different gas atmospheres. The stability region of SFCA-I within the Fe\textsubscript{2}O\textsubscript{3}(FeO)–CaO–Al\textsubscript{2}O\textsubscript{3}–SiO\textsubscript{2} pseudo-quaternary system is yet to be determined. The synthesis of SiO\textsubscript{2}-containing SFCA-I has not been yet been achieved (even though SFCA-I in industrial sinters has been reported to contain SiO\textsubscript{2}).
- further work is required to understand the significance of Fe-rich/Ca-deficient ‘SFCA’ - whether this material is present in industrial sinters, for example – and the effect of sinter variables (T, composition, cooling rate etc.) on its formation. Webster et al.\textsuperscript{31)} briefly examined the effect of Al\textsubscript{2}O\textsubscript{3} concentration on the crystallisation temperature of Fe-rich SFCA, but an opportunity exists for further work examining the effect of gas atmosphere, basicity, MgO content and Ti addition on the crystallisation of this phase.

3. Crystal Structure of ‘SFCA’ Phases

The section on composition of ‘SFCA’ phases indicates that it should be easy to distinguish between SFCA and SFCA-I based on composition. In practice however the rapid, non-equilibrium nature of the sintering process causes complexity, resulting in highly chemically zoned crystals often exhibiting fine-grained, intergrown textures. A combination of composition, morphology/texture and XRD have been all used to differentiate the different ‘SFCA’ phases, with reliable differentiation of the phases only achieved via XRD.\textsuperscript{33)} The following section reviews current state of knowledge regarding the crystal structure of ‘SFCA’ phases.

3.1. ‘SFCA’ Structure Nomenclature

The ‘SFCA’ group of iron ore sinter phases are related to the group of minerals belonging to the sapphirine super-group (Grew et al.\textsuperscript{34}). Minerals within this supergroup are part of a polysomatic series which consist of pyroxene-like (P) and spinel-like (S) modules known as polysomes, in several distinct proportions. The P modules are one chain-width broad (010) slices of pyroxene structure whereas the S modules are one octahedron/tetrahedron broad (010) slices.

Fig. 6. Backscattered electron (BSE) micrograph collected for a pot-grate sinter sample showing the presence of the Fe-rich ‘SFCA’ phase. Also present in the sample is dicalcium silicate, C\textsubscript{2}S (2CaO.SiO\textsubscript{2}). (Sinter pot bulk composition nominally 59.00 wt% T-Fe; 8.30 wt% CaO; 5.24 wt% SiO\textsubscript{2}; 1.64 wt%Al\textsubscript{2}O\textsubscript{3} and 1.16 wt% MgO).
of spinel structure (so-called ‘winged-octahedra’). In phases belonging to the ‘SFCA’ group, the \(<PS>\) polysomes are arranged in such a way that the pyroxene chain unit has S octahedra attached leading to branched chains.

The \(<P_{n}S_{m}>\) polysomatic series has two subseries one with \(m > n\) which generates pyroxene-like chains \(<PP>\) in the structure parallel to the \(x\) axis while the other has \(m < n\) in which only fully-branched \(<PS>\) chains are inserted into each other occur. ‘SFCA’ phases found in iron ore sinter belong to the latter subseries giving rise to the following potential phases: SFCA-\(<PS>\) or M\(_6\)O\(_{29}\), SFCA-I (\(<PSS>\) or M\(_{29}\)O\(_{29}\)) and SFCA-II (\(<SSPS>\) or M\(_{31}\)O\(_{29}\)). The structure of all three ‘SFCA’ types therefore consists of alternating intergrowths of spinel (M\(_4\)T\(_2\)O\(_8\)) and Ca-rich clinopyroxene-type (P = Ca\(_3\)M\(_2\)Si\(_4\)O\(_{12}\)) structural slabs. Using this classification, crystal structure representations of the SFCA and SFCA-I types are provided in Fig. 7. The cations form layers with Fe, Ca and Mg in octahedral sites alternating with predominantly tetrahedral layers containing Fe, Al and Si tetrahedral layers.

### 3.2. SFCA Structure Type

Ahsan\(^{35}\) originally analysed industrial sinter samples with scanning electron microscopy (SEM) and transmission electron microscopy (TEM) and suggested SFCA had a similar crystal structure to magnetite and that the SFCA structure was a superlattice of magnetite. CF\(_2\) was also suggested to have the same crystal structure. In a similar study, Mulvaney\(^{36}\) examined industrial and laboratory sinters by TEM and EPMA. He determined that the crystal structure of SFCA was not a magnetite superlattice but instead had a crystal structure identical to the CaSi\(_2\)Fe\(_4\)O\(_{10}\) phase previously identified by Lister.\(^{29}\) Later research,\(^{19,37}\) subsequently showed that the crystal structure of SFCA differs from both a magnetite superlattice and CaSi\(_2\)Fe\(_4\)O\(_{10}\).

The crystal structure of SFCA was determined by Mumme\(^{37}\) and Hamilton et al.\(^{19}\) using flux-grown crystals and remains the one most used for phase identification and quantification. SFCA crystallises in the triclinic space group \(P\overline{1}\) and has M\(_6\)O\(_{29}\) stoichiometry (\(<PS>\) and is composed of alternating layers, one with octahedral ribbons four octahedra wide, the other a continuous tetrahedral layer (Fig. 7(a)). Based on the refinement of the crystal structure, it was suggested that the Fe\(^{3+}\) occupies octahedral and tetrahedral sites, Ca\(^{2+}\) occupies octahedral sites, Si\(^{4+}\) and Al\(^{3+}\) is substituted into the tetrahedral sites and Mg\(^{2+}\) is substituted into the octahedral sites.\(^{22}\) SFCA cell parameters determined by Hamilton et al.\(^{19}\) are provided in Table 2.

Kim et al.\(^{38}\) determined the crystal structures of calcium ferrite solid solution phases in real and synthetic iron ore sinters using results from powder XRD. The compositions have been calculated assuming they conform to SFCA stoichiometry and are included in Table 2. The data from Kim et al.\(^{38}\) should be viewed with some caution due to the considerable variation in lattice parameters suggesting likely mis-identification of phases.

