A Phase Equilibrium of the Iron-rich Corner of the CaO–FeO–Fe₂O₃–SiO₂ System in Air and the Determination of the SFC Primary Phase Field

Jiang CHEN, Maksym SHEVCHENKO,* Peter Charles HAYES and Evgueni JAK

Pyrometallurgy Innovation Centre, School of Chemical Engineering, The University of Queensland, Brisbane, Queensland, 4072 Australia.

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Experimental studies of the CaO–FeO–Fe₂O₃–SiO₂ system in air from 1 200°C to 1 260°C have been carried out in the Fe-rich region with particular focus on the phase equilibria associated with silico-ferrite of calcium (SFC) phase. The measurements have been made possible through the use of a modified experimental technique involving high temperature equilibration and rapid quenching followed by electron probe X-ray microanalysis (EPMA). Isothermal sections for 1 220°C, 1 240°C, 1 255°C and 1 260°C are reported providing information on the limits of stability of the SFC solid solution and the liquidus in the SFC primary phase field for the first time.

KEY WORDS: SFC; phase equilibria; liquidus; slags; CaO–FeO–Fe₂O₃–SiO₂.

1. Introduction

The system CaO–FeO–Fe₂O₃–SiO₂ forms the basis for the description of the chemical behaviour of slags encountered in a wide range of metallurgical ferrous and non-ferrous processing systems. For this reason, there has been considerable research effort to characterise the phase equilibria and liquidus of this system. Most of the research has been undertaken at slags having relatively high silica concentrations since these compositions are of direct application to steelmaking slags and non-ferrous smelting systems.

The iron-rich, low-silica corner of the system is of particular interest to ironmaking practice. The production of high quality iron ore sinter is an important factor in achieving high productivity, and high thermal and chemical efficiencies in modern blast furnace practice. Control of sinter microstructure is the key factor in attaining optimum physical and chemical properties. Research to date has suggested that particular phases, namely silico-ferrite of calcium (SFC)^{1–3)} and/or silico-ferrite of calcium and aluminium (SFCA),^{4–16)} formed during the sinter making process, play a dominant role in determining the sinter microstructure,^{17,18)} and important metallurgical properties of iron ore sinter, such as, reducibility, mechanical strength and softening temperature. From the point of view of improving sinter quality, it is vitally important to understand the critical conditions necessary to form this phase. Relatively few fundamental phase equilibrium studies have been undertaken on these high-iron, low-silica slags, since experimental investigations

of these systems are extremely difficult to carry out due to difficulties in quenching the liquid slag. This, however, is the focus of the present investigation.

The currently accepted version of the liquidus of the CaO–Fe₂O₃–SiO₂ system in air reported in the Slag Atlas¹⁹⁾ is shown in **Fig. 1** and is based on the previous studies.^{20,21)} It can be seen that there is no liquid primary phase field for the SFC phase included in the diagram, nor are any thermodynamic data on the SFC phase included in any of the chemical thermodynamic databases currently available. In addition, the saddle point at 1 242°C on the boundary line between dicalcium silicate (Ca₂SiO₄) and calcium diferrite (CaFe₄O₇) is inconsistent with the 1 226°C peritectic (L + Fe₂O₃ = CaFe₄O₇) and 1 205°C eutectic (L = CaFe₂O₄ + CaFe₄O₇) on the pseudo-binary calcium diferrite liquidus; the latter points taken from Phillips and Muan.²²⁾

The results obtained by Schurmann and Krause²³⁾ using thermal analysis for the liquidus for the C₂F and CF primary fields agree closely with those of²²⁾ but they reported the L + C₂F → CF peritectic temperature to be at 1 228°C rather than 1 216°C. It should be noted that thermal analysis may give significant errors in systems where absorption or loss of oxygen from atmosphere is involved in solid-liquid transitions, such as the Ca–Fe–O system in air. More recent measurements of liquid and solid compositions have been made in the CaO–Fe₂O₃ pseudo-binary system in air using the equilibration, quenching and microanalysis technique.²⁴⁾ The experimental results obtained by Liu²⁴⁾ indicated good agreement with the data reported by^{22,23)} on the positions of the liquidus of the H, C₂F and CF₂ primary phase fields. The direct measurement of melt compositions, however, indicated that the eutectic temperature and the peritectic

* Corresponding author: E-mail: m.shevchenko@uq.edu.au
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Fig. 1. Previous diagram for the CaO–“Fe₂O₃”–SiO₂ system in air.¹⁹⁾ The insert is drawn by the present authors to zoom the area of interest in.¹⁹⁾

Fig. 2. The CaO–“Fe₂O₃” pseudo-binary system in air.^{22,24,28,29)}

temperatures for CF and CF₂ phases are higher by 5–10°C than reported by Phillips and Muan.²²⁾

The liquidus compositions predicted by FactSage thermodynamic calculation software with FToxid database^{25–28)} for the C₂F, CF, H and CF₂ primary phase fields are at consistently higher Fe₂O₃ concentrations than all measured experimental data,^{22–24)} whereas the newer optimisation by Hidayat *et al.*²⁹⁾ gave lower temperatures of liquidus and invariant reactions. Comparisons of the reported phase and invariant equilibria in the CaO–“Fe₂O₃” system in air are given in Fig. 2 and Table 1.

