Solidification of Melts in the CaO-“Fe₂O₃”-SiO₂ System

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Abstract

In order to provide further insight into the chemical reactions and phase transformations taking place during iron ore sintering fundamental studies have been undertaken on the solidification of liquids in the $\text{Fe}_2\text{O}_3$-CaO-$\text{SiO}_2$ system in air. A new experimental technique and analysis methodology has been developed that enables the phases and microstructures formed at selected temperatures to be identified. The technique involves the melting and solidification of a small mass of an oxide powder mixture at a controlled cooling rate followed by rapid quenching. The resulting microstructures and phases present in the sample are characterised through the use of electron probe micro X-ray analysis (EPMA) measurements. The new approach makes it possible to systematically investigate the influence of key process variables and to accurately measure the compositions of the phases and their sequence of formation. In addition, an improved experimental technique has been used to measure the temperatures and oxygen partial pressures experienced by the materials in the sinter bed during pilot scale sintering.

The phases formed during the cooling of high iron melts have been shown to critically depend on the thermodynamic properties of the system, the crystal structures of the phases and the kinetics of the solidification processes.

Of particular interest to industrial iron ore sintering operations is the formation of the silico-ferrite of calcium (SFC) phase, which is isomorphic with silico-ferrite of calcium and aluminium (SFCA). The focus of the experimental study has been on bulk liquid compositions for which it is anticipated that the silico-ferrite of calcium (SFC) phase would form on equilibrium solidification. The effects of melt composition, the initial primary phase field, $\text{Fe}_2\text{O}_3$ concentration, CaO/$\text{SiO}_2$ ratio, and cooling rate were investigated.

The phases identified in the solidified products include, hematite, dicalcium silicate, calcium diferrite, calcium monoferrite, SFC-I and $\text{Ca}_{7.2}\text{Fe}^{2+}_{0.8}\text{Fe}^{3+}_{3.0}\text{O}_{57}$. The results of the experimental studies show that the solidification paths do not follow those anticipated from equilibrium or Sheil-Gulliver cooling. Significantly, the SFC phase does not form from the solidification of the melts at any of the conditions investigated in the $\text{Fe}_2\text{O}_3$-CaO-$\text{SiO}_2$ system in air.

The complex morphologies and phase assemblages in the final products are shown to be the result of solidification of the melt and include; equiaxed facetted hematite and magnetite; dendritic di-calcium silicate; divorced and coupled structures of di-calcium silicate and hematite; individual calcium diferrite crystals; coupled structures of calcium diferrite and di-calcium silicate; individual calcium monoferrite crystals; coupled structures of calcium monoferrite and di-calcium silicate; coupled structures of calcium diferrite, di-calcium silicate and calcium monoferrite.

The sequences of phases formed on solidification of iron rich compositions are more closely described by Sheil-Gulliver cooling of a metastable liquidus of the $\text{Fe}_2\text{O}_3$-CaO-$\text{SiO}_2$ system that does not include the SFC primary phase field.

The heterogeneous nucleation of SFC on hematite appears not to be favoured. The SFCA-I phase, having a crystal structure related to SFCA, is observed to nucleate homogeneously from the melt and preferentially the surfaces of magnetite under conditions where this latter phase is present.

The formation of secondary hematite in industrial sinter has been shown to take place through the oxidation of magnetite at sub-liquidus and sub-solidus temperatures.
The study lays the foundation for further systematic studies in the system “Fe₂O₃”-CaO-SiO₂ system in the iron rich region including minor concentrations of Al₂O₃ and MgO, for compositions that more closely resemble those produced in industrial processing operations.
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**Published manuscripts included in this thesis**


2. "Controlled solidification of liquids within the SFC primary phase field of the \( \text{Fe}_2\text{O}_3 \)-\( \text{CaO-SiO}_2 \) system in air", Nicol, S., Jak, E., and Hayes P. C., Met. Trans. B, 2019, Online first

3. “Measurement of Process Conditions Present in Pilot Iron Ore Sintering”, Stuart Nicol\(^1\)*, Jiang Chen\(^3\), Wei Qi\(^2\), Xiaoming Mao\(^2\), Evgueni Jak\(^1\) and Peter C Hayes\(^1\), Minerals, 2019, 9(6), 374, p1-28

**Submitted manuscripts included in this thesis**

4. “Effect of cooling rate on the controlled solidification of \( \text{Fe}_2\text{O}_3 \)-\( \text{CaO-SiO}_2 \) liquidus in iron ore sinter”, Nicol, S., Jak, E., and Hayes P. C., submitted 2019

5. “Effect of \( \text{Fe}_2\text{O}_3 \) on the controlled solidification of \( \text{Fe}_2\text{O}_3 \)-\( \text{CaO-SiO}_2 \) liquidus in iron ore sinter”, Nicol, S., Jak, E., and Hayes P. C., submitted 2019

**Manuscripts prepared for submission included in this thesis**

6. “Effect of \( \text{CaO/SiO}_2 \) ratio on the controlled solidification of \( \text{Fe}_2\text{O}_3 \)-\( \text{CaO-SiO}_2 \) liquidus in iron ore sinter”, Nicol, S., Jak, E., and Hayes P. C.

7. “Silico Ferrite of Calcium (SFC) Formation in the \( \text{Fe}_2\text{O}_3 \)-\( \text{CaO-SiO}_2 \) system”, Nicol, S., Jak, E., and Hayes P. C.

**Other Publications during candidature**


2. “Experimental liquidus studies of the Pb-Cu-Si-O system in equilibrium with metallic Pb-Cu alloys”,, Shevchenko, M., Nicol, S., Hayes, P. C., Jak, E., Met. Trans B, 2018, 49(4), 1690-1698

Contributions by others to the thesis

Significant contributions to the thesis were made by Professor Peter Hayes, Professor Evgueni Jak and Dr Jeff Chen in the assistance in experimental design, analysis of results and preparing this thesis.

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Sintering, Solidification, Iron Ore, “Fe₂O₃”- CaO-SiO₂

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1. Introduction

Over one billion tonnes of steel are produced annually using the iron blast furnace/basic oxygen steelmaking route. The sintering process is a key high temperature processing step used in the preparation of a competent feed for the iron blast furnace, with some furnaces operated almost entirely on sinter feed (Lu and Ishiyama, 2015). Iron sinter bulk compositions vary significantly between operations, and typically involve the use of a blend of ores and flux materials. The principal chemical components are Fe$_2$O$_3$, Fe$_3$O$_4$, CaO, MgO, SiO$_2$ and Al$_2$O$_3$. In the sintering process, solid materials are heated, and partly melted, to produce bonded particles. Sintering enables iron ore fines, typically <5mm diameter, to be economically processed and used in the blast furnace process.

Agglomerating the furnace feed increases the productivity of iron blast furnaces (Lloyd, 1922) and allows less expensive feeds and fine recycled material to be processed. The use of agglomerated feed increases the bed voidage, decreases the pressure drop through the furnace allowing for an increased blast rate. This increases the productivity of blast furnaces, and improves fuel, reductant utilisation and overall technical and economic performance. Since the physical and chemical properties of iron ores are inherently variable, and variations in composition and microstructure of the sinter product are observed, it is desirable to develop a more fundamental understanding of the reactions taking place in the process and in doing so to be able to predict outcomes for different materials and process conditions. The improvement of the iron ore sinter process represents a significant technical and scientific challenge. The sinter process is a complex heterogeneous reaction system, and there have been many attempts to characterise and understand the changes taking place during this process. The focus of the current research is on aspects of the solidification of melts during iron ore sintering.

The principle aims of the present study are to identify the phases, microstructures and processes occurring on the solidification of “Fe$_2$O$_3$”-CaO-SiO$_2$ melts. This represents the principal chemical subsystem describing these iron oxide rich materials.

The ternary “Fe$_2$O$_3$”-CaO-SiO$_2$ system was selected as;

1. The ternary phase diagram describing the liquidus in air has been well defined.
2. All major sinter phases observed in industrial sinters are present in this ternary system
3. The ternary system contains the major components in sinter

These aims are to be achieved through:

1. Critical analysis of the elementary processes taking place during the sintering process.
2. Identifying the key process variables influencing the solidification process.
3. Designing and implementing appropriate experimental methodologies and techniques.
4. Characterising, analysing and measuring key features of the sinter product microstructures formed during solidification.
5. Developing quantitative relationships between key process parameters and sinter microstructures.

1.1 Iron Ore Sintering in Industry

1.1.1 Iron Ore Characteristics and Mineralogy

The iron ore used in industrial operations comes from a wide variety of sources globally. Most of the iron ore mined and processed in Australia is currently from deposits in Western Australia. These deposits originate from Banded Iron Formations (BIF), which formed as a result of photosynthesis or
photo oxidation in the earth’s oceans. This resulted in the oxidation of dissolved \( \text{Fe}^{2+} \) and subsequent precipitation of iron from solution as \( \text{Fe(OH)}_3(s) \) (Hagemann et al., 2016). With the precipitation of iron hydroxides, the ocean also became more acidic and this, along with a change in the potential of the solutions, \( E_h \), led to the precipitation of other minerals, including silica. The precipitated phases formed large deposits of iron hydroxides and silica. These were buried and underwent metamorphism to form a BIF. The metamorphism converted the iron hydroxides \( \text{Fe(OH)}_3 \) into hematite \( \text{Fe}_2\text{O}_3 \) and then in some cases into magnetite \( \text{Fe}_3\text{O}_4 \). The other minerals, including the silica, are transformed into more stable phases and morphologies.

Some of the BIF deposits have undergone enrichment processes to form a variety of different iron deposits, including Banded Iron Deposits (BID), Detrital Iron Deposits (DID) and Channel Iron Deposits (CID) (Dalstra, 2011, Morris and Kneeshaw, 2011, Morris and Ramanaidou, 2007). An unenriched BIF contains typically 20 - 40 wt% Fe and 43 - 56 wt% \( \text{SiO}_2 \). A BIF is enriched to form a BID, which in turn weathers to form a DID and CID. These three deposits have higher iron concentrations than their parent materials, typically containing approximately 60 wt% Fe.

The mineralogy of iron ores is highly dependent on the orebody, with significant variation in both the minerals present and their compositions. Common iron minerals found in these orebodies include (Clout and Manuel, 2015);

- Hematite \( \text{Fe}_2\text{O}_3 \)
- Magnetite \( \text{Fe}_3\text{O}_4 \)
- Goethite \( \text{FeOOH} \) (or \( \text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O} \))
- Maghemite \( \text{Fe}^{3+}_(1.67,\text{Va}_{0.33})\text{O}_4 \)
- Kenomagnetite \( \text{Fe}_{5.4}(\text{Va})_4\text{O}_4 \)
- Martite \( \text{Fe}_2\text{O}_3 \) (pseudomorph after magnetite)
- Hydrohematite \( \text{Fe}_{2-x/3}(\text{OH})_x\text{O}_{3-x} \)

(note: \( \text{Va} \) denotes a vacancy in the crystal structure)

The gangue minerals in iron ores include (Clout and Manuel, 2015);

- Quartz \( \text{SiO}_2 \)
- Kaolinite \( \text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_8 \)
- Gibbsite \( \text{Al(OH)}_3 \)
- Minnesotaite \( (\text{Mg,Fe})_2\text{Si}_6\text{O}_{10}(\text{OH})_2 \)
- Stilpnomelane \( (\text{K,Na,Ca})_2.6(\text{Mg,Fe}^{2+},\text{Fe}^{3+})_6\text{Si}_8\text{Al}(\text{O,OH})_{27-24}\text{H}_2\text{O} \)
- Chlorite \( (\text{Fe,Al,Mg})_4(\text{Si,Al})_2\text{O}_5(\text{OH})_6 \)
- Pyrite \( \text{FeS}_2 \)
- Pyrolusite \( \text{MnO}_2 \)
- Ankerite \( \text{Ca}(\text{Fe,Mg,Mn})(\text{CO}_3)_2 \)

The minerals present in ore and the bulk iron concentrations vary both between orebodies, and within a single orebody. The most common gangue mineral in iron ore is quartz, with clays and other silicates present depending on the orebody. Of the iron ore minerals, goethite is able to contain a significant concentration of impurity elements, including silicon, aluminium and phosphorus (Clout and Manuel, 2015). These elements can be in a solid solution or in separate compounds. The iron ore minerals and the gangue minerals present influence the outcomes of the sinter process. Iron ore fines for sintering are marketed as particles less than 6 mm diameter (Wei, 2017); variations in ore mineralogy, texture
and composition are accommodated at the mine site by blending and targeted mining and mineral separation practices.

1.1.2 Iron Ore Sintering in Practice

The process technology used industrially for the sintering of iron ore is the Dwight-Lloyd moving grate machine (Ball, 1973). The downdraft sintering process is continuous, with the process steps illustrated schematically in Figure 1-1.

![Figure 1-1: A schematic diagram illustrating the typical process steps undertaken in iron ore sintering (Lu and Ishiyama, 2015)](image)

The material to be sintered is mixed and blended, with coke, limestone and dolomite to form granules (Ball, 1973). Typically iron fines from a number of different sources are used, including but not limited to (Lloyd, 1922): blast furnace flue dust, iron ore concentrates, iron hydrates, iron oxides, and mill scale. A number of different agglomeration strategies are used industrially to control the distribution of the materials within the granules. The agglomerated solids, typically less than 8mm (Lu and Ishiyama, 2015) in diameter, are charged onto the top of sinter grates with a feeder designed to ensure even feeding and an unsegregated charge. The sinter bed charge is typically 0.5 to 1.0 m thick and 4 to 6 m wide (Lu and Ishiyama, 2015). Oil or gas burners are used to initially heat up the top layer and ignite the surface of the charge. Air is drawn down through the charge with downdraft fans. The sinter grates are moved over the wind boxes at 2 to 3 m/min (Lu and Ishiyama, 2015). As the air passes through the bed, the coke combustion provides additional heat to the charge, allowing the bed to heat up to typically between 1300°C and 1375°C (Lu and Ishiyama, 2015).

The solids discharged from the sinter machine are cooled, crushed and sized to produce particles approximately 50 mm diameter, appropriate feed for the blast furnace. The fine materials produced during these preparation processes are returned to the sinter machine to be reprocessed into a coarser material. The coarse sintered material needs to be strong and reduce well in the blast furnace.

1.1.3 Iron Ore Sinter Input Parameters

A number of process parameters are used to control the sintering process. The majority of these are associated with the blending, selection and pre-processing of the feed materials, with relatively few
machine variables able to be controlled in the operation of the sintering machine. These parameters include (Ball, 1973, Lu and Ishiyama, 2015, Lloyd, 1922);

- Ore type and composition
- Ore and flux size distribution
- Coke particle size distribution
- Coke reactivity
- Coke in charge (wt% of charge)
- Feed moisture concentration
- CaO/SiO$_2$ ratio in the sinter (limestone or lime addition)
- MgO in the sinter (dolomite addition)
- Return sinter addition
- Granulation process and sequence
- Granule size distribution
- Sintering gas composition and recycle
- Distribution of phases within the sinter feed granules
- Air flowrate or suction pressure

The composition of the individual feed materials are controlled by purchasing particular feeds and blending in the stockyard. The ratio of the materials in the feed is typically controlled in blending and granulation, through the measurement and control of the mass flowrates. The feed moisture is controlled with the water flowrate at the granulation process. The principle parameter controlled during sintering is the air suction, which is typically fixed by the fan and motors installed.

1.1.4 Iron Ore Sintering Output Characteristics

The output targets are typically, a high sinter throughput, low sinter cost and good quality sinter. The output characteristics measured are (Ball, 1973, Lu and Ishiyama, 2015, Lloyd, 1922);

- Sinter productivity (t.m$^{-2}$.d$^{-1}$)
- Sintering temperature (°C)
- Sinter composition (CaO/SiO$_2$, MgO)
- Sinter strength
- Sinter reducibility

In industrial processes, the downdraft fan pressure drop is generally constant along the sinter strand and is set to achieve the desired sinter productivity onsite. The rate of air drawn through the sinter bed and the sinter strand speed limit the throughput and production rate of a sintering machine.

To obtain the desired thermal profile, the coke breeze particle size and addition rate is controlled to ensure that there is a match between the heat front and the flame front velocities to achieve the highest peak bed temperature (Ball, 1973) and plant throughput.

The CaO/SiO$_2$ ratio and the MgO concentration in the sinter are controlled to achieve a high sinter strength and reactivity, along with the desired blast furnace slag composition. Superfluxed sinter has a significantly higher CaO/SiO$_2$ ratio to that in the blast furnace slag. Initial research on the effects of composition on sinter strength found that a high lime sinter (i.e. >1.5 CaO/SiO$_2$ (wt/wt)) and low lime sinter (i.e. <1.5 CaO/SiO$_2$) were strongest (Ball, 1973). Sinters with a CaO/SiO$_2$ ratio of approximately 1.5 wt/wt were observed to have a low strength. The high lime sinter was believed to be strong due to the presence of calcium ferrite bonding phases and the low lime sinter was strong due to silicate glasses (Ball, 1973). An additional benefit of fluxing at the sinter machine, rather than the blast
furnace, is that the decarbonation of limestone and dolomite is performed with a cheaper fuel. Currently, the majority of sinter used in industry has a CaO/\text{SiO}_2\text{ ratio of 1.7 or above (Lu and Ishiyama, 2015). The flux additions made to the sinter are selected to achieve the desired chemical compositions in bosch and tapping slags in the blast furnace.

1.1.5 Processes in Iron Ore Sintering

During the sintering process, heat and mass transfer occurs. The cumulative microscale heat transfer processes lead to the macroscale heat transfer. On the macroscale, as the combustion front travels down through the charge, the thermal profiles move progressively down through the sinter bed (Ball, 1973). The rates of heating, peak bed temperatures, times at temperature and cooling rates vary with vertical position within the bed. However, the same overall temperature profile is observe at all heights within the sinter bed. The movement of the heat front is the result of the heat transfer between hot solids and cold gas at the top of the sinter bed and between hot gas and cold solids at the bottom of the bed.

The macroscale thermal history of sinter in different parts of the bed have been determined from sinter pot tests. These tests are laboratory bench scale tests used for quality control and optimisation of sintering. They are routinely performed to determine the effects of changes in feed composition, moisture, suction pressure and other parameters on the sinter properties and production. To measure the temperatures thermocouples are positioned at different heights in the sinter pot. This allows the thermal history of sintering to be determined and extrapolated to industrial conditions. An example temperature profile from a sinter pot test is shown below in Figure 1-2 (Garbers-Craig et al., 2003). The temperature profiles in the sinter pot tests have been shown to reflect those within an industrial sinter bed.

![Figure 1-2: The measured thermal history of sinter in a sinter pot test (Garbers-Craig et al., 2003)](image)

These temperature profiles have three distinct stages, heating, peak bed temperature and cooling. During the heating stage, the green sinter is heated by hot gas and coke combustion to the peak bed temperature. The peak bed temperature is the maximum temperature attained in the sintering
process, with a high peak bed temperature and maximum time close to the peak bed temperature typically desired. The temperature and time above the solidus temperature increases the proportion of melt present in the sinter. The cooling is the result of the contact of cold air with the hot sinter.

The thermal history of the sinters in industrial operations vary considerably (Garbers-Craig et al., 2003, Tahanpesaranedezful and Moghadam, 2012, Umadevi et al., 2014, Dabbagh et al., 2013)

- Heating rate – 4 to 24 °C/s
- Peak bed temperature – 1200 - 1400°C
- Cooling Rate – 0.8 to 4 °C/s
- Flame front speed – 0.01 to 0.04 cm/sec

Burlingame (Burlingame et al., 1957) undertook a series of sinter pot tests to determine the macroscale processes and heat transfer occurring during sintering. The sinter pot tests were stopped part way through by the addition of nitrogen, which stopped the combustion of coke and cooled the sinter. The sinter pot was dissected and analysed both visually and with wet chemical analysis of the materials. In the testwork, five zones were identified; the cooling zone, the combustion zone, the preheat zone, the drying or dehydration zone and the recondensation zone (Burlingame et al., 1956). The zones and the key reactions in each are shown in Figure 1-3.

In the cooling zone, fresh air is drawn through hot sinter and cools it down. The hottest sinter in this zone has just left the combustion zone and has little or no coke remaining. The solids and air temperature profiles in this zone are counter current and this improves the heat transfer efficiency. The air is heated up in this zone and this improves the energy efficiency of the combustion in later zones.

In the combustion zone, warm air is drawn through the hot solids and the oxygen in the air reacts with the coke. The coke combustion provides heat and partly melts the solids. This creates the hottest point in the sinter bed. This zone is quite thin and is commonly called the flame front. In this zone, the presence of solid carbon has the potential to create locally reducing conditions.

![Figure 1-3: Schematic showing the five zones in sintering and key reactions occurring.](image-url)
The hot air from the combustion zone is drawn into dry solids and heats them up. This increases the solids temperature and recovers heat from the hot air. Some of the solids in this zone are able to undergo dehydroxylation (e.g. Fe(OH)$_{252}$) and decarbonation (e.g. CaCO$_{390}$).

In the drying zone, the hot air heats up the wet solids and evaporates physically entrained water. The solids are dried and all physically entrained water is removed. The hot air leaving the drying zone is cooled further in the recondensation zone. If the temperature is low enough and the air is saturated, some of the water condenses.

On a microscale, heat is transferred between oxide solids in a sinter and the gas phase. The heat transfer processes are important and require control. The following diagram illustrates these processes during the heating of the sinter:

![Figure 1-4: Schematic diagram showing the microscale heat transfer between gas and solids during sintering.](image)

The processes identified include:

- $q_{\text{rad}}$ – radiative transfer of heat from the surface of the particle to the surrounding gas phase and other solid particles
- $q_{\text{conv}}$ – convective transfer of heat from the surface particle to the gas phase
- $q_{\text{cond}}$ – conductive transfer of heat from the centre of the particle to the surface
- $q_{\text{comb}}$ – heat generated by the combustion of coke with oxygen in the gas
- $q_{\text{solid}}$ – heat generated by the solidification of oxides in the melt
- $q_{\text{mix}}$ – enthalpy associated with the change in solution composition due to changes to the heat of mixing with composition
- $q_{\text{oxid}}$ – heat generated by the oxidation of oxides in the particle with oxygen in the gas atmosphere

During heating, solid state reactions occur and phases in the sinter melt and dissolve (Scarlett et al., 2004b) to form a liquid oxide. In the cooling process the melt solidifies to form strong bonds (Webster et al., 2012). The heating and cooling rates of the solids, particularly that above the solidus temperature, has the potential to have a significant impact on the microstructure and properties of the sinter. The solidification of solids from the melt is of high importance to the final phases and
microstructures observed, and the formation of strong bonds in the sinter product. These processes are illustrated in Figure 1-5.

![Figure 1-5: A schematic of the iron ore sintering process. Four stages are shown, the initial mixing of solids (1), the formation of a melt at high temperatures (2), the solidification of the melt (3) and the final solidified sinter (4). (German, 2014)](image)

On a microscale, there are three types of chemical processes occurring in sintering, solid state reactions, dissolution and solidification. These three processes can occur concurrently during iron ore sintering, during both heating and cooling. These processes are transient, with the compositions of the solids and melt varying with time. These three processes are illustrated schematically in Figure 1-6.

![Figure 1-6: The three chemical processes occurring during sintering, solid state reactions, dissolution and solidification.](image)

All three processes involve mass transfer and reaction steps. Typically, the processes involving the melt are faster than for the solid phases as there is a larger surface area and a higher diffusivity in the melt compared to the solid phases.

1.2 Chemical Characteristics of Iron Ore Sinters

1.2.1 Iron Ore Sinter Composition and Phases

Iron sinter compositions vary significantly between operations, with the sinter typically high in Fe$_2$O$_3$, Fe$_3$O$_4$, CaO, MgO, SiO$_2$ and Al$_2$O$_3$. These phases typically exhibit solid solutions and multiple microstructure types. Iron ore sinter compositions are typically within the following range (Yang and Loo, 1997):

- Fe – 52 to 57 wt%
- CaO/SiO₂ – 1.4 to 1.8 wt/wt
- Al₂O₃ – 0.4 to 3 wt%
- MgO – 2.0 to 4 wt%
- TiO₂ – 0.03 to 0.3 wt%

The phases formed during sintering have been identified, typically using optical microscopy, scanning electron microscopy (SEM), electron probe X-ray microanalysis (EPMA) and X-ray Diffraction (XRD). The phases identified include; hematite (Fe₂O₃), magnetite (Fe₃O₄), Silico-Ferrite of Calcium and Aluminum (SFCA and SFCA-I), Larnite (Ca₂S, Ca₂SiO₄), Gehlenite (Ca₂AlFeSiO₇) and Glass (Ostwald, 1981). The glass phase is variable in composition, however it is consistently observed to contain a significant concentrations of SiO₂. The SFCA, magnetite, and hematite phases, along with others, are commonly in the form of solid solutions. Of these, the most complex and common phases in sintering are the SFCA phases; these have a significant impact on sinter properties (Ostwald, 1981).

1.2.2 Impact of Kinetic Processes on Iron Ore Sinter

Research on sinters has identified the microstructures present and the composition of the phases, typically using optical microscopy, electron microscopy and microanalysis techniques (Ostwald, 1981, Ahsan et al., 1983, Mukherjee and Whiteman, 1985). Using these techniques, a number of structures present in iron ore sinter have been identified.

Initial work (Dawson, 1993, Egundebi and Whiteman, 1989) identified that sinters showed a heterogenous microtexture, indicating that there were different reactions occurring within the sample. In some areas of the sample, unreacted or partly reacted ore was identified. Sinter at one industrial site was found to contain 30 to 40% unreacted material in the sinter, with unreacted material associated with lower quality sinter (Mukherjee and Whiteman, 1985). Cracks were also commonly found in unreacted areas.

During sintering, four main steps have been observed to occur. These are solid-state reactions, melting and dissolution of solids, solidification and oxidation (Ostwald, 1981, Webster et al., 2012, Dawson, 1993, Egundebi and Whiteman, 1989). The rates of each of these processes are limited by kinetics and this controls the microstructures and phases that form during sintering processes.

The first step at sub-solidus conditions is solid state reactions, occurring at the interface between solid particles present in sinter. It has been observed that solid state reactions occur between the ore and fluxes to form a variety of calcium ferrites and SFCA phases (Scarlett et al., 2004a, Scarlett et al., 2004b, Webster et al., 2012, Webster et al., 2013a, Webster et al., 2014). These solid state reactions are limited by solid state diffusion and the contact area between particles. As such, the reactions occurring and their extents in industrial sinters is limited by the particle size distribution and the extent of the particle mixing.

At higher temperatures, it was observed that the ferrites and SFCA phases melt and dissolve to form a molten oxide liquid (Scarlett et al., 2004a, Scarlett et al., 2004b, Webster et al., 2012, Webster et al., 2013a, Webster et al., 2014). This melt is able to dissolve other components in the sinter, including those that did not undergo solid-state reactions. In industrial sinters, the extent of dissolution can be limited by the mass transfer of material from the interface with coarse particles of ore and flux.

During cooling, the melt has been found to crystallise to form crystalline oxide phases. These phases have been observed to include SFCA, spinel and C₆S (Webster et al., 2012). Due to variations in local composition, there will be variable CaO/SiO₂ contents of the melt through the sinter. The morphology and phases formed in industrial sinters during solidification will be influenced by nucleation and mass transfer processes, surface reactions and the local chemical composition.
Due to the variable gas composition through the sinters thermal history, both reduction and oxidation of the sinter occurs. The oxidation of magnetite to hematite has been observed to occur on the edges of sinter lumps, indicating that the air reacts with the magnetite (Ostwald, 1981). The presence of this reaction at the surface indicates that it occurred on cooling after solidification had completed, otherwise there would be hematite evenly distributed throughout the sinter. The extent of this reaction will be limited by the solid-state diffusion of oxygen through the solids, which is in turn limited by the gas composition, temperature and time.

1.2.3 Microstructure of Iron Ore Sinter

Industrial sinter exhibits a wide range of microstructures, both between different sinter lumps and within a single lump of sinter. The phases observed in sinters have been observed to vary with bulk composition, with a higher proportion of glass and magnetite observed in sinters with a low CaO/SiO$_2$ ratio and a higher proportion of SFCA phases and C$_2$S in sinters with a high CaO/SiO$_2$ ratio. The proportion of other phases present, hematite, magnetite, pyroxene and other silicates, are observed to change as well. The variation in phases with bulk CaO/SiO$_2$ ratio is illustrated in Figure 1-7 (Bagnall, 1977). The change in phases present with composition occurs gradually, suggesting that there is heterogeneity in the local compositions with a sample in addition to the multi-phase equilibria. This further suggests that there are a number of different microstructures present in sinter.

![Figure 1-7: Variation in the proportion of phases in iron ore sinters with CaO/SiO$_2$ ratio. (Bagnall, 1977). Three types of sinters were suggested, based on the predominant phases, type A with magnetite and glass, type B with hematite, and Type C with calcium ferrite.](image)

Within a single sinter lump, multiple microstructures have been observed to form (Ostwald, 1981). This indicates differences in local composition, formation processes and resulting properties. Between different microstructures in the sinter lumps, there is either diffuse or distinct borders (Chen, 2017). While the microstructures present may not vary with a moderate change in bulk composition, it is
likely that the proportions of these microstructures vary. This would allow the system to achieve the required bulk composition, while maintaining the same microstructures and phases.