Sugiyama et al.\(^{21}\) determined the structure of two synthetic magnesium-containing crystals prepared by solid state reaction. Up to 20 and 26.6 wt% MgO was present in the SFCA prompting Sugiyama et al.\(^{21}\) to denote these as Mg-rich SFCA, or SFCAM. Cell parameters are indicated in Table 2. They confirmed the triclinic space group however in contrast to Hamilton et al.\(^{19}\) indicated some Al occurred in octahedral sites. The distribution of Al\(^{3+}\) at the octahedral sites appears to be a unique feature found in the structure of Mg-rich SFCAM.

Recently Liles et al.\(^{39}\) determined the cell parameters of a synthetic crystal of SFCA prepared from a slow-cooled melt (Table 2). They considered that the calculated diffraction pattern of SFCA derived using the crystal structure data of Hamilton et al.\(^{19}\) differed substantially from the observed pattern of pure synthesised material and used the new data to correct and refine the previously published crystal structure data.

Murao et al.\(^{40}\) performed X-ray absorption of near edge structure (XANES) spectra analysis of SFCA to determine the site occupancy of the cations. Based on the spectra analysis, and in agreement with that suggested based on the refinement of the crystal structure,\(^{19,21,22,39}\) it was suggested that the octahedral sites in SFCA was occupied by both Fe\(^{3+}\) and Ca\(^{2+}\) and the tetrahedral sites were occupied by Fe\(^{3+}\), Si\(^{4+}\) and Al\(^{3+}\). Further work is required with this technique to confirm the sites which Fe\(^{3+}\) and Mg\(^{2+}\) occupies.

Naturally-occurring SFCA has been reported by Chesnokov et al.\(^{41}\) and more recently by Galuskina et al.\(^{42}\) – see Table 2. Chesnokov et al.\(^{41}\) described a new phase from the burned dumps of the Chelyabinsk coal basin, Urals, Russia. Spontaneous combustion and self-sustained burning of coal spoil heaps led to thermal alteration and melting of pre-existing sedimentary rocks with the formation of the phase ‘malakhovite’. Similarly, Galuskina et al.\(^{42}\) described a new mineral, khesinite, discovered in veins of lavas of the Hatrukhov Complex in the Negev Desert, Israel. Both minerals are chemically and structurally similar to synthetic SFCA and SFCAM.

### 3.3. SFCA-I Structure Type

Determination of the crystal structure of synthetic SFCA-I by Mumme et al.\(^{22}\) proved that it has a triclinic structure and M\(_{29}\)O\(_{29}\) stoichiometry (\(<PSS>\)). In contrast to SFCA, SFCA-I has no identified natural analogue (Grew et al., 2008).\(^{34}\)

SFCA-I contains two types of alternating layers in its structure: the first is a continuous layer of single ribbons

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Fig. 7. Representative crystal structures for; a) SFCA and b) SFCA-I using the crystal structure data reported in Hamilton et al.\(^{19}\) and Mumme et al.\(^{22}\) respectively. The notation \(P\) indicates pyroxene modules while \(S\) indicates spinel modules.
The Fe\textsuperscript{3+} SFCA may therefore be predicted on the basis of this series. Preference for tetrahedral sites. (Table 2). This material was referred to as CaFe\textsubscript{3}AlO\textsubscript{7} in iso-structural with SFCA-I.22) Differences were observed in the unit cell parameters of SFCA and SFCA-I required refinement for each industrial sinter due to their highly variable compositions. Takayama et al.45) suggested further improvements should include the use of internal standards during XRD analysis plus a more comprehensive analysis of compositions (EDS). This enabled a better fit to the XRD pattern and a more accurate Rietveld analysis. Results indicated the unit cell parameters for SFCA and SFCA-I differed between the sinter pot samples and also between values obtained by past researchers. The research demonstrated that the unit cell parameters for SFCA and SFCA-I are members of a homologous series M\textsubscript{14}O\textsubscript{28} where n = 0 for SFCA and n = 1 for SFCA-I. The structures of higher homologues of SFCA may therefore be predicted on the basis of this series. The Fe\textsuperscript{3+} was suggested to be located in tetrahedral and octahedral sites, the Ca\textsuperscript{2+} in octahedral sites and the Al\textsuperscript{3+} substituted into the tetrahedral sites.

Zoll43) prepared synthetic FCAM-I from pure oxides, with analysis by powder XRD and EPMA to determine the structure. The research demonstrated that the unit cell parameters for SFCA and SFCA-I are members of a homologous series M\textsubscript{14}O\textsubscript{28} where n = 0 for SFCA and n = 1 for SFCA-I. The XRD data for SFCA-I are provided in Table 2. Mumme22) performed XRD on samples obtained from sinter pot tests. The proportion of phases was determined via Rietveld analysis using existing structural models for SFCA and SFCA-I with the unit cell parameters refined to suit the compositions of SFCA and SFCA-I as measured by Energy Dispersive Spectroscopy (EDS). This enabled a better fit to the XRD pattern and a more accurate Rietveld analysis. Results indicated the unit cell parameters for SFCA and SFCA-I are members of a homologous series M\textsubscript{14}O\textsubscript{28} where n = 0 for SFCA and n = 1 for SFCA-I. The structures of higher homologues of SFCA may therefore be predicted on the basis of this series. The Fe\textsuperscript{3+} was suggested to be located in tetrahedral and octahedral sites, the Ca\textsuperscript{2+} in octahedral sites and the Al\textsuperscript{3+} substituted into the tetrahedral sites.