The phase equilibria related to the SFC solid solution have been studied previously by a number of researchers. A study by Inoue and Ikeda³⁰⁾ has found the SFC to be stable between 1 100°C and 1 250°C in air. A later study

Table 1. Comparison of the reported invariant equilibria in the CaO–“Fe₂O₃” system in air.

Reaction	Temperature, °C	Composition wt.% CaO	wt.% “Fe ₂ O ₃ ”	Reference
L → CF + CF ₂	1 205	20.0	80.0	²²⁾ exp
eutectic	1 205	20.3	79.7	²³⁾ exp
	1 207 (1 atm O ₂)	21.3	78.7	³⁶⁾ model
	1 214	20.8	79.2	²⁸⁾ model
	1 210–1 215	22.0	78.0	²⁴⁾ exp
	1 208	20.9	79.1	²⁹⁾ model
	1 210			Accepted in present study
L + C ₂ F → CF	1 216	24.5	75.5	²²⁾ exp
peritectic	1 228	24.6	75.4	²³⁾ exp
	1 219 (1 atm O ₂)	24.2	75.8	³⁶⁾ model
	1 220	21.2	78.8	²⁸⁾ model
	1 220–1 230	24.6	75.4	²⁴⁾ exp
	1 220	23.3	76.7	²⁹⁾ model
	1 220			Accepted in present study
L + H → CF ₂	1 226	18.9	81.1	²²⁾ exp
peritectic	1 226	19.2	80.8	²³⁾ exp
	1 229 (1 atm O ₂)	19.4	80.6	³⁶⁾ model
	1 225	19.7	80.3	²⁸⁾ model
	1 230–1 240	20.4	79.6	²⁴⁾ exp
	1 223	19.4	80.6	²⁹⁾ model
	1 230			Accepted in present study

L = liquid; CF = calcium monoferrite (CaO·Fe₂O₃), CF₂ = calcium diferrite (CaO·2Fe₂O₃), C₂F = dicalcium ferrite (2CaO·Fe₂O₃), H = hematite (Fe₂O₃)

by Hamilton *et al.*⁵⁾ reported the SFC solid solution phase to be stable between 1 067°C to 1 192°C. More comprehensive phase equilibria studies¹⁾ of the CaO–“Fe₂O₃”–SiO₂ system in air were undertaken for the iron-rich corner of the phase diagram between 1 240 and 1 300°C. Synthetic chemical mixtures (3.5 g) supported by Pt foil were equilibrated in air before quenching into water. The samples were then examined using optical microscopy, EPMA and XRD analysis. The authors reported the phases present after equilibration and plotted the results onto isothermal sections of the CaO–“Fe₂O₃”–SiO₂ ternary phase diagram. They found the SFC phase to be stable up to 1 252°C in air and to melt incongruently at higher temperatures to form hematite and liquid. The compositional range of the SFC stability was measured by electron probe microanalysis and reported to be between 3.9 wt% and 6.8 wt% SiO₂. Using this experimental technique, it was possible to identify the primary phases formed on equilibration but it was of great challenge to measure the compositions of the coexisting liquid phases since the liquid phase rapidly crystallised on cooling of the sample.

Further studies³⁾ have demonstrated that the SFC phase forms a crystal structure of M₁₄O₂₀ and the SFC solid solution is stable over a range of compositions on the pseudo-binary CF₃–C₄S₃. This stoichiometry of the phase has been shown to be consistent with the substitution reaction $2\text{Fe}^{3+} = \text{Ca}^{2+} + \text{Si}^{4+}$.

Using these data, a number of schematic isothermal sections have been constructed.^{2,3)} The results have provided a valuable initial guide to the phases present in the CaO–FeO–Fe₂O₃–SiO₂ subsystem in the composition ranges of interest to iron ore sintering; however, not all the observed phase compositions were reported. It was clear that using this technique it was not possible to retain the low-SiO₂ liquids present at temperature as a glass phase on cooling to room temperature; this meant it was not possible at that time to accurately determine the liquidus surface in the high-iron region of the system or the conjugate phase relations between solid and liquid solutions.