The microstructures observed in sinter can be classified with a variety of different systems. One of these classifies microstructures into four types (Chen, 2017). These four are illustrated in Figure 1-8. These are;

1. SFCA – Spinel (magnetite) – Liquid
2. Dense Cores of spinel and SFCA
3. Secondary hematite
4. Spinel/Hematite-Liquid

The SFCA-Spinel-Liquid microstructure is typically observed to be a significant proportion of sinter mass. This microstructure is shown in Figure 1-8a and Figure 1-8b. The SFCA and magnetite (spinel) are the major contributors to this microstructure, with the melt and C₃S minor contributors. Based on the microstructure it can be suggested that the magnetite (spinel) is potentially present at temperature and the other phases, along with the magnetite, crystallised from a melt during cooling. Two morphologies were observed for SFCA, platy and blocky (Ostwald, 1981). The SFCA is observed to have a faceted and regular shape, while the magnetite is subhedral.

In some instances, a dense core microstructure has been found inside the sinter and contains magnetite and SFCA. This microstructure is shown in Figure 1-8c. The SFCA is a minor contributor to the mass of this microstructure. The magnetite is typically coarse irregular in size and shape. Based on the microstructure, it is proposed that the SFCA is the continuous phase and the magnetite is the matrix phase. This suggests that at temperature, the magnetite is present and that the SFCA formed during melt solidification.

Hematite is found at the edges of the sinter lump, with a skeletal morphology. This microstructure is shown in Figure 1-8d. Other phases are observed in this microstructure. The hematite is typically faceted and large. This microstructure is typically observed at the edges of the sinter, suggesting that it formed from the oxidation of magnetite in air during sinter cooling.

In the iron oxide-glass microstructure, unlike the other microstructures, the spinel and/or hematite are observed without SFCA. This microstructure is shown in Figure 1-8e. The major phase is the iron oxides, with the liquid a small contributor. The iron oxides are typically fine grained and irregular and anhedral in shape. This microstructure is poor in CaO, suggesting that this microstructure formed in areas isolated from the limestone flux (Chen, 2017). The melt in this region is rich in SiO₂, which leads to difficulty in melt solidification due to the low diffusivity of species within the melts.
Figure 1-8: SEM Micrographs showing the microstructures observed in sinter, a) – Type 1, Blocky SFCA, b) – Type 1, Platy SFCA, c) – Type 2, Dense Cores, d) – Type 3, Secondary Hematite, e) – Type 4, Spinel/Hematite and Liquid (Chen, 2017).

note: SFCAM is an endmember of the SFCA phase, referring to SFCA with MgO included in the crystal structure
1.2.4 Iron Ore Sinter Properties and Performance

Iron ore sinter is smelted with coke to produce pig iron in the iron blast furnace. To produce the iron efficiently, the feed material must meet a number of requirements with regards to physical properties to promote gas flow through the furnace. These requirements ensure that the throughput and efficiency of the blast furnace is maximised.

The blast furnace is a counter current process, with gases flowing up through solids. The solids travel down the shaft of the furnace and pass through different zones. Based on the physical requirements of the solids, the furnace can be divided into three zones. These are the lumpy zone, the cohesive zone and the lower blast furnace, as illustrated in Figure 1-9 (Lu et al., 2015).

In the lumpy zone, the sinter is heated and undergoes gas/solid reduction. To be processed efficiently, the sinter must be resistant to degradation by tumbling, crushing and abrasion, should be reduced easily and not degrade during reduction (Lu et al., 2015). These sinter properties are measured by standard industrial tests, the Abrasion Index (AI), Tumble Index (TI), Reducibility Index (RI) and Reduction Disintegration Index (RDI) (Lu et al., 2015).

The sinter in the cohesive zone is heated, is deformed and partly melted. To maximise the furnace throughput, this zone needs to be as narrow as possible (Lu et al., 2015). This is achieved by having material that softens at as high a temperature as possible, measured by the softening temperature. There are a variety of standard tests used to determine the softening temperature, with a wide range of different procedures (Lu et al., 2015).

The oxide material in the lower blast furnace is fully molten, with reactions occurring in the liquid phase (Lu et al., 2015). The material in this zone must have appropriate chemistry to give the molten
oxide (slag) a low viscosity and for deleterious elements to partition preferentially into the slag. Typically, these properties are inferred from the composition of the slag, rather than through standard tests.

To measure the TI and AI, a sample of the material is rotated in a 1 m diameter drum for 200 revolutions at 25 rpm (Lu et al., 2015). The proportion of the resulting material that is >6.3 mm is the TI and the proportion <0.5mm is the AI. The RDI is measured with a number of different standard tests, but typically involves holding a sample in a reducing gas for an extended period of time followed by tumbling in a drum, with the proportion of material in a set size fraction after tumbling measured. The RI test is performed by determining the extent of oxygen removed after holding the material at temperature in a reducing atmosphere. A number of different standards exist, which specify different atmospheres, temperatures and times. The typical targets for these parameters are summarised in the Table 1-1 below.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Target Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tumble Index</td>
<td>&gt;65</td>
<td>% + 6.3 mm</td>
</tr>
<tr>
<td>Abrasion Index</td>
<td>&lt;7</td>
<td>% - 0.5 mm</td>
</tr>
<tr>
<td>Reduction Disintegration Index</td>
<td>&lt;35</td>
<td>% + 2.8 mm</td>
</tr>
<tr>
<td>Reducibility Index</td>
<td>&gt;65</td>
<td>%</td>
</tr>
</tbody>
</table>

It was suggested by Ostwald (Ostwald, 1981) that the phases present influence the strength and reducibility of sinter. An increased strength and reducibility was associated with a higher proportion of SFCA than glass. Loo (Loo et al., 1988) performed the Vickers hardness test and knoop indentation test on industrial sinters collected from an Australian steelworks to determine the impact of sinter mineralogy on sinter strength. Based on the observation that the breakage of sinter was random in samples observed by the researcher, it was suggested that a composite fracture toughness could be calculated based on the volume fraction of phases in sinter. It was also observed that pores do not contribute significantly to the sinter volume and as such were assumed to have a negligible impact on the sinter hardness and strength. The ‘composite’ microhardness was calculated assuming that the different phases contributed to the sinters hardness as per their volume proportions (Loo and Leung, 2003). The calculated ‘composite’ microhardness was compared to the tumble index, with a trend showing that the tumble index increased with composite hardness. This suggests that the strength of sinter, as measured by the TI and AI, is related to the phases present and their microstructure.

Ostwald (Ostwald, 1981) reviewed past work on reducibility and reduction degradation and suggested that the phases present impacted these properties. The reduction degradation has been linked to the proportion of hematite in the sinter, with an increase in hematite leading to an increased proportion of fines. This is suggested to be caused by a volume change associated with the reduction of hematite to magnetite. Recent reviews and work have indicated that both the phase present and their microstructure impacts the reducibility of the sinter (Fernández-González et al., 2017). The reducibility of SFCA has been found to be strongly related to its morphology, porosity and glass coating (Fernández-González et al., 2017). Similarly, the porosity of the hematite microstructure was observed to influence its reducibility. This research indicates that the reducibility and reduction degradation is impacted by the phases present and their microstructure.
2. Review of Literature

2.1 Phase Equilibria

The phases formed during sintering are determined by both phase equilibria and kinetics. Due to the high temperatures involved, the kinetic processes are relatively rapid and phase equilibria provide a starting point for determining the phases and reaction mechanisms in sintering.

Iron ore sintering is most simply represented by the FeO-Fe₂O₃-CaO phase diagram. The next system, with respect to complexity, able to represent sintering is the FeO-Fe₂O₃-CaO-SiO₂ phase diagram. The region of relevance to industrial processes is illustrated in Figure 2-1.

![Figure 2-1: Region of interest in the Fe₂O₃-SiO₂-CaO system to iron ore sintering (Yang and Loo, 1997). Note: conditions at smelters are expected to be within this region, but not necessarily within this area.](image)

The FeO-Fe₂O₃-CaO-SiO₂-Al₂O₃ system contains nearly all major components in the iron ore sintering process. This system can be used to understand the phases present and the conditions in industrial sinters, with some differences expected with respect to phase stabilities, due to the presence of minor elements in industrial sinters such as MgO, TiO₂, P₂O₅, etc.

2.1.1 CaO-“Fe₂O₃”

Phase equilibria in the Ca-Fe-O system has been studied by a number of researchers, in air, 1 atm O₂, iron saturation and in a closed system with Fe₂O₃-Fe₃O₄. Of the research, the most relevant conditions to the present study are those performed in air and in equilibrium with magnetite.

Schuermann (Schuermann and Kraume, 1976b) investigated the ‘FeO’-CaO system in equilibrium with iron. This system, due to the presence of metallic iron is not highly relevant to industrial sintering, but
is relevant to the low temperature reduction occurring in a blast furnace. The phase diagram for this system is shown in *Figure 2-2*.

![Figure 2-2: Binary phase diagram for the CaO-“FeO” system in equilibrium with iron from Schuermann (Schuermann and Kraume, 1976b).](image)

Philips (Phillips and Muan, 1958) and Liu (Liu, 2013) performed experimental work on the iron rich regions of the "Fe₂O₃"-CaO system in air. This work, along with others in this system, was used by Hidayat et al (Hidayat et al., 2016) to optimise the system with computational thermodynamics, with the resulting phase diagram shown in *Figure 2-3*.
Figure 2-3: Pseudo-binary phase diagram for the CaO-Fe\textsubscript{2}O\textsubscript{3} system in air from Hidayat et al (Hidayat et al., 2016). Mono2 refers to the CaO-FeO monoxide solid solution phase.

The region of interest to this study is the high iron region of the system, the C\textsubscript{2}F (Ca\textsubscript{2}Fe\textsubscript{2}O\textsubscript{5}), CF (CaFe\textsubscript{2}O\textsubscript{4}), CF\textsubscript{2} (CaFe\textsubscript{4}O\textsubscript{7}) and Fe\textsubscript{2}O\textsubscript{3} primary phase fields, at temperatures between 1100°C (1373 K) and 1300°C (1573 K). This region was studied in detailed by Liu (Liu, 2013) and only briefly by Philips (Phillips and Muan, 1958). For the region relevant to iron ore sintering, the hematite primary phase field, the melt crystallises hematite until the peritectic temperature for CF\textsubscript{2} (1223°C, 1496 K). At this temperature, the peritectic reaction between the melt and hematite occurs to form CF\textsubscript{2}. Depending on the bulk composition of the melt, further solidification can occur until the eutectic temperature (1208°C, 1481 K) of CF and CF\textsubscript{2}. The melt is also to first form at 1208°C (1481 K) at the CF-CF\textsubscript{2} eutectic.

Phillips (Phillips and Muan, 1960) investigated the ternary C\textsubscript{2}F-Fe\textsubscript{3}O\textsubscript{4}-Fe\textsubscript{2}O\textsubscript{3} system. In this work, two ternary compounds were found, 4CaO.FeO.4Fe\textsubscript{2}O\textsubscript{3} and 4CaO.FeO.8Fe\textsubscript{2}O\textsubscript{3}. It was suggested that these phases could be non-stoichiometric and exist as solid solutions, however this was not confirmed experimentally. The work also identified the C\textsubscript{2}F, CF and CF\textsubscript{2} phases as being present in the samples. Limited information was obtained on the liquidus isotherms for the two ternary phases, further work is needed to define their primary phase fields and liquidus isotherms.
Schurmann (Schuermann and Kraume, 1976a) performed experimental work to determine the phase equilibria and liquidus in the FeO-Fe₂O₃-CaO system away from the pseudo binary “Fe₂O₃”-CaO system. One ternary compound, CaO.FeO.Fe₂O₃ was detected in the experimental work. The region of interest to iron ore sintering, the Fe₂O₃ rich corner, shows the same solidification sequence and phases as the binary “Fe₂O₃”-SiO₂ system. The phase diagram sketched for this system is shown in Figure 2-5.

2.1.2 “Fe₂O₃”-CaO-SiO₂
The SiO₂-“Fe₂O₃”-CaO system is the simplest ternary system applicable to sintering. Phase equilibria in the SiO₂-“Fe₂O₃”-CaO system has been investigated by a number of researchers. Early work was performed in air and at iron saturation as no control over the gas atmosphere is required for these
conditions. The pseudo-ternary phase diagram for the SiO$_2$-'FeO'-'CaO in equilibrium in iron and air has been investigated for a wide range of temperatures and compositions. Limited experiments have been performed on the SiO$_2$-'FeO'-'CaO system at oxygen partial pressures relevant to sintering.

Allen (Allen and Snow, 1955) performed phase equilibria on the CaO-'FeO'-SiO$_2$ system in equilibrium with iron, with the resulting phase diagram shown in Figure 2-6. The research investigated a series of pseudo-binary phase diagrams, Ca$_2$SiO$_4$-FeO, CaFeSiO$_4$-FeO, Fe$_2$SiO$_4$-FeO and CaO-FeO, along with the ternary system in equilibrium with iron. This system, while relevant to ironmaking, is not highly relevant to sintering, as sintering is performed at conditions more oxidising than iron saturation.

Phillips (Phillips and Muan, 1959) investigated the phase equilibria in the CaO-'Fe$_2$O$_3$'-SiO$_2$ system in air at a wide range of temperatures. In the region of interest to iron ore sintering, the "Fe$_2$O$_3$" rich corner of the phase diagram, six primary phase fields were identified. These were magnetite, hematite, CF$_2$, CF, CF$_2$ and CsS. The magnetite and hematite had large primary phase fields, with an increase in CaO leading to a decrease in the liquidus and primary phase stability. The calcium ferrites had a narrow primary phase field and the dicalcium silicate was observed to have a larger primary phase field. All the primary phase fields, except dicalcium silicate, were observed to have a relatively shallow liquidus. The phase diagram is shown in Figure 2-7.
Figure 2-7: The phase diagram $\text{SiO}_2$-"$\text{Fe}_2\text{O}_3$"-CaO in air from Phillips, showing the region of interest to iron ore sintering (Phillips and Muan, 1959).
Pownceby (Pownceby et al., 1998b) revisited the “Fe$_2$O$_3$”-CaO-SiO$_2$ system in air, focusing on the high Fe$_2$O$_3$ region of the phase diagram. Experiments were performed by mixing pure oxide samples and equilibrating them in a platinum crucible in air. The samples were examined using optical metallography. On the basis of the starting compositions and phases observed following isothermal treatment the phase boundaries within the isothermal sections were inferred. This approach was used to interpolate a liquidus isotherm, since it was not possible using this technique to measure the liquid compositions. Four temperatures were investigated, 1300°C, 1270°C, 1255°C and 1240°C. Unlike previous work, the presence of SFC was detected, along with some differences in the liquidus isotherms. In particular, the liquid only region in this study was larger than that observed in previous work. While the technique used only allowed estimates to be made for the isotherms, sufficient information was obtained to an estimate of the liquidus and phase diagram.

Hayes (Hayes et al., 2016) revisited the CaO-SiO$_2$-“Fe$_2$O$_3$” system in air to determine the phase equilibria and liquidus of the system relevant to sintering. By using a technique involving the use of samples of low mass, less than 0.1 g, and ultra-rapid cooling, it was possible to quench the samples from the equilibration temperature and use electron probe X-ray microanalysis (EPMA) to measure the compositions of the resulting phases. The research was focussed on the slag liquidus of the iron rich corner at temperatures between 1200°C and 1300°C. The results obtained from isothermal sections enabled the liquidus surface of the ternary phase diagram to be constructed and the extent of the SFC solid solution as a function of temperature and composition to be determined. The estimate liquidus isotherms and boundary curves were later updated by Chen (Chen et al., 2019). There is
general agreement with the results of earlier work by Pownceby (Pownceby et al., 1998a), with both works identifying the SFC phase and general arrangement of primary phase fields.

The phase diagram constructed by Hayes (Hayes et al., 2016) and recently updated (Chen et al., 2019), (see Figure 2.9) is most relevant to the present study. Based on this work, six primary phase fields in the high iron region can be identified by the research, Hematite, CF, SFC, C$_2$S, and C$_2$F. Of these, the areas of interest to iron ore sintering conditions are the low silica region in hematite primary phase field and the adjoining boundary curves. In this region, the melt forms at 1192°C at the ternary eutectic point between C$_2$S, CF and C$_2$F.

### 2.1.3 “Fe$_2$O$_3$”-CaO-SiO$_2$-Al$_2$O$_3$

The SiO$_2$-“Fe$_2$O$_3$”-CaO-Al$_2$O$_3$ system contains the major elements present in iron ore sinter, Fe$_2$O$_3$, SiO$_2$ and CaO, as well as the largest minor element in sintering, Al$_2$O$_3$. Despite the importance to industrial processes, little information is available on this system.

Pownceby (Pownceby and Clout, 2003) reported phase equilibria work on the Fe$_2$O$_3$-SiO$_2$-CaO system with Al$_2$O$_3$ additions, in air at temperatures between 1240°C and 1300°C. Alumina additions, between 1 and 3 wt\%, were found to change the liquidus temperatures and increase the temperature range in which SFCA is formed. The region of liquid phase stability was not significantly impacted, with a minor decrease in area with alumina addition. The maximum alumina concentration in SFCA was observed to be approximately 31.5 wt\%. SFCA-I was believed to be present, but this was not confirmed with EPMA analysis.
Figure 2-10: The impact of Al$_2$O$_3$ on the "Fe$_2$O$_3"-CaO-SiO$_2$ system in air (Pownceby and Clout, 2003).

The research performed to date on the "Fe$_2$O$_3"-SiO$_2$-CaO-Al$_2$O$_3$ system is quite limited. The work has focused on a narrow composition and temperature range. Limited information on the effect of P$_{O2}$ on the system is available. Due to the limited range of conditions investigated in this system, little is known of the phase equilibria and relations relevant to sintering.

### 2.1.4 SFCA

SFCA phases are present in the majority of modern iron ore sinters. The identification of this phase has been performed with XRD and EPMA. To date three SFCA phases, SFCA, SFCA I and SFCA II, have been identified. The three SFCA phases have distinct crystal structures, but are similar in composition and morphology, leading to difficulties in differentiating between these phases.

Research by Bristow (Bristow and Waters, 1991) has found that sinter containing SFCA was more porous and more reducible at high temperatures but less reducible at low temperatures. As a result, SFCA phases are believed to positively impact the sinter properties. Significant research has been performed on the SFCA phases present in iron ore sinter.

The SFCA phase was the first SFCA identified by researchers (Mumme, 1988, Hamilton et al., 1989, Sugiyama et al., 2005, Liles et al., 2016). A number of crystal structures and compositions have been proposed, mostly from the stoichiometry of composition measurements, including phases such as CF$_3$. It is currently believed that SFCA is a solid solution in the CF$_3$-CA$_3$-C$_6$S$_3$ series (Patrick and Pownceby, 2002).

The SFCA-I phase was more recently identified and characterised (Mumme et al., 1998, Zöll et al., 2017). The SFCA-I phase is believed to impart beneficial properties to the sintering process, with some research performed to maximise the formation of this phase (Webster et al., 2012). The SFCA-I phase has been identified with XRD and other techniques. The composition range for SFCA-I has not been
determined, but a number of compositions have been determined including, $\text{Ca}_{3.18}\text{Fe}^{3+}_{14.66}\text{Al}_{1.34}\text{Fe}_{10.82}\text{O}_{28}$, $\text{Ca}_3\text{MgAl}_6\text{Fe}_{10}\text{O}_{28}$, $\text{Ca}_2\text{Mg}_2\text{Al}_7\text{Fe}_9\text{O}_{28}$, $\text{Fe}_{15.27}\text{Ca}_{3.22}\text{Al}_{1.20}\text{O}_{28}$ (Zöll et al., 2017, Koryttseva et al., 2017, Mumme et al., 1998).

The SFCA II phase is currently believed to be a small contributor to the mass of industrial sinters. Limited work has been completed on the SFCA-II phase and the solid solution series it belongs to (Mumme, 2003) (Mumme and Gable, 2018). The solid solution series for this phase has not been determined, but two compositions have been determined $\text{Ca}_{5.1}\text{Al}_{9.3}\text{Fe}^{3+}_{18.7}\text{Fe}^{2+}_{0.9}\text{O}_{48}$ (Mumme, 2003) and $\text{Ca}_{2.6}\text{Fe}^{3+}_{8.0}\text{Fe}^{2+}_{3.4}\text{Al}_{4}\text{O}_{24}$ (Mumme and Gable, 2018). Significant work is required to confirm the composition, structure and solid solution series for this phase.

### 2.2 Crystal Structures of Iron Rich Sinter Phases

#### 2.2.1 Hematite

Hematite is composed of $\text{Fe}^{3+}$ cations and $\text{O}^{2-}$ anions in a hexagonal close packing arrangement of oxygen ions. The unit cell for hematite is rhombohedral, with the unit cell dimensions of $a = 0.5034$ nm and $c = 1.3752$ nm (Cornell and Schwertmann, 2003).

The oxygen anions are arranged in alternating close packed sheets in the [001] plane with an ABAB... arrangement (Cornell and Schwertmann, 2003). The $\text{Fe}^{3+}$ cations occupy two thirds of the tetrahedral interstitial sites, in a regular arrangement of two filled sites, followed by one vacant site in the (001) plane, resulting in the formation of sixfold rings.

The hematite crystal structure has a relationship with both the magnetite and CF$_2$ crystal structures. Specifically, these three crystals all possess a close packed oxygen plane.

#### 2.2.2 Magnetite

Magnetite is an endmember of the spinel group of minerals. Magnetite is composed of $\text{Fe}^{3+}$ and $\text{Fe}^{2+}$ cations and $\text{O}^{2-}$ anions, the oxygen ions forming a cubic close packed arrangement. The unit cell for magnetite is cubic, with the unit cell dimensions of $a = 0.8396$ nm (Cornell and Schwertmann, 2003).

The oxygen anions are arranged in close packed sheets in the [111] plane with an ABCABC... arrangement (Cornell and Schwertmann, 2003). The $\text{Fe}^{3+}$ cations are preferentially located in octahedral sites. Within the magnetite crystal structure, $\text{Fe}^{2+}$ preferentially occupies the octahedral sites and the tetrahedral sites are fully occupied by $\text{Fe}^{3+}$. Cation substitution is possible, resulting in a wide range of solid solutions and associated changes in the unit cell edge length.

#### 2.2.3 SFCA Group

The SFCA group is a polysomatic series of structures, and includes the minerals SFCA, SFCA-I and SFCA-II. The SFCA group consists of pyroxene-like <Py> and spinel-like <Sp> polysomes, arranged in a regular and repeating structure (Grew et al., 2008)). The pyroxene polysomes are slices of the pyroxene structure, along the [010] plane and consisting of one silicate chain. The spinel polysomes are slices of the spinel structure, along the [010] plane and consisting of one tetrahedral/octahedral unit.

The SFCA mineral consists of alternating layers of the spinel <Sp> and pyroxene <Py> polysomes, <SpPy>. This mineral has a triclinic unit cell, with $a = 1.0395$ nm, $b = 0.906$ nm, $c = 1.0546$ nm, $\alpha = 95.67^\circ$, $\beta = 109.58^\circ$ and $\gamma = 118.45^\circ$ (Hamilton et al., 1989). The SFCA-I mineral consists of alternating layers of two spinel <SpSp> and pyroxene <Py> polysomes, <SpSpPy>. This mineral has a triclinic unit cell, with $a = 1.0431$ nm, $b = 1.1839$ nm, $c = 1.0610$ nm, $\alpha = 94.14^\circ$, $\beta = 110.27^\circ$ and $\gamma = 117.62^\circ$ (Mumme et al., 1998). SFCA-II is considered as an intergrowth of SFCA and SFCA-I, <SpSpPy>. This mineral has a triclinic unit cell, with $a = 1.0338$ nm, $b = 1.0482$ nm, $c = 1.7939$ nm, $\alpha = 90.384^\circ$, $\beta = 89.770^\circ$ and
γ = 109.398° (Mumme, 2003). Due to the similarities in compositions and crystal structures, the X-ray powder diffraction (XRD) techniques is the only reliable method to differentiate between the minerals in the SFCA group.

The SFCA group has crystallographic relationship with both magnetite and pyroxene, but no simple relationship to the hematite or other calcium ferrite phases.

The magnetite is crystallographically related to the SFCA, SFCA-I, SFCA-II, hematite and CF$_2$ crystal structures. The SFCA group and CF$_2$ are both polysomatic, containing polysomes of magnetite. The SFCA group contains the spinel polysomes, a slice of the spinel structure along the [010] plane. The CF$_2$ consists of two polysomes, Motif-F and spinel, with the spinel polysomes being a slice of the spinel structure along the [111] plane (Million et al., 1986). The spinel polysome consists of three anion layers, ABCABC.

2.2.4 Ca$_{7.2}$Fe$_{2+0.8}$Fe$_{3+30}$O$_{53}$

Limited information is available for this phase, limited to XRD patterns. It has been proposed that this phase is structurally related to CaFe$_4$O$_7$ (Hughes et al., 1967). It is possible that this mineral potentially bears a relationship with hematite, magnetite and the SFCA group.

2.2.5 CaFe$_2$O$_4$

Monocalcium ferrite, CaFe$_2$O$_4$ is an endmember of a solid solution series. The CaFe$_2$O$_4$ has an orthorhombic unit cell with $a = 0.916$ nm, $b = 1.060$ nm and $c = 0.301$ nm(Hills et al., 1956). The crystal structure consists of Fe$^{3+}$ octahedral and calcium cation with eight-fold co-ordination. The Fe$^{3+}$ octahedra share edges and corners, surrounding the Ca$^{2+}$ cations. This crystal structure bears no relationship to the other iron rich phases in iron ore sinter.

2.2.6 CaFe$_4$O$_7$

Calcium ferrite, CaFe$_4$O$_7$ (CF$_2$) is a polysomatic mineral, consisting of spinel <Sp> and ‘Motif-F’ polysomes arranged in alternating layers. CF$_2$ has a monoclinic unit cell, with $a = 1.0409$ nm, $b = 0.6005$ nm, $c = 3.1640$ nm, and $β = 96.30°$ (Million et al., 1986). The spinel polysome is a slice of the spinel structure along the [111] plane. The ‘Motif-F’ polysome consists of a plane of trigonal FeO$_5$ bipyramids, with a mixed Fe-Ca layer either side of this layer. Other minerals have been identified as belonging to the same polysomatic group as CF$_2$, including Ca$_4$Fe$_9$O$_{17}$ and Ca$_3$Fe$_{15}$O$_{25}$ (Gerardin et al., 1988).

The CF$_2$ crystal structure is crystallographically related with the spinel and hematite crystals since all three minerals have close packed planes of oxygen anions. In addition, the CF$_2$ consists of spinel polysomes, and can be considered an intergrowth of spinel and ‘Motif-F’.

2.3 Solidification Pathways

There are three principal solidification pathways in the SiO$_2$-CaO-“Fe$_2$O$_3$” system in air. The pathways illustrated in Figure 2-11 result, under equilibrium cooling, in the eutectic reactions SiO$_2$-Fe$_2$O$_3$-CaSiO$_3$ (pathway 1), Ca$_5$SiO$_7$-Ca$_3$Si$_2$O$_7$-Fe$_2$O$_3$ (pathway 2) and Ca$_3$SiO$_4$-CaFe$_2$O$_4$-CaFe$_4$O$_7$ (pathway 3).
In the “$\text{Fe}_2\text{O}_3$”-CaO-SiO$_2$ system in air at the bulk CaO/SiO$_2$ ratios relevant to iron ore sintering, two pathway of cooling can be identified. These are as illustrated in Figure 2-12 and Figure 2-13. These two pathway align with pathways 2 and 3 illustrated in Figure 2-11. The two regions were identified by Pownceby (Pownceby et al., 1998a), with the saddle point at a mole ratio of 2 at 1270°C. The saddle point is located at the intersection of the Fe$_2$O$_3$-Ca$_2$SiO$_5$ boundary curve and Alkemade line. The compositions richer in silica form glasses on cooling under industrial conditions, while those poor in silica form crystalline phases. The CaO-Fe$_2$O$_3$-rich melts are highly fluid and behave like ionic melts, with a number of calcium ferrites able to form. The SiO$_2$-rich melts are highly viscous and have low diffusivity, typically leading to difficulties in crystallising silicate phases from the melt.
Figure 2-12: The phase diagram SiO$_2$-Fe$_2$O$_3$-CaO from Pownceby and Clout divided into two pathways of cooling (Pownceby and Clout, 2000).

Figure 2-13: The phase diagram SiO$_2$-Fe$_2$O$_3$-CaO from Pownceby identifying two pathways of melt during cooling (Pownceby et al., 1998a).

The equilibrium cooling for the high iron compositions are of importance to kinetics study in iron ore sintering. The final phase assemblage under open system cooling at equilibrium conditions is determined by Alkemade triangles. For compositions relevant to iron ore sintering, there are six
Alkemade triangles. These are; SFC-Fe₂O₃-C₂S, SFC-Fe₂O₃-CF₂, SFC-C₂S-CF₂, Fe₂O₃-C₂S-C₃S₂, SFC-CS-C₃S₂, and Fe₂O₃-C-S-CS. These Alkemade triangles are illustrated in Figure 2-14.