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### 3.5. Summary and Future Directions for ‘SFCA’ Crystallographic Research

Extensive research has been performed to determine the crystal structure of the ‘SFCA’ group of phases. Three distinct crystalline phases which form part of a polysomatic series have been identified and described. The simplest form is SFCA which has a triclinic crystal structure \((a = 9.06, b = 10.02, c = 10.92\, \text{Å})\), and, has the general formula \(M_4\text{O}_{28}\) (\(M = \text{Fe, Ca, Si, Al}\)). The second ‘SFCA’ type is designated SFCA-I. It is structurally different to SFCA but is part of the homologous series \(M_{14+6n}\text{O}_{20+8n}\) (\(n = 0\) and 1 for SFCA and SFCA-I, respectively). The structure of SFCA-I is triclinic \((a = 10.43, b = 10.61, c = 11.84\, \text{Å})\) and has the general formula \(M_{30}\text{O}_{28}\), \(i.e. n = 1\). A third member of the SFCA homologous series, with \(M_4\text{O}_{28}\) stoichiometry and designated SFCA-II is also known. SFCA-II however, has not been found in iron ore sinter.

Further work is required to determine the effect of composition on the unit cell parameters of the ‘SFCA’ phases. While comprehensive information is available for SFCA, the SFCA-I phase has been less extensively researched, the unit cell parameters and crystal structure has been determined for only a limited number of compositions in the solid solution range – for example, an \(\text{SiO}_2\)-containing SFCA-I phase equivalent to that found in industrial plant sinters has not been fully characterised due to an inability...

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**Fig. 8.** Simulated X-ray powder diffractions patterns (Cu Kα radiation) for SFCA and SFCA-I using the crystal structures reported in Hamilton\(^{19}\) and Mumme \textit{et al.}\(^{22}\) respectively.

**Fig. 9.** Rietveld fit to XRD data (Co Kα radiation) collected for an industrial sinter sample. Experimental data are shown as a blue (scattered) solid line and the calculated profile as a red (smooth) solid line. The short vertical lines are the Bragg peak markers for (top to bottom) hematite, magnetite, SFCA, SFCA-I, larnite, mordenite and quartz. The long vertical lines represent peaks which have been inserted in order to model the broad hump of the amorphous material in the range \(-35–45°\). Relative wt\% values for the crystalline phases: 48 wt\% hematite, 14 wt\% magnetite, 17 wt\% SFCA, 13 wt\% SFCA-I, 7 wt\% larnite, 0.5 wt\% mordenite, 0.5 wt\% quartz.
to synthesise a phase of this composition. In addition to a lack of comprehensive, high-quality data regarding SFCA-I, crystal structure data for the Fe-rich (Ca-deficient) SFCA phase have not been determined (although whether this phase is important in industrial sinter is yet to be clarified).

4. SFCA Morphology

One of the salient features of ‘SFCA’ is its appearance in iron ore sinter in different morphologies. The chain-like crystal structure of the ‘SFCA’ group of minerals (Fig. 7) gives rise to crystals with elongated aspect ratios. While this type of morphology is common for both SFCA and SFCA-I, the effects of cooling, composition, kinetics, melt viscosity etc. in industrially prepared sinter samples can also impart morphological effects. This has resulted in a wide variety of ‘SFCA’ morphologies observed and described by past researchers. There is therefore, significant inconsistency with the naming and classification of ‘SFCA’ phases with the same morphology and ‘SFCA’ phase being described differently between authors.

Descriptive names for the ‘SFCA’ group of minerals most commonly encountered in literature include, but are not limited to:48)

- Monocalcium Ferrite
- Acicular calcium ferrite
- Acicular SFCA
- Platy SFCA
- SFCA-I
- Fibrous SFCA
- Finely Fibrous SFCA
- Irregularly- Shaped SFCA
- Low T Morphology SFCA
- Needle- Like SFCA
- Dendritic SFCA
- Columnar SFCA
- Tabular SFCA
- Blocky SFCA
- Prismatic SFCA
- Lath-Shaped SFCA
- Crystalline SFCA
- Eutectic SFCA
- Complex Calcium Ferrite

Even though the previous section indicated that XRD is crucial in distinguishing between SFCA and SFCA-I, at present the most commonly used approach by researchers is based on observed texture by microscopic examination (optical or SEM). Using these approaches, current researchers typically classify ‘SFCA’ into at least two microstructures, with one typically suggested to be SFCA (prismatic or columnar in habit) and the other SFCA-I (platy in habit)31,49) (Fig. 10). Examination of Fig. 10(b) however illustrates that depending on the orientation of the crystals, the platy SFCA-I often exhibits a fine needle-like or fibrous texture. To add to the confusion, recent work by Hapugoda49) indicated that they are further able to differentiate three morphologies, SFCA-I which exhibits a micro-platy texture and two SFCA types, dense SFCA and prismatic (columnar) SFCA. Similarly, Gan50) differentiates between four morphologies, with two having similar compositions to SFCA (acicular and columnar) and the other two, SFCA-I (platy and granular).

Frequently, a relation between morphology and chemical composition is presented in literature, but as shown previously, analyses tend to differ substantially and are often incomplete. For example, needles are thought to have high Ca and low Al contents, as opposed to plates which have low Ca and high Al (Ahsan et al.35). Different opinions concerning a relation between the attained sintering temperature and the subsequent morphology exist as well (e.g. Sasaki and Hida51). Mezibricky33) recently performed work to determine the differences between acicular (SFCA-I) and columnar (SFCA) structural types, with the work indicating that the different ‘SFCA’ phases can form similar microstructures at certain conditions. The similarities in composition of the two phases gives them a similar colour and contrasts in both optical and electron microscopes giving rise to significant difficulties in differentiation between both different phases and microstructures. This indicates that more advanced techniques than that currently used may be required to differentiate between the phases.

Honeyands et al.46) compared and contrasted the terminology and classification of SFCA phases and microstructures between labs, with four types of SFCA in the final classifications system. These were, platy SFCA-I, prismatic SFCA, blocky SFCA and dendritic SFCA, with blocky and dendritic considered as sub-types of prismatic. Three techniques were used to attempt to differentiate phases: XRD, reflected light microscopy (incorporating optical image analysis)
and EPMA. Of the four techniques, only XRD was able to clearly differentiate between SFCA and SFCA-I but did not differentiate between different microstructures for these two phases. Reflective light microscopy and EPMA were used to determine the microstructures present, but were unable to determine what ‘SFCA’ phase was present in any particular microstructure. It was concluded that a number of complementary techniques are required to fully determine the phases present and microstructures in an iron ore sinter.