The aim of the present study is to use an improved experimental technique (including open support substrate – platinum wire – and quenching into iced water to ensure maximum cooling rates; careful control of achievement of equilibrium; use of additional standards for electron probe microanalysis) to accurately determine the slag liquidus compositions and the solid/liquid phases that coexist at equilibrium with focus on the SFC primary phase field.

2. Experimental

Experimental procedures for phase equilibrium measurements have been developed by the Pyrometallurgy Innovation Centre (PYROSEARCH) at the University of Queensland.³¹⁾ The technique involves high temperature equilibration of a synthetic oxide sample in a controlled gas atmosphere. The sample is then rapidly quenched so that the phase assemblage present at high temperature remains unaltered. The quenched sample is mounted in epoxy resin, polished for metallographic examination and microanalysis, and the compositions of the crystalline solid and glass phases are measured by electron probe X-ray microanalysis (EPMA) with wavelength dispersive detectors (WDD).

2.1. Preparation of Oxide Mixtures

The starting mixtures were made from CaO (prepared by heating 99.98 wt.% purity CaCO₃ in air at 1 000°C for 18 hours), Fe₂O₃ (99.98 wt.% purity) and SiO₂ (99.98 wt.% purity) supplied by Sigma-Aldrich Co, NSW, Australia. Mixtures of selected bulk compositions were prepared by weighing the high purity powders and mixing them thoroughly using an agate mortar and pestle for 30 minutes. The initial compositions of the mixtures were selected in such a way that at least 2 condensed phases are present in equilibrium. Each mixture was then compacted with pressure of 40 MPa to produce a small pellet weighing approximately 0.2 gram.

In the present study, to address the difficulty in quenching a high-fluidity low-SiO₂ liquid, an open support technique was adopted. A dish-shaped container with diameter approximately 10 mm was made from a 0.5 mm thick platinum-rhodium alloy (6–30 wt.% Rh) wire supplied by AGR Matthey (Melbourne, Australia) by winding the wire into a spiral shape. The pelletized sample was then placed on the container and secured by Pt-Rh wire. During equilibration, the sample became partially molten and flowed into the gaps between the spirals and was held onto the wire by the surface tension. In this way, on quenching the sample the liquid slag phase was the first phase to come in direct contact with the quenching medium (water). This results in very high quenching rate and minimizes the extent of crystallisation of the liquid during the quenching process. It was found that platinum, under the conditions investigated, did not dissolve in or contaminate the slag samples.

2.2. High Temperature Equilibration Technique

All equilibration experiments were conducted in a vertical reaction tube (impervious re-crystallized alumina, 30-mm i.d.) in electrical resistance-heated furnaces with silicon carbide (SiC) elements. The sample was introduced from the bottom of the vertical tube furnace and suspended by a sample holder constructed using Pt wire. The 30-mm i.d. re-crystallized alumina reaction tube was preconditioned at the target temperature for more than 30 minutes, and the specimen was then raised into the uniform temperature hot zone of the furnace. After the equilibration, the specimen was rapidly quenched by dropping it directly into the iced water. The samples were mounted in epoxy resin, polished using conventional metallographic polishing techniques and carbon coated for subsequent electron probe X-ray microanalysis (EPMA).

2.3. Control of Temperature

To monitor the actual temperature surrounding the sample, a working thermocouple of 6 wt.% Rh/Pt – 30 wt.% Rh/Pt was placed in a re-crystallised alumina thermocouple sheath immediately adjacent to the sample. The working thermocouple was calibrated against a standard thermocouple 6 wt.% Rh/Pt – 30 wt.% Rh/Pt (supplied by the National Measurement Institute of Australia, NSW, Australia). The temperature of the experiment was continuously controlled within 1°C of the target temperature. It is estimated that the overall absolute temperature accuracy of the experiment is within 5°C.

2.4. Analysis Technique and Selection of Measurement Points

The rapid quenching technique successfully retains phase assemblages present at the equilibration temperatures. The compositions of the various phases were measured using JEOL 8200L EPMA with wavelength dispersive detectors (JEOL is a trademark of Japan Electron Optics Ltd., Tokyo). A 15-kV accelerating voltage and 15 nA probe current were selected for the microanalyser operation. The standards (Charles M. Taylor, Stanford, CA) used in the EPMA measurements were as follows: wollastonite (CaSiO_3) for Ca and Si, hematite (Fe_2O_3) for Fe. The Duncumb–Philibert correction based on atomic number, absorption, and fluorescence (ZAF correction, supplied by JEOL) was applied. The accuracy of compositions measured was expected to be within 1 wt%. Only the metal cation concentrations were measured with EPMA; the oxide concentrations for presentation purposes were recalculated using assigned oxidation states.