![Figure 2-14: Schematic Alkemade triangles for the ternary SiO₂-Fe₂O₃-CaO system in air, based on (Chen, 2017, Phillips and Muan, 1959).](image)

The solidification path of compositions within these Alkemade triangles can be determined from the phase diagram constructed by Chen (Chen, 2017) and Philips (Phillips and Muan, 1959) for the low and high silica compositions respectively. For each pathway, there are between 3 and 4 steps, with eutectic and/or peritectic reactions occurring. The pathways for melt solidification have been illustrated in Figure 2-15 and Figure 2-16.

![Figure 2-15: Predicted solidification pathways for melts relevant to iron ore sintering in air, low in silica and with C/S >2, based on (Chen, 2017, Phillips and Muan, 1959).](image)
2.4 Previous Research on Iron Ore Sinter Microstructures

The focus of the present review is on the phases and microstructures observed in industrial and synthetic iron ore sinters, and previous attempts to identify the reaction sequences in the formation of these structures. General reviews of iron ore sintering are available from Dawson (Dawson, 1993).

A review of the research on SFCA phase formation has been performed in a collaborative publication with other researchers (Nicol et al., 2018).

2.4.1 Microstructure Identification in Industrial Sinters

The focus of much of the research undertaken on iron ore sinters prior to the 1980’s was on the examination of structures obtained in industrial sinter operations.

Ostwald (Ostwald, 1981) reviewed iron ore sinters produced in Australia at that time and reviewed previous research on the mineralogy of sinters. Two types of sinter were observed, acid sinters (no fluxing) and basic sinters (limestone fluxed). The acid sinters formed iron oxides and glasses, with the glasses forming by the assimilation of various oxides in a silica rich melt. The basic sinter was observed to consist of iron oxides, hematite and magnetite, and calcium ferrites. Ostwald comprehensively reviewed the phases present in the sinter, but did not provide any details on their mechanisms of formation.

In the study by (Matsuno and Harada, 1981), the iron oxides were reported to originate from unassimilated relict ore, solidification during cooling or by oxidation at lower temperatures. A large number of calcium ferrites were reported, CF, C₂F, C₃F, C₄F, C₄AF, CFA and SCFA, along with a number of calcium silicates, C₂S, CS, C₃MS₂ and CMS. Olivine was also occasionally observed. The minor elements were observed to distribute differently between phases, with magnesia, zinc and manganese reporting to the magnetite and phosphate, potassia, and soda to the glass. Sinter property tests indicated that increasing SFCA increased the sinter strength and reducibility. Hematite was observed to be more reducible than magnetite, but was more prone to reduction degradation.

Ahsan (Ahsan et al., 1983) analysed two industrial sinters with optical microscopy, SEM, EPMA, and TEM to determine the mechanisms of formation and phases present in sinters. The researchers found that the main phases present included hematite, magnetite, calcium ferrites, silicates and glass. The iron oxides in the sample were classified as either originating from unassimilated relict ore, solidification during cooling or oxidisation during cooling. The different iron oxides were found to have
differences in composition, with the crystallised magnetite having a higher impurity content (i.e. CaO, MgO, MnO and Al₂O₃) and the hematite a lower content when compared to the relict ore. The presence of a number of calcium ferrites was reported, SCFA, CF and CF₂. The CF₂ and SCFA described was believed to have the same crystal structure by electron diffraction, a superlattice of magnetite. It was also suggested that the formation of calcium ferrites is promoted by low magnesia content. Ahsan described the formation of the iron oxides present in the sinter and differentiated them based on their composition.

The research on microstructure identification was able to classify and determine the phases present in sinters. The work identified that there were different regions and processes occurring in the sinter. Research was unable to determine the processes by which the complex calcium rich phases formed.

2.4.2 Sinter Pot Tests
To provide further insight into the processes taking place in iron ore sintering, tests were undertaken on a pilot scale, using conditions replicating those in industrial processes. In these studies sintering was stopped part way through the process, the sinter bed dissected and analysis of the different layers present in the sinter pot undertaken.

Shigaki (Shigaki et al., 1984, Shigaki et al., 1985) performed sinter pot tests and laboratory furnace tests to study the formation of liquids in sinters. The work was supported by phase equilibria research, completed prior to the kinetics research. Industrial ore, limestone and coke samples were used in the testwork to simulate industrial conditions. The sinter pot test was stopped part way through with the use of nitrogen as a coolant. The samples collected from these tests were subjected to EPMA and chemical analysis. The sinter from the sinter pot test was found to contain a “melt”, which was classified as quaternary calcium ferrite melt, binary calcium ferrite and silicate melt. Based on supporting research, it was suggested that the binary calcium ferrite melt formed first, and then dissolved SiO₂ and Al₂O₃. The CaO was believed to dissolve into this melt and precipitate C₂S and then Fe₃O₄ at low oxygen partial pressures. A high silica melt was observed to form in some regions and this was attributed to uneven distribution of CaO in the sinter. The silica melt was proposed to dissolve C₂S at high temperatures to form a more basic melt.

Wang (Wang et al., 1998) quenched a sinter pot test using nitrogen gas, with sintering performed on both hematite and magnetite ores. The phases present and the bulk composition was determined with chemical analysis, XRD and SEM with EDS. In the combustion zone, for magnetite sinters, C₂S, Fe₂O₃ and calcium ferrite was detected. On cooling, the calcium ferrite morphology changes, the proportion of C₂S decreased and glasses were observed to be present. In the hematite sinter a larger proportion of calcium ferrite and hematite was observed in the sintered material. The calcium ferrite was believed to be SFCA based on XRD and EDS. The SFCA phase was suggested to form through the reaction of C₂S, CaO and Fe₂O₃.

Choudhary (Choudhary, 2007) carried out sinter pot tests on industrial feed materials and stopped the sintering process part way by introducing nitrogen gas from the bottom of the sinter pot. The bulk composition of the sinter from different depths of the sinter pot was measured with Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and the microstructures were examined and measured with an SEM equipped with EDS. Based on the ICP-MS analysis, it was concluded that reduction occurred prior to melt formation and that oxidation occurred during. At the flame front, it was found that the phases consisted of melt, magnetite and ferrite. During cooling, two iron silicates are formed and the proportions of melt and magnetite has decreased. Further oxidation of the sinter resulted in the formation of a ferrite and a phase with a composition close to CF₃ and containing SiO₂ and Al₂O₃, potentially SFCA.
Based on the sinter pot tests, some of the processes occurring during sintering could be identified. Solid state reactions were suggested to occur during heating, followed by the formation of a complex melt and then solidification of complex oxides during cooling. Calcium ferrites, calcium silicates and SFCA phases were said to form during heating, but there were differences in the processes proposed. The processes and phased formed during melt solidification were not investigated or proposed.

2.4.3 Controlled Heating Tests

To assist in the determination of the processes occurring during heating and cooling of sinters laboratory scale tests were undertaken to reproduce sintering with small sample sizes. Both synthetic and natural samples have been heated and cooled under controlled conditions.

Matsuno (Matsuno, 1978) performed experimental studies on the phase formation in the Fe$_2$O$_3$-SiO$_2$-CaO system relevant to iron ore sintering. Pure oxides were mixed and heated in an electric furnace open to air, as well as in a DTA furnace. The samples produced in the electric furnace were analysed with XRD and SEM equipped with EPMA. The DTA analysis of two samples (CaO/SiO$_2$ of 1.2 and 3) showed that there were three reactions occurring, Ca(OH)$_2$ dehydroxylation, CaCO$_3$ decarbonation, and melting of the oxides. It was observed that at about 950 °C to 1000 °C calcium ferrite formed from CaO and iron oxides. As temperature increased to approximately 1200 °C, the CF$_2$, SiO$_2$ and Fe$_2$O$_3$ reacted to form a melt at low basicities, CF$_2$ and C$_2$S at high basicities, and CF$_2$ and glass at intermediate basicities. At higher temperatures (approximately 1320 °C), the hematite was found to be reduced to form magnetite. This research, while able to identify the formation of calcium ferrites, was unable to differentiate between the different forms present.

Ikeda (Ikeda et al., 1981) prepared synthetic oxides and heated the material in air under controlled cooling (5 °C/min) and heating rates or equilibrated the material at temperature. At equilibrium, at 1200 °C, four phases were observed to be stable, hematite, calcium ferrite, spinel and melt. With an increase in temperature, it was observed that there was an increase in the proportion of spinel and melt and a decrease in hematite and calcium ferrite present. At temperature greater than 1300 °C, the calcium ferrite was stable. With an increase in temperature, the alumina and iron in the melt increased and the magnesium in the melt decreased. MgO increased the stability of both spinel and calcium ferrite. Al$_2$O$_3$ increased the stability of calcium ferrite. In agreement with the equilibrium tests, controlled cooling tests with higher temperatures was associated with a decrease in the proportion of calcium ferrite and an increase in the melt and spinel present.

Matsuno (Matsuno and Harada, 1981) heated industrial iron ore sinter feeds (15 g total) heated in an electric furnace for 10 minutes. The effect of variations in, lime, coke and temperature was examined. Optical microscopy was used to determine the phases and the microstructures formed, with a select number of samples examined using EPMA and XRD. Coke was observed to influence the predominant phases formed, but not the microstructures formed. It was suggested that lime and iron reacted to form calcium ferrite on heating, which subsequently forms a melt and iron oxides through a reaction with gangue materials and silica. On cooling, based on phase equilibria, the magnetite was suggested to be crystallised with the dissolution of SiO$_2$. At a low silica concentration, calcium ferrite and C$_2$S were observed and a high silica concentration, a glass was observed.

Dawson (Dawson et al., 1985) performed experimental work on pure oxide materials in an infrared image furnace. The oxide mixtures pelletised (6.33 mm Ø, 3 mm), heated in air at a rate of 20 °C/s, held at temperature (1250 to 1350°C) and cooled at 2 °C/s to simulate industrial sintering processes. The CaO/SiO$_2$ in the samples varied from 1.2 to 8.5, the total Fe from 58.8 to 33.2 wt% and the Al$_2$O$_3$ 0.5 to 8.7 wt%. The resulting samples were analysed with SEM with EDS to determine phases present and their compositions. Both temperature and alumina in the sintering process was explored. In the
experiments performed with variation in the peak temperature, SFCA formed on heating and melted to form liquid and hematite at temperatures above 1300 °C. The SFCA was observed to form, dense, columnar and fibrous microstructures. The SFCA was proposed to be a CF2 phase based on the measured composition. The proportion of SFCA present increased with alumina. The SFCA was suggested to form through a series of reactions. On heating CF was suggested to be the first ferrite to form, followed by CA. These two phases were suggested to react to form a solid solution C(F,A).

Marliere (Marliere et al., 1986) simulated industrial sintering processes in a vertical tube furnace. Industrial ores were ground to <50 μm and mixed to homogenise the material. Approximately 1g was contained in a platinum sintering cell and moved through the hot zone of the furnace to simulate the sintering process. In the testwork, the heating and cooling rates (0.8 °C/s, 1.7 °C/s and 8.3 °C/s) were controlled along with the peak temperature (1140 to 1320 °C), while the atmosphere was maintained as air. The results led the researchers to believe that there were three stages to sintering, with the transitions between the stages brought on by temperature. The first stage was limited melting and solid state reactions to form calcium ferrites. The second stage was associated with an increase in melt, the precipitation of hematite and magnetite, a decrease in calcium ferrites and the transformation of their shape into columnar. The last stage was associated with a large amount of slag, further precipitation of magnetite and the increase in the size of calcium ferrite. It was found that the cooling rate (0.8 °C/s, 1.7 °C/s) had little effect on the phases formed, but it increased the size of the crystals formed.

Hida (Hida et al., 1987) investigated acicular SFCA formation mechanisms. Two pellets, one containing iron ore and the other CaO, were pressed and heated in air at 1150 °C and 1180 °C to explore the solid state reactions between the two components. The calcium ferrite formed differed to that observed in industrial sinters, suggesting that acicular SFCA was not formed through solid state reactions. Samples with the same composition to that observed in industrial sinters were prepared from pure oxides and heated to 1350 °C, followed by cooling at a variety of rates, 10 to 1000 °C/min. The microstructures observed to form under cooling differed to that observed in industrial samples, suggesting that the SFCA was not formed through solidification. Ore and lime were heated in a furnace equipped with SEM with EDS to observe the processes occurring at temperature and to enable the measurement of phase composition at temperature. On heating the initial melt was measured to have a composition similar to CF, forming at approximately 1205 °C. On further heating the other components present dissolve into this melt. On cooling an acicular calcium ferrite and hematite was observed to form. This research investigated the formation mechanisms of the acicular SFCA, but did not determine the phase that was referred to as acicular SFCA. The research focused on replicating the microstructures in industrial sinters and lab tests to determine the conditions and processes occurring in industrial sinters.

Hsieh and Whiteman (Hsieh and Whiteman, 1989b) undertook experiments on industrial feed materials to determine the microstructures formed and the mechanisms of their formation. Industrial hematite, limestone, silica and kaolin were used. Experiments were carried out by heating the samples, contained in a fireclay boat, in a horizontal tube furnace. The gas atmosphere in the furnace was controlled with CO/CO2/N2/O2, with the pO2 controlled between 0.21 atm and 10^{-7.05} atm. A variety of cooling conditions were used, both low cooling and rapid cooling, and in air or controlled gas atmospheres. The samples were analysed by optical microscope, and the point and count method. The results of the tests showed that as P_{O2} increased, the proportions of glass and hematite increased and the calcium ferrite and magnetite decreased. It was also found that increasing the peak bed temperature from 1210 °C to 1255 °C resulted in an increase in the proportion of glass and hematite relative to calcium ferrite. The results also suggested that the phase assemblage was strongly affected
by the oxidation occurring during cooling. The phases and phase assemblages formed in a sinter pot test were compared to that formed under controlled laboratory tests. The phase assemblages formed in the sinter pot were suggested to be replicated by laboratory tests performed at a maximum temperature of 1255 °C, a heating \( P_{O_2} \) of 4×10\(^{-7}\) atm and slow cooling in air.

Hsieh and Whiteman (Hsieh and Whiteman, 1989a), examined the processes occurring on the heating and cooling of sinter. Samples were prepared from industrial feeds and heated under different atmospheres, a \( P_{O_2} \) between 0.21 atm and 10\(^{-7}\) atm, to simulate the conditions in industrial processes. The processes were determined by examining the samples with an optical microscope, and the phase composition by SEM with EDS. The heating experiments showed that a calcium ferrite phase formed at low temperatures (<1185 °C), and increases until around 1260 °C at which point a melt formed along with magnetite. Oxidising conditions were associated with a larger proportion of calcium ferrites and reducing conditions led to the formation of a larger proportion of magnetite and slag. On cooling at intermediate oxygen partial pressures, calcium ferrite was observed to form. Based on the composition as determined by SEM, the calcium ferrite was suggested to be CF\(_2\) with Al\(_2\)O\(_3\) and SiO\(_2\) substituted into the crystal structure.

Hsieh and Whiteman (Hsieh and Whiteman, 1993) explored the influence of MgO and Al\(_2\)O\(_3\) on sintering. Al\(_2\)O\(_3\) was observed to be associated with an increased proportion of calcium ferrites and magnetite and a decrease in the proportion of glass. The testwork showed that Al\(_2\)O\(_3\) increased the proportion of calcium ferrites in the sinter and MgO stabilised the magnetite phase.

Egundebi (Egundebi and Whiteman, 1989) heated industrial iron ores in horizontal tube furnaces to between 1100 °C and 1350 °C. A variety of gas atmospheres were used, air, nitrogen and CO/CO\(_2\) (0.2 to 0.8 vol/vol). With a variation in peak bed temperature and time, composition and gas atmosphere, changes in the phases present were observed. At low temperatures (1100 °C), CF and CF\(_2\) were observed, SCFA at higher temperatures (1150 °C) and magnetite and C\(_2\)S at the highest temperatures (>1150 °C) investigated. The sintering time at peak temperature was extended for a number of samples, and this showed that SCFA formed more rapidly at higher temperatures but contributed less to the sinter mass. With longer times, SFCA initially increased in mass and then decreased. Under reducing conditions, the proportions of SFCA and CF\(_2\) decreased and C\(_2\)F increased. It was proposed that CF\(_2\) or C\(_2\)F formed on heating through solid state reactions. At the peak bed temperature, these phases were no longer present. The SFCA phase was proposed to form through solidification from the melt.

Da Costa (Costa et al., 1995) investigated the reactions occurring during sintering in the aim to improve the performance of segregated sintering. Segregated sintering was proposed to improve the performance by creating strong sinters of different compositions and blending these sinters to achieve the target blast furnace slag composition. Three stages of test work was performed, all were performed with coke present. In the first, natural ores and flux were blended and heated to determine the melting temperature of the sinter. The heating tests determined the onset of softening. The second stage of the test work was performed by heating ore samples, with or without fluxes, and cooled. The samples were examined by optical microscopy with image analysis and EPMA. It was found that the proportion of hematite present decreased with temperature. The magnetite phase was observed to form at temperatures above 1257 °C. The SFCA phase was observed, forming at high temperatures and later melting as temperature increased further.

Yang (Yang and Davis, 1999) used an infrared image furnace to simulate sintering with hematite and magnetite ores. The temperature profile used in the experimental work reproduced that measured in industrial test work. The gas atmosphere in the experiments either air, N\(_2\) or 10 vol% O\(_2\). The samples
produced were analysed with optical microscopy and the proportion of phases by the point count method. It was believed that the proportion of melt formed at higher temperature and the assimilation of surrounding the melt was the cause for differences in the amount of SFCA in the sinter. The experimental results were reported to indicate that a higher proportion of fines believed to lead to more extensive bonding in the sintering. Sinters with a higher basicity (CaO/SiO₂), higher sintering temperatures (1300 vs 1250 °C) and higher gangue levels were also found to lead to a higher degree of assimilation and reaction in the sintering process. It was found that the magnetite did not assimilate and react as well as the hematite.

Experiments by Loo and Leung (2003) were undertaken by heating synthetic oxides in Infrared Image Furnace to simulate the thermal history in sintering; this involved heating the samples at a rate of 2°C/s to 800 °C, holding for 60s then heating at 20 °C/s to 1300 °C, holding at 120s then cooling at 2 °C/s. The samples were analysed with optical microscopy and SEM, with image analysis. It was found that the sinter composition and the maximum temperature influenced the formation and proportion of pores in the sinter. With an increase in basicity (CaO/SiO₂), silica, alumina or magnesia, the contribution of the pores to the total sinter volume increased. Similarly, at lower temperatures, the proportion of pores present increased. This was linked to melt properties, with the belief that a lower viscosity, higher surface tension and lower density decrease the proportion of pores.

In the study by (Clout and Manuel, 2003) iron ores and limestone were sintered with a similar heating profile to that seen in industrial sintering. The samples were heated to 1270 °C in a gas atmosphere with a pO₂ of 10⁻³ atm. The samples were examined using optical microscopy and tumbler tests (TI) were carried out. It was found that the sinters consisted of iron oxides, SFCA, SFCA-I and glass. Strength in the magnetite sinters was achieved by sintering at high temperatures, leading to the formation of fused magnetite-magnetite grains. The strength in hematite ores was attributed to the formation of SFCA and SFCA-I. It was suggested that magnetite concentrates did not form SFCA readily at high temperatures, due to the large phase field for the magnetite+liquid region at temperature in the binary CaO-SiO₂-Fe₂O₃ phase diagram.

Scarlett (Scarlett et al., 2004a, Scarlett et al., 2004b) mixed and heated synthetic hematite (Fe₂O₃), quarts (SiO₂), calcite (CaCO₃) and gibbsite (Al(OH)₃) with a platinum resistance heater equipped with an in-situ XRD. Three starting compositions with different alumina content prepared to explore the impact of alumina on the reactions occurring on heating. The proportion of phases was determined through Reitveld refinement of the XRD pattern. On heating, a heating rate of 10°C/min was used to heat the sample to 600 °C. Above 600 °C, the samples were heated at 5 °C/min. On heating, based on the reitveld refinement of the XRD patterns, gibbsite and calcite decomposition and the formation of CF₂, CF, SCFA and SCFA-I were detected. Gibbsite and calcite decomposed at approximately 250 °C and 600 °C respectively. At between 650 °C and 780 °C, CF₂ formed. This phase formation was suggested to occur as a result of a solid state reaction between Fe₂O₃ and CaO. The CF was proposed to form through a solid state reaction between CF₂ and Fe₂O₃ when the proportion of CF₂ in the material was greatest, approximately 920 °C to 1000 °C. The SFCA and SFCA-I was proposed to form through a solid state reaction at a similar temperature to that at which CF formed. The temperature at which the reactions occurred varied with the alumina content of the material. The formation of a melt at temperature was determined through DTA. The melt was observed to form at around 1230 °C, through the melting of SCFA-I (Scarlett et al., 2004c).

Jeon (Jeon et al., 2010) completed testwork to determine the mechanisms of calcium ferrite formation from iron oxides and lime. Fe₂O₃ and CaCO₃ were heated to approximately 1000 °C with thermogravimetric analysis, (TGA) in an alumina crucible under a controlled gas atmosphere at a pO₂ of 10⁻⁵.23 to 10⁻¹⁴.48 atm. The resulting products were also investigated with XRD. Based on the TGA and
temperatures to form SCFA-I, which in turn decomposed into melt and Fe with the formula of Ca to the formation of γ-CFF at temperature, rather than SFCA. The γ-CFF phase is a binary calcium ferrite low silica samples underwent different reactions upon heating to temperature. The lack of silica lead compositions of these samples were selected such that they had a similar composition to SFCA-I. Using the same experimental technique, low silica samples were analysed in air and a p oxidising conditions. Webster (Webster et al., 2013a) further expanded the compositional range in their previous work. On heating, Fe-rich SCFA solidification (1223 – 1288 C), Fe rich SCFA, and the temperature at which melt formed decreased under more oxidising conditions, FeO reacts with O2 and CaO to form C2F. The different iron oxides reacted with the CaO at different rates, with more reducing conditions leading to a faster reaction rate.

Fan (Fan et al., 2011) performed laboratory sintering tests with iron ore and pure oxides in a horizontal tube furnace open to air. The samples were cooled down for a number of selected cooling rates and for interrupted cooling test conditions, and analysed with optical microscopy. The effects of SiO2 and Al2O3 in the feed were tested. The results of the tests showed that as SiO2 increased the proportion of glassy phase and the proportion of calcium ferrites decreased; as Al2O3 increased the proportions of calcium ferrite increased and proportion of hematite decreased. Increasing the cooling rate decreased the size of the calcium ferrite crystals. The tests where quenching was performed part way through cooling showed that calcium ferrites formed from a melt on cooling.

Webster (Webster et al., 2012) carried out in-situ XRD tests on synthetic oxides in a reducing atmosphere (P02 of 10^-2.3 atm) under both heating and cooling. Samples were also tested by heat/quench experiments under reduction conditions (P02 of 10^-2.3 atm), with analysis by EPMA and XRD. During the in-situ XRD, 11 reactions were observed. The first three were associated with single component reactions, specifically Al(OH)3 dehydroxylation (170 °C to 260 °C), quartz transformation (603 °C), and CaCO3 decarbonation (587 °C). Five other events were observed on heating, C2F formation (~771 °C), CF/CFA formation (968 - 979 °C), SFCA-I formation (1054 – 1119 °C), SFCA formation (1107 – 1140 °C), and Fe3O4 and melt formation (1213 – 1308 °C). Three events were observed on cooling, Fe-rich SFCA solidification (1223 – 1288 °C), SFCA solidification (1145 – 1270 °C) and Fe3O4 formation (1085 – 1145 °C). All ferrites formed through solid state reactions on heating, which is consistent with previous research (Scarlett et al., 2004b, Scarlett et al., 2004a). On heating, CaO and Fe2O3 underwent a solid state reaction C2F. The CF3 reacted with Fe2O3 and CaO to form CF and Fe2O3, CaO and Al2O3 reacted to form CFA. It was suggested that SFCA-I is formed through a solid state reaction between Fe3O4, C2F and SiO2, and SFCA from CF, SFCA-I, CFA, SiO2 and Al2O3. The SCFA decomposed to form a melt and Fe3O4 at higher temperatures. On cooling, the Fe-rich SCFA crystallised first, followed by SCFA. The Fe-rich SCFA was observed to decompose into SCFA.

Webster (Webster et al., 2013c) examined the impact of P02 on the phase changes occurring on heating synthetic oxides. Samples were examined using in-situ XRD and heat/quench experiments, with analysis performed by EPMA, XRD, and wet chemical analysis. The reactions and phase changes observed agreed with those previously observed (Scarlett et al., 2004b, Scarlett et al., 2004a). The P02 values investigated were 0.21, 10^-2.3 and 10^-4 atm. Under oxidising conditions, Fe2O3 forms rather than Fe3O4 and under reducing conditions, a new calcium ferrite phase formed rather than SCFA-I. The temperatures at which phases were formed were found to be dependent on P02; SCFA-I, SCFA, and the temperature at which melt formed decreased under more oxidising conditions.

Webster (Webster et al., 2013a) further expanded the compositional range in their previous work. Using the same experimental technique, low silica samples were analysed in air and a P02 of 10^-2.3. The composition of these samples were selected such that they had a similar composition to SFCA-I. The low silica samples underwent different reactions upon heating to temperature. The lack of silica lead to the formation of γ-CFF at temperature, rather than SFCA. The γ-CFF phase is a binary calcium ferrite with the formula of CaF2 x=1.82O2y. Unlike the high silica samples, the γ-CFF reacted at high temperatures to form SCFA-I, which in turn decomposed into melt and Fe3O4 at around 1554 K.
Kimura (Kimura and Murao, 2013) performed experimental studies on the phase changes in the binary Fe$_2$O$_3$-CaO system in air. Samples were heated and analysed with in-situ XRD, and in a laser microscope. The heating rate during XRD was 0.5 °C/s and the cooling rate was 0.83 °C/s and 0.083 °C/s above 400 °C. The experimental work with the in-situ XRD showed that the phase changes in the CaO-Fe$_2$O$_3$ system varied with the bulk composition. Samples rich in iron underwent four reactions, C$_2$F formation, CF formation, CF$_2$ formation and liquid formation. Samples with moderate levels of iron underwent three reactions, CF formation, CF$_2$ formation and liquid formation. Samples rich in lime underwent two reactions, C$_2$F formation and CF formation. It was found that C$_2$F formed at the lowest temperatures from solid state reactions between CaO and Fe$_2$O$_3$. At higher temperatures, CF formed from either a reaction with C$_2$F and Fe$_2$O$_3$ or a solid state reaction between CaO and Fe$_2$O$_3$. The last solid state reaction is the formation of CF$_2$, which was observed to form from a solid state reaction between CF and Fe$_2$O$_3$ at 1240 °C. The reactions observed in the binary CaO-Fe$_2$O$_3$ system were also observed in the complex SiO$_2$-Fe$_2$O$_3$-CaO and SiO$_2$-Fe$_2$O$_3$-CaO-Al$_2$O$_3$ systems.

Webster (Webster et al., 2014) later examined the impact of basicity on the phase changes and reactions occurring on heating synthetic oxide samples at a p$_{O_2}$ of 10$^{-2.3}$ atm. The CaO/SiO$_2$ ratio investigated varied from 2.5 to 4.9. The oxide samples were performed using in-situ XRD and neutron diffraction techniques. The phases and reactions observed in the experiments were similar to that seen in past work (Scarlett et al., 2004b, Scarlett et al., 2004a), with the only major difference being that gehlenite (Ca$_2$Al$_2$SiO$_7$) was observed. With an increase in basicity (CaO/SiO$_2$), it was observed that the proportions and stability of SFCA-I increased and gehlenite decreased.

Ding (Ding and Guo, 2014) performed experimental research on the formation of SFC from calcium ferrites. Samples were prepared from pure oxides and heated in platinum crucibles for 24 hours in a muffle furnace open to air. Five starting compositions were prepared and analysed. The samples were subsequently analysed by XRD, SEM and EPMA. The low silica samples were found to contain Ca$_{2.5}$Fe$_{15.5}$O$_{25}$, with increasing silica leading to the formation of SFC. This led the researchers to suggest that SFC formed from Ca$_{2.5}$Fe$_{15.5}$O$_{25}$. It was proposed that this was achieved by substituting Si$^{4+}$ into the crystal structure, with the transformation of the crystal structure as a result.

Pownceby (Pownceby et al., 2016) studied the phase transformations and strength of sintered iron ores. Natural iron ores were heated in an in-situ XRD, on a platinum resistance heater, with an oxygen partial pressure of 10$^{-2.3}$ atm. The phase transformations and processes occurring in the sample were the same as that observed in earlier work by Webster (Webster et al., 2012, Webster et al., 2013b, Webster et al., 2013c), indicating that the synthetic oxides were able to simulate ore samples. In the natural ore samples, MgO was present, which was believed to stabilise SFCA-I. Sinter strength was tested by the tumbler index (TI). It was found that the sinter strength was greatest when SFCA was present but SFCA-I was not, which disagrees with the conclusions drawn by other researchers (Sasaki and Hida, 1982).