Takayama et al. determined the proportion of phases present in sinter pot samples. The proportion of phases was determined via XRD with Rietveld analysis using initial structural models for SFCA and SFCA-I. The calculated proportion of phases was back checked with the sinter composition and shown to be accurate within an appropriate accuracy. This research, while unable to relate the SFCA and SFCA-I to specific microstructures, supported the conclusions of Honeyands et al. in which SFCA and SFCA-I can only be definitively differentiated based on XRD.

4.1. Summary and Future Directions for ‘SFCA’ Morphological Research

The use of morphological features to identify and distinguish between SFCA and SFCA-I structure has resulted in the generation of a number of conflicting textural terms used for the same phase. It is likely that many of the diverse textural features result from differences sintering conditions in temperature and cooling rates with the possibility of one or both ‘SFCA’ phases generating a similar, if not the same, textural feature. Fundamental research is required to determine the conditions at which different ‘SFCA’ morphologies form and the properties of these resulting microstructures.

Current characterisation techniques allow either the microstructures or the proportion of phases present to be determined, but not the phases present in particular microstructures. This information would enable the morphologies observed in industrial sintering to be identified and quantified. Given the ability of XRD to unequivocally distinguish between SFCA and SFCA-I (Fig. 8), we suggest that future research should focus on a detailed optical and chemical (e.g. SEM or EPMA) study, followed by quantitative examination of the microtextures identified using a technique such as micro-XRD. Such a study linking the textural information with structure and would need to use well-constrained synthetic sinter samples to enable isolation of the effects of parameters such as T and cooling rate on the textures formed.

5. Formation of ‘SFCA’ Phases in Sintering Practice

An extensive body of research is available which examines the reactions occurring in the sintering process. The various techniques to determine the reaction mechanisms include information from sinter pot tests, tube furnace tests, infrared furnace tests and in-situ XRD. Early researchers examining phase formation in iron ore sinter systems did not uniquely identify the ‘SFCA’ phases and differentiate them from other calcium-rich ferrite phases. These papers typically report such phases as ‘calcium ferrites’. Due to the uncertainty in the relationship between ‘calcium ferrites’ and SFCA and SFCA-I, only research that uniquely identi-
Table 3. SFCA formation test conditions.

| Researcher | Year | Technique | Atmosphere | Fe (wt%) | CaO/SiO₂ (or CaO wt%) | Al₂O₃ (wt%) | MgO (wt%) | Heating Rate | Temperature (°C) | Time at Temp. | Cooling Rate |
|------------|------|-----------|------------|---------|---------------------|-------------|-----------|-------------|-----------------|---------------|--------------|
| Ikeda⁴)   | 1981 | Laboratory Furnace | Air        | 60      | 1.0–2.2             | 0–3.5       |           | 0 – 2.0     | 15°C/min | 1 200–1 320 | 0–30 min |
| Matsuno⁵⁻⁶) | 1981 | Electric Furnace | Air/Coke   | 59.5–68 | 0.02–0.25           | 0.4–3.4     |           | 0.1 - 2.1   | ? | 1 200–1 350 | 10 min   |
| Dawson⁷)  | 1985 | Infrared Furnace Tubefurnace, Electric Furnace | Air | 58.8–33.2 | 1.2–8.5 | 0.5–8.7 | 0 | 20°C/s | 1 250–1 350 | 40 s | 2°C/s |
| Hida⁵⁻⁷)  | 1987 | Air, O₂ | 45.5      | 2.5     | 4.2     | 0     | ? | 1 000–1 350 | ? | 10–1 000 °C/min |
| Hsieh⁵⁻⁷)  | 1989 | Tube Furnace | P₀₂=0.21, 9×10⁻³, 4×10⁻⁷, 5×10⁻³, 2×10⁻⁸ | 53.9 | 2.08 | 3 | 0 | ? | 1 185–1 260 | ? | ? |
| Egundebi⁸) | 1989 | Tube Furnace | Air, nitrogen, various CO/ (CO+CO₂) conditions | 52.9 | 1.93 | 0.3 | 0 | ? | 1 100–1 350 | ? | ? |
| Da Costa⁵) | 1995 | Tube Furnace | Air/Coal | 57.4–59.3 | 2.09–2.10 | 0.7–2.2 | 0.1 - 0.2 | ? | 1 300 | 180 s | ? |
| Wang⁹)    | 1998 | Sinter pot | Air/Coal  | ? | ? | ? | 0 | ? | ? | ? | ? |
| Patrick and Pownceby³) | 2002 | Laboratory Furnace | Variable | Variable | 0.0–40.0 | 0 | ? | 1 240–1 390 | 24 hrs | ? |
| Pownceby and Clout³) | 2003 | Laboratory Furnace | Air | Variable | Variable | 0.0–3.0 | 0 | ? | 1 240–1 300 | 24 hrs | ? |
| Scarlett⁵⁻⁵) | 2004 | In-situ XRD | Air | 57.6–54.1 | 3.95 | 0–5 | 0 | 5°C/min | 1 260 | – | n/a |
| Webster¹) | 2012 | In-situ XRD | P₀₂=5×10⁻³ | 50.6–56.91 | 3.96 | 1–5 | 0 | 10°C/min | 1 260 | – | 5°C/min |
| Webster²) | 2013 | In-situ XRD | P₀₂=0.21, 5×10⁻⁴, 1×10⁻⁴ | 54.1 | 3.96 | 5 | 0 | 10°C/min | 1 350 | – | ? |
| Webster³) | 2014 | In-situ XRD | P₀₂=5×10⁻⁴ | 51.9–45.6 | 2.5–4.9 | 10 | ? | 1 350 | – | ? |
| Webster⁴) | 2013 | In-situ XRD | Air, P₀₂=5×10⁻³ | 58.2–58.8 | 12.6 wt% CaO, 13 C/S | 2–4.2 | 0 | 10°C/min | 1 350 | – | ? |
| Webster⁴) | 2014 | In-situ XRD | P₀₂=5×10⁻³ | 53.9 | 4.07 | 4.56 | 0.12 | 10°C/min | 1 350 | – | ? |
| Ding⁵) | 2016 | In-situ XRD | P₀₂=5×10⁻³ | 53.9 | 4.07 | 4.56 | 0.12 | 10°C/min | 1 350 | – | ? |