It was found³²⁾ that JEOL ZAF correction gives systematic deviations of measured cation ratios in the Fe–Si–O system. In particular, measured mol. fraction Si/(Si+Fe) in fayalite Fe_2SiO_4 is 34.3% instead of actual 33.3%. Therefore, fayalite has been accepted as an additional standard, and a custom correction is applied for the measured Si/(Si+Fe) ratio. A dedicated series of experiments has been conducted to synthesize $\text{Ca}_2\text{Fe}_2\text{O}_5$, CaFe_2O_4 and CaFe_4O_7 crystals by heating the elemental oxides at temperature just below solidus, in proportion that gives mixtures of these compounds in equilibrium with each other. Theoretically, the listed compounds may undergo limited substitution of Ca^{2+} by Fe^{2+} , which lowers the Ca/(Ca+Fe) ratios from stoichiometric values (0.5 for $\text{Ca}_2\text{Fe}_2\text{O}_5$, 0.333 for CaFe_2O_4 , and 0.2 for CaFe_4O_7). However, all synthesized crystals showed higher Ca/(Ca+Fe) ratios: 0.506 for $\text{Ca}_2\text{Fe}_2\text{O}_5$, 0.336–0.340 for CaFe_2O_4 , and 0.205 for CaFe_4O_7 , indicating deviation of JEOL ZAF correction in Ca–Fe–O system towards overestimated fraction of Ca up to 0.6 mol.%. This information for Fe–Si–O and Ca–Fe–O systems has been combined into a formula that allows to correct all cation concentrations in the ternary CaO –“ Fe_2O_3 ”– SiO_2 system:

$$x(\text{SiO}_2)^{\text{corr}} = x(\text{SiO}_2) - 0.0637x(\text{SiO}_2)x(\text{FeO}_{1.5})(1 - x(\text{SiO}_2))$$

$$x(\text{CaO})^{\text{corr}} = x(\text{CaO}) - x(\text{CaO})x(\text{FeO}_{1.5}) \\ (0.0208 + 0.0119(x(\text{FeO}_{1.5}) - x(\text{CaO})))$$

$$x(\text{FeO}_{1.5})^{\text{corr}} = 1 - x(\text{SiO}_2)^{\text{corr}} - x(\text{CaO})^{\text{corr}}$$

where $x(\text{SiO}_2)$, $x(\text{CaO})$, $x(\text{FeO}_{1.5})^{\text{corr}}$ are corrected cation molar fractions.

As mentioned previously, due to the high fluidity of low- SiO_2 liquid, it was impossible to obtain well-quenched liquid phase across the whole sample even when the open support method was used. Mounted samples were examined carefully under the electron microscope at high magnifications and well-quenched areas were selected when carrying out the EPMA measurement for the liquid phase. A typical example of back-scattered electron micrograph of a sample containing hematite–SFC–liquid three condensed phase equilibrium assemblage is shown in **Fig. 3**. It consists of large crystalline hematite and SFC grains surrounded by a

Fig. 3. Example of microstructures observed (in backscattered electron mode) in the CaO –“ Fe_2O_3 ”– SiO_2 system in air at 1 240°C showing the hematite–liquid–SFC phases in equilibrium.

liquid phase. Within the liquid phase and at the interface of liquid and solids, clusters of fine needle-shaped microcrystalline phases were observed; these phases were believed to have precipitated out of the liquid during quenching (e.g. region A). It is generally found that better quenching was obtained at the edges of the sample where direct contact with quenching media was expected. Measurement of the liquid composition should then be carried out on the well-quenched areas, such as B, rather than those of type A, where there is the presence of microcrystalline precipitates. The direct observation of the phase assemblage makes it possible to distinguish phases that were present at the equilibration temperature. In this sense, the present technique is superior to the use of XRD, although the latter can provide useful information on the crystal structures and confirm the individual phases present. The cracks in the sample have formed after cooling as evidenced by the continuity of the crack position across the phase boundaries between solid and (liquid) glass phases, and the solid/solid interface boundaries.

2.5. Assessment of Attainment of Equilibrium

In the present study, particular attention was paid to achievement of equilibrium. For each condition this was confirmed by i) equilibration for different times, ii) checking the uniformity of phase compositions across the samples, iii) approaching equilibrium from different starting conditions, and iv) considering possible reactions specific to the investigated system taking place in the sample during equilibration.

Selected experiments were carried out at different times in order to determine the minimum time required to attain equilibrium; for example; **Table 2** reports the results of experiments with samples equilibrated for 2, 8 and 24 hours.

It can be seen that both compositions of liquid and SFC were noticeably different after 8 h equilibration compared with sample equilibrated for 2 hours. After 24 h equilibration, the changes in composition are within the measurement uncertainty of EPMA. Therefore, the minimum time for equilibration was selected as 8 h.