Ding (Ding and Guo, 2016) experimentally investigated the reactions and phase changes that occurred during the heating of SiO$_2$ Fe$_2$O$_3$ and CaO during sintering. Pure oxides were mixed and heating in platinum crucibles for 120 minutes in a vertical tube furnace open to air. The samples were analysed with XRD and SEM to determine phases present, their composition and microstructure. The testwork showed that CF reacted with SiO$_2$ to form C$_2$S and Fe$_2$O$_3$ at approximately 1000 °C. The C$_2$S and Fe$_2$O$_3$ then reacted to form SFC at approximately 1100 °C. These reactions were observed by analysis of the microstructures and the XRD patterns.
2.5 Summary of Findings from Previous Research

The phase equilibria in the $\text{Al}_2\text{O}_3$-$\text{CaO}$-$\text{FeO}$-$\text{Fe}_2\text{O}_3$-$\text{MgO}$-$\text{SiO}_2$ system have not been characterised over the whole range of compositions relevant to iron ore sintering. Sub-liquidus equilibria in the iron rich region of the “$\text{Fe}_2\text{O}_3$”-$\text{CaO}$-$\text{SiO}_2$ system and the liquidus for the “$\text{Fe}_2\text{O}_3$”-$\text{CaO}$-$\text{SiO}_2$ in air have been established. Some information on the range of stability of the SFC solid solution in air at temperatures at which liquid oxide is present has been obtained. The mechanism of substitution within the crystal lattice for this phase established, this phase being primarily described by a solid solution with the $\text{CF}_3$, $\text{CA}_3$, and $\text{C}_3\text{S}_4$ endmembers. Only limited data is available on the “$\text{Fe}_2\text{O}_3$”-$\text{CaO}$-$\text{SiO}_2$ systems containing $\text{Al}_2\text{O}_3$ and $\text{MgO}$ as minor components.

The majority of the research undertaken to date on the phases and microstructures formed during sintering has not involved the separate investigation of heating and cooling steps. This makes it difficult to unambiguously determine whether the microstructures were formed in the heating or cooling stages. These previous studies and conditions investigated are shown in Table 2-1 and Table 2-2.

The research undertaken using in-situ XRD partly addressed this issue, but the heating and cooling rates investigated were significantly slower than those experienced in industrial sinter processes and were unable to determine the microstructures formed and their formation mechanisms. The processed during heating were well defined, however there are significant uncertainties about the sequence and phase associations formed on cooling.
Table 2-1: Summary of experiments performed on kinetic processes in sintering (Nicol et al., 2018)

<table>
<thead>
<tr>
<th>Researcher</th>
<th>Year</th>
<th>Technique</th>
<th>Atmosphere (atm)</th>
<th>Fe (wt%)</th>
<th>CaO/SiO₂ (or CaO wt%)</th>
<th>Al₂O₃ (wt%)</th>
<th>MgO (wt%)</th>
<th>Heating Rate</th>
<th>Peak Temp. (°C)</th>
<th>Time at peak temperature</th>
<th>Cooling Rate</th>
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<td>Electric Furnace</td>
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<tr>
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<td>0</td>
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<tr>
<td>Matano</td>
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<td>Air/CO₂</td>
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<td>0</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
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<td>-</td>
<td>-</td>
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<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Abian</td>
<td>1983</td>
<td>Industrial Sinters</td>
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<td>-</td>
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<tr>
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<td>1985</td>
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<tr>
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<td>Sinter pot</td>
<td>Air/CO₂</td>
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<td>-</td>
<td>-</td>
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<td>-</td>
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<tr>
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<tr>
<td>Ichishii</td>
<td>1989</td>
<td>Tube Furnace</td>
<td>Air, nitrogen, CO₂/CO₂ (0.2; 0.8) (various psi)</td>
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<tr>
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<tr>
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<td>1998</td>
<td>Sinter pot</td>
<td>Air/CO₂</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Yang</td>
<td>1999</td>
<td>In-situ Furnace</td>
<td>CO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Liu</td>
<td>2004</td>
<td>In-situ Furnace</td>
<td>Air</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>Chou</td>
<td>2005</td>
<td>Laboratory Furnace</td>
<td>Air</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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<tr>
<td>Scarlett</td>
<td>2004</td>
<td>In-situ XRD</td>
<td>Air</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Chen</td>
<td>2007</td>
<td>Sinter pot</td>
<td>Air/CO₂ (unknown)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Jeon</td>
<td>2010</td>
<td>Tube Furnace</td>
<td>P: 5 x 10⁻³</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Tan</td>
<td>2011</td>
<td>Tube Furnace</td>
<td>Air</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Webster</td>
<td>2011</td>
<td>In-situ XRD</td>
<td>P: 5 x 10⁻³</td>
<td>50.6 &amp; 56.91</td>
<td>3.96</td>
<td>1 - 5</td>
<td>0</td>
<td>10 °C/min</td>
<td>1260</td>
<td>0 - 5 °C/min</td>
<td>1200</td>
</tr>
<tr>
<td>Webster</td>
<td>2011</td>
<td>In-situ XRD</td>
<td>P: 1.01; 5 x 10⁻³</td>
<td>54.1</td>
<td>3.96</td>
<td>5</td>
<td>0</td>
<td>10 °C/min</td>
<td>1350</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Webster</td>
<td>2011</td>
<td>In-situ XRD</td>
<td>Air</td>
<td>44.7 &amp; 62.0</td>
<td>10 - 36 °C/CO₂</td>
<td>-</td>
<td>-</td>
<td>30 °C/min</td>
<td>1500</td>
<td>0 °C - 5 °C/min</td>
<td>-</td>
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<tr>
<td>Webster</td>
<td>2011</td>
<td>In-situ XRD</td>
<td>P: 5 x 10⁻³</td>
<td>58.2 &amp; 48.9</td>
<td>4.9</td>
<td>10</td>
<td>0</td>
<td>10 °C/min</td>
<td>1350</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ding</td>
<td>2014</td>
<td>Lab Furnace</td>
<td>Air</td>
<td>56.3 &amp; 60.9</td>
<td>4.7</td>
<td>70.6</td>
<td>-</td>
<td>-</td>
<td>1200</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ding</td>
<td>2015</td>
<td>Lab Furnace</td>
<td>Air</td>
<td>56.8 &amp; 60.9</td>
<td>4.7</td>
<td>70.6</td>
<td>-</td>
<td>-</td>
<td>1200</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Powlesley</td>
<td>2016</td>
<td>In-situ XRD</td>
<td>P: 5 x 10⁻³</td>
<td>52.9</td>
<td>4.67</td>
<td>4.56</td>
<td>0.12</td>
<td>10 °C/min</td>
<td>1350</td>
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<td>-</td>
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</tbody>
</table>

Note: NA – not suggested by researcher, ND – not detected by researcher.
3. Aims and Objectives

The review of the literature has demonstrated that despite the widespread use of the Dwight-Lloyd sintering technology in iron ore industrial practice, there remains a limited understanding of the detailed chemical reactions and phase transformations taking place during the process. These reactions are complex and involve multiple reaction steps. In addition, the phase equilibria in the \( \text{Al}_2\text{O}_3-\text{CaO-FeO-Fe}_2\text{O}_3-\text{MgO-SiO}_2 \) system have not been well characterised over the whole range of compositions relevant to iron ore sintering. The number of degrees of freedom in this six-component system, and the lack of phase equilibrium data available at the present time in the composition ranges critical to iron ore sintering, therefore makes it difficult to systematically investigate this system.

The research to date on the system has relied principally on the post mortem evaluation of the final sinter microstructures. The complexity of the reaction sequence and phases formed has meant there is no clear understanding of the reaction sequence and the phase assemblages and associations in the products. In-situ monitoring of the system during heating and cooling using X-ray diffraction techniques has provided some indication of potential reaction sequences but the process conditions investigated to date are not representative of industrial sintering processes. In addition, this approach does not provide critical information on microstructural relationship and structures formed during the process.

The aim of the present project is to identify the relationships between process variables and sinter product microstructures in the production of iron ore sinter.

A key assumption made at the outset of the project was that the phases and microstructures formed in iron ore sintering are primarily the result of reactions taking place during solidification of the melts. The results reported in the present study focus on the solidification processes taking place during controlled cooling in the \( \text{Fe}_2\text{O}_3-\text{CaO-SiO}_2 \) system in air. This pseudo-ternary system was selected for the study rather than the six-component system as:

- The phase equilibria and liquidus isotherms in the ternary system in air are now well defined, enabling comparisons to be made between the phases and structures formed in equilibrium and non-equilibrium conditions.
- This system contains all major phases observed in industrial iron ore sinters,
- This simplified system reduces the number of compositional and process variables so that the effects of these key variables can be systematically investigated and the magnitude of their impact unambiguously identified.

The objectives of the research are to:

- Develop a new experimental methodology that will enable the characterisation of the solidification processes taking place in these oxide melts. The approach should be one that enables the sequence of phase formation to be clearly identified and linked to the final microstructures
- Undertake a systematic study on the effects of key process variables on the processes and product microstructures formed during the solidification processes in iron oxide rich compositions in the “\( \text{Fe}_2\text{O}_3-\text{CaO-SiO}_2 \)” system in air. These variables include, cooling rate, \( \text{CaO/SiO}_2 \) ratio and \( \text{Fe}_2\text{O}_3 \) concentration.
4. Experimental Techniques

An experimental technique has been designed to enable controllable cooling, in a controlled gas atmosphere, on a microscale. The samples are heated to temperature, cooled at a controlled rate to a specific temperature, rapidly quenched to room temperature, followed by analysis by scanning electron microscope and electron probe x-ray microanalysis (EPMA) techniques. The cooling rate, sample composition and gas atmosphere are to be controlled within the range expected in industrial sintering process and then well outside those experience in industrial processes.

4.1 Initial Mixtures and Substrate

High purity oxide powders of Fe$_2$O$_3$ (>99.5 wt%, Alfa Aesar), CaCO$_3$ (>99.95 wt%, Alfa Aesar), and SiO$_2$ (>99.9 wt%, Alfa Aesar) are used in the present study as starting materials. The CaCO$_3$ is calcined to produce CaO free of carbonates and moisture.

The masses of the powders and mixtures are weighed on a digital balance to four decimal points to obtain the target bulk composition. The powders are mixed to achieve intimate contact with an agate mortar and pestle. The mixed powders are pressed into a pellet (6 mm ø) with a steel die at approximately 400 bar. The pellets are affixed to the substrate for experimentation.

The oxide samples are supported on a Pt-Rh (70 wt% Pt, 30 wt% Rh) wire substrate in a tube furnace. This support material was selected as it is not likely to react with the oxide sample at conditions relevant to sintering. It is only appropriate at conditions more oxidising than iron saturation and at temperatures less than about 1400°C. The wire is formed into a spiral, to which the pellet was affixed, as illustrated in Figure 4-1.

4.2 Sample Heating and Cooling

The oxide pellet and substrate are heated and cooled in a vertical tube furnace. The furnace has SiC electrical heating elements surrounding an alumina tube (38 mm OD, 30 mm ID) in which the sample is heated. The temperature profile of the furnace is kept constant and controlled via a feedback controller with a thermocouple positioned beside the alumina tube. This maintains the temperature inside the hot zone of the furnace within 2 K of the set point under steady state conditions. This is schematically shown in Figure 4-2.

The sample is vertically suspended in the furnace with an alumina rod. The vertical position of the alumina rod, and in turn the sample, is controlled with a positioning motor affixed to the top of the furnace. The positioning motor rotates the positioning screw, which in turn moves the moving stage up and down. The alumina tube is fixed to the moving stage with the fixing nut. This allows the sample to move through the hot zone of the furnace in a controlled manner to achieve a target heating and cooling rate.

The sample can be quenched at any point in the heating or cooling process with the specimen holder wire. The sample is quenched in water to maintain the same phase assemblages and compositions as
those that are present at the quench temperature. Prior to quenching the sample, the furnace end is
removed with the quenching fluid underneath to maintain the gas atmosphere in the furnace. The
cooling medium, substrate and sample mass are selected to provide a high enough cooling rate to
transform the liquid phases into a glass.

4.3 Sample Temperature Control and Calibration
The temperature of the sample is measured by the specimen thermocouple. This thermocouple is a
B-type, installed along with the specimen holder wire, in a four hole alumina tube. The thermal mass
of the sample and substrate is sufficiently small that the thermal profile within the sample is uniform. As the thermocouple is close to the sample, the measured temperature is assumed to be representative of the temperature within the centre of the sample. There is expected to be a small difference between the temperature of the sample and that measured by the thermocouple, but it is not currently possible to quantify this difference.

To control the sample temperature, a calibration was performed by moving a sample at a constant velocity through the tube furnace. The temperature is recorded and this, along with the speed, is used to calculate the temperature of the sample at different positions through the furnace. The desired cooling rate, a constant \( \frac{dT}{dt} \), is input and the controller moves the sample to achieve the target-cooling rate. The computer control is performed for the entire cooling process. This system achieves a cooling rate within 0.1 °C/s of the target.

The computer controller was calibrated with samples and substrates identical to that used in the cooling tests. The calibration was run at a constant speed of 0.4 mm/s, with calibration once per day to accommodate for changes in the surrounding temperature and humidity.

Three trial runs were performed to confirm the accuracy and control of the cooling rates. A range of cooling rates were used, from 0.25 °C/s to 7 °C/s to determine the accuracy and reproducibility of the experimental set up. The controller was able to achieve a reproducible and constant cooling rate. The cooling profiles observed are shown in the Figure 4-3.

![Variation in temperature with time](image)

**Figure 4-3: Cooling profiles recorded for initial calibration and control tests**

### 4.4 Phase Characterisation

Quenched samples are washed and dried prior to mounting in epoxy resin. The mounted samples are subsequently polished with a Struers polishing system, a conventional metallographic technique. This sections and prepares a flat and clean surface for analysis under SEM and EPMA. Samples are polished in three steps, wet sandpaper (4 stages), polishing discs with diamond paste in a water suspension (1 stage) and finally polishing discs with diamond paste in a kerosene suspension (2 stages). The polished samples are coated with carbon to create a conductive surface for electron microscopy.

The sample cross sections were characterised. Initially using optical microscopy for phase and microstructure identification using a reflected light microscope (Olympus Provis AX70TRF). For electron microscope analysis, the polished surfaces were carbon coated using a carbon coater (Quorum Technologies, QT150TES). For high-resolution imaging, a field emission scanning electron microscope (FE-SEM) (JEOL 7001F; Japan Electron Optics Ltd., Tokyo, Japan) was used with an
accelerating voltage of 15 keV in backscatter mode. A scanning electron microscope (JEOL 6610; Japan Electron Optics Ltd., Tokyo, Japan) equipped with an Electron Backscatter Diffraction (EBSD) detector was used to determine if crystal twinning was present.

Phase compositions were measured by an electron probe X-ray microanalysis (EPMA) technique with wavelength dispersive spectroscopy (WDS) (JEOL 8200L EPMA; Japan Electron Optics Ltd., Tokyo, Japan). An electron beam was provided at a voltage of 15 keV and current of 20 nA. The standard Duncumb–Philibert atomic number, absorption, and fluorescence correction (ZAF-correction) supplied with the probe was used. Selected point analysis of phases within the sample was performed. Three standards were used for calibration, pure CaSiO$_3$, Fe$_2$O$_3$, and Al$_2$O$_3$ (all standards from the Charles M. Taylor Co., Stanford, CA). The accuracy of the composition measurements was estimated to be within 1 % of the measured value. The EPMA was not used to measure the proportion of different oxidation states. The iron in the sample was assumed to be in the Fe$^{3+}$ state for presentation purposes.

Repeated experiments, cooling from 1623 K to 1073 K (1350 °C to 800 °C) at 2 K/s, with 0.2 g of starting oxides were performed to obtain 1g of material. The material was crushed and ground with an agate mortar and pestle. The resulting powder was analysed with powder X-Ray Diffraction (XRD) (Bruker D8), with a Cu kα radiation source at a voltage of 40 kV and a current of 40 mA. The phases present were identified by comparison with previously characterised XRD patterns reported in the literature.

4.5 Thermodynamic Calculations
Thermodynamic calculations are undertaken to predict the phase assemblages formed under equilibrium cooling. These calculations were undertaken using the FactSage 7.1 (2017) computer package, using the FToxid database and a custom solution model for the SFC phase. The Equilib module was used, with equilibrium calculations performed for a range of temperatures, with set temperature steps.
5. Results

The outcomes of the research that has been undertaken are presented in this thesis in a series of sections or sub-chapters. These sections demonstrate the new systematic approach taken to the examination of microstructures formation from iron ore sinter melts. These sections address the following research questions;

1. Establishment of the research methodology and approach to analysis of results
2. The effect of cooling rate on phase formation and microstructure solidification
3. The effect of bulk chemical composition on the phases formation and microstructure solidification
4. The measurement and analysis of process conditions present in industrial iron ore sintering
5. The formation of the SFCA phases at conditions relevant to iron ore sintering

Of particular interest to industrial sinter practice is the formation of silico-ferrites of calcium (SFC) and silico-ferrites of calcium and aluminium (SFCA) phases. For this reason, the range of bulk compositions selected for this study were chosen such that the SFC phase was predicted to form under equilibrium cooling.

6. Microstructure Evolution During Controlled Solidification of “Fe$_2$O$_3$”-CaO-SiO$_2$ Liquids in Air

A new experimental technique and analysis methodology required to determine processes occurring during the solidification of liquids with the “Fe$_2$O$_3$”-CaO-SiO$_2$ system in air has been developed. This technique enables each process occurring on solidification and the evolution of microstructures to be observed and identified in isolation in the sequence in which they form. To develop the technique and to provide a base case for later comparison, samples with a bulk composition of 73.2 wt% Fe$_2$O$_3$ and a CaO/SiO$_2$ mass ratio of 3.46 wt/wt were heated above the liquidus temperature and cooled to below the solidus temperature. The bulk composition was selected such that the melt composition passed through the Silico-Ferrite of calcium (SFC) primary phase field on cooling. A series of samples were cooled at 2 K/s from 1623 K to 1073 K and quenched at 5 K intervals from 1533 K to 1453 K. The phases formed and microstructures of the with quenched samples were analysed using Scanning Electron Microscopy (SEM) and Electron Probe Micro X-Ray Analysis (EPMA).

On cooling, four phase assemblages were observed. These were, in the order of formation, Liquid+H(I), Liquid+H+C$_2$S(II), Liquid+C$_2$S+CF$_2$(III) and C$_2$S+CF$_2$+CF (IV), where H corresponds to Hematite, C$_2$S is dicalcium silicate, CF$_2$ is calcium diferrite and CF is calcium ferrite. The phase assemblages differed from that predicted under equilibrium and Scheil-Gulliver Cooling. Importantly, no Silico-Ferrite of Calcium (SFC) phase was formed on solidification of the liquid.

Based on the liquid compositions as measured by EPMA and the morphologies of the solids formed, the complex solidification sequence was determined to be as follows; nucleation and growth of the primary phase hematite, nucleation of C$_2$S followed by the formation of a C$_2$S layer on hematite, C$_2$S dendrites and a coupled C$_2$S-hematite microstructure, nucleation of CF$_2$ followed by the formation of individual CF$_2$ crystals and a coupled CF$_2$-C$_2$S microstructure and finally the nucleation of CF followed by the formation of individual CF crystals and coupled C$_2$S-CF and C$_2$S-CF-CF$_2$ microstructures.

Details of the microstructures formed during the solidification sequence are given in the paper in Appendix A.
The study clearly demonstrates the importance of thermal history in determining phase formation and product microstructure during solidification of these “Fe₂O₃”-CaO-SiO₂ liquids. A solidification pathway for melts solidifying from within the hematite primary phase field and passing through the SFC primary phase field was established.

7. Controlled Solidification of Liquids Within the SFC Primary Phase Field of the “Fe₂O₃”-CaO-SiO₂ System in Air

Further experimental studies were undertaken on samples with a bulk composition within the Silico-Ferrite of Calcium (SFC) primary phase field. It was predicted on equilibrium solidification that the SFC phase would form homogenously from the melt. Samples with a bulk composition containing 69.24 wt% Fe₂O₃ and a CaO/SiO₂ ratio of 4.0 wt/wt were cooled from 1623 K to 1453 K. A series of samples were cooled at 2 K/s from 1623 K to 1073 K and quenched at 5 K intervals from 1533 K to 1453 K, with quenched samples analysed using Scanning Electron Microscopy (SEM) and Electron Probe Micro X-Ray Analysis (EPMA).

On cooling, an intergrowth of SFC-I and Ca₇.₂Fe²⁺₀.₈Fe³⁺₃₀O₅₃ was observed to form referred to here as ‘SFC-I’. This intergrowth was confirmed with the use of powder X-Ray Diffraction (XRD). On cooling, three phase assemblages were observed to form, in the following order, Liquid+'SFC-I' (I), Liquid+'SFC-I'+C₂S+CF₂ (II), and CF+CF₂+C₂S (III). The SFC phase was not observed to form, despite this phase predicted to form under both equilibrium and Scheil-Gulliver Cooling.

Based on the phases identified, the microstructures formed and the liquid compositions, as measured by Electron Probe Micro X-Ray Analysis (EPMA), the solidification sequence was determined as follows; nucleation and growth of the SFC-I and Ca₇.₂Fe²⁺₀.₈Fe³⁺₃₀O₅₃ intergrowth, nucleation and growth of C₂S dendrites and a coupled C₂S-SFC-I+Ca₇.₂Fe²⁺₀.₈Fe³⁺₃₀O₅₃ microstructure, nucleation and growth of individual CF₂ crystals and a coupled CF₂-C₂S microstructure, and finally the nucleation and growth of CF, coupled C₂S-CF and C₂S-CF-CF₂ microstructures.

Details of the microstructures formed during the solidification sequence are given in the paper in Appendix B.

This study demonstrates that the non-equilibrium phases SFC-I and Ca₇.₂Fe²⁺₀.₄Fe³⁺₃₀O₅₃ are able to form on cooling. A solidification pathway for melts solidifying from within the SFC primary phase field was established.

8. Effect of Cooling Rate on the Controlled Solidification of “Fe₂O₃”-CaO-SiO₂ Liquidus in Iron Ore Sinter

The impact of cooling rate on the solidification of melts within the “Fe₂O₃”-CaO-SiO₂ was examined using samples within the hematite primary phase field, the same composition as that used in Chapter 10 and Appendix A. Samples were cooled from 1623 K to 1073 K at 0.5 K/s and 0.1 K/s. The microstructures formed were identified by Scanning Electron Microscopy (SEM). The melt compositions were measured by Electron Probe Micro X-Ray Diffraction (EPMA) formed at different cooling rates were compared.

On cooling, two separate solidification pathways were observed. The pathways established in Chapter 6, a hematite pathway, and Chapter 7, a ‘SFC-I’ pathway, were observed to occur in separate regions.
The ‘SFC-I’ intergrowth was observed to form in slow cooled samples (0.1 K/s) in regions free of hematite. The equilibrium Silico-Ferrite of Calcium (SFC) phase was not observed at any of the cooling rates investigated.

The phases formed and their sequence of formation were found to be independent of cooling rate in the range of conditions studied. A slower cooling rate was observed to result in larger and fewer individual crystals, and larger and coarser coupled microstructures. Slower cooling rates result in the liquid compositions during cooling approaching equilibrium conditions more closely.

Details of the research findings are given Appendix C.

It has been demonstrated that the cooling rate influences the phases, microstructures and the proportions of phases formed. Non-equilibrium conditions were observed at all cooling rates.

9. Effect of Fe$_2$O$_3$ on the Controlled Solidification of “Fe$_2$O$_3$”-CaO-SiO$_2$ Liquidus in Iron Ore Sinter

Based on the solidification pathways established for liquids with the hematite and SFC primary phase field, the effect of the bulk Fe$_2$O$_3$ composition on the solidification of melts within the “Fe$_2$O$_3$”-CaO-SiO$_2$ system at a selected CaO/SiO$_2$ ratio was examined. Samples within the hematite primary phase field, with the same CaO/SiO$_2$ ratio as that used in Chapter 10, and containing 70.3 wt%, and 85.0 wt% Fe$_2$O$_3$ were cooled from 1623 K to 1073 K at 2 K/s. The microstructures formed and the melt composition were determined by Scanning Electron Microscopy (SEM) and Electron Probe Micro X-Ray Diffraction (EPMA) respectively. The melt composition and microstructures formed at different compositions were compared to determine the impact of the Fe$_2$O$_3$ concentration on solidification.

On cooling, two separate solidification pathways were observed to be possible. The pathways established in Chapter 6, a hematite pathway, and Chapter 7, a ‘SFC-I’ pathway, were observed to occur in separate regions. The ‘SFC-I’ intergrowth was observed to form in regions free of hematite, present in samples with a low bulk Fe$_2$O$_3$ concentration. The equilibrium Silico-Ferrite of Calcium (SFC) phase was not observed at any of the compositions investigated.

The morphologies of the hematite phase formed on cooling, and in turn, the subsequent microstructures that formed in the remaining areas was influenced by the bulk Fe$_2$O$_3$ concentration. Hematite formed on cooling was found to form dendritic structures, while that which was originally present at the sub-liquidus peak temperature formed euhedral equiaxed structures. With a decrease of the bulk Fe$_2$O$_3$ concentration, the proportion of hematite formed on cooling decreased and the proportion of coupled microstructures relative to individual crystals increased.

Details of the research findings are given in Appendix D.

It has been demonstrated that the bulk Fe$_2$O$_3$ concentration influences the phases, microstructures and the proportion of phases formed. Non-equilibrium conditions were observed for all compositions investigated.
10. **Effect of CaO/SiO\(_2\) Ratio on the Controlled Solidification of “Fe\(_2\)O\(_3\)”-CaO-SiO\(_2\) Liquidus in Iron Ore Sinter**

Based on the solidification pathways established for liquids with the hematite and SFC primary phase field, the effect of the bulk CaO/SiO\(_2\) ratio on the solidification of melts within the “Fe\(_2\)O\(_3\)”-CaO-SiO\(_2\) system was determined. Samples within the hematite primary phase field with a CaO/SiO\(_2\) ratio (wt/wt) of 2.78 and 4.75 were cooled from 1623 K to 1073 K at 2 K/s. These compositions contained 69.23, 72.74 and 74.94 wt% Fe\(_2\)O\(_3\) respectively. The compositions selected were predicted to follow the same equilibrium solidification pathway. The microstructures formed were determined by Scanning Electron Microscopy (SEM) and the melt composition as measured by Electron Probe Micro X-Ray Diffraction (EPMA) formed at different compositions were compared to determine the effect of the CaO/SiO\(_2\) ratio on the solidification processes.

On cooling, two separate solidification pathways were observed. The pathways established in Chapter 6 and 7 were observed to occur in separate regions. The ‘SFC-I’ intergrowth was observed to form in regions free of hematite, present in samples with a high CaO/SiO\(_2\) ratio. The equilibrium Silico-Ferrite of Calcium (SFC) phase was not observed at any of the compositions investigated.

The CaO/SiO\(_2\) ratio influenced the both proportions of the phases formed and morphologies of the microstructures. Details of the research findings are given in Appendix E.

It has been demonstrated that the CaO/SiO\(_2\) ratio influences the phases, microstructures and the proportion of phases formed on solidification of these “Fe\(_2\)O\(_3\)”-CaO-SiO\(_2\) melts. Non-equilibrium conditions were observed for all compositions investigated.

11. **Measurement of Process Conditions Present in Pilot Iron Ore Sintering**

It has been demonstrated previously that the phases and microstructures formed during sintering are dependent on bulk composition, gas atmosphere and cooling history. Due to the lack of data available on the process conditions within the sinter bed during the sintering process, measurements of the temperatures and oxygen partial pressures experienced during the actual sintering process were undertaken.

An improved experimental technique was developed to measure, concurrently, the oxygen partial pressures (p\(_{O_2}\)) and temperatures within a pilot scale iron ore sinter pot as a function of time. Based on the measured oxygen partial pressure and temperature, supported by laboratory experiments, processes occurring during sintering were identified.

Repeatable trends and relationships between the p\(_{O_2}\) and temperature profile during sintering were obtained using this experimental design and procedure. Based on the measured p\(_{O_2}\) and thermodynamic calculations, it has been demonstrated that at the peak bed temperature and during cooling, the conditions can be oxidising or reducing relative to hematite. Laboratory experiments demonstrated that oxidation of magnetite on cooling to form hematite can occur at both at sub-liquidus and sub-solidus conditions.
The relative impacts of changes to coke rate and draft pressure drop on the process conditions and proportions of the phases formed in the sinter have been measured. Increasing coke rate was shown to result in a faster sinter heating rates, higher peak bed temperatures and times at peak temperature. Higher draft pressures across the sinter bed resulted in faster sinter heating rate and a shorter time at peak temperature.

The sintering stages have been classified in terms of the process conditions present during sintering to enable the influence of sintering process variables on the resulting microstructure to be more clearly identified.

This results of this research is detailed in Appendix F.

12. Silico Ferrite of Calcium (SFC) Formation in the “Fe₂O₃”-CaO-SiO₂ system

The SFCA phases constitute major proportions of the mass of iron ore sinter. These phases are believed to improve the properties of sinter and in turn their performance in an iron blast furnace.

The mechanisms of formation of SFC in the “Fe₂O₃”-CaO-SiO₂ system have been studied through undertaking targeted thermal treatments of selected oxide samples. This research is detailed in Appendix G.