Table 4. Proposed ‘SFCA’ phase formation mechanisms.

| Author      | SFCA/ SFCA-I | Solid State Reaction | SFCA | Reaction Temp. (°C) | Melting Temp. (°C) | Crystallisation Temp. (°C) | SFCA-I | Solid State Reaction | Reaction Temp. (°C) | Melting Temp. (°C) |
|-------------|--------------|----------------------|------|---------------------|-------------------|--------------------------|--------|----------------------|-------------------|-------------------|
| Dawson⁴)    | ‘SFCA’       | aluminous hemicalcium ferrite + SiO₂ → SFCA | 1 200–1 250 | 1 300 | NA | – | – | – | – | – |
| Hsieh⁵⁻⁷)   | ‘SFCA’       | unknown              | <1 180 | 1 255 | ND | – | – | – | – | – |
| Egundebi⁸)  | ‘SFCA’       | NA                   | NA | NA | ND | – | – | – | – | – |
| Da Costa⁵⁻⁷) | ‘SFCA’       | unknown              | ND | ND | NA | – | – | – | – | – |
| Wang³)      | ‘SFCA’       | 9(Fe₆Al₂O₁₉) + 2C₂S + CaO → SFCA | ND | ND | NA | – | – | – | – | – |
| Scarlett⁵⁻⁵) | Both         | CF + Fe₂O₃ + SiO₂ + Al₂O₃ → SFCA | 1 000 | ND | – | – | – | – | – | – |
| Webster³)   | Both         | CF + CFA + SiO₂ + Al₂O₃ → SFCA | 1 107–1 140 | 1 213–1 308 | 1 145–1 270 | – | – | – | – | – |
| Webster³)   | Both         | Fe₂O₃ + CF + SiO₂ + Al₂O₃ → SFCA | 1 165–1 173 | 1 206–1 321 | – | – | – | – | – | – |
| Webster⁴)   | Both         | Fe₂O₃ + CF + SiO₂ + Al₂O₃ → SFCA | 1 227 | 1 334 | – | – | – | – | – | – |
| Webster⁷)   | SFCA-I       | –                    | – | – | – | – | – | – | – | – |
| Webster⁴)   | SFCA-I       | –                    | – | – | – | – | – | – | – | – |
| Ding³)      | SFCA         | C₂S + Fe₂O₃ → SFCA   | 1 100 | 1 200 | NA | – | – | – | – | – |
| Pownceby⁸)  | Both         | Fe₂O₃ + CF + CFA + SiO₂ + Al₂O₃ → SFCA | >1 148 | >1 267 | >1 267 | – | – | – | – | – |
| Ding⁵)      | SFCA         | C₂S + CF → SFCA      | 1 100 | 1 200 | NA | – | – | – | – | – |

Note: NA – not suggested by researcher, ND – not detected by researcher.
analysis, ‘SFCA’ was believed to be a CF$_2$ solid solution but as the amount of alumina was increased, the amount of ‘SFCA’ increased, leading the researchers to believe that the alumina was crucial for the formation of the ‘SFCA’. It was suggested that on sintering, the CF formed first, followed by CA, then the reaction of CF and CA to form aluminous monocalcium ferrite solid solution, and finally ‘SFCA’. Determined to be.

Hsieh$^{53}$ performed laboratory tests to determine the formation mechanisms for ‘acicular SFCA’. This research was performed prior to the differentiation of SFCA and SFCA-I via XRD. As such, the ‘acicular SFCA’ was not confirmed to be either SFCA or SFCA-I. However, due to its morphology, this phase is likely to be SFCA-I. Three potential formation mechanisms for ‘acicular SFCA’; solid state reaction, melt crystallisation and melt-solid reaction were investigated. To investigate the solid state reaction mechanism, separate pellets of CaO and iron ore were heated in air at 1 500°C and 1 800°C. The dense microstructure observed and composition of the calcium ferrite formed was significantly different to that observed in industrial sinter feed and it was concluded that the ‘acicular SFCA’ formed in industrial sinter feeds did not form as a result of solid state reactions. To investigate the mechanism of ‘acicular SFCA’ formation via crystallisation from melt, samples were prepared from pure oxides to achieve a bulk composition the same as that observed for ‘acicular SFCA’ in industrial sinters. The pure oxide samples were heated to 1 350°C and cooled at a variety of rates. The microstructures observed, consisting of matrix and coarse dendrites, were different to that in industrial samples and it was concluded that ‘acicular SFCA’ did not form by melt crystallisation. The solid-liquid reaction mechanism was investigated by heating iron ore and lime in a SEM equipped with a furnace. In these tests, it was observed that the first melt to form was close to the composition of CF and formed at around 1 205°C. At higher temperatures, other oxides dissolved into the melt with iron oxides remaining. On cooling, a similar microstructure to that seen in industrial sinters was observed. As such, it was suggested that in industrial sinters, ‘acicular SFCA’ forms during cooling by the reactions between the melt and iron oxides. This research was able to differentiate the mechanisms formed, but did not identify the ‘SFCA’ phases forming in the sinter, causing potential issues in differentiating SFCA, SFCA-I and other calcium ferrites.