Table 2. Measured phase compositions for samples in the CaO–Fe₂O₃–SiO₂ system equilibrated at different times. Legend: L=liquid; SFC=SFC solid solution.

Time of equilibration/ hours	Temperature °C	$P(\text{O}_2)$, atm.	Phase at equilibrium	Composition wt. %		
				CaO	Fe_2O_3	SiO_2
2	1 240	0.21 (air)	L	25.2	64.9	9.9
			SFC	14.9	84.4	0.8
L			24.7	67.7	7.6	
SFC			13.3	83.2	3.5	
L			25.2	67.4	7.3	
SFC			13.4	83.0	3.6	

3. Results

3.1. CaO–Fe₂O₃–SiO₂ System in Air

3.1.1. Phase Compositions

The following phases have been identified in the range of compositions investigated: liquid (L), silico-ferrite of calcium solid solution (SFC), hematite H (Fe₂O₃), dicalcium silicate C₂S (2CaO·SiO₂), calcium diferrite CF₂ (CaO·2Fe₂O₃) and calcium monoferrite CF (CaO·Fe₂O₃). The phases observed in the present study and their compositions measured by EPMA are given in **Table 3**. Each of the reported phase compositions represents an average of at least six measurements in different areas across the sample and normalised to 100 wt. pct. The measured composition of iron is reported as Fe₂O₃ for presentation purposes.

3.2. Microstructures

Examples of typical microstructures observed in equilibrated samples in the CaO–Fe₂O₃–SiO₂ system are shown in **Fig. 4**. In Figs. 4(a) and 4(b), where a liquid phase is present, the equilibrated phases were found to have good contact with each other and a dense microstructure was obtained. Figure 4(a) shows the microstructure of the three-condensed-phase SFC–hematite–liquid equilibrium. The hematite and SFC phases are principally present in the form of large blocky grains, 50–100 μm diameter. The majority of the liquid has formed a homogenous glassy (liquid) phase indicating the liquid was well quenched; a small area of crystallization containing fine, solid SFC crystals is observed in the bulk matrix. In Fig. 4(b), at equilibrium the SFC crystals exhibit a plate-like structure and are evenly distributed amongst the homogeneous liquid phase. Inspection of a number of samples indicates that the very fine (sub-micron) SFC crystals observed in Figs. 4(a) and 4(b) are formed during cooling of the melt and are not present at the equilibration temperature.

Each of the crystallised solid phases exhibited different shapes of faceted crystals within the liquid oxide matrix. In Figs. 4(c) and 4(d), where only the solid phases hematite, SFC and dicalcium silicate (C₂S) are present, that is no liquid is present, the equilibrated samples are found to be more porous in structure than in samples with presence of the liquid phase. All the phases are irregular in shape but have good contact and interconnect with each other, which suggests that the samples are well-equilibrated. This was confirmed with multiple EPMA measurements undertaken

Table 3. Compositions of the phases measured by EPMA in the CaO–Fe₂O₃–SiO₂ system in equilibrium in air. Legend: L = liquid; H = hematite; C₂S = dicalcium silicate; CF₂ = calcium diferrite; CF = calcium ferrite; SFC = SFC solid solution.

Temperature (°C)	Experiment No.	Phases	Composition (wt.%)		
			CaO	Fe ₂ O ₃	SiO ₂
1 260	1	L	22.6	73.7	3.6
		H	0.1	99.9	0.0
	2	L	24.8	67.2	8.0
		H	0.1	99.8	0.1
	3	L	28.5	58.2	13.3
		H	0.2	99.7	0.1
1 255	4	L	24.5	69.0	6.4
		SFC	14.4	81.5	4.1
		H	0.2	99.8	0.0
	5	L	26.4	63.1	10.5
		SFC	14.7	80.7	4.6
		C ₂ S	65.0	0.5	34.5
	6	L	22.9	73.3	3.7
		H	0.1	99.9	0.0
	7	L	25.2	67.4	7.3
		SFC	13.4	83.0	3.6
	8	L	25.8	66.6	7.5
		SFC	14.6	80.7	4.7
1 240	9	L	24.8	68.6	6.5
		SFC	13.0	83.6	3.4
	10	L	22.7	73.4	3.8
		SFC	13.4	83.5	3.1
	11	H	0.3	99.7	0.0
		L	22.3	74.7	3.0
	12	H	0.2	99.8	0.0
		L	26.0	65.8	8.2
	13	SFC	14.7	80.5	4.9
		SFC	14.9	80.1	5.1
		H	0.2	99.8	0.0
1 220	14	C ₂ S	64.6	0.9	34.5
		SFC	13.1	84.8	2.1
		H	0.1	99.9	0.0
	15	CF ₂	14.6	85.2	0.3
		SFC	14.6	80.3	5.2
		H	0.1	99.9	0.0
	16	C ₂ S	65.0	0.6	34.4
		SFC	13.6	83.7	2.8
		H	0.2	99.8	0.0
	17	L	25.7	69.2	5.1
		SFC	14.5	80.7	4.9
		C ₂ S	65.1	0.2	34.7
1 210	18	L	21.8	76.4	1.8
		CF ₂	14.7	85.3	0.0
	19	L	24.4	72.8	2.8
		CF	25.7	74.2	0.1