It has been shown that the SFC group minerals nucleate heterogeneously upon existing magnetite crystals. The SFC group minerals were not nucleated in close proximity to hematite. The nucleation and growth of the SFC-I/\(\text{Ca}_2\text{Fe}^{3+0.8}\text{Fe}^{3+30}\text{O}_{57}\) intergrowth was observed at conditions in which SFC was predicted to form based on phase equilibria. The SFC phase was formed on heating and retained in oxide samples when the peak temperature was lower than the SFC liquidus temperature.

It has been demonstrated in these targeted thermal treatments, at conditions relevant to iron ore sintering, that the SFCA phases are able to form on both heating and cooling and under both oxidising and reducing conditions, relative to hematite. The SFCA crystals formed vary in size, composition and association with the formation conditions.
13. Summary

A new experimental technique and analysis methodology has been developed to enable the study of the solidification of liquids within the \( \text{Fe}_2\text{O}_3-\text{CaO}-\text{SiO}_2 \) system in air. The technique enables the cooling rate of a melt of a specific bulk composition to be accurately controlled. The microstructures present at a given temperature are able to be determined and the composition of the phases are able to be measured. This represents a significant advance in research capability. Not only can the sequences of phase formation and phase associations be clearly identified but also the compositions of the phases produced at any stage in the process can be measured.

Pilot scale iron ore sintering tests have been undertaken to establish the oxygen partial pressures \( p_{\text{O}_2} \) and temperatures within the sinter bed during iron ore sintering. It has been shown that the effective oxygen partial pressure at peak bed temperature and cooling approached that in air.

The focus of the experimental laboratory study has been on bulk liquid compositions for which it is anticipated that the silico ferrite of calcium (SFC) phase would form on equilibrium solidification. The effects of melt composition, the initial primary phase field, \( \text{Fe}_2\text{O}_3 \) concentration, \( \text{CaO}/\text{SiO}_2 \) ratio, and cooling rate were investigated. These included:

- Cooling at 2K/s and \( \text{CaO}/\text{SiO}_2 = 3.46 \) and 73.2\%\( \text{Fe}_2\text{O}_3 \),
- Cooling at 2 K/s with \( \text{CaO}/\text{SiO}_2 (\text{wt/wt}) = 4 \) at 69.2 wt\%\( \text{Fe}_2\text{O}_3 \) in the SFC primary phase field
- Cooling melts with \( \text{CaO}/\text{SiO}_2 (\text{wt/wt}) = 3.46 \) at 73.2 wt\%\( \text{Fe}_2\text{O}_3 \) at cooling rates between 0.01 and 4 K/s,
- Cooling at 2 K/s with \( \text{CaO}/\text{SiO}_2 (\text{wt/wt}) = 3.46 \) between 70 and 85 wt\%\( \text{Fe}_2\text{O}_3 \) in the hematite primary phase field
- Cooling at 2 K/s with \( \text{CaO}/\text{SiO}_2 (\text{wt/wt}) \) between 2.78 and 4.75,

The phases identified in the solidified products include, hematite, dicalcium silicate, calcium diferrite, calcium ferrite, SFC-I and \( \text{Ca}_{7.2}\text{Fe}^{2+}_{0.8}\text{Fe}^{3+}_{30}\text{O}_{57} \). The results of the experimental studies show that the solidification paths do not follow those anticipated from equilibrium or Sheil-Gulliver cooling. Significantly, the Silico-Ferrite of Calcium (SFC) phase was not observed to form at the conditions investigated when the peak temperature was above the SFC liquidus.

The complex morphologies and phase assemblages in the final products are shown to be the result of the formation, on solidification of the melts, of equiaxed faceted hematite; dendritic dicalcium silicate; divorced and coupled dicalcium silicate and hematite; calcium diferrite; coupled calcium diferrite and dicalcium silicate; calcium monoferrite; coupled calcium monoferrite and dicalcium silicate; coupled calcium diferrite, dicalcium silicate and calcium monoferrite.

According to equilibrium cooling in the samples having a \( \text{CaO}/\text{SiO}_2 \) ratio less than approximately 2 wt/wt, at temperatures below the SFC peritectic temperature, the hematite primary phase should redissolve or react to form SFC; this did not take place under the cooling conditions studied. In addition, the metastable hematite phase did not dissolve or react on cooling below the peritectic temperature, as anticipated for the reaction \( \text{L} + \text{H} + \text{C}_2\text{S} \rightarrow \text{L} + \text{C}_2\text{S} + \text{CF}_2 \).

The sequences of phases formed on solidification of iron rich compositions are more closely described by Sheil-Gulliver cooling of a metastable liquid of the “\( \text{Fe}_2\text{O}_3 \)-\text{CaO}-\text{SiO}_2 \) system that does not include the SFC primary phase field.
The heterogeneous nucleation of SFC on hematite appears not to be favoured, rather the SFC-I phase, having the same crystal structure as SFCA-I, is observed to form directly from the melt and preferentially in association with the surfaces of magnetite under conditions where this latter phase is present.

The observations made in the present study indicate that significant undercooling is required to enable the formation of new phases during the solidification sequence. This was demonstrated by the supercooling of the melt with respect to dicalcium silicate prior to the nucleation of this phase. This was additionally supported by the observation of both individual crystals of dicalcium silicate, calcium diferrite and calcium monoferrite and coupled microstructures containing these phases in the solidified material.

The formation of secondary hematite in industrial sinter has been shown to take place through the oxidation of magnetite at sub-liquidus and sub-solidus temperatures. The microstructures of the secondary hematite differ depending on the oxidation mechanism. Large facetted hematite crystals are formed if the oxidation takes place in the presence of liquid oxide. Gas/solid oxidation of magnetite can result in the formation of two different structures i) a two phase material consisting of hematite and an as yet undetermined calcium ferrite phase and ii) a dense lath hematite formed by a transformation along common close packed oxygen planes in the crystals.

The study lays the foundation for further systematic studies of the solidification of complex multicomponent melts. This includes the systems directly relevant to iron ore sintering, $\text{Al}_2\text{O}_3$-$\text{Fe}_2\text{O}_3$-CaO-SiO$_2$ and $\text{Fe}_2\text{O}_3$-CaO-SiO$_2$-MgO. Minor modifications to the experimental design mean that studies of solidification in the presence of other gas compositions are also possible, in effect exploring solidification reactions in the FeO-Fe$_2$O$_3$-CaO-SiO$_2$ system. As has been the case in the present study, the design of the experiments, the analysis and the interpretation of the experimental results are best undertaken with the support of phase equilibrium information on these systems.
14. References


HAMILTON, J., HOSKINS, B., MUMME, W., BORBIDGE, W. & MONTAGUE, M. 1989. The crystal structure and crystal chemistry of Ca$_{2.3}$Mg$_{0.8}$Al$_{1.5}$Si$_{1.1}$Fe$_{8.3}$O$_{20}$ (SFCA): solid solution limits and selected phase relationships of SFCA in the silica-ferric oxide-calcium oxide (-alumina) system. *Neues Jahrb. Mineral., Abh.*, 161, 1-26.


LIU, X. G. 2013. Experimental phase equilibria studies in oxide systems for copper smelting slags. The University of Queenslands, School of Chemical Engineering.


MUMME, W., CLOUT, J. & GABLE, R. 1998. The crystal structure of SFCA-I, Ca$_{13.18}$Fe$_{14.66}$Al$_{1.34}$Fe$_{0.82}$O$_{28}$, a homolog of the aenigmatite structure type, and new crystal structure refinements of β-CFF, Ca$_{2.99}$Fe$_{14.30}$Fe$_{0.55}$O$_{25}$ and Mg-free SFCA, Ca$_{2.45}$Fe$_{0.04}$Al$_{1.74}$Fe$_{0.16}$Si$_{0.6}$O$_{20}$. *Neues Jahrb. Mineral., Abh.*, 173, 93-117.

MUMME, W. G. 1988. A note on the relationship of Ca$_{2.3}$Mg$_{0.8}$Al$_{1.5}$Si$_{1.1}$Fe$_{8.3}$O$_{20}$ (SFCA) with aenigmatite group minerals and sapphireine. *Neues Jahrb. Mineral., Abh.*, 8.

MUMME, W. G. 2003. The crystal structure of SFCA-II, Ca$_{5.1}$Al$_{9.3}$Fe$_{18.7}$Fe$_{2+0.9}$O$_{48}$ a new homologue of the aenigmatite structure-type, and structure refinement of SFCA-type, Ca$_{3}$Al$_{5}$Fe$_{7}$O$_{20}$. Implications for the nature of the "ternary-phase solid-solution" previously reported in the CaO-Al$_2$O$_3$-iron oxide system. *Neues Jahrb. Mineral., Abh.*, 178, 307-335.

MUMME, W. G. & GABLE, R. W. 2018. Crystal structures of monoclinic variants of two SFCA structure-types containing significant Fe2+: crystal structure of monoclinic SFCA-II, Ca$_{2.6}$Fe$_{3+8.0}$Fe$_{2+3.4}$O$_{24}$; and proposed crystal structure of monoclinic SFCA-I, ideally, Ca$_{2}$Fe$_{2+8}$Fe$_{3+8}$Al$_{4}$O$_{28}$. *Neues Jahrb. Mineral., Abh.*


SUGIYAMA, K., MONKAWA, A. & SUGIYAMA, T. 2005. Crystal structure of the SFCAM phase Ca$_2$(Ca,Fe,Mg,Al)$_5$(Fe,Al,Si)$_4$O$_{20}$. ISIJ Int., 45, 560-568.


WEI, Q. 2017.


Appendix A: Microstructure Evolution During Controlled Solidification of “Fe$_2$O$_3$”-CaO-SiO$_2$ Liquids in Air
Microstructure evolution during controlled solidification of “Fe$_2$O$_3$”-CaO-SiO$_2$ liquids in air

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Abstract

The principal chemical components in iron ore sintering are Fe$_2$O$_3$, CaO and SiO$_2$. The sintering process consists of three key steps, heating, holding at peak temperature and cooling. During the cooling stage, a liquid oxide solidifies to form the final sinter microstructures.

To investigate the fundamental processes taking place during the cooling of sinters, a new experimental technique has been developed that allows the stages of solidification to be determined in isolation, rather than inferred from the final microstructures. Fe$_2$O$_3$-CaO-SiO$_2$ oxide samples of a bulk composition having a CaO/SiO$_2$ mass ratio of 3.46 and 73.2 wt% Fe$_2$O$_3$, were cooled in air from 1623 K (1350 °C) at 2 K/s, quenched at 5 K temperature intervals from 1533 K (1260 °C) to 1453 K (1180 °C) and analysed using Electron Probe Micro X-Ray Analysis (EPMA). During cooling, four distinct stages were observed, consisting of the phase assemblages liquid+hematite (I), liquid+hematite+C$_2$S (II), liquid+C$_2$S+CF$_2$ (III) and C$_2$S+CF$_2$+CF (IV). This solidification sequence differs from that predicted under equilibrium and Scheil-Gulliver Cooling. Importantly, no Silico-Ferrite of Calcium (SFC) phase was observed to form on solidification of the liquid.

Based on the microstructures formed and liquid compositions, measured by EPMA, it was demonstrated that kinetic factors play a major role in determining the phases and microstructures formed under the conditions investigated.

Keywords: Iron ore sinter; microstructure; solidification; “Fe$_2$O$_3$”-CaO-SiO$_2$

1.0 Introduction

Over one billion tonnes of steel are produced annually using the iron blast furnace/basic oxygen steelmaking route. The sintering process is a key process step in the preparation of a competent feed from iron ore fines for the iron blast furnace, with some furnaces operated almost entirely on sinter [1]. In the sintering process the iron oxide fines, flux, coke and return sinter are heated and partly melted, to produce bonded multi-phase particles. The use of sinter in the furnace feed increases the productivity of iron blast furnaces [2] and enables a wide range of low cost ore feed and recycled materials to be processed.

It was suggested [3] and later confirmed [4] [5] [6], that the phases present and microstructures in sinter influence their strength and reducibility, and in turn the efficiency and productivity of the iron blast furnace. For this reason, there are ongoing efforts to identify optimal sinter microstructures and how they are produced.

It has been observed [6] [7] [8] [9] that there are three key stages in the sintering process; heating, peak temperature and cooling. Solid state reactions have been observed to occur on heating, with new
phases and microstructures being formed in the oxide material. As the peak temperature is approached, some of these phases melt or dissolve. During cooling, the liquid solidifies to form new crystalline and amorphous (glassy) phases. Given the complexity of the sintering processes, understanding and controlling the processes to obtain the desired microstructures and properties presents an ongoing technical and scientific challenge.

The principal elements present in iron ore sinters are Fe-Ca-Si-Al-Mg-O; iron can be in the form of ferric or ferrous iron depending on the temperature and oxygen partial pressure. There is a lack of information available for the range of compositions and temperatures observed in iron ore sinters.

Pilot scale sinter pot tests are undertaken routinely as a form of quality control to determine the effects of changing ore blends and key process variables \[10\]. This approach whilst reproducing industrial sintering conditions does not explain why or how particular phases and microstructures are formed as analysis is only able to be performed ex-situ.

Laboratory based techniques used to investigate iron ore sintering have included the use of infrared heating furnaces \[7\]\[8\]\[6\], electrically heated tube furnaces \[11\] and in-situ X-ray powder diffraction (XRD) \[12-13\][14-16][17]. Of these techniques, the infrared furnaces and in-situ XRD provide the most control over the heating and cooling processes. The infrared furnace technique allows samples to be prepared at heating and cooling rates representative of sintering conditions, but using this approach it is only possible to observe the initial and final states of the mixtures \[7\]\[8\]\[6\]. The in-situ XRD technique enables the phases and the temperature at which they form to be determined, but it is not possible to heat and cool samples at rates representative of sintering conditions and does not provide microstructural information \[12-13\][14-16][17].

These previous studies have demonstrated that there are many factors that influence the outcomes of the sintering process. These factors include material characteristics, such as, feed composition and mineralogy, and process characteristics, such as, coke addition and draft suction. The large number of process variables are such that developing empirically based models to predict product microstructure presents an extremely difficult if not intractable problem.

A very different and fundamentally based approach is proposed by the authors based on the hypothesis that the principal phases and microstructures are formed in sinter during the solidification of the oxide liquids. A series of studies have been undertaken to demonstrate the validity of this view, these include;

- Establishing the phase equilibria, and in particular the liquidus surface, in selected oxide systems
- Systematic studies of the solidification processes taking place as a function of key process variables

As part of the first stage of this approach, experimental techniques have been developed \[18\] to accurately measure the solidus and liquidus compositions in these low silica liquids. These techniques have been applied to the characterisation of phase equilibria in selected oxides systems relevant to iron ore sintering. The Fe$_2$O$_3$-rich corner of the “Fe$_2$O$_3$”-CaO-SiO$_2$ system in air is the simplest ternary oxide system that can be used to represent iron ore sintering. Following earlier studies \[19\], the liquidus surface and the primary phase field for the SFC (silico-ferrite of calcium) solid solution have now been established \[20\][18][21]. This provides the solid basis for further systematic studies to be undertaken to understand the influence of kinetic processes on the resulting sinter microstructures in this system.
The second stage involves the development of suitable experimental techniques that enable the phases formed on solidification, the sequence of formation and the resulting microstructures to be characterised under known and controllable process conditions. This is the focus of the present article.

### 2.0 Experimental Technique

A new technique has been developed to enable the determination of the processes occurring during the controlled cooling of synthetic sinter. Unlike previously used techniques, the new approach enables samples to be quenched from any temperature during the solidification sequence, preserving the phases and liquid present at temperature. This allows each of the processes taking place during solidification to be observed in isolation, separate from the processes occurring during heating. The ability to rapidly quench the sample and to accurately capture the microstructures and phase compositions present at temperature are critical to the experimental design. The controlled cooling rates achievable with the new experimental technique are within the range measured in industrial iron ore sintering\(^{[22]}\).

Synthetic sinters have been prepared from mixtures of high purity oxide powders of Fe\(_2\)O\(_3\) (>99.5 wt%, Alfa Aesar), CaCO\(_3\) (>99.95 wt%, Alfa Aesar), and SiO\(_2\) (>99.9 wt%, Alfa Aesar). Before mixing, all the oxides were calcined in air to remove absorbed and chemically bonded water, and to decarbonate CaCO\(_3\). CaCO\(_3\) was heated above 1173 K (900 °C) for at least 5 hr, and the SiO\(_2\) and Fe\(_2\)O\(_3\) were pre-heated above 673 K (400 °C) for 4 hr. The masses of the individual powders were weighed on a digital balance to four decimal points to obtain the target mass. The powders were mixed with an agate mortar and pestle to achieve intimate contact. The mixed powders are pressed by a hydraulic press in a tool steel die into a pellet (0.1 g, 6 mm ø). The oxide samples are supported on a Pt-Rh (70 wt% Pt, 30 wt% Rh) wire (0.5 mm ø) spiral.

The oxide pellet and wire support are heated and cooled in air in an electrically heated vertical tube furnace (alumina reaction tube, 38 mm OD, 30 mm ID), with lanthanum chromate heating elements. The peak temperature and the temperature profile within the furnace (Pyrox) are maintained at constant values using a feedback controller (Eurotherm 2404) and a Pt/Rh controller thermocouple positioned immediately adjacent to the uniform hot zone of the furnace alumina tube.

The sample is vertically suspended within the reaction tube in the furnace from an alumina rod, see Figure 1. The vertical position of the alumina rod, and in turn the sample, is controlled with a positioning motor affixed to the top of the furnace. The temperature of the sample is measured by a separate specimen thermocouple (B type, 70%Pt/30%Rh-94%Pt/6%Rh) positioned immediately above the sample. This thermocouple cannot be immersed in the slag since to do so would destroy the alumina rod and in turn the thermocouple. The accuracy of the thermocouple reading is estimated to be within 3 °C of the standard thermocouple, calibrated by the Australian Government National Measurement Institute, within the temperature range investigated.

The factors contributing to differences between the measured and actual sample temperature were identified as, sample position, sample size and solidification processes. Since the sample is positioned approximately 5 mm lower than the specimen thermocouple tip, during cooling it is in a lower temperature region of the furnace than the specimen thermocouple tip. Measurements made during cooling with and without a sample present showed that the presence of a sample leads to a higher temperature measurement by the thermocouple tip. This difference is believed to be due to the thermal mass of the sample and the occurrence of exothermic processes (i.e. heat of transformation and heat of reaction) during cooling, resulting in a higher specimen temperature and the transfer of heat from the sample to the thermocouple tip. Due to these processes, the specimen temperature
approaches that measured by the thermocouple tip. For the conditions selected for these experiments, this difference estimated to be approximately 5 K based on the maximum thermal gradient in the tube furnace (°C/mm) and the vertical difference between the sample and thermocouple tip. The results presented hereafter refer to the temperature measured by the thermocouple.

Figure 1: Schematic diagram of the experimental apparatus for the controlled cooling of oxide liquids.

The experiment is set up by first setting the peak temperature in the furnace hot zone and allowing the temperature profile to come to a pseudo-steady state condition. The sample is cooled at a controlled rate by moving the sample and thermocouple down through the hot zone of the furnace. The rate of movement, and hence the cooling rate, is controlled by programmable computer software, written specifically for this purpose.

To perform a controlled cooling, the programmable computer software is first calibrated. The calibration is performed by moving the alumina rod supporting the sample at a constant velocity (0.5 mm/s) through the tube furnace. This provides the software with a temperature profile able to predict the temperature at each position in the furnace during cooling.

The temperature profile of the furnace is used by the computer software to calculate the change in position with time required to achieve the target constant cooling rate (K/s). Once calibrated and the position variation with time is calculated by the software, the sample is able to be cooled at a constant rate. The sample is moved through the furnace at the calculated rate by the positioning motor, controlled by the programmable computer software. This system is able to achieve a cooling rate within 10% of the target value.
To perform an experiment, the alumina support tube is lowered to the bottom of the reaction tube, the sample is attached to the tube with the platinum wire. The moving stage is raised to the hot zone of the furnace, and the sample is held for four minutes at or above 1623 K (1350 °C) for melting and homogenisation. After homogenisation, the sample is lowered to achieve a constant cooling rate. On reaching the target temperature the sample is quenched in water by releasing the sample, which falls under gravity into the quenching medium. Quenched samples were washed briefly in water and air dried prior to mounting in epoxy resin. The samples are polished with conventional metallographic techniques, using the Struers system. Samples were first ground with SiC paper to section the sample, followed by the polishing. The first stages of polishing were performed with diamond suspended in water (9 μm) and the last two stages were with diamond paste (3 μm, 1 μm) suspended in kerosene. The later procedure is undertaken to ensure that phases that are reactive with water in the microstructure are not damaged or removed during sample preparation.

The sample cross-sections were characterised, initially using optical microscopy for phase and microstructure identification using a reflected light microscope (Olympus Provis AX70TRF). For electron microscope analysis, the polished surfaces were carbon coated using a carbon coater (Quorum Technologies, QT150TES). For high resolution imaging, a field emission scanning electron microscope (FE-SEM) (JEOL 7001F; Japan Electron Optics Ltd., Tokyo, Japan) was used with an accelerating voltage of 15 keV in backscatter mode.

Phase compositions were measured by an electron probe X-ray microanalysis (EPMA) technique with wavelength dispersive spectroscopy (WDS) (JEOL 8200L EPMA; Japan Electron Optics Ltd., Tokyo, Japan). An electron beam was provided at a voltage of 15 keV and current of 20 nA. The standard Duncumb–Philibert atomic number, absorption, and fluorescence correction (ZAF-correction) supplied with the probe was used. Selected point analysis of phases within the sample was performed. Three standards were used for calibration, pure CaSiO$_3$, Fe$_2$O$_3$, and Al$_2$O$_3$ (all standards from the Charles M. Taylor Co., Stanford, CA). The accuracy of the composition measurements was estimated to be within 1 % of the measured value. The proportion of elements in different oxidation states were not measured; the iron in the sample was assumed to be in the Fe$^{3+}$ state for presentation purposes.

The experimental conditions were selected to reflect conditions in industrial processes, provide controllable and repeatable results, and to investigate the processes of interest to industrial sinter using the phase equilibria data available for the “Fe$_2$O$_3$"-CaO-SiO$_2$ system in air $^{[18]}$. The bulk composition of the samples was selected such that the liquid was in the hematite primary phase field, fully molten at the peak temperature and forms the silico-ferrite of calcium (SFC) phase on equilibrium cooling. The fully molten state at the peak temperature ensures uniformity in the starting material and that all crystalline phases are only formed during cooling, providing reproducibility and control.

The bulk composition of the oxide mixture, 72.74 wt% Fe$_2$O$_3$, 6.11 wt% SiO$_2$ and 21.14 wt% CaO (CaO/SiO$_2$ ratio of 3.46 wt/wt), was selected as this was predicted to form the SFC, Fe$_2$O$_3$ and C$_2$S phases during equilibrium cooling of the liquid in air $^{[18]}$. The liquidus temperature is estimated to be 1568 K (1295 °C). A constant cooling rate of 2 K/s was selected as this is typical of the cooling rate in industrial processes and reduces the number of variables in the experiments $^{[22]}$.

In a sinter bed, there is both macroscale and microscale heat transfer. The aim of the experimental work is to replicate the microscale processes, and as such, the microscale heat transfer requires replication with the experimental technique. The combination of all the microscale processes results in the overall temperature profile within a sinter bed, which appears to indicate directional solidification. However, directional solidification may not necessarily occur within the individual sinter particles.
The Biot number \cite{23} for sinter particle cooling in industrial sinter machines was calculated, using the following assumptions:

- Temperature of air – 473 K (200°C)
- Temperature of sinter – 1573 K (1300°C)
- Thermal conductivity of solids – 2 W/m.K
- Gas velocity – 2 m/s
- Sinter particle diameter – 0.02 m

Using these parameters, and using the heat transfer correlations for both forced and natural convection around a spherical particle \cite{23}, the Biot number was found to be less than 0.1. This indicates that the rate of heat conduction within the particles is greater than the rate of heat transfer by forced convection from the surrounding gas phase to the particles surface. As such, it can be concluded that the temperature within individual sinter particles is relatively uniform and constant, resulting in volumetric solidification rather than directional solidification. The experimental technique is thus designed to reproduce the volumetric solidification by selecting appropriate experimental conditions.

Initial tests were performed to confirm that the selected conditions allowed for liquid formation and homogenisation prior to solidification. Samples were held at 1623 K (1350 °C) for 4 min, then quenched to room temperature. In the resulting amorphous (glassy) material, the sample composition, as measured by EPMA, was found to be uniform across the whole sample cross section. As such, it was concluded that these conditions were sufficient to ensure the sample was fully molten and homogeneous in composition at the start of the controlled cooling process.

Preliminary tests were performed to determine the conditions that enable volumetric solidification to occur within the samples. Samples sizes between 0.1 and 0.2 g were tested and they were found to have a uniform microstructure with position within the sample, indicating that this sample size range provides a uniform composition and temperature profile during cooling. Samples with higher masses, e.g. 0.4 g, were found to have an uneven distribution of microstructures within the solidified samples. These preliminary tests were repeated multiple times to confirm that these conditions are able to produce reproducible results and a uniform temperature profile within the sample. For this reason, a sample size of 0.1 g, with an spheroid diameter of 0.4 mm and height of 0.3 mm once molten was selected for the main study.

### 3.0 Theoretical Solidification Sequences

#### 3.1 Equilibrium Cooling

Equilibrium cooling assumes infinitely rapid mass transfer in all phases and infinitely fast reaction kinetics. This results in equilibrium phases and phase assemblages forming at all temperatures during the cooling process. Under equilibrium cooling of the liquid, with the bulk composition (72.7 wt% Fe₂O₃, 6.1 wt% SiO₂ and 21.1 wt% CaO) shown as X in Figure 2, from 1623 K (1350 °C) to below 1423 K (1150 °C) five stages of solidification occur. The liquidus of the selected composition is approximately 1548 K (1275 °C). The first stage is the nucleation and growth of the primary phase, hematite, from the liquid (L \(\rightarrow\) Fe₂O₃ + L). At the conclusion of this stage, the maximum proportion of hematite present in the system is approximately 10 wt%. Stages 2 and 3 involve the formation of SFC. During stage 2, SFC is formed through the peritectic reaction between the liquid and hematite (L + Fe₂O₃ \(\rightarrow\) L + SFC). The peritectic reaction occurs over a small temperature range, over which the liquid composition follows the Fe₂O₃-SFC boundary curve away from the saddle point (d) towards the CF₂-SFC-Fe₂O₃ peritectic point (a) (approximately 1225 °C, 1498 K). The SFC phase is a solid solution with the end
members $\text{CF}_3\text{C}_4\text{S}_3$, with the composition of this phase in equilibrium with liquid changing during cooling \[^{18}\]. The reaction proceeds to completion such that no hematite remains at temperatures below approximately 1529 K, (~1256 °C). On further cooling during stage 3, the SFC continues to form ($L \rightarrow \text{SFC}$) with the liquid composition moving across the SFC primary phase field. Stage 4 starts at approximately 1508 K (1235 °C) with the formation and precipitation of $\text{C}_2\text{S}$ together with SFC ($L \rightarrow \text{SFC} + \text{C}_2\text{S}$). Stage 5 occurs with the SFC reacting with the liquid at 1489 K (1216 °C) to form $\text{C}_2\text{S}$ and $\text{CF}_2$ ($L + \text{SFC} \rightarrow \text{C}_2\text{S} + \text{CF}_2$) until all the liquid is transformed. The phases present after this final reaction is complete are SFC, $\text{C}_2\text{S}$ and $\text{CF}_2$.

![Schematic diagram](image)

Figure 2: Predicted liquid compositions on equilibrium cooling of bulk composition X (72.74 wt% $\text{Fe}_2\text{O}_3$, 6.11 wt% $\text{SiO}_2$ and 21.14 wt% $\text{CaO}$) from 1623 K to 1453 K (1350 °C to 1180 °C) in the “$\text{Fe}_2\text{O}_3$”-CaO-$\text{SiO}_2$ system in air \[^{18}\]. The insert refers to the various stages discussed in the text.

### 3.2 Scheil-Gulliver Cooling

The predicted Scheil-Gulliver cooling is different from equilibrium cooling and provides a second point of comparison for the observed processes. This cooling process assumes that solid state reactions, peritectic reactions and solid phase diffusion do not occur, diffusion in the liquid is rapid and solidification reactions achieve equilibrium. This results in solid phases, once formed, remaining and not changing in composition with further solidification or formation of other phases. Under Scheil-Gulliver cooling, for the same bulk composition (72.74 wt% $\text{Fe}_2\text{O}_3$, 6.11 wt% $\text{SiO}_2$ and 21.14 wt% $\text{CaO}$), indicated as X in Figure 3, and temperature range (1623 K to 1423 K, 1350 °C to 1150 °C), five processes occur (see Figure 3). The liquidus of this liquid under Scheil-Gulliver cooling is the same as equilibrium cooling, 1548 K (1275 °C). The first stage is the nucleation and growth of stoichiometric primary phase hematite from the liquid ($L \rightarrow \text{Fe}_2\text{O}_3 + L$). The second stage of solidification occurs with the
solidification of the SFC phase (L → SFC), starting at 1529 K (1256 °C). Unlike equilibrium cooling, the hematite does not react with the liquid and remains present during the solidification of SFC, contributing to approximately 10 wt% of the total mass. Stage 3 occurs with SFC and C2S solidifying concurrently (L → SFC + C2S), starting at approximately 1508 K (1235 °C). The formation of SFC under Sheil-Gulliver cooling is characterised by coring, with the composition in the SFC solid solution changing during cooling. Stage 4 occurs with the concurrent formation of C2S and CF2 (L → C2S + CF2), starting at 1489 K (1216 °C). The fifth and final solidification process is the formation of the ternary eutectic C2S, CF2 and CF (L → C2S + CF2 + CF) at 1465 K (1192 °C). The final phase assemblage under this non-equilibrium cooling process consists of hematite, SFC, C2S, CF2, and CF. This differs from equilibrium cooling as the peritectic reactions, the redissolution of hematite (L + H → SFC) and SFC (L + SFC → CF2), do not occur and as a result hematite remains at low temperature and CF forms during the final stage of solidification.