Hsieh$^{5,6}$ performed experiments to determine the processes occurring during sintering. Samples were industrial sinter feed heated under various gas atmospheres in a laboratory furnace. The gas atmosphere was controlled with a CO/CO$_2$/N$_2$ mix with a log(pO$_2$) of -1.3 to -7.7. After heating to the maximum temperature (1 85°C to 1 260°C) the samples were cooled by room temperature gas or slow cooled at 1 40°C for 2 minutes. Results showed that a calcium ferrite phase formed at low temperatures (< 1 85°C), and the proportion increased until around 1 260°C at which point magnetite and a melt formed. A higher proportion of calcium ferrites formed under more oxidising conditions from reactions between hematite and the Ca-rich flux. Cooling experiments showed that cooling under oxidising conditions favoured the formation of hematite while under reducing conditions magnetite and slag formed. ‘SFCA’ was formed during cooling at an intermediate oxygen partial pressure, with the greatest proportion formed at a pO$_2$ of 5 x 10$^{-3}$ atm. A sinter pot test was performed, with the mineralogy and phase assemblage matching that created in the laboratory tests with a maximum temperature of 1 255°C, a heating pO$_2$ of 4 x 10$^{-7}$ atm and slow cooling in air. The calcium ferrite formed during different stages of the sintering was determined to be CF$_2$, with Al$_2$O$_3$ and SiO$_2$ substitution. This phase is likely to be the SFCA identified in industrial sinters by other researchers. The calcium ferrite phase was observed to form from both solid state reactions and from the crystallisation of a melt, both mechanisms agree with later research into the formation of SFCA. The solid state reactions were not identified, but the breakdown into melt and iron oxides was successfully observed.

Hsieh and Whiteman$^7$ later extended their work to explore the effects of MgO and Al$_2$O$_3$ on sinter phase formation. The testwork showed that Al$_2$O$_3$ increased the proportion of ‘SFCA’ in the sinter, decreased the glass and increased the stability of magnetite relative to hematite. The effect of MgO was found to vary with the form in which it was added; dolomite was found to inhibit the amount of ‘SFCA’ which formed while serpentine was found to increase the amount.

Egunde$^8$ performed laboratory tests on industrial ore to determine the formation mechanisms of sinter phases. The samples were heated up to 1 100°C to 1 350°C in a horizontal tube furnace in air, nitrogen and CO/CO$_2$. Three distinct assemblages were observed; at low temperatures (1 100°C) CF and CF$_2$ formed, ‘SFCA’ and C$_2$S were present at higher temperatures (1 150°C to 1 300°C) and finally magnetite formed at the highest temperatures (1 50°C to > 1 300°C). Under reducing atmospheres it was found that the stability of ‘SFCA’ decreased and CF$_2$ formed in preference to CF$_2$. The authors concluded that during sintering, CF$_2$ or CF$_2$ formed first from solid state reactions, followed by melting of these ferrites and crystallisation of ‘SFCA’ on cooling from the liquid with crystallisation promoted by the presence of a viscous melt. A melt having a low viscosity was considered to solidify too rapidly to allow crystallisation of ‘SFCA’ from the melt.

Da Costa$^9$ heated ore samples in air with or without fluxes to examine sinter phase formation. It was found that hematite decreased with temperature, magnetite was formed above 1 257°C and ‘SFCA’ formed at high temperatures, with most ‘SFCA’ present at temperatures between 1 225°C and 1 300°C. At higher temperatures, the ‘SFCA’ phase diminished and the proportion of melt and magnetite increased. This research did not explore the mechanisms of ‘SFCA’ formation in detail, but the stability range of ‘SFCA’ agreed with other researchers.

Wang$^{10}$ performed a sinter pot test with both hematite and magnetite ores and interrupted sintering part way through. The sinter pot was dissected and analysed. In the combustion zone, for magnetite sinters, C$_2$S, Fe$_2$O$_3$ and minor calcium ferrite between the two was present. With a decrease in temperature, the calcium ferrite changed in shape (sheet-like to acicular), C$_2$S decreased and the proportion of glass increased. In the hematite sinter, similar microstructures and phases were seen, with the exception of a greater proportion of calcium ferrite and hematite. The
calcium ferrite was analysed with EDS and XRD and was considered to be SFCA. Based on the observed phases present and their location in the sinter pot, it was suggested that SFCA formed via a reaction between C2S, CaO and Fe2O3 initially forming a calcium ferrite and that incorporation of Al2O3 resulted in SFCA. Wang considered SFCA forms from solid state reactions, but the reacting phases conflicted with that of previous researchers i.e. CF and CF2 phases were not observed. These are both key phases observed by others in the formation of SFCA.

As indicated previously, Patrick and Pownceby systematically investigated the solid solution range and thermal stability of SFCA within the four-component Fe2O3–CaO–Al2O3–SiO2 system using a high temperature equilibrium quenching method. They presented schematic phase diagrams showing the relationship of SFCA with surrounding phases and estimated that SFCA containing high alumina contents (up to ~31.5 wt%) were stable up to temperatures above ~1480°C.

Pownceby and Clout experimentally determined the phase relations in the model sinter systems such Fe2O3–Al2O3–CaO–SiO2 to examine the links between iron ore chemical composition and the temperatures used during sintering. Results from experiments to determine the effect of 1·0, 2·0 and 3·0 wt% Al2O3 on phase relations between 1240 and 1300°C in air are shown in Fig. 11. SFCA was stabilised to higher temperatures by the addition of alumina (dark solid line in Fig. 11). Pownceby and Clout noted that in many high-Fe charges SFCA-I was present as an equilibrium phase. The texture exhibited by SFCA-I was generally very fine grained and ‘meshlike’ in appearance (e.g. Fig. 10) making it impossible to distinguish from other calcium ferrite phases. The stability range of SFCA-I was therefore not determined during this study although its approximate position within the FACS quaternary is shown schematically in Fig. 11 by the circled area at high Fe contents.