Fig. 4. Examples of microstructures observed (in backscattered electron mode) in the CaO–“Fe₂O₃”–SiO₂ system in air. a: Hematite–liquid–SFC equilibrium at 1 240°C; b: Liquid–SFC equilibrium at 1 240°C; c: Hematite–CF₂–SFC equilibrium at 1 220°C; d: SFC–C₂S–Hematite equilibrium at 1 255°C. Legend: H = Hematite, SFC = SFC, L = Liquid, C₂S = Dicalcium silicate, P = Pores.

in each phase in different sample locations, which demonstrated that each of the individual grains was uniform in composition and that the compositions of the hematite, SFC and dicalcium silicate in all phases were independent of position in the sample. It should be pointed out that the dicalcium silicate crystals present in Fig. 4(d) on cooling have gone through the structural transition from α' -Ca₂SiO₄ to γ -Ca₂SiO₄ during which a significant density change has occurred. As a result, the Ca₂SiO₄ phase in the sample tends to be mechanically weak and to readily disintegrate. Close examination of the C₂S phase shown in Fig. 4(d) reveals the presence of microcracks in this phase.

3.3. Isothermal Sections of the CaO–“Fe₂O₃”–SiO₂ System in Air

The experimental results obtained following equilibration in air at 1 220°C, 1 240°C, 1 255°C and 1 260°C are plotted in isothermal, pseudo-ternary sections of the CaO–“Fe₂O₃”–SiO₂ system shown in **Figs. 5** through **8**. The binary and ternary phase fields associated with the SFC have been identified at each temperature and are also marked on the figures. The phase fields present and the shapes of the intersecting

Fig. 5. Isothermal section of the CaO–“Fe₂O₃”–SiO₂ system in air at 1 220°C. Solid lines are phase boundaries determined by present study; dashed lines are phase boundaries estimated based on present study, CaO–“Fe₂O₃” pseudo-binary data²⁹⁾ and CaO–“Fe₂O₃”–SiO₂.¹⁹⁾

Fig. 6. Isothermal section of the CaO–“Fe₂O₃”–SiO₂ system in air at 1 240°C. Solid lines are phase boundaries determined by present study; dashed lines are phase boundaries estimated based on present study, CaO–“Fe₂O₃” pseudo-binary data²⁹⁾ and CaO–“Fe₂O₃”–SiO₂.¹⁹⁾

Fig. 7. Isothermal section of the CaO–Fe₂O₃–SiO₂ system in air at 1255°C. Solid lines are phase boundaries determined by present study; dashed lines are phase boundaries estimated based on present study, CaO–Fe₂O₃ pseudo-binary data²⁹⁾ and CaO–Fe₂O₃–SiO₂.¹⁹⁾

Fig. 8. Isothermal section of the CaO–Fe₂O₃–SiO₂ system in air at 1260°C. Solid lines are phase boundaries determined by present study; dashed lines are phase boundaries estimated based on present study, CaO–Fe₂O₃ pseudo-binary data²⁹⁾ and CaO–Fe₂O₃–SiO₂.¹⁹⁾

phase fields have been constructed so as to comply with the phase diagram rules,³³⁾ including the Schreinemaker's rule.³⁴⁾ In constructing the isothermal sections and the liquidus for the CaO–Fe₂O₃–SiO₂ system in the present study, the eutectic and peritectic temperatures for the CF and CF₂ phases as well as liquidus on the CaO–Fe₂O₃ binary reported by Hidayat *et al.*²⁹⁾ for the CaO–Fe₂O₃ pseudo-binary system in air have been used.

It can be seen in the temperature range investigated, the phase assemblages at the Fe₂O₃-rich corner of the system were found to be very sensitive to bulk composition and temperature. The SFC solid solution was found to be stable at temperatures in the range 1220°C to 1255°C in air and to melt incongruently to form the liquid and hematite phases at 1257°C.