Figure 3: Predicted liquid composition on cooling of the bulk composition X (72.74 wt% Fe2O3, 6.11 wt% SiO2 and 21.14 wt% CaO) from 1623 K to 1453 K (1350 °C to 1180 °C) under Sheil-Gulliver cooling in the "Fe2O3"-CaO-SiO2 system in air [18].

4.0 Results

The initial experiments were performed with samples cooled at 2 K/s from fully liquid conditions at 1523 K to 1073 K (1350 °C to 800 °C). Within this range, complete solidification was found to have taken place and there was no residual liquid at 1073 K (800 °C). An example of the typical microstructure formed under these conditions is given in Figure 4.
Using FE-SEM and EPMA measurements, the phases present in the sample were identified to be hematite (H, Fe₂O₃), dicalcium Silicate (C₂S, 2CaO·SiO₂), calcium ferrite (CF, CaO·Fe₂O₃) and calcium diferrite (CF₂, CaO·2Fe₂O₃). Notably, the SFC phase was absent in all the samples examined. The preliminary analysis of the phases and microstructures demonstrated that those present were different from those anticipated for both equilibrium and Scheil-Gulliver cooling.

To provide a clear understanding of the sequence of reactions, a series of experiments were performed. These experiments were undertaken with samples cooled from the same starting
temperature (1350 °C), and the same cooling rate (2 K); samples were quenched from selected temperatures between 1543 K (1270 °C) and 1453 K (1180 °C).

Between a fully homogeneous liquid and the final microstructure after complete solidification, four intermediate stages of solidification were observed in these experiments, each resulting in the formation of specific phases and phase assemblages. The four, in the order of formation, are as follows, liquid+H (Assemblage I), liquid+H+C\textsubscript{2}S (Assemblage II), liquid+C\textsubscript{2}S+calcium diferrite (Assemblage III) and finally C\textsubscript{2}S+calcium diferrite+calcium ferrite (Assemblage IV). Although the resultant total phase assemblage is additive, consisting of all solids that formed in the previous stages, for ease of description of the solidification phenomena, each of the phase assemblages are presented as occurring independently of the pre-existing solids. The temperatures at which the different phase assemblages were observed are illustrated in Figure 5. Over a range of temperature, two microstructures were observed to occur concurrently within the same sample. The two microstructures, within the same sample, had different local melt compositions. This overlap is shown in Figure 5.

![Phase assemblages observed at temperature during liquid solidification (72.74 wt% Fe\textsubscript{2}O\textsubscript{3}, 6.11 wt% SiO\textsubscript{2} and 21.14 wt% CaO)](image)

**4.1 L + H (Assemblage I)**

Assemblage I, involving the formation of hematite crystals, was the first phase assemblage observed during cooling from 1533 K to 1528 K (1260 °C to 1225 °C). Figure 6 shows a micrograph illustrating the typical hematite primary phase and microstructure.
Figure 6: Backscattered electron micrograph showing the locations of liquid compositions able to be measured Assemblage I, samples cooled from 1623 K to 1518 K (1350 °C to 1245 °C) at 2 K/s in air (72.74 wt% Fe$_2$O$_3$, 6.11 wt% SiO$_2$ and 21.14 wt% CaO). Line 1 – close to hematite and a distance from the sample surface, Line 2 – far from the hematite and close to the sample surface (H – Hematite, L – Liquid, Pt – Platinum).

The hematite was observed to be in the form of large, faceted dendritic (skeletal) crystals (>100 μm long, ~30 μm wide), distributed throughout the liquid; a larger proportion of solids was observed to be present near the platinum substrate. The hematite crystals increased in size and number with decreasing temperature. At the highest temperatures, just below the liquidus, these crystals were only observed in association with the substrate.

The composition of the liquid perpendicular to a planar hematite crystal was measured by point analysis with EPMA. The concentration profile is illustrated in Figure 7 with data from Table 2, which shows the liquid composition as a function of distance from hematite.
The liquid composition was found to vary with distance from the hematite/liquid interface. The composition of the liquid remote from the hematite found to have a Fe$_2$O$_3$ concentration close to that predicted by the liquidus surface [18] between hematite and liquid (i.e. the hematite and liquid equilibrium) at the temperature from which it was quenched. The liquid close to the hematite surface was observed to be poor in Fe$_2$O$_3$ relative to the high temperature equilibrium [18]. This indicated that the concentration profiles observed are a result of crystal growth during the quenching processes rather than present during crystal growth on controlled cooling.

It was observed that the liquid composition was closest to equilibrium when measured at least 40μm from hematite and within 40 μm of the surface of the sample. The liquid composition close to the sample surface and far from hematite, was measured to have typically 5 wt% more Fe$_2$O$_3$ than the other regions of the sample. This is illustrated in Figure 6, where Line 1 was measured to have an average Fe$_2$O$_3$ concentration of 65.2 wt% and Line 2 with 70.7 wt%. On quenching, the surface of the sample is the first to solidify while the centre of the sample was still molten, allowing a short time for mass transfer to the liquid in the centre of the sample and for further solidification of hematite to take place.

**4.2 Liquid + H + C$_2$S (Assemblage II)**

Assemblage II was observed to form between 1508 K and 1473 K (1235 °C and 1200 °C) and was the second phase assemblage observed on cooling following the formation of the initial hematite dendrites. Figure 8 shows typical micrographs illustrating this phase assemblage.
In this phase assemblage, the C$_2$S phase was observed to be present as both individual crystals and in a coupled microstructure with hematite. The different microstructures were either formed concurrently or separately as cooling occurred. The C$_2$S/liquid interface in all cases was non-faceted.

The C$_2$S was observed as a thin layer on the primary hematite (IIa), individual C$_2$S dendrites (IIb), and a coupled H+C$_2$S microstructure (IIc). The layer of C$_2$S on hematite (IIa) was observed on most of the hematite crystals, and was only 2 to 3 micrometres in thickness.

The coupled microstructure (H-C$_2$S) (IIc) was found to surround all the individually formed hematite crystals, forming on either the hematite or the thin layer of C$_2$S. In the coupled microstructure, hematite is the continuous phase and C$_2$S is present as either rods or as an irregular unfaceted microstructure. The phase ratio is approximately 2 H:1 C$_2$S by volume, as determined by the melt composition. The volume fraction of this coupled microstructure increased with decreasing temperature.

The individual C$_2$S (IIb) appeared as unfaceted crystals either isolated in the liquid, or dendritic structures surrounded by either the coupled (H-C$_2$S) microstructure or the liquid. Analysis of the 2D
microstructure indicates that the individual and isolated C$_2$S crystals are in fact part of the dendritic structures. The individual crystals were not observed in all regions of assemblage II, increasing in proportion and occurrence with decreasing temperature. These individual crystals appear to occasionally split to form two main branches. The crystals themselves are smaller than the hematite, and are observed to be up to 10 μm in width and 50 μm in length. The isolated crystals are not directly associated with the hematite, with only a Liquid/C$_2$S interface observed. The crystals themselves are larger than the C$_2$S crystals in the coupled microstructure.

4.3 L + C$_2$S + CF$_2$ (Assemblage III)

Phase assemblage III was observed to form between 1488 K and 1473 K (1215 and 1200 °C). Figure 9 shows a micrograph illustrating this phase assemblage. The high proportion of solids present in this temperature interval lead to difficulties in retaining liquid on quenching the sample.
Figure 9: Microstructures observed in Assemblage III, samples cooled from 1623 K to 1488 K (1350 °C to 1215 °C) at 2 K/s in air (72.74 wt% Fe₂O₃, 6.11 wt% SiO₂ and 21.14 wt% CaO). (H – Hematite, C₂S – Dicalcium Silicate, L – Liquid, CF₂ – Calcium Diferrite) b), c) detail of a) (BSE)

The microstructure observed consists of individual CF₂ crystals and a coupled C₂S-CF₂ microstructure. The individual CF₂ crystals, as confirmed by EPMA, were observed to form on the hematite and the coupled C₂S-CF₂ microstructure on the individual CF₂ crystals. No measurable dissolution of previously solidified hematite was observed.

The individual CF₂ crystals (IIIa) were observed to form thin faceted needles or plates (up to ~80 μm long and 5 μm wide), with an interface with both hematite, liquid and occasionally C₂S. Some of the individual CF₂ crystals were curved, providing an indication of the direction of growth or solidification. The individual crystals were observed to be thin and formed splitting tips. The splitting tips potentially...
indicated that the CF\textsubscript{2} formed as a series of parallel plates, resulting in the appearance as an individual needle or plate. The length of the crystals appeared to be physically limited by the presence of solids formed following solidification at higher temperature. The smallest crystals were observed to form an interface with one solid phase, Hematite. The CF\textsubscript{2} crystals were observed to have similar orientations and associations with other solids, but differed in size. The CF\textsubscript{2} crystals were observed to form around the individual C\textsubscript{2}S crystals.

The coupled C\textsubscript{2}S-CF\textsubscript{2} microstructure (IIIb) was only observed in some regions of assemblage III. The coupled microstructure is illustrated with Figure 10, as this microstructure is more clearly illustrated in Assemblage IV. The CF\textsubscript{2} formed the continuous phase and C\textsubscript{2}S as rods (<1 μm diameter), indicating that CF\textsubscript{2} formed a larger volume proportion of the microstructure. The coupled microstructure was always located in association with the individual CF\textsubscript{2} crystals, forming both in close proximity to and far from the solidified hematite. At the interface with the liquid, the C\textsubscript{2}S formed ahead of the CF\textsubscript{2} with an unfaceted interface while the CF\textsubscript{2} formed a faceted interface.

**4.4 L + C\textsubscript{2}S + CF\textsubscript{2} + CF (Assemblage IV)**

The final microstructures to form consisted of individual CF crystals (IVa), coupled C\textsubscript{2}S+CF microstructures (IVb) and a coupled C\textsubscript{2}S+CF\textsubscript{2}+CF microstructure (IVc). These phases are the last to form during or before the complete solidification of the liquid at between 1200 and 1195 °C.

![Figure 10: Microstructures observed to form in Assemblage IV, samples cooled from 1623 K to 1073 K (1350 °C to 800 °C) at 2 K/s in air (72.74 wt% Fe\textsubscript{2}O\textsubscript{3}, 6.11 wt% SiO\textsubscript{2} and 21.14 wt% CaO). (BSE)](image)
The individual CF crystals (IVa) were observed to form interfaces with the individual CF$_2$ crystals (IIIa), the coupled C$_2$S-CF$_2$ microstructure (IIIb) and the coupled C$_2$S-CF (IVb) and coupled C$_2$S-CF$_2$-CF (IVc) microstructures. The interfaces between CF and CF$_2$ were irregular and appeared as diffuse in SEM imaging. These individual crystals were smaller than the CF$_2$ and C$_2$S individual crystals present in the sample and constrained in all dimensions by the previously formed solids.

The fine interdispersion of the phases make it difficult to characterise individual phases in the coupled C$_2$S-CF (IVb) and coupled C$_2$S-CF$_2$-CF (IVc) microstructures. The phases present in these two microstructures were determined by line analysis with EPMA. The diameter of the excitation volume created by the electron beam in these materials is of the order of 1 μm. As the position of the probe is moved across these fine microstructures, the mean composition therefore changes with the proportion of each material within the interaction volume. The measured compositions should however be on the binary join between the end members or within the alkemade triangles, assuming that the accuracy of the measurements is not affected by the heterogeneous nature of the material in the interaction volume. The line measurements were compared to the joins on the ternary phase diagram, as illustrated in Figure 11. Based on the line analysis, the four coupled microstructures were confirmed, C$_2$S-Hematite (Microstructure IIc), C$_2$S-CF$_2$ (Microstructure IIIb), C$_2$S-CF (Microstructure IVb), and C$_2$S-CF$_2$-CF (Microstructure IVc). The measured compositions for the C$_2$S-CF$_2$-CF coupled microstructure were found to be within the C$_2$S-CF$_2$-CF Alkemade triangle rather than along the C$_2$S-CF or C$_2$S-CF$_2$ joins. This was attributed to either the presence of a ternary coupled microstructure or the interaction volume of the EPMA sampling two microstructures at the same time.

The C$_2$S-CF$_2$-CF coupled microstructure and the C$_2$S-CF coupled microstructures were both observed to share interfaces with the CF and CF$_2$ individual crystals and the C$_2$S-CF$_2$ coupled microstructure. Both coupled microstructures were observed to consist of either rods of C$_2$S (<1μm diameter) in a CF or CF$_2$/CF matrix or as an irregular coupled microstructure. The C$_2$S in this microstructure extended from surface microstructures to the coupled microstructure.

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Figure 11: EPMA line analysis of coupled structures formed when cooling a liquid from 1623 K to 1073 K (1350 °C to 800 °C) at 2 K/s in air (72.74 wt% Fe$_2$O$_3$, 6.11 wt% SiO$_2$ and 21.14 wt% CaO).

### 4.5 Liquid Composition

In the current study, the compositions of the liquid at selected temperatures were measured with EPMA. The measured liquid compositions are shown in Figure 12 and given in Table 1.
During the initial solidification of hematite (I), with decreasing temperature the liquid composition moved from the hematite primary phase field into the C$_2$S primary phase field. As this occurred, some regions of the samples were observed to be of assemblage II (L+H+C$_2$S). Once C$_2$S was present, the coupled hematite+C$_2$S microstructure (IIC) and individual C$_2$S crystals (IId) solidified from the liquid. The liquid composition in Assemblage II (L+H+C$_2$S) moved away from the C$_2$S primary phase field as the temperature decreased. This continued as the liquid approached the CF$_2$ primary phase field. In some regions of the sample, CF$_2$ nucleated and these regions transitioned into Assemblage III (L+C$_2$S+CF$_2$). When compared to the composition of the liquid in the surrounding area (Assemblage II), only CF$_2$ had solidified from the liquid in these regions (Assemblage III).

The proportion of the phases in Assemblage II (L+H+C$_2$S) at each temperature can be determined by undertaking a mass balance using the measured liquid composition, as summarised in Table 1. The calculated proportions of these phases present for this assemblage are shown in Figure 13. From this figure, it is seen that the proportion of hematite in the assemblage did not significantly change in the temperature range over which Assemblage II (L+H+C$_2$S) was observed to form, only increased by 3 wt% between 1508 K and 1498 K (1235 °C and 1225 °C). The C$_2$S was observed to undergo a significant change, increasing from 0 wt% to 10 wt% between 1513 K and 1488 K (1240 °C and 1215 °C). The C$_2$S increased from 0 to 8 wt% between 1240 °C to 1225 °C. In this range, the increase in C$_2$S with time was approximately constant, at approximately 1 wt%/s. This could be taken to indicate that the C$_2$S solidified independently from hematite from 1513 K and 1498 K (1240 °C to 1225 °C). At temperatures between 1498 K and 1488 K (1225 °C and 1215 °C), both the C$_2$S and hematite solidified simultaneously.
5.0 Discussion

There are significant differences between the observed microstructures and those predicted from both equilibrium and Scheil-Gulliver cooling. In the solidified material obtained by cooling the liquid from 1623 K to 1073 K (1350 °C to 800 °C) at 2 K/s;

1. No SFC phase is formed at any stage
2. The liquid composition on cooling does not follow that predicted by equilibrium or Scheil-Gulliver solidification
3. There is no evidence of redissolution of solid phases once formed, as expected for equilibrium cooling and required for peritectic reactions

However, based on the experiments undertaken, the sequence of solidification and origins of microstructures can be determined. An example of the microstructures formed is illustrated in figure 14.
5.1 Formation of Assemblage I (L+H)

Based on the results of the present study for the selected bulk composition and cooling rate, on initial cooling of the liquid, stoichiometric hematite is the first phase to be formed. Metallographic observations indicated that this takes place through heterogeneous nucleation on the platinum substrate and possibly later homogenously from the liquid. The proportion of hematite and the number of hematite crystals increases with decreasing temperature. The growth at the faceted hematite/liquid interface results in the formation of skeletal faceted dendritic structures. Despite the fact that the liquid is subsequently cooled to below the SFC-Hematite peritectic temperature, continued solidification of the hematite takes place. The resulting liquid composition was found to move progressively from the hematite primary phase field through the SFC primary phase field and into the C₂S primary phase field.

No SFC was observed within the sample when the liquid composition was cooling through the SFC primary phase field. It appears that it is more kinetically favourable to continue hematite solidification than to nucleate a new liquid/SFC interface.

The measured liquid compositions on cooling are illustrated in Figure 15. Since SFC is not formed on cooling, this primary phase field has been replaced in Figure 15 with the metastable hematite liquidus, which is close to but slightly above the SFC liquidus. It can be seen that the temperature at which the L+H and L+C₂S liquidus isotherms intersects differs from that at which the L+SFC and L+C₂S liquidus isotherms intersect in Figure 12. Consistent with the hematite liquidus, a decrease in temperature resulted in the removal of Fe₂O₃ from the liquid as a result of hematite formation, while maintaining a constant CaO/SiO₂ ratio. The majority of the measured liquid compositions were lower in Fe₂O₃ than that predicted by equilibrium or the hematite liquidus extension. This was despite the measurements being performed in regions of the sample that appeared to be well quenched, that is close to the sample surface and far from solidified material. For hematite solidification to occur, the liquid composition should be richer in Fe₂O₃ than that indicated by the L+H liquidus isotherm at all temperatures. The fact that the measured compositions are lower in iron than anticipated indicates that some hematite continued to precipitate on quenching the samples. This is observed in Figure 15 where the measured liquid composition is always to the left of the liquids isotherm.
During the final stages of Assemblage I, the liquid compositions were inside the C2S primary phase field, i.e. below the L+C2S liquidus, showing the supersaturation of the liquid with respect to C2S. Despite this, the hematite continued to solidify as cooling progressed.

Examining the shape and position of the metastable hematite liquidus extension it can be seen that it closely follows that of the equilibrium phase SFC liquidus. In effect the thermodynamic driving forces for both hematite SFC formation are similar within this range of conditions. The crystal structure of the SFC phase is relatively complex compared to the orthorhombic hematite, which is close to a hexagonal close packed oxygen arrangement with interstitial ferric ions \(^{24}\). The SFC phase in contrast consists of alternating layers of spinel (M\(_4\)T\(_2\)O\(_8\)) and pyroxene (M\(_2\)Si\(_4\)O\(_{12}\)). This results in alternating layers of octahedral and tetrahedral layers, with the tetrahedral layer continuous in tetrahedral units and the octahedral layer consisting of ribbons 4 octahedral units wide \(^{25}\). It is anticipated that the nucleation frequency of this more complex crystal structure would be lower than that of hematite for the same bulk liquid composition for a given undercooling. This in part explains the absence of the SFC phase during cooling under the conditions investigated in the present study.

### 5.2 Formation of Assemblage II (L+H+C2S)

All microstructures observed in Assemblage II were all later observed in Assemblages III and IV, indicating that all microstructures formed during this stage were a result of cooling, rather than quenching. As observed in Figure 12, the composition of the liquids in close proximity to Assemblage II was found to be within the C2S primary phase field. At the highest temperatures (1508 K to 1503 K, 1235 °C to 1230 °C), the liquid composition was observed to be close to that measured for Assemblage I within the same sample. As temperature decreased, the liquid compositions moved towards the C2S-SFC boundary curve. During the solidification of Assemblage II, both hematite and C2S were found to be solidifying, indicating that the liquid was supercooled with respect to both C2S and hematite. This is despite the liquid composition being in the C2S primary phase field on the ternary phase diagram, as illustrated by Figure 16.
Metallographic evidence indicates that a thin layer of C\textsubscript{2}S (IIa) nucleated heterogeneously and grew at the hematite-liquid interface or homogenously in liquid adjacent to the hematite-liquid interface. The other two microstructures, the individual C\textsubscript{2}S crystals (IIb) and the coupled C\textsubscript{2}S-H (IIc) microstructures, were subsequently formed.

From the calculated proportions of phases (Figure 13) and the liquid compositions (Table 1) at each temperature, the order of formation of the remaining microstructures (IIb, IIc) can be determined, as illustrated by Figure 16. During the initial stage of solidification, the rate of C\textsubscript{2}S solidification was faster than hematite solidification, indicating that the coupled H+C\textsubscript{2}S microstructure (IIc) was not forming. At the highest temperatures, only the individual C\textsubscript{2}S crystals (IIb) were forming. As temperature decreased further, the rate C\textsubscript{2}S formation decreased and was similar to the rate of hematite formation. At the lower temperatures in which this assemblage was observed, the coupled C\textsubscript{2}S-hematite microstructure (IIc) was the predominant microstructure forming. The mass ratio of C\textsubscript{2}S/H in the coupled microstructure is approximately 0.7, which is consistent with that expected from the phase diagram in Figure 12.

From the metallographic evidence it is concluded that C\textsubscript{2}S layer formed first (IIa), followed by the individual C\textsubscript{2}S crystals (IIb) and lastly the coupled H+C\textsubscript{2}S microstructure (IIc). The individual C\textsubscript{2}S crystals were not associated with hematite, indicating that the hematite was unable to nucleate on the C\textsubscript{2}S phase. The individual C\textsubscript{2}S crystals solidified as dendrites.

![Figure 16: Schematic representation of the change in liquid composition as solidification occurred for Assemblage I and II assuming a metastable liquidus in which SFC is absent (72.74 wt% Fe\textsubscript{2}O\textsubscript{3}, 6.11 wt% SiO\textsubscript{2} and 21.14 wt% CaO).](image)

The microstructures formed in phase assemblage II can also be related to the kinetic phenomena taking place during cooling. It was demonstrated in Figure 15 that the undercooling of the liquid with respect to SFC is relatively small. Inspection of this figure shows that on continued cooling the undercooling with respect to the C\textsubscript{2}S phase increases as the temperature of the liquid decreases. For example at 1493 K (1220 °C) and 32 wt% CaO+SiO\textsubscript{2} the undercooling with respect to the C\textsubscript{2}S liquidus is approximately 50 K, which is considerable. The nucleation and growth of the C\textsubscript{2}S from the liquid results in the release of the heat of solidification. The effect of the heat release counters the heat loss to the surroundings, locally changing the rate of cooling of the sample. The extent of this change is determined by the rates of heat conduction and convection within the liquid and solids, and the rate of solidification. This change in thermal conditions is illustrated schematically in Figure 17. The large thermodynamic driving force also leads to rapid C\textsubscript{2}S growth and the formation of the C\textsubscript{2}S crystal dendrite structure. As the C\textsubscript{2}S crystals are formed the local increase in temperature and the change in liquid composition lowers the thermodynamic driving force for C\textsubscript{2}S growth and the rate of growth of...
the individual crystals decrease. This then leads to the transition from single crystal \( \text{C}_2\text{S} \) growth to the coupled growth of \( \text{C}_2\text{S}+\text{H} \) and the formation of the binary eutectic structure.

![Figure 17: The schematic representation of local temperature and time during \( \text{C}_2\text{S} \) nucleation and growth][26].

### 5.3 Formation of Assemblage III \((\text{L}+\text{C}_2\text{S}+\text{CF}_2)\)

The formation of assemblage III was found to take place over a small temperature range. The individual \( \text{CF}_2 \) (IIIa) crystals were principally observed to be adjacent to hematite, suggesting heterogeneous nucleation of \( \text{CF}_2 \) on the hematite. The \( \text{CF}_2 \) was observed as individual \( \text{CF}_2 \) crystals (IIIa) in all regions of assemblage III, while the coupled \( \text{CF}_2-\text{C}_2\text{S} \) microstructure (IIIb) was in limited areas. As such, this suggests that the \( \text{CF}_2 \) individual crystals formed first in a liquid supercooled with respect to \( \text{CF}_2 \), growing faster than the other phases present. These crystals were constrained by the microstructures formed in Assemblage I and II, solidifying around them. The shape of these crystals and the presence of splitting tips suggests that this phase solidified as a series of parallel plates rather than as individual crystal.

The coupled \( \text{C}_2\text{S}-\text{CF}_2 \) microstructure (IIIb) is believed to have formed after the individual \( \text{CF}_2 \) crystals (IIIa), most likely via a coupled growth mechanism. This microstructure was observed to be associated with the individual \( \text{CF}_2 \) crystals (IIIa), indicating that the \( \text{C}_2\text{S} \) nucleated heterogeneously on the \( \text{CF}_2 \) or in the liquid adjacent to the liquid-\( \text{CF}_2 \) interface. Based on the microstructure and image analysis, it appears that the \( \text{CF}_2 \) formed a larger proportion of the volume in this coupled microstructure (see Figure 7). This is consistent with the ratio of the \( \text{C}_2\text{S}/\text{CF}_2 \), predicted to be 0.25 based on the phase diagram (Figure 12) and estimated to be 0.29 based on image analysis of the micrographs.
Based on the order of solidification, the liquid composition can be inferred followed a path similar to that illustrated in Figure 18. Prior to the formation of the CF$_2$, within the CF$_2$ primary phase field, the liquid composition would have been supersaturated with respect to CF$_2$. Initially, the individual CF$_2$ crystals (IIIa) are formed. At some point, C$_2$S is nucleated on the CF$_2$ Crystals (see Figure 18). Once the C$_2$S-CF$_2$ coupled microstructure (IIlb) started to form, the composition would have moved towards the C$_2$S-CF$_2$ boundary curve and the C$_2$S-CF$_2$-CF ternary eutectic point. These processes give two-step changes in the liquid composition. There are small differences and changes in the liquid compositions that could not be accurately measured in the present study primarily due to quenching difficulties and low volume fraction of liquid.

**5.4 Formation of Assemblage IV (C$_2$S+CF$_2$+CF)**

The CF was observed in the final microstructure, and present in three microstructures, individual CF crystals (IVa), a C$_2$S-CF coupled microstructure (IVb) and a C$_2$S-CF$_2$-CF coupled microstructure (IVc). Based on the mechanisms observed for the other observed assemblages, the possible mechanism for the final stages of solidification can be inferred, as illustrated by Figure 19. The liquid composition during the three stages of solidification are illustrated schematically in Figure 19. The order of formation is likely to be individual CF crystals (IVa), the coupled C$_2$S-CF microstructure and finally the coupled C$_2$S-CF$_2$-CF microstructure. It is likely that the CF formed from a liquid supercooled with respect to CF, with solidification initially forming individual crystals of CF (IVa). Once the individual CF crystals solidified, the liquid composition would have decreased in CaO and Fe$_2$O$_3$ in equal proportions on a molar basis. The CF phase appears to have nucleated heterogeneously on CF$_2$. The remaining liquid would have solidified to form the C$_2$S-CF coupled microstructure (IVb) via a coupled growth mechanism and finally the C$_2$S-CF$_2$-CF coupled microstructure (IVc) with the same mechanism. Once the formation of the C$_2$S-CF microstructure was initiated, the liquid composition would have moved towards the C$_2$S-CF boundary curve and towards the C$_2$S-CF$_2$-CF ternary eutectic point, where the final solidification (IVb) would have occurred.

![Figure 18: Schematic representation of the changes in liquid composition as solidification occurred for Assemblage III (72.74 wt% Fe$_2$O$_3$, 6.11 wt% SiO$_2$ and 21.14 wt% CaO).](image-url)
Figure 19: The change in liquid composition as solidification occurred for Assemblage IV (72.74 wt% Fe$_2$O$_3$, 6.11 wt% SiO$_2$ and 21.14 wt% CaO).

Once solidification had been completed, no other phase changes were observed to occur. The cumulative microstructures and phase assemblages are illustrated in Figure 20.

Figure 20: a) The cumulative phase assemblages and microstructures during the formation of the four phase assemblages (72.74 wt% Fe$_2$O$_3$, 6.11 wt% SiO$_2$ and 21.14 wt% CaO), b) sequence of phase assemblages observed to form from the liquid on cooling in air at 2 K/s
5.5 Overall Impacts of Kinetics

The results of the present study have demonstrated that kinetic factors can play a significant role in determining the phases and microstructures formed on the solidification of these oxide liquids. Whilst most of the reactions and resultant product morphologies are consistent with those anticipated from solidification theory, for example, the formation of dendritic structures, pseudo-binary and ternary eutectics, the outstanding feature not previously anticipated was the role of nucleation.