5.2. High Temperature in situ Studies
Scarlett et al. used a quantitative in situ XRD technique to research the phase changes occurring during the heating of synthetic iron ore sinter mixtures in air. The XRD analysis indicated a number of phase changes occurred during heating including C2F formation, CF formation, SFCA-I formation and SCFA formation. C2F was observed to form at between 650°C and 780°C (depending on alumina content) from a solid state reaction between CaO and Fe2O3. CF was then observed to form by a reaction between C2F and Fe2O3 at around 920°C to 1000°C, when the proportion of C2F was greatest. SFCA and SFCA-I formed at roughly the same temperature via solid state reactions. With increasing alumina at a similar CaO/SiO2 ratio and Fe2O3 content, the temperature at which both SFCA and SFCA-I began to form was decreased, and for samples containing 1 wt% and 5 wt% Al2O3, SFCA and SFCA-I appeared to form at similar temperatures. The temperature at which the two phases occurred varied with sample composition. DTA was also performed to identify the formation of a melt in the sample, which occurred via the melting of SCFA-I at around 1230°C. The experimental technique used a much slower heating rate to that in industrial processes (10 to 20°C/s),

![Fig. 11. Series of diagrams showing effect of increasing alumina on phase relations in the high Fe2O3-part of the Fe2O3–Al2O3–CaO–SiO2 system between 1240 and 1300°C in air. The approximate location of the stability field for SFCA-I is shown by the circled area. Modified from Pownceby and Clout.](image-url)
potentially affecting the reaction mechanisms on heating and leading to a different series of reactions being observed to that occurring in industrial processes.

Webster et al.\textsuperscript{31}) performed \textit{in-situ} synchrotron XRD experiments on synthetic oxides to examine the formation of SFCA and SFCA-I iron ore sinter phases during heating and cooling of synthetic iron ore sinter mixtures in the range 25°C to 1 350°C and at oxygen partial pressure of $5 \times 10^{-3}$ atm. During heating, SFCA-I formation at 1 054°C to 1 119°C (depending on composition) was associated with the reaction of Fe$_2$O$_3$, C$_2$F, and SiO$_2$. SFCA formation (1 107°C to 1 164°C) was associated with the reaction of CF, SiO$_2$, and a CFA phase (with average composition average composition 71.7 wt% Fe$_2$O$_3$, 12.9 wt% CaO, 0.3 wt% SiO$_2$ and 15.1 wt% Al$_2$O$_3$). Increasing Al$_2$O$_3$ concentration increased the temperature range over which SFCA-I was stable before the formation of SFCA, and it stabilised SFCA to a higher temperature before it melted to form a Fe$_3$O$_4$+melt phase assemblage (1 213°C to 1 308°C). During cooling, the first phase to crystallize from the melt (1 179°C to 1 288°C) was the phase designated Fe-rich SFCA which, as discussed earlier. At lower temperatures (1 145°C to 1 270°C), this phase reacted with melt to form SFCA. Increasing Al$_2$O$_3$ increased the temperature at which crystallisation of the Fe-rich phase occurred, increased the temperature at which crystallisation of SFCA occurred, and suppressed the formation of Fe$_2$O$_3$ (1 085°C to 1 145°C) to lower temperatures. The set of reaction sequences determined by Webster et al.\textsuperscript{31}) are shown in Fig. 12. This research investigated conditions closer to industrial sintering processes when compared to the earlier work by Scarlett,\textsuperscript{54,55}) but like the earlier work the heating and cooling rates are not directly comparable with industrial conditions.

Webster et al.\textsuperscript{28}) expanded their initial \textit{in-situ} XRD work to investigate the formation mechanisms of SFCA and SFCA-I during heating of a synthetic iron ore sinter mixture in the range 25–1 350°C and at pO$_2 = 0.21, 5 \times 10^{-3}$ and $1 \times 10^{-4}$ atm. Oxygen partial pressure was observed to have a significant effect on the formation of SFCA-I and SFCA. If the oxygen partial pressure was too low, SFCA-I did not form. Instead, a Ca-rich ferrite phase, CFAAlSi$_3$, formed through a reaction between C$_3$(F$_{1-x}$A$_x$)$_3$, CF, SiO$_2$ and Fe$_2$O$_3$. Conversely, if the pO$_2$ was too high, the thermal stability range of SFCA-I before the formation of SFCA (see Webster et al.\textsuperscript{31}) was reduced. In addition, SFCA, which had previously been determined to be a key precursor phase in the formation of SFCA at pO$_2 = 5 \times 10^{-3}$ atm, was also observed to form at pO$_2 = 0.21$ and $1 \times 10^{-4}$ atm with the proportion decreasing with increasing pO$_2$.

Webster et al.\textsuperscript{37}) further expanded their \textit{in situs} XRD work to examine the formation mechanism of SFCA-I using synthetic sinter mixtures in the temperature range 25–1 350°C in air and at pO$_2$ of $5 \times 10^{-3}$ atm. In air, the initial formation of SFCA-I at ~1 165°C (depending on composition) was associated with reaction of precursor phases Fe$_2$O$_3$, CaO·Fe$_2$O$_3$, SiO$_2$, amorphous Al-oxide and the CFA phase. At temperatures above ~1 165°C, the decomposition of another phase, γ-CFF, resulted in the formation of additional SFCA-I. At lower oxygen partial pressure the initial formation of SFCA-I occurred at similar temperatures and was associated with reaction between similar phases as its formation in air. However, the decomposition of γ-CFF did not result in the formation of additional SFCA-I, with the maximum SFCA-I concentration (25 wt%) lower than the values attained in air (54 and 34 wt%). Hence, more oxidising conditions was observed to favour the formation of SFCA-I phase.

Webster et al.\textsuperscript{58}) also investigated the effects of basicity (CaO: SiO$_2$ ratio (wt/wt)) on the thermal range, concentration, and formation mechanisms of SFCA and SFCA-I using \textit{in-situ} XRD and, for the first time, \textit{in-situ} neutron diffraction. Increasing basicity significantly increased the range of temperatures at which SFCA-I is present, from 1 090°C to 1 260°C for a mixture with a basicity of 2.48 to ~1 050°C to 1 320°C a basicity of 4.94. Increasing basicity increased the proportion of SFCA-I formed, from 18 wt% for the mixture with B = 2.48 to 25 wt% for the B = 4.94 mixture. The basicity did not appear to influence the formation mechanism of SFCA-I. It did, however, affect the formation mechanism of SFCA, with the decomposition of SFCA-I coinciding with the formation of a significant proportion of additional SFCA in the mixtures with a basicity of 2.48 and 3.96 but only a small proportion in the highest basicity mixture, a basicity of 4.94. \textit{In situ} neutron diffraction enabled characterisation of the behaviour of magnetite after melting of SFCA produced a magnetite plus melt phase assemblage.