3.4. Liquidus between 1200°C to 1260°C

The liquidus surface of the iron-rich corner of the CaO–Fe₂O₃–SiO₂ system in air deduced from the results of the present investigation is shown in Fig. 9. The eutectic and peritectic temperatures on the CaO–Fe₂O₃ pseudo-binary system in air were taken from Hidayat *et al.*²⁹⁾ The CF and CF₂ phases melt incongruently and form a binary

eutectic at 1210°C. This eutectic reaction extends into the SiO₂-containing system and an invariant equilibrium point involving air, liquid, C₂S, CF and CF₂ phases estimated to be at 1192°C (point *e* on Fig. 9) and approximately 3.9 wt.% SiO₂.

The primary phase field of SFC (labelled as "S") was found to exist in a narrow range of compositions between ~3.3–11.0 wt.% SiO₂. The SFC field is bounded by the primary phase fields of hematite (labelled as "H"), calcium diferrite (labelled as "CF₂") and dicalcium silicate (labelled as "C₂S"). The points *abcd* on Fig. 9 mark the limits of the SFC primary phase field.

- Point *a* marks the coexistence of the liquid–SFC–CF₂–H phases;
- point *b* marks the coexistence of the liquid–C₂S–CF₂–SFC phases;
- point *c* marks the coexistence of the liquid–C₂S–SFC–H phases; and
- point *d* marks the coexistence of the liquid–SFC–H, point *d* represents the maximum temperature at which SFC can exist in air; above this temperature only liquid and hematite are present. The dashed lines marking the particular isotherms indicate their estimated positions. A summary

Fig. 9. Liquidus of the CaO–Fe₂O₃–SiO₂ system in air including the SFC primary phase field based on the results of the present study and binary data reported by.²⁹⁾ SFC = SFC solid solution; “CF₃” = imaginary compound that has chemical formula of CaO·3Fe₂O₃; “C₄S₃” = imaginary compound that has chemical formula of 4CaO·3SiO₂. Temperatures in °C. Thin dashed lines are estimated liquidus isotherms; thin solid lines are measured liquidus isotherms; thick dashed lines are estimated univariant lines. The invariant points and univariant lines are estimated from the present experimental results.

Table 4. Estimated Invariant points in the CaO–Fe₂O₃–SiO₂ system in air in the iron oxide-rich region. Refer to Fig. 10 for point a–e.

Reaction		Temperature, °C	Liquid Composition, wt. %			
			CaO	“Fe ₂ O ₃ ”	SiO ₂	CaO/SiO ₂
L + C ₂ F → L + CF + C ₂ S	Peritectic	1 195	25.7	71.3	3.0	8.6
L → CF + CF ₂ + C ₂ S	Eutectic	1 192 (point e)	25.0	71.2	3.7	6.7
L + SFC → L + CF ₂ + C ₂ S	Peritectic	1 216 (point b)	24.8	70.7	4.5	5.5
L + H → L + CF ₂ + SFC	Peritectic	1 225 (point a)	23.1	73.7	3.2	7.3
L + H → L + C ₂ S + SFC	Peritectic	1 256 (point c)	26.9	62.4	10.7	2.5
L + H → L + SFC	Peritectic	1 257 (point d)	23.9	69.2	6.8	3.5

of estimated invariant temperatures and compositions in this subsystem is given in **Table 4**.

4. Discussion

4.1. Isothermal Sections

The previous study by Pownceby *et al.*¹⁾ reported SFC to be present at 1 240°C but not at 1 255°C or above. The previously constructed isothermal section at 1 240°C compared to the present results is shown in **Fig. 10**. The limits of the fully liquid region in the low-silica slags obtained in the present study was found to be narrower than reported.¹⁾ In particular, the 1 240°C isotherm in the C₂S primary phase field has been found at ~2 wt.% higher Fe₂O₃ compared to;¹⁾ the 1 240°C isotherm in the SFC primary phase field agrees with¹⁾ within the experimental uncertainty. At the same time, what is different between the sections shown in Figs. 5 through 8 (present study) and those previously reported in Fig. 10^{1,2)} is the interpretation of the phase boundaries and conjugate lines in the sub-liquidus regions of the sections. In the 1 240°C isothermal section in Fig. 6 determined in present study, both the liquid + hematite (L+H) and SFC+dicalcium silicate (SFC+C₂S) two-phase regions are

Fig. 10. Isothermal section of the CaO–Fe₂O₃–SiO₂ system in air at 1 240°C constructed by Pownceby *et al.*¹⁾ Shaded areas denoted by α and β are the fully liquid regions. Dashed lines: liquid region determined by present study; dotted lines: SFC solid solution determined in present study.

included, but these are absent from the previously presented diagram.^{1,2)}

4.2. Liquidus

The liquidus obtained in the present study for the CaO–

“Fe₂O₃”–SiO₂ system, shown in Fig. 9, differs from the accepted diagram for this system to date¹⁹⁾ as illustrated in Fig. 1. The SFC phase did not appear in the previous version of the liquidus. The present study provides information on the limits of the SFC primary phase field. This information is essential to identify the compositions and temperatures at which this phase will form from the liquid.