In the system, and for the bulk composition selected for study, it was anticipated from the equilibria studies that the SFC phase would be formed on cooling of the liquids, however this was not the case. Nowhere in the solidification sequence was this phase formed. In addition, considerable undercoolings of the liquids were observed before the formation of the dicalcium silicate, calcium diferrite and calcium ferrite phases. These phenomena resulted in the formation of complex metastable phase assemblages. The rates of diffusional mass transfer of species in these low-silica ionic liquids are high relative to high-silica liquids [27]. The formation of these non-equilibrium structures is then all the more unexpected.

In the present study, only a single cooling rate was investigated. The results however indicate that the thermal history is a potentially important factor influencing the resultant sinter microstructures and phase assemblages.

6.0 Summary

A new experimental technique has been developed that enables the cooling rates of oxide liquids to be accurately controlled. Using this new approach, the sequence of phase formation and the product microstructures formed in specific temperature ranges can be identified.

The solidification of liquids in the system “Fe₂O₃”-CaO-SiO₂ having a bulk composition with a CaO/SiO₂ ratio of 3.46 and 73.17 wt% Fe₂O₃, within the hematite primary phase field and predicted to form SFC during equilibrium have been studied. The experiments were carried out in air and with a cooling rate of 2 K/s. The phases present in the final microstructure were, hematite, C₂S, CF and CF₂. No SFC was formed indicating non-equilibrium cooling. The solidification sequence was determined to be as follows; nucleation and growth of the primary phase hematite, nucleation of C₂S followed by the formation of a C₂S layer on hematite, C₂S dendrites and a coupled C₂S-hematite microstructure, nucleation of CF₂ followed by the formation of individual CF₂ crystals and a coupled CF₂-C₂S microstructure and finally the nucleation of CF followed by the formation of individual CF crystals and coupled C₂S-CF and C₂S-CF-CF₂ microstructures.

The study clearly demonstrates the importance of thermal history in determining phase formation and product microstructure during solidification of these “Fe₂O₃”-CaO-SiO₂ liquids. As demonstrated in this study, the supercooling prior to nucleation, the homogenous nucleation of new phases and the suppression of equilibrium phases due to kinetic factors are some of the key parameters that require consideration in iron ore sintering.

7.0 Acknowledgements

The authors would like to thank BHP Billiton for financial support to enable this research to be carried out, and to the Centre of Microstructure and Microanalysis (CMM), the University of Queensland for providing electron microscope facilities that enabled the microanalytical measurements to be
undertaken. This research was supported by an Education Endowment Fund (EEF) scholarship from the Australasian Institute of Mining and Metallurgy (AusIMM) and an Australian Government Research Training Program (RTP) Scholarship.

Table 1: Liquid compositions measured by EPMA, formed on cooling a liquid (72.74 wt% Fe$_2$O$_3$, 6.11 wt% SiO$_2$ and 21.14 wt% CaO) from 1623 K at 2 K/s

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Assemblage I (L+H)</th>
<th>Assemblage II (L+C$_2$S+H)</th>
<th>Assemblage III (L+C$_2$S+CF$_2$)</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Fe$_2$O$_3$ (wt%)</td>
<td>SiO$_2$ (wt%)</td>
<td>CaO (wt%)</td>
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<tr>
<td>1200</td>
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</table>
Table 2: Liquid compositions measured by EPMA for a line perpendicular to hematite-liquid interface, formed on cooling to 1543 K (see Figure 7)

<table>
<thead>
<tr>
<th>Distance from hematite (μm)</th>
<th>$\text{Fe}_2\text{O}_3$ (wt%)</th>
<th>$\text{SiO}_2$ (wt%)</th>
<th>CaO (wt%)</th>
</tr>
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<td>7.9</td>
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<td>72.1</td>
<td>6.7</td>
<td>21.3</td>
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</tbody>
</table>
References

Appendix B: Controlled Solidification of Liquids Within the SFC Primary Phase Field of the “Fe₂O₃”-CaO-SiO₂ System in Air
Controlled solidification of liquids within the SFC primary phase field of the “Fe$_2$O$_3$”-CaO-SiO$_2$ system in air

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Abstract
To provide fundamental information on the phases and microstructures formed during sintering, a liquid with a bulk composition within the silico ferrite of calcium (SFC) primary phase field in the ternary “Fe$_2$O$_3$”-CaO-SiO$_2$ system in air was solidified at a controlled rate. Samples of a bulk composition with a CaO/SiO$_2$ ratio of 4.00 wt/wt and 69.24 wt% Fe$_2$O$_3$, were cooled from 1623 K (1350 °C) at 2 K/s, with samples quenched at temperatures between 1553 K (1260 °C) to 1073 K (800 °C). The silico ferrite of calcium I (SFC-I) and Ca$_{7.2}$Fe$_{5+0.8}$Fe$_{3+30}$O$_{53}$ phases were observed to form an intergrowth (‘SFC-I’) rather than the anticipated SFC phase. Solidification was found to occur in three stages, Liquid+‘SFC-I’, Liquid+‘SFC-I’+C$_2$S+CF$_2$, and C$_2$S+CF$_2$+CF, where C$_2$S denotes dicalcium silicate, CF denotes calcium ferrite and CF$_2$ denotes calcium diferrite. The phases formed and the solidification sequence differ from those predicted under equilibrium and Scheil-Gulliver Cooling.

Keywords: Iron ore sinter; microstructure; solidification; SFCA; SFC; SFC-I; “Fe$_2$O$_3$”-CaO-SiO$_2$

1.0 Introduction
A number of different phases have been identified in Iron ore sinters, including hematite (Fe$_2$O$_3$), magnetite (Fe$_3$O$_4$), C$_2$S (2CaO.SiO$_2$), silico ferrite of calcium and aluminium (SFCA) and silica containing glass [1]. It has been reported that the strength and reducibility of the sinters increase with an increasing proportion of the SFCA phases [1]. This increase in strength and reducibility increases the throughput and decreases the operating costs of the Iron Blast Furnace. To be able to design optimal sinter microstructures, an improved understanding of the formation mechanisms of these SFCA phases is required. In the text and figures provided in the present paper, the following terminology is used S=SiO$_2$, F=Fe$_2$O$_3$, C=CaO and A=Al$_2$O$_3$.

Three SFCA phases have been identified to date, SFCA, SFCA-I and SFCA-II[2-4]. SFC, SFC-I and SFC-II are endmembers of these phases, having identical cation and anion arrangements but with different compositions and site occupancies. The SFCA phases belong to a polysomatic series of phases, consisting of pyroxene <Py> and spinel <Sp> polysomes arranged in regular and repeating sequences[5]. The arrangement of the pyroxene <Py> and Spinel <Sp> polysomes in SFCA is illustrated in Figure 1. The spinel polysome is a module or section of the spinel crystal structure consisting of one combination of octahedral/tetrahedral oxygen polyhedron present on the (110) plane of the spinel structure, with the sections oriented normal to the close packed oxygen plane [6]. The pyroxene polysome is a module of the pyroxene crystal structure containing both tetrahedral and octahedral units, with the polysome one silicate (tetrahedral oxygen polyhedra) chain present on the (010) plane of the pyroxene structure, with the sections oriented normal to the close packed oxygen plane. The SFCA phases, despite containing pyroxene polysomes, do not contain an
appreciable concentration of silica, cations substitution occurring such that these tetrahedral sites are occupied by other metals. The SFCA phase consists of alternating <Sp> and <Py> polysomes, i.e. <SpPy> . It is currently believed that SFCA is a solid solution in the CF$_3$-CA$_3$-C$_4$S$_3$ series. The SFCA-I phase consists of a regular arrangement of two <Sp> and one <Py> polysome, i.e. <SpSpPy> . The full composition range over which SFCA-I is stable has not been determined, but a number of compositions have been reported including, \( \text{Ca}_{3.18}\text{Fe}_{3+14.66}\text{Al}_{1.34}\text{Fe}^{2+0.82}\text{O}_{28} \), \( \text{Ca}_3\text{MgAl}_{6}\text{Fe}_{10}\text{O}_{28} \), \( \text{Ca}_3\text{MgAl}_{12}\text{Fe}_{28}\text{O}_{28} \), \( \text{Fe}_{15.27}\text{Ca}_{3.22}\text{Al}_{12.20}\text{O}_{28} \) \([\text{2, 11-12}]\). SFCA-II is believed to have a polysome arrangement of <SpPySpPy>, with a single composition, \( \text{Ca}_3\text{Al}_{9.3}\text{Fe}^{3+18.7}\text{Fe}^{2+0.9}\text{O}_{48} \) reported to date \([\text{4}]\). The three SFCA phases, along with other calcium containing ferrites, are similar in chemical composition and appearance under both optical and electron microscopy examination, leading to difficulties in differentiating between these phases. The three SFCA phases can only be reliably distinguished through the use of X-Ray Powder Diffraction (XRD) \([\text{13}]\).

The solidification mechanisms of the SFCA phases has not been determined, despite the understanding of the crystal structure. The crystal structure suggests the potential for these phases to nucleate upon the hematite and magnetite phases. Recent research \([\text{14}]\) has demonstrated that the SFC phase does not form on cooling a liquid with 69.24 wt% Fe$_2$O$_3$, 6.16 wt% SiO$_2$ and 24.61 wt% CaO (CaO/SiO$_2$ ratio of 3.46) in air at 2 K/s from 1623 K (1350 °C) to 1073 K (800 °C), despite the formation of SFC under equilibrium cooling. The focus of the present research is to determine the phases and microstructures formed when a liquid of bulk composition within the SFC primary phase field of the “Fe$_2$O$_3$“-CaO-SiO$_2$ system is cooled in air at conditions relevant to iron ore sintering. In particular, the sequence and temperatures at which each of the microstructures formed during cooling of liquids from 1623 K to 1073 K (1350 °C to 800 °C) at 2 K/s are identified.

### 2.0 Experimental Technique

Details of the experimental technique used have been reported in a previous publication by the authors \([\text{14}]\). The technique enables each stage of the solidification process to be identified in isolation and differentiated from the processes occurring during heating. The ability to rapidly quench the sample, and to accurately capture the microstructures and phase compositions present at temperature, are critical to the experimental design. The controlled cooling rates achievable with the new experimental technique are within the typical range of cooling rates measured in industrial iron ore sintering \([\text{15}]\).

An oxide pellet (0.1 g, 6 mm diameter) and substrate (70/30 Pt/Rh wire, 0.5mm diameter) is heated and cooled in air in an electrically heated vertical tube furnace (alumina reaction tube, 38mm OD 30
mm ID). The sample is vertically suspended within the reaction tube in the furnace with an alumina rod. The vertical position of the alumina rod, and in hence the position of the sample, is controlled with a positioning motor affixed to the top of the furnace. The sample is raised into the hot zone of the furnace, and the sample is held for four minutes at or above 1623 K (1350 °C) for complete melting and homogenisation with respect to composition of the sample. After homogenisation, the sample is lowered down through the furnace with the use of a computer controlled motor drive to achieve a constant cooling rate. On reaching the target temperature the sample is quenched in water by releasing the sample, which falls under gravity into the quenching medium.

The samples are characterised initially by examining polished cross sections of the material using optical microscopy for phase and microstructure identification using a reflected light microscope (Olympus Provis AX70TRF) and scanning electron microscopy (SEM) in back scattered mode (BSE). Phase compositions were measured by an electron probe X-ray microanalysis (EPMA) technique with wavelength dispersive spectroscopy (WDS) (JEOL 8200L EPMA; Japan Electron Optics Ltd., Tokyo, Japan). An electron beam was provided at a voltage of 15 keV and current of 20 nA. Three standards were used for calibration, pure CaSiO$_3$, Fe$_2$O$_3$, and Al$_2$O$_3$ (all standards from the Charles M. Taylor Co., Stanford, CA). The iron concentration in phases were recalculated to Fe$_2$O$_3$ for presentation purposes.

To identify the phases formed using XRD, repeated experiments, cooling from 1623 K to 1073 K (1350 °C to 800 °C) at 2 K/s, with 0.2 g of starting oxides were performed to accumulate 1 g of material. The material was crushed and ground with an agate mortar and pestle. The resulting powder was analysed with powder X-Ray Diffraction (XRD) (Bruker D8), with a copper Kα radiation source at a voltage of 40 kV and a current of 40 mA.

The bulk composition of the oxide mixture, 69.24 wt% Fe$_2$O$_3$, 6.16 wt% SiO$_2$ and 24.61 wt% CaO (CaO/SiO$_2$ ratio of 4.00 wt/wt), was selected as the SFC phase is predicted to form on equilibrium cooling of the liquid, based on the compositional limits of the SFC primary phase field in the “Fe$_2$O$_3$”-CaO-SiO$_2$ system in air [16]. The compositions of the samples were selected such that the liquid was in the SFC primary phase field, and fully molten, at the peak temperature of 1623 K (1350 °C). The tests were performed in air, as the oxygen partial pressure (p$_{O_2}$) during sintering cooling in industrial processes have been measured to be close to 0.21 atm and phase equilibria data is available for the “Fe$_2$O$_3$”-CaO-SiO$_2$ system in air [16]. A constant cooling rate of 2 K/s was selected as this is typical of the cooling rate in industrial iron ore sintering processes.

### 3.0 Theoretical Cooling Structures

#### 3.1 Equilibrium Cooling

Equilibrium cooling assumes infinitely rapid mass transfer and reaction kinetics, providing a point of comparison with the observed processes. The predicted equilibrium cooling path for a sample with a bulk composition of 69.24 wt% Fe$_2$O$_3$, 6.16 wt% SiO$_2$ and 24.61 wt% CaO is illustrated in Figure 2 [16]. The liquidus of the selected composition is approximately 1511 K (1238°C). During equilibrium cooling of the liquid from 1623 K (1350 °C) to below 1423 K (1150 °C), four stages occur, as illustrated by paths 1 to 4 on Figure 2. The first stage is the formation and growth of the primary phase, SFC, from the liquid. The SFC phase composition varies during solidification. The formation of SFC occurs at approximately 1513 K (1240 °C) for the bulk composition indicated by X in Figure 2. Based on the phase diagram and the tie lines from Chen et al [16], on further cooling, the SFC continues to solidify from the melt (L → SFC), and the melt composition moves across the SFC
primary phase field away from the SFC solid composition. Stage 2 occurs when the melt composition reaches the SFC-C$_2$S boundary line. Stage 2 occurs from approximately 1503 K (1230 °C) to 1489 K (1216 °C) with both SFC and C$_2$S solidifying from the melt (L → SFC+C$_2$S). As solidification progresses, the melt composition changes along the SFC-C$_2$S boundary curve. At 1216 °C, Stage 3 occurs with the SFC reacting with the liquid to form C$_2$S and CF$_2$ (L+SFC → L+C$_2$S+CF$_2$). There is excess liquid to that required for the peritectic reaction, resulting in the complete reaction of the SFC. On further cooling, the C$_2$S and CF$_2$ solidify concurrently (stage 3) (L → C$_2$S+CF$_2$) and the liquid composition moves along the C$_2$S-CF$_2$ boundary line to the C$_2$S-CF$_2$-CF ternary eutectic point (1465 K (1192 °C)). At the ternary eutectic point, complete solidification of the remaining melt occurs (L→ C$_2$S+CF$_2$+CF) to form C$_2$S, CF$_2$, and CF. The phases present after this final reaction is complete are SFC and CF$_2$, CF.

![Figure 2: Predicted cooling paths for equilibrium cooling and Scheil-Gulliver Cooling in the Fe$_2$O$_3$-CaO-SiO$_2$ system in air for a bulk composition 'X' (69.24 wt% Fe$_2$O$_3$, 6.16 wt% SiO$_2$ and 24.61 wt% CaO) [16].](image)

### 3.2 Scheil-Gulliver Cooling

The Scheil-Gulliver cooling process assumes that solid state reactions, peritectic reactions and solid phase diffusion do not occur, diffusion in the liquid is rapid and solid/liquid reactions achieve equilibrium. During this cooling regime, for the bulk composition X (69.24 wt% Fe$_2$O$_3$, 6.16 wt% SiO$_2$ and 24.61 wt% CaO), four processes occur between 1513 K (1240 °C) and 1465 K (1192 °C). The first stage is nucleation and subsequent solidification of SFC (L → SFC), occurring from approximately 1511 K (1238 °C) to 1503 K (1230 °C). The second stage occurs with the concurrent solidification of SFC and C$_2$S (L → SFC + C$_2$S) from 1503 K (1230 °C) to 1489 K (1216 °C). During stage 1 and 2, the formation of SFC under Scheil-Gulliver cooling is characterised by coring, with the composition in the solidifying SFC changing during cooling. Unlike equilibrium cooling, SFC does not react with the liquid to form CF$_2$ on reaching the peritectic temperature of 1489 K (1216 °C). Stage 3 occurs from 1489 K (1216 °C) to 1465 K (1192 °C) with the concurrent solidification of C$_2$S and CF$_2$ (3) (L → C$_2$S+CF$_2$). The fourth and final stage of solidification is the formation of the ternary eutectic C$_2$S, CF$_2$, and CF (L →
The final phase assemblage under this cooling process consists of SFC, C$_2$S, CF$_2$, and CF.

### 4.0 Results

Initial experiments were performed with samples cooled at 2 K/s from fully liquid conditions at 1623 K to 1073 K (1350 °C to 800 °C). Within this range, complete solidification was found to have taken place and there was no residual liquid at 1073 K (800 °C). An example of the typical microstructure formed under these conditions is given in Figure 3.

![Backscattered electron micrograph showing the typical microstructures formed on a liquid (69.24 wt% Fe$_2$O$_3$, 6.16 wt% SiO$_2$, 24.61 wt% CaO) cooling from 1623 K to 1073 K (1350 °C to 800 °C) at 2 K/s. (dicalcium silicate (C$_2$S, 2CaO·SiO$_2$), calcium ferrite (CF, CaO·Fe$_2$O$_3$), complex calcium silico ferrite ("S") and Calcium Diferrite (CF$_2$, CaO·2Fe$_2$O$_3$))](image)

The phases present in the sample were identified using EPMA point and line measurements. In addition to the three identifiable phases, dicalcium silicate (C$_2$S, 2CaO·SiO$_2$), calcium ferrite (CF, CaO·Fe$_2$O$_3$), calcium silico ferrite ("S") and calcium diferrite (CF$_2$, CaO·2Fe$_2$O$_3$), a complex calcium silico ferrite was observed, marked “S” in Figure 3.

### 4.1 Unknown calcium silico ferrite ‘S’

The composition of the unknown calcium silico ferrite ‘S’ was measured by EPMA and found to contain 86.2 to 87.2 wt% Fe$_2$O$_3$, 0.01 to 0.3 wt% SiO$_2$ and 12.8 to 13.7 wt% CaO, as summarised in Table 1. Care was taken during the analysis to avoid including C$_2$S in the EPMA interaction volume. The molar Fe$_2$O$_3$/CaO ratio for this composition range varied from 2.21 to 2.39. A comparison of the compositions of the SFCA, SFCA-I, β-CFF and Ca$_{2.2}$Fe$_{1.9}$Fe$^{3+}$.Fe$^{3+}$.O$_{5.3}$ phases is shown in Table 2. The compositions of these phases are normalised to the binary CaO-Fe$_2$O$_3$ by assuming the CaO + SiO$_2$ → Fe$_2$O$_3$ and Al$_2$O$_3$ → Fe$_2$O$_3$ substitution reactions take place. These normalised compositions are shown in Table 3.
Table 1: Mean compositions of the unknown calcium silico ferrite, ‘S’, as measured by EPMA, formed by cooling a liquid from 1623 K to 1473 K (1350 °C to 1200 °C) at 2 K/s in air.

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Table 2: Reported compositions of complex ferrite phases

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<tr>
<td>SFCA [2]</td>
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<td>73.5</td>
</tr>
<tr>
<td>Ca₀.₇₂Fe²⁺₀.₈Fe³⁺₀.₃O₅.₃ [17]</td>
<td>14.1</td>
<td>85.9</td>
</tr>
</tbody>
</table>

Table 3: Normalised compositions of complex ferrite phases using Al₂O₃ and SiO₂ substitution reactions.

<table>
<thead>
<tr>
<th>Phase</th>
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<th>mol%</th>
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<td>SFCA</td>
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<tr>
<td>Ca₀.₇₂Fe²⁺₀.₈Fe³⁺₀.₃O₅.₃</td>
<td>14.1</td>
<td>85.9</td>
</tr>
</tbody>
</table>

The mean composition of the unknown calcium silico ferrite was found to differ from the phases previously reported [2, 17]. Examples of the observed typical microstructures of these calcium silico ferrite crystals are shown in Figure 4, specifically C₃S inclusions (Figure 4a), banding (Figure 4b), and parallel plates at the melt-solid interface (Figure 4c). The image contrast of the crystals observed under the SEM in Backscattered Electron (BSE) mode is dependent of the mean atomic number of the phase. The mean composition of the crystals may vary due to solid solutions, the formation of an intergrowth containing multiple phases or the presence of twinned crystals. The unknown calcium silico ferrite crystals with C₃S inclusions were observed to have significant banding in BSE imaging. The compositions of the bands could not be measured independently since the size of the interaction volume of the probe exceeds the size of these bands. The bands were also examined using electron backscatter diffraction (EBSD) in a scanning electron microscope, however the presence of different crystal orientations (e.g. twinning) could not be detected.
Figure 4: SEM micrographs of a calcium silico ferrite ‘S’ crystal, showing different regions in backscatter electron (BSE) mode. Liquid (69.24 wt% Fe$_2$O$_3$, 6.16 wt% SiO$_2$ and 24.61 wt% CaO) cooled at 2 K/s in air from 1623 K (1350°C) to a,c) 1488 K (1215°C) and b) 1073 K (800°C). (S- calcium silico ferrite, L-Liquid)

Additional characterisation of the samples to determine the unknown calcium silico ferrite, ‘S’ phase, was undertaken using XRD analysis. Samples for XRD were prepared from liquids cooled from 1623 K to 1073 K (1350 °C to 800 °C) at 2 K/s. The XRD pattern obtained for the sample is shown in Figure 5, compared to known XRD patterns for SFCA, SFCA-I and Ca$_{7.2}$Fe$_{2+0.8}$Fe$_{3+30}$O$_{53}$. The low angle XRD peaks are used for phase differentiation as the SFCA minerals have triclinic unit cells and have similar unit cell dimensions leading to difficulties in phase differentiation at the higher diffraction angles.

Based on the low angle XRD peaks observed in the diffraction pattern, SFCA-I and Ca$_{7.2}$Fe$_{2+0.8}$Fe$_{3+30}$O$_{53}$ were identified as phases present in the sample. The SFC phase having an similar crystal structure to SFCA, which was anticipated to form based on phase equilibria considerations, was not observed with XRD. Additionally, the β-CFF phase was not observed in the XRD pattern obtained. Some
differences in the unit cell dimensions of SFCA and SFCA-I are to be expected as these parameters vary with composition \[2, 4, 7\]. The SFCA-I peaks were observed at a slightly lower 2θ values relative to those previously reported, indicating a slightly larger unit cell size.

The mean compositions of the unknown calcium silico ferrite, given in Table 1, are between the SFCA-I and \(\text{Ca}_{7.2}\text{Fe}^{2+}_{0.8}\text{Fe}^{3+}_{30}\text{O}_{53}\) phase compositions at all temperatures investigated. It appears that the unknown ferrite crystals are composed of two phases, SFCA-I and \(\text{Ca}_{7.2}\text{Fe}^{2+}_{0.8}\text{Fe}^{3+}_{30}\text{O}_{53}\). The composition of the intergrowth varied between the different individual crystals measured; this is suggested to be as a result of variations in the proportions of the two phases. From the mass balance based on the calcium concentration in the crystals, the material is calculated to contain between 45 and 83 wt% \(\text{Ca}_{7.2}\text{Fe}^{2+}_{0.8}\text{Fe}^{3+}_{30}\text{O}_{53}\) with the remainder SFCA-I. On average the proportion of SFCA-I increases with decreasing temperature.

Based on the phases identified with XRD and phase compositions measured by EPMA, the unknown calcium-silico ferrite appears to be an intergrowth of SFCA-I and \(\text{Ca}_{7.2}\text{Fe}^{2+}_{0.8}\text{Fe}^{3+}_{30}\text{O}_{53}\). For presentation purposes, the intergrowth of SFCA-I and \(\text{Ca}_{7.2}\text{Fe}^{2+}_{0.8}\text{Fe}^{3+}_{30}\text{O}_{53}\) is hereafter referred to as ‘SFC-I’.

### 4.2 Phase assemblages present during cooling

To understand the sequence of reactions taking place during solidification and the evolution of the product microstructure, a series of experiments were performed. These experiments were undertaken with samples cooled from the same starting temperature of 1623 K (1350 °C), held for 240 s, cooled (2 K/s) and quenched at 5 K temperature intervals in the temperature range of 1513 K to 1453 K (1240 °C to 1180 °C).

Between a fully homogenous liquid and the final microstructure, three intermediate stages of solidification were observed in these experiments, each resulting in the formation of specific phases and phase assemblages. Three phase assemblages were observed, Liquid+‘SFC-I’ (Assemblage I), Liquid+‘SFC-I’+\(\text{C}_2\text{S}\)+calcium diferrite (CF\(_2\)) (Assemblage II), and finally \(\text{C}_2\text{S}\)+CF\(_2\)+calcium ferrite (CF) (Assemblage III) (figure 6). Assemblage II, based on phase equilibria and equilibrium cooling, consists of two separate stages, first ‘SFC-I’ and \(\text{C}_2\text{S}\) solidification (1225 °C to 1216 °C) and then \(\text{C}_2\text{S}\) and CF\(_2\) solidification (1216 °C to 1190 °C). For ease of description of the solidification phenomena, the sequence of phase assemblages are presented as occurring in isolation. The temperature at which the different phase assemblages were observed are illustrated in Figure 6, with the suggested two stages of Assemblage II shown by dashed lines.
4.3 Liquid Composition

The compositions of the liquids at selected temperatures are shown in Figure 7 and given in Table 4.

In the experiments performed, fine crystals were sometimes observed in the regions that were liquid at temperature, as illustrated in Figure 8. In addition, in well quenched regions, variations in the shade of grey in the image under SEM in back scatter electron (BSE) mode were observed in this residual liquid with distance from the crystalline material. These observations both indicate that during quenching, further solidification of the liquid occurred. Despite this, as illustrated in Figure 7, the change in liquid composition with temperature could be determined with EPMA using the line analysis technique.
As illustrated in Figure 7, during the formation of individual ‘SFC-I’ (I) crystals, the liquid composition moved from the SFC primary phase field into the C\textsubscript{2}S primary phase field. As temperature decreased further, C\textsubscript{2}S was formed and the liquid composition moved away from the C\textsubscript{2}S composition towards the CF\textsubscript{2} primary phase field. Two distinct stages for the melt composition were observed in Assemblage II. This first stage involves the formation of C\textsubscript{2}S and ‘SFC-I’ and the second the formation of C\textsubscript{2}S and CF\textsubscript{2}. This change in liquid composition continued until the liquid approached the CF primary phase field. Below 1463 K (1190 °C) no liquid remained, the final stage of solidification was the formation of C\textsubscript{2}S, CF\textsubscript{2} and CF. At lower temperatures, Assemblage III was present and no liquid remained.

The first stage of Assemblage II was observed at higher temperatures, with an average liquid composition of 69.0 wt% Fe\textsubscript{2}O\textsubscript{3}, 4.1 wt% SiO\textsubscript{2} and 26.9 wt% CaO. The second stage was observed at lower temperatures, with an average liquid composition of 69.8 wt% Fe\textsubscript{2}O\textsubscript{3}, 3.6 wt% SiO\textsubscript{2} and 26.6 wt% CaO. The difference in composition between the two stages was approximately the same as the difference observed between the C\textsubscript{2}S-CF\textsubscript{2}-SFC peritectic and the C\textsubscript{2}S-CF\textsubscript{2}-CF eutectic invariant points. As such, the first stage is suggested to be associated with C\textsubscript{2}S and ‘SFC-I’ solidification and the second with C\textsubscript{2}S and CF\textsubscript{2} solidification.

### 4.4 Liquid+’SFC-I’ (Assemblage I)

‘SFC-I’ crystals formed upon cooling a homogenous liquid, leading to the observation of Assemblage I. Figure 9 shows micrographs illustrating the typical morphologies of ‘SFC-I’ crystals formed.
Figure 9: Examples of microstructures observed in Assemblage I, with the formation of the ‘SFC-I’ crystals from a liquid (69.24 wt% Fe$_2$O$_3$, 6.16 wt% SiO$_2$ and 24.61 wt% CaO) cooled from 1623 K (1350 °C) to a) 1508 K (1235 °C) and b) 1483 K (1210 °C) at 2 K/s in air (S-‘SFC-I’) (BSE).

The ‘SFC-I’ was observed to be in the form of long faceted plates (~300 μm long, ~10 μm thick), distributed throughout the liquid. Larger crystals were observed to have side arms (Figure 9a)), with the arms potentially forming from the nucleation of a crystal on the existing ‘SFC-I’. The large crystals were observed to form from parallel plates, with liquid between the plates as these crystals grew larger (Figure 4, section 4.1). This indicated that the ‘SFC-I’ phase grew as a series of parallel crystals. A layer of ‘SFC-I’ was observed at the interface with the gas phase. The ‘SFC-I’ crystals increased in size and number with decreasing temperature.

The composition of the liquid as a function of distance from the ‘SFC-I’ crystals was measured by point analysis with EPMA. An example of these measurements is given in Table 5 and summarised in Figure 10. The melt composition close to the ‘SFC-I’-liquid interface was lower in Fe$_2$O$_3$ than in the surrounding melt, indicating that mass transfer of iron and further solidification had occurred during quenching. In this figure, the composition measured at 12.6 μm from the ‘SFC-I’ crystals differed from the general trend, with a lower Fe$_2$O$_3$ concentration than anticipated. This difference can be attributed to quench crystal formation, intersection of the interaction volume with phases below the sample surface, or cracks and porosity within the sample.

Figure 10: Liquid composition variation with distance from ‘SFC-I’-liquid interface as measured by EPMA. Sample prepared by cooling a homogenous liquid (69.24 wt% Fe$_2$O$_3$, 6.16 wt% SiO$_2$ and 24.61 wt% CaO) from 1623 K to 1483 K (1350 °C to 1210°C) at 2 K/s in air, followed by quenching to room temperature.
4.5 Liquid+‘SFC-I’+C₂S+CF₂ (Assemblage II)

Assemblage II, involving the formation of ‘SFC-I’, C₂S and CF₂, was observed at 1498 K to 1463 K (1225 °C to 1190 °C). Figure 12 shows a micrograph illustrating this phase assemblage. The chemical compositions of the CF₂ and ‘SFC-I’ phases are similar, leading to significant difficulties in differentiating between these phases with the SEM in BSE mode. The compositions of the coupled microstructures observed in Assemblage II were measured by EPMA line analysis to determine the phases present, as summarised by Figure 11. From the line analysis, two coupled microstructures were confirmed ‘SFC-I’-C₂S (IIb) and C₂S-CF₂ (IId).

Figure 11: The result of EPMA line analyses of eutectic structures formed on cooling a liquid (69.24 wt% Fe₂O₃, 6.16 wt% SiO₂ and 24.61 wt% CaO) from 1623 K (1350 °C) to 1073 K (800 °C) at 2 K/s.

In this phase assemblage, the C₂S phase was observed at all temperatures and appears to be present in a coupled microstructure with either ‘SFC-I’ (IIb) or CF₂ (IId) and occasionally as individual C₂S crystals (IIa). The individual crystals of CF₂ (IIc) were also observed to form between adjoining coupled microstructures.

Figure 12: Microstructures observed in Assemblage II, liquid (69.24 wt% Fe₂O₃, 6.16 wt% SiO₂ and 24.61 wt% CaO) cooled from 1623 K (1350 °C) to 1488 K (1215 °C) at 2 K/s in air.

The individual C₂S (IIa) crystals appeared infrequently as unfaceted crystals either isolated in the liquid or on the individual ‘SFC-I’ crystals. The individual C₂S crystals were observed to be up to 5 μm
in width and 30 μm in length, smaller than the individual ‘SFC-I’ crystals and larger than the C$_2$S crystals in the coupled microstructure (IIb).

The coupled microstructure ‘SFC-I’-C$_2$S (IIb) was associated with the individual ‘SFC-I’ crystals and appeared to have originated from this microstructure. The coupled microstructures, ‘SFC-I’-C$_2$S (IIb) and C$_2$S-CF$_2$ (IIId), occur with ‘SFC-I’ or CF$_2$ as the continuous phases and C$_2$S present as either rods or as an irregular unfaceted microstructure. The individual rods or irregular shapes were observed to vary in size, with fine and coarse eutectics observed. All the C$_2$S eutectic rods were observed to be less than 1μm in diameter.

At higher temperature, one coupled microstructure was observed, ‘SFC-I’-C$_2$S. At lower temperatures, a second coupled microstructure was present, C$_2$S-CF$_2$. The C$_2$S-CF$_2$ coupled microstructure appears to be isolated from the ‘SFC-I’ phase by unfaceted individual CF$_2$ crystals. The C$_2$S rods in the ‘SFC-I’-C$_2$S and C$_2$S-CF$_2$ coupled microstructures are commonly oriented differently and are of a different size. This further suggests that they formed at different stages.

### 4.6 C$_2$S+CF$_2$+CF (Assemblage III)

Assemblage III involves the formation of C$_2$S, CF$_2$ and CF, at approximately 1463 K (1190 °C). As illustrated in Figure 13, this assemblage consisted of coupled microstructures and individual CF crystals (IIIa). The individual crystals CF (IIIa) were irregularly shaped and constrained in all dimensions by the previously formed solids. The coupled microstructures consisted of either rods of C$_2$S (<1μm) in a calcium ferrite matrix or as irregular coupled microstructures. The differentiation of the C$_2$S-CF$_2$ and ‘SFC-I’-C$_2$S coupled microstructures is based on phase analysis and microstructure associations as described in section 4.5.

The compositions of the coupled microstructures present in Assemblage III were measured by line analysis with EPMA to determine the phases present, as summarised in Figure 11. The line measurements were compared to the C$_2$S-CF and C$_2$S-CF$_2$ joins on the ternary phase diagram. Based on the line analysis, the two coupled microstructures were confirmed, C$_2$S-CF (IIIb) and C$_2$S-CF$_2$-CF (IIIc). The measured compositions for the C$_2$S-CF$_2$-CF coupled microstructure were within the C$_2$S-CF$_2$-CF Alkemade triangle rather than along the C$_2$S-CF and C$_2$S-CF$_2$ joins. The final structure formed after complete solidification is shown in Figure 14, also showing the other phase assemblages and microstructures formed.

Figure 13: Microstructures observed to form in Assemblage III, liquid (69.24 wt% Fe$_2$O$_3$, 6.16 wt% SiO$_2$ and 24.61 wt% CaO) cooled from 1623 K (1350 °C) to 1073 K (800 °C) at 2 K/s in air (BSE).
5.0 Discussion

5.1 Formation of Assemblage I (L+’SFC-I’)

On initial cooling of the liquid, the ‘SFC-I’ formed first, by heterogeneous nucleation on the platinum substrate, at the liquid-gas interface and later homogenously in the liquid. The number of ‘SFC-I’ crystals increased with decreasing temperature. The individual ‘SFC-I’ crystals were observed to grow with two intergrowth phases, SFCA-I and $\text{Ca}_{7.2}\text{Fe}^{2+}_{0.8}\text{Fe}^{3+}_{30}\text{O}_{53}$, forming bands within the individual crystal structure.

During solidification of the ‘SFC-I’, further homogenous and heterogeneous nucleation of ‘SFC-I’ occurred with decreasing temperature. The ‘SFC-I’ continued to solidify, changing in composition, until the liquid was supercooled with respect to $\text{C}_2\text{S}$. The liquid composition moved through the SFC primary phase field and into the $\text{C}_2\text{S}$ primary phase field.

5.2 Formation of Assemblage II (L+’SFC-I’+$\text{C}_2\text{S}$+$\text{CF}_2$)

This phase assemblage was observed from 1463 K to 1498 K (1190 °C to 1225 °C), with the liquid compositions inside the $\text{C}_2\text{S}$ primary phase field. From the observed microstructures, liquid compositions and phase equilibria, the formation sequence of Assemblage II can be determined, as illustrated schematically in Figure 15.

This assemblage formed in two stages, $\text{C}_2\text{S}$-‘SFC-I’ solidification and then $\text{C}_2\text{S}$-$\text{CF}_2$ solidification. At the highest temperatures at which this assemblage was observed, the melt is supercooled relative to $\text{C}_2\text{S}$. To form the coupled ‘SFC-I’-$\text{C}_2\text{S}$ microstructure, only $\text{C}_2\text{S}$ needs to be nucleated. It is statistically and thermodynamically likely that the ‘SFC-I’-$\text{C}_2\text{S}$ coupled microstructure forms prior to the nucleation of $\text{CF}_2$. 
During the solidification of C$_2$S and ‘SFC-I’, the individual C$_2$S (IIa) crystals are formed by heterogeneously nucleation on the ‘SFC-I’ or homogenously in the liquid in the concentration gradient established adjacent to the ‘SFC-I’-liquid interface. Prior to the formation of this phase, the supercooling with respect to C$_2$S was observed in Assemblage I. As individual C$_2$S crystals (IIa) are formed, the liquid composition moves towards the C$_2$S-SFC boundary curve. The composition of the ‘SFC-I’ and C$_2$S in the coupled ‘SFC-I’-C$_2$S (IIb) microstructure results in the liquid composition moving to and then following the ‘SFC-I’-C$_2$S boundary curve. This solidification process is shown schematically in Figure 15.

To enable the nucleation and growth of the individual CF$_2$ crystals (IIc), the liquid must be supercooled with respect to this phase. As such, at the conclusion of the ‘SFC-I’-C$_2$S coupled growth and prior to the nucleation of the CF$_2$, the melt composition would be in the CF$_2$ primary phase field. Based on the microstructure of the individual CF$_2$ crystals (IIc), the CF$_2$ nucleated heterogeneously on the ‘SFC-I’ or homogenously in the concentration gradient at ‘SFC-I’-liquid interface. Once nucleated, the individual CF$_2$ crystals (IIc) would rapidly solidify, in the supercooled liquid. The liquid composition would move towards the C$_2$S-CF$_2$ boundary curve.

The C$_2$S-CF$_2$ coupled microstructure (IIId) was observed with rods of C$_2$S in the CF$_2$ matrix. This indicated that there was a larger volume fraction of CF$_2$ than C$_2$S in this microstructure, in agreement with that predicted from the C$_2$S-CF$_2$-CF Alkemade triangle.

**5.3 Formation of Assemblage III (C$_2$S+CF$_2$+CF)**

The CF was observed in the final microstructure, and present in the three microstructures, individual CF crystals (IIla), a C$_2$S-CF coupled microstructure (IIlb) and a C$_2$S-CF$_2$-CF coupled microstructure (IIlc). This solidification process is shown schematically in Figure 16.

It appears that the CF phase forms first as individual crystals of CF (IIla). The CF phase appears to have nucleated heterogeneously on CF$_2$, initially growing faster than the other phases present. The remaining liquid solidifies to form the C$_2$S-CF coupled microstructure (IIlb) and finally the C$_2$S-CF$_2$-CF coupled microstructure (IIlc).
The present study has demonstrated that kinetic factors play a significant role in determining the nucleation and subsequent growth of phases and microstructures during oxide solidification. The phases formed during cooling, were similar to those expected from solidification theory. The major difference was that the SFC phase was not formed. Instead, the SFCA-I and \( \text{Ca}_{7.2}\text{Fe}^{2+}_{0.8}\text{Fe}^{3+}_{30}\text{O}_{53} \) phases homogenously nucleated in the liquid and formed an intergrowth. This suggests that some phases formed on the solidification of oxide liquids are potentially metastable phases. In addition, the peritectic reaction involving the dissolution of the ‘SFC-I’ intergrowth was not observed under the cooling rates investigated. The present study reinforces the results of previous research \cite{14}, and further demonstrates that nucleation phenomena play a key role in determining the phases and resultant microstructures formed during cooling of these liquid oxides.

6.0 Summary

The phases and microstructures formed on solidification of a liquid (69.24 wt% \( \text{Fe}_2\text{O}_3 \), 6.16 wt% \( \text{SiO}_2 \) and 24.61 wt% \( \text{CaO} \)) within the SFC primary phase field of the ternary \( \text{Fe}_2\text{O}_3 \)-CaO-SiO\(_2\) system in air have been determined. A liquid of this composition was expected to form SFC upon cooling based on the ternary phase diagram. However, it was demonstrated that the SFC phase does not form under these conditions.

The phases formed on cooling were determined by EPMA and XRD to be SFCA-I, \( \text{Ca}_{7.2}\text{Fe}^{2+}_{0.8}\text{Fe}^{3+}_{30}\text{O}_{53} \), \( \text{C}_2\text{S} \), CF, and \( \text{C}_2\text{S} \). The SFCA-I and \( \text{Ca}_{7.2}\text{Fe}^{2+}_{0.8}\text{Fe}^{3+}_{30}\text{O}_{53} \) phases were observed to occur as intergrowths, giving the appearance of a single crystal. The solidification sequence was determined to be as follows; nucleation and growth of the SFCA-I and \( \text{Ca}_{7.2}\text{Fe}^{2+}_{0.8}\text{Fe}^{3+}_{30}\text{O}_{53} \) intergrowth, nucleation and growth of \( \text{C}_2\text{S} \) dendrites and a coupled \( \text{C}_2\text{S}-(\text{SFC-I+Ca}_{7.2}\text{Fe}^{2+}_{0.8}\text{Fe}^{3+}_{30}\text{O}_{53}) \) microstructure, nucleation and growth of individual \( \text{CF}_2 \) crystals and a coupled \( \text{CF}_2-\text{C}_2\text{S} \) microstructure, and finally the nucleation and growth of CF, coupled \( \text{C}_2\text{S}\text{-CF} \) and \( \text{C}_2\text{S}\text{-CF}\text{-CF}_2 \) microstructures.

The study clearly demonstrates that during continuous cooling, the solidification of oxide liquids, non-equilibrium phases can nucleate and grow, emphasising the importance of kinetic processes in determining the phases formed and microstructures present during the solidification of these
‘Fe₂O₃’-CaO-SiO₂ liquids. This observation is significant in that it provides valuable insight into the key processes taking place during industrial iron ore sintering.

7.0 Acknowledgements

The authors would like to thank the Australian Research Council Linkage Program and BHP for financial support to enable this research to be carried out, and the Centre of Microstructure and Microanalysis (CMM), the University of Queensland for providing electron microscope facilities that enabled the microanalytical measurements to be undertaken. This research was supported by an Education Endowment Fund (EEF) scholarship from the Australasian Institute of Mining and Metallurgy (AusIMM) and an Australian Government Research Training Program (RTP) Scholarship.
Table 4: Liquid compositions measured by EPMA, formed on cooling a liquid (69.24 wt% Fe$_2$O$_3$, 6.16 wt% SiO$_2$ and 24.61 wt% CaO) from 1623 K (1350°C) at 2 K/s in air

<table>
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<th>Temperature (°C)</th>
<th>Assemblage I (L+$'SFC$-I'))</th>
<th>Assemblage Ila/b (L+Ca$_2$S+$'SFC$-I'))</th>
<th>Assemblage Ilc/d (L+Ca$_2$S+CF$_2$)</th>
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Table 5: Liquid compositions measured by EPMA for a line perpendicular to ‘SFC-I’ formed on cooling to 1483 K (1210 °C) at 2 K/s in air (69.24 wt% Fe$_2$O$_3$, 6.16 wt% SiO$_2$ and 24.61 wt% CaO).

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References

Appendix C: Effect of Cooling Rate on the Controlled Solidification of “Fe$_2$O$_3$”-CaO-SiO$_2$ Liquidus in Iron Ore Sinter
Effect of cooling rate on the controlled solidification of “Fe₂O₃”-CaO-SiO₂ liquids in air in synthetic iron ore sinter

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Abstract

Iron ore sinter is the principal feed to the iron blast furnace. During the cooling of iron ore sinter, liquid oxide solidifies to form the final sinter microstructures. The phases and microstructures formed influence the technical and economic performance of the blast furnace.

The cooling rate of the liquid oxide can be controlled in industrial sintering processes through the draft pressure and has the potential to influence microstructure formation. The solidification of a liquid within the hematite primary phase field in the ternary “Fe₂O₃”-CaO-SiO₂ system in air was undertaken at different cooling rates to determine the impact of cooling rate on the formation of product microstructures. Samples with a bulk composition of 72.7 wt% Fe₂O₃ and a CaO/SiO₂ ratio of 3.46 (6.11 wt% SiO₂ and 21.14 wt% CaO), were cooled from 1623 K (1350 °C) at 2 K/s, 0.5 K/s, 0.1 K/s and 0.01 K/s and quenched at 5 K temperature intervals from 1533 K (1260 °C) to 1453 K (1180 °C). During cooling, four stages of phase assemblage formation were consistently observed at all cooling rates; in order of formation these are, Liquid+hematite (I), Liquid+hematite+dicalcium silicate(C₂S)(II), Liquid+C₂S+calcium diferrite (CF₂)(III) and C₂S+CF₂+calcium ferrite (CF)(IV). An intergrowth of silico-ferrite of calcium and aluminium-I (SFCA-I) and Ca₇.2Fe²⁺₀.8Fe³⁺30O₅₃ was observed to form in some conditions in regions free of hematite, present in liquids solidifying at 0.5 K/s and 0.1 K/s. The sizes and shapes of microstructures were observed to systematically change with cooling rate, with a slower cooling rate typically resulting in coarser coupled microstructures and larger individual crystals. A larger proportion of coupled microstructures are observed at slower cooling rates, this appears to be related to the degree of undercooling prior to the nucleation of new phases. The equilibrium silico-ferrite of calcium (SFC) phase was not observed at any of the cooling rates investigated.

Based on the microstructures formed and liquid composition, as measured by EPMA, it was demonstrated that the cooling rate of the melt influences the microstructures formed.

Keywords: Iron ore sinter; microstructure; formation mechanisms; solidification; “Fe₂O₃”-CaO-SiO₂

1.0 Introduction

A number of processes have been identified to occur during the heating, peak temperature and cooling of iron ore sinters [1-4]. During cooling, the liquid solidifies to form new crystalline and amorphous phases. Limited control of the cooling rate during sintering is possible in industrial sintering processes. For example, the sinter draft pressure can be changed to vary the overall cooling rate of the sinter [5]. Differences in the rate of cooling within the sinter bed may occur as a result of heterogeneity within the sinter feed [6], the position in the bed, the agglomeration practice and particle packing in the bed. An understanding of the impact of cooling rate on the solidification processes occurring during cooling will assist in determining the optimal conditions for iron ore sintering.
The solidification processes for melts in the “Fe\textsubscript{2}O\textsubscript{3}”-CaO-SiO\textsubscript{2} system in air, within the hematite and Silico Ferrite of Calcium (SFC) primary phase fields, at cooling rates (2 K/s) and temperatures (1623 K to 1073 K, 1350 °C to 800 °C) have been investigated [7, 8]. It was shown that there were significant differences in the phases formed, and the product microstructure formed, from those anticipated under equilibrium cooling. It was observed that nucleation processes play a key role in the formation of the phases present in the final product. For the liquid within the hematite primary phase field, with a CaO/SiO\textsubscript{2} ratio of 3.46 wt/wt and 72.7 wt% Fe\textsubscript{2}O\textsubscript{3}, four phase assemblages were observed. These were in the order in which these assemblages formed on cooling: Liquid+H, Liquid+H+Si, Liquid+Si+CF\textsubscript{2}, and Si+CF\textsubscript{2}+CF, where H is hematite (Fe\textsubscript{2}O\textsubscript{3}), Si is 2CaO.SiO\textsubscript{2}, CF\textsubscript{2} is CaO.2Fe\textsubscript{2}O\textsubscript{3}, and CF is CaO.3Fe\textsubscript{2}O\textsubscript{3}. For the liquid within the SFC primary phase field, with a CaO/SiO\textsubscript{2} ratio of 4.00 and 69.24 wt% Fe\textsubscript{2}O\textsubscript{3}, four phase assemblages were observed. These were, in the order of formation, Liquid+SFC-I, Liquid+SFC-I+Si, Liquid+Si+CF\textsubscript{2}, and Si+CF\textsubscript{2}+CF. The ‘SFC-I’ was shown to be an intergrowth of SFC-I and Ca\textsubscript{2}Fe\textsuperscript{2+}Fe\textsuperscript{3+}\textsubscript{30}O\textsubscript{53}, forming at conditions in which the SFC phase was expected.

The focus of the present study is to determine the effects of cooling rate on the phases and microstructures formed during the solidification of a liquid within the hematite primary phase field of the “Fe\textsubscript{2}O\textsubscript{3}”-CaO-SiO\textsubscript{2} system in air.

### 2.0 Experimental Technique

Details of the experimental technique used in this study have been reported in a previous publication by the authors [7]. The technique enables oxide melts to be cooled at controlled rates over a range of temperatures, it allows each stage of the solidification process to be observed in isolation and differentiated from the processes occurring during heating. The ability to rapidly quench the sample and to accurately capture the microstructures and phase compositions present at temperature are critical to the experimental design. The controlled cooling rates achievable with the new experimental technique are within the range of cooling rates measured in industrial iron ore sintering [9].

An oxide pellet (0.1 g, 6 mm diameter) and substrate (70/30 Pt/Rh wire, 0.5 mm diameter) was heated and cooled in air in an electrically heated vertical tube furnace (alumina reaction tube, 38mm OD 30 mm ID). The sample was suspended vertically within the reaction tube in the furnace with an alumina rod. The vertical position of the alumina rod, and hence the position of the sample, was controlled with a positioning motor affixed to the top of the furnace. The sample is raised into the hot zone of the furnace, and the sample was held for four minutes at or above 1623 K (1350 °C) for melting and homogenisation. After homogenisation, the sample was lowered through the furnace with the use of a computer controlled motor drive to achieve a constant cooling rate. On reaching the target temperature the sample was quenched in water by releasing the sample, which falls under gravity into the quenching medium.

The samples were characterised initially by preparing polished cross sections using conventional metallographic techniques. The phases and microstructures formed were examined using a reflected light microscope (Olympus Provis AX70TRF) and scanning electron microscope (SEM) in back scattered electron mode (BSE). Phase compositions were measured by an electron probe X-ray microanalysis (EPMA) technique with wavelength dispersive spectroscopy (WDS) (JEOL 8200L EPMA; Japan Electron Optics Ltd., Tokyo, Japan). The EPMA was operated at a voltage of 15 keV and current of 20 nA. Two standards were used for calibration, pure CaSiO\textsubscript{3} and Fe\textsubscript{2}O\textsubscript{3} (all standards from the Charles M. Taylor Co., Stanford, CA). The iron concentration in phases were recalculated to Fe\textsubscript{2}O\textsubscript{3} for presentation purposes.
The bulk composition of the oxide mixture, 72.74 wt% Fe$_2$O$_3$, 6.11 wt% SiO$_2$ and 21.14 wt% CaO (CaO/SiO$_2$ ratio of 3.46 wt/wt), was selected as this was predicted to form SFC, Fe$_2$O$_3$ and C$_2$S on equilibrium cooling of the liquid in air [10]. For this bulk oxide composition, the liquidus temperature is estimated to be 1568 K (1295 °C). Constant cooling rates between 2 K/s and 0.01 K/s were selected.

### 3.0 Results

Experiments were performed with samples cooled at 2 K/s [7] 0.5 K/s, 0.1 K/s and 0.01 K/s from fully liquid conditions at 1623 K to 1073 K (1350 °C to 800 °C). Within this range of temperatures and cooling rates, complete solidification of the liquid was found to have taken place, with no residual liquid observed at 1073 K (800 °C). At all cooling rates, hematite (Fe$_2$O$_3$), dicalcium silicate (C$_2$S, 2CaO·SiO$_2$), calcium ferrite (CF, CaO·Fe$_2$O$_3$) and calcium diferrite (CF$_2$, CaO·2Fe$_2$O$_3$) were observed to form. The SFC-I/CF$_2$Fe$_{2.8}$Fe$_{30}$O$_{53}$ intergrowth, hereafter referred to as ‘SFC-I’, was occasionally observed at slow cooling rates (0.5 K/s and 0.1 K/s). An example of the typical phases and microstructures formed on cooling at 0.5 K/s is given in Figure 1. Examples of the final microstructures formed at cooling rates of 0.1, 0.5 and 2 K/s are presented for comparison in Figure 2 a-c.

Figure 1: a) Example of final solidified structure formed on cooling a liquid (72.74 wt% Fe$_2$O$_3$, 6.11 wt% SiO$_2$ and 21.14 wt% CaO) from 1523 K to 1478 K (1250 °C to 1205 °C) at 0.5 K/s in air. b) detail of a). (H - Hematite, C$_2$S - 2CaO·SiO$_2$, CF – CaO·Fe$_2$O$_3$, CF$_2$ – CaO·2Fe$_2$O$_3$, (Backscattered electron (BSE) micrographs)
Figure 2: Examples of the phases and microstructures observed on cooling a liquid (72.74 wt% Fe$_2$O$_3$, 6.11 wt% SiO$_2$ and 21.14 wt% CaO) from 1623 K (1350 °C) at a) 0.1 K/s to 1463 K (1190 °C), b) 0.5 K/s to 1463 K (1190 °C) and c) 2.0 K/s to 1468 K (1195 °C) in air (BSE micrographs).

In experiments undertaken at a cooling rate of 0.01 K/s, it was found that on quenching from temperature all samples disintegrated into a fine powder on quenching. The resulting powder was examined by Scanning Electron Microscopy (SEM) equipped with Energy Dispersed Spectrometer (EDS) and identified to contain C$_2$S, CF$_2$, CF and hematite. An example of the typical phases and microstructures formed on cooling at 0.01 K/s is given in Figure 3. The individual crystals observed were significantly larger than that observed at faster cooling rates. The C$_2$S crystals were an order of magnitude larger (>200μm vs ~20 μm) than those obtained on cooling at 0.1 K/s and contained cracks or fissures. These cracks or fissures appeared to be associated with particular planes within the C$_2$S crystals. These observations suggest that the disintegration of the sample is related to the fracturing of the C$_2$S as a result of the phase transformation on cooling.
At all cooling rates, the phases and microstructures observed differed from that anticipated under both equilibrium and Scheil-Gulliver cooling. To provide a clear understanding of the sequence of reactions and the effect of cooling rate on these processes, a series of experiments were performed. These experiments were undertaken with samples cooled from the same starting temperature 1623 K (1350 °C) and quenched from selected temperatures between 1523 K (1250 °C) and 1453 K (1180 °C).

Between a fully homogenous liquid and the final microstructure, four intermediate stages of solidification were observed for all cooling rates as illustrated in Figure 4. These stages were, in the order of formation, liquid+hematite (Assemblage I), liquid+hematite+C\textsubscript{2}S (Assemblage II), liquid+C\textsubscript{2}S+calcium diferrite(CF\textsubscript{2}) (Assemblage III) and finally C\textsubscript{2}S+CF\textsubscript{2}+calcium ferrite(CF) (Assemblage IV). In some samples, liquid+‘SFC-I’ phase assemblage (Assemblage V) and a liquid+‘SFC-I’+C\textsubscript{2}S phase assemblage (Assemblage VI) were observed. As assemblage V and VI were minor phase assemblages, they are discussed and described separately. The temperatures at which assemblages I though IV were observed are illustrated in Figure 4.
3.1 Liquid + Hematite (Assemblage I)

Assemblage I, involving the formation of hematite crystals, was the first phase assemblage observed to form from a homogenous melt. Figure 5 a-c) shows micrographs illustrating the typical Assemblage I microstructures formed at different cooling rates.

At all cooling rates, the hematite was observed to be in the form of large, faceted dendritic (skeletal) crystals. A slower cooling rate resulted in larger crystals, observed to be approximately 100 μm long and 30 μm wide at 2 K/s; 150 μm long and 75 μm wide at 0.5 K/s; and 200 μm long and 100 μm wide at 0.1 K/s. These crystals almost exclusively formed on the substrate or the sample surface. With slower cooling rates, the hematite dendrites were observed to increase in length from 5 μm at 2 K/s to 10 μm at 0.5 K/s and 30 μm at 0.1 °C/s. With an increase in the size of the hematite crystals, the distance between hematite crystals increased. For all cooling rates, the hematite crystals increased in size and number with decreasing temperature.

3.2 Liquid + Hematite + C$_2$S (Assemblage II)

The formation of Assemblage II followed and is additive to Assemblage I. Figure 6 shows micrographs typical of this phase assemblage.
For all cooling rates, C$_2$S was observed in three forms; a thin C$_2$S layer on the primary hematite (IIa), individual C$_2$S dendrites (IIb) and a coupled hematite+C$_2$S microstructure (IIc). The morphologies of these microstructures have been previously reported [7]. At all cooling rates, the 2 to 3 μm layer of C$_2$S on hematite (IIa) was observed on a most of the hematite (I) crystals.

The individual C$_2$S (IIb) appeared as unfaceted crystals either isolated in the liquid, or as dendritic structures, originating from the coupled H-C$_2$S microstructure. The individual crystals were not observed in all regions of assemblage II. The overall volume fraction of C$_2$S increased with decreasing temperature. The volume of the individual crystals themselves were also observed to increase with decreasing cooling rate, with the length of the dendrites increasing from 5 μm to 20 μm when the cooling rate decreased from 2 K/s to 0.1 K/s.

The coupled microstructure (H-C$_2$S) (IIc) was found to surround all the individually formed hematite crystals, forming on either the hematite (I) or the thin layer of C$_2$S. In the coupled microstructure, hematite wa the continuous phase and C$_2$S was present as either rods or as an irregular unfaceted crystals. The diameter of the C$_2$S rods increased with a decreasing cooling rate. The extent of formation of this microstructure (IIc) was observed to increase with a decreased cooling rate.
3.3 Liquid + C₂S + CF₂ (Assemblage III)

Phase assemblage III (L+C₂S+CF₂) was observed to form at all cooling rates. Figure 7 shows typical microstructures of this phase assemblage, formed at different cooling rates. Difficulties in quenching all phase assemblages and retaining the liquid as a glass or amorphous phase on cooling was experienced due to the large proportions of solids present.

![Microstructure](image)

**Figure 7:** Examples of typical microstructures observed in Assemblage III (L+C₂S+CF₂), liquid (72.74 wt% Fe₂O₃, 6