The most recent \textit{in-situ} XRD work by Webster et al.\textsuperscript{28,59,60}) investigated the effects of titanomagnetite addition (in the form of New Zealand ironsand), the form of the alumina (i.e. gibbsite vs kaolinite vs aluminous goethite), and the addition of millscale on the formation of SFCA and SFCA-I. Results are summarised as follows:

- Increasing titanomagnetite ironsand addition in an otherwise synthetic sinter mixture composition designed to form SFCA-I did not significantly affect the thermal stability range of SFCA-I (~1 100–1 250°C), I, nor did it significantly affect the proportion of SFCA-I attained. (42–46 wt%). The

Fig. 12. Summary of the reaction sequences in the formation of the SFCA phases during heating (zone 1) and cooling (zone 3) in the range 25°C to 1 350°C and at pO$_2$ = $5 \times 10^{-3}$ atm. Zone 2 is the regime where Fe$_3$O$_4$ and melt coexist. T = temperature. (from Webster et al.\textsuperscript{31}).
main effect of iron sands addition was observed to be a small reduction in the thermal stability range of the γ-CFF phase. In comparison, increasing titanomagnetite iron sand addition from 2.4 to 3.9 and to 11.6 wt% in a mixture designed to form SFCA resulted in a decrease in the maximum SFCA-I concentration, from 30, to 24 and 16 wt%, respectively, with a corresponding increase in the proportion of SFCA (16, to 23 and 33 wt%).

- Iron ore in which the primary source of alumina is gibbsite is less likely to form high ‘SFCA’ phases due to the low reactivity of the amorphous alumina which forms from gibbsite decomposition leading to low proportions of SFCA-I and SFCA. Alumina in the form of kaolinite or aluminous goethite, however, produced larger proportions of both SFCA-I and SFCA and at lower temperatures due to higher reactivity of the intermediate phases.

- Increasing mill scale addition from 2.6 to 10.6 and to 21.2 wt% in an otherwise synthetic sinter mixture composition designed to form SFCA did not significantly affect the thermal stability ranges of SFCA-I or SFCA. In addition, it did not significantly affect the amount of each of SFCA or SFCA-I, which formed. This was attributed to the relatively high chemical purity of the mill scale. Also, the transformation to hematite during heating of the wüstite and magnetite present in the mill scale meant that all of the Fe₂O₃ was in a reactive form.

The formation of calcium ferrites during heating and cooling was investigated by in situ and real-time observation using a newly developed quick X-ray diffraction (Q-XRD) system to identify the phases formed and an in situ laser microscope to examine the microstructures. In the new Q-XRD, a specimen was heated up to 1 773 K, and X-ray diffraction patterns were measured using a pixel-array area detector with an interval as short as a few seconds. Cooling rates of \(-8.3 \times 10^{-1}\) or \(-8.3 \times 10^{-2}\) K/s were achievable which is more realistic of cooling rates in industrial processes. In situ observation both of crystal structure and microstructure successfully revealed the effects of heating and cooling rates on the sintering reaction in the CaO–Fe₂O₃ system with special attention to overheating and overcooling phenomena. While to work has only been applied to phases in the CaO–Fe₂O₃ system, the technique should prove useful when other oxides such as SiO₂ and Al₂O₃ are present, the mechanism of formation of composite oxides such as SFCA and SFCA-I.

5.3. Summary and Future Directions for ‘SFCA’ Formation Research

The formation of SFCA and SFCA-I at sintering conditions close to, or at those relevant to industrial sintering, has been investigated by a large number of researchers using a variety of ex situ and in situ techniques. Research using in situ techniques has shown that these two phases can form via solid state reactions with significant differences in the proposed reactions, and phases formed, under different conditions and compositions. These techniques however, are unable to replicate the time scale of industrial sintering. In contrast, some researchers have proposed that the SFCA phases form during solidification in industrial sintering, but there has been limited research investigating these processes. Only a limited range of compositions and conditions relevant to industrial conditions have been studied without the quantification of process kinetics or a systematic evaluation of the sensitivity of the processes to process conditions. Further research is required to generate a complete understanding of the conditions required for the formation of ‘SFCA’ bonding phases. This includes conditions both relevant to, and differing from, industrial sintering thus enabling the comprehensive understanding of the formation and reactions between phases in industrial sintering.

Suggested areas of research include:

- The impact of the bulk composition on the formation of SFCA-I is yet to be established. No data currently exists as to: a) the stability region, and b) solid solution limits of the SFCA-I phase.
- It has been established that the proportion and form of Al₂O₃ and TiO₂ affect the formation of SFCA and SFCA-I. Further research into the impacts of the proportion and form of other minor components requires further investigation, specifically MgO and phosphorous.
- Significant work is required to determine the mechanisms occurring during melt solidification. It is believed that these processes determine the final phases observed.
- Research on the mechanisms and kinetics of SFCA and SFCA-I formation during heating and cooling need to be performed at conditions relevant to industrial processes. Limited research has been performed to date at conditions replicating industrial sintering.

6. Conclusion

Laboratory and pilot scale studies have been surveyed to review the chemical composition, thermochemistry, structure and formation conditions for the ‘SFCA’ group of phases, considered to be the major bonding phases in iron ore sinter-making. A formidable body of data exists and a high level understanding of the fundamentals of the ‘SFCA’ group of phases has been established. There are however, significant discrepancies in data reported in literature and missing information due to the high complexity of the chemical systems and operation conditions involved in sinter-making. Future studies have been suggested to comprehensively understand the ‘SFCA’ fundamentals.

Another key aspect that is of great interest to sinter producers is the relationship between the various ‘SFCA’ phases such as SFCA and SFCA-I and sinter properties such as strength, reducibility and softening behaviour in the blast furnace. A detailed summary of this information is out of the scope of present review and we note very few systematic studies are available in literature. It is further recommended that future research focuses on establish this relationship at a fundamental level through controlled experimental studies. The outcome is expected to help plant operators to make informed decision rather fully relying on empirical correlation based on sinter pot tests.

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