The narrow composition range over which the SFC phase can be formed as well as similar morphology of SFC and CF₂ crystals helps to explain why the presence of this SFC primary phase field was not recognised in the earlier investigations that used optical microscopy method for phase identification.

4.3. Liquid Composition in Equilibrium with the SFC Phase

Using the liquidus data in Fig. 9, the projected limiting compositions for liquid in equilibrium with the SFC phase in air are plotted as a function of temperature vs CaO/SiO₂ weight ratio in Fig. 11. The points a–d represent the invariant points at the liquidus involving the SFC phase;

Fig. 11. Projection of liquid composition in equilibrium with SFC solid solution.

the lines joining these points give the liquid compositions and coexisting phases. It can be seen from the figure, when in equilibrium with SFC phase, the CaO/SiO₂ of the liquid ranges from approximately 2.5 to 7.1.

4.4. SFC Solid Solution

In the present study, at the temperatures investigated, the SFC phase was found to be stable up to 1257°C, and to decompose to form hematite and liquid. The range of the SiO₂ concentration in the SFC solid solution phase in air is plotted against temperature as shown in Fig. 12. It can be seen that for the temperature range investigated, both the lower and upper limits of SiO₂ solubility in SFC increase with the decrease of temperature. At 1240°C the SFC is stable in the SiO₂ concentration ranges from 3.3 wt.% to 5.1 wt.% while temperature decreases to 1220°C, the SFC is stable in the SiO₂ concentration expands and ranges from 2.2 wt.% to 5.4 wt.%; this is different from what has been reported by Pownceby and Patrick suggesting temperature has little effect on the solid solution range of SFC phase.³⁾

Fig. 12. Schematic illustration of the limits of stability of the SFC solid solution in air determined in the present study and by Pownceby and Patrick.³⁾ Legend: SFC=SFC solid solution.

Fig. 13. Plot of compositions of SFC phases in the CaO–Fe₂O₃–SiO₂ ternary system.

4.5. Substitution Mechanism

A number of different mechanisms to explain the range of the SiO₂ solubility in the SFC phase have been proposed previously.^{1,5,30,35)} In the study by Inoue and Ikeda³⁰⁾ it was proposed that the composition of SFC lies between the end members CaO·3Fe₂O₃ (CF₃) and CaO·SiO₂ (CS). An alternative substitution mechanism with CaO·2Fe₂O₃ (CF₂) and CaO·3SiO₂ (CS₃) as end members of SFC was proposed by Dawson *et al.*³⁵⁾ Hamilton *et al.*⁵⁾ suggested the SFC lies along the join of CaO·3Fe₂O₃ (CF₃) and 4CaO·3SiO₂ (C₄S₃). This later substitution reaction can be described by the replacement of ferric ions in the crystal structure with silicon 4+, and calcium and iron 2+ ions, as follows:

The results from the study by¹⁻³⁾ were in agreement with proposed substitution with Hamilton *et al.*⁵⁾

The compositions of all the SFC phases measured in the present study are plotted in a CaO–Fe₂O₃–SiO₂ ternary phase diagram together with all previously proposed substitution binary lines as shown in Fig. 13. It can be seen that the compositions of the SFC at high SiO₂ concentrations appear to lie on the C₄S₃–CF₃ line indicating agreement with the substitution mechanism proposed by Hamilton *et al.*⁵⁾ The SFC phase formed at low-SiO₂ compositions appears as fine, plate-like structures. It appears that further detailed analysis of these results are necessary before firm conclusions about this trend can be made.

5. Summary

Experimental techniques have been developed for the rapid quenching of low-SiO₂, iron-rich, high-fluidity liquids to room temperature and in doing so preventing the crystallisation of the liquid phase. This has enabled phase equilibria in the CaO–FeO–Fe₂O₃–SiO₂ system in air to be determined with particular focus on identifying the limits of stability of the SFC phase.

Isothermal sections in the CaO–“Fe₂O₃”–SiO₂ system in air have been constructed for 1 220°C, 1 240°C, 1 255°C and 1 260°C. The SFC solid solution was found to be stable below 1 257°C in air and to melt incongruently to form hematite and liquid above this temperature. The experimental data have been used to define the primary phase field of SFC and the liquidus between 1 200°C to 1 260°C.

The substitution mechanism of SFC solid solution was found to be in good agreement with the reaction $\text{Si}^{4+} + (\text{Ca}^{2+}, \text{Fe}^{2+}) = 2\text{Fe}^{3+}$. The phase assemblages in the temperature range investigated were found to be highly sensitive to bulk composition and temperature.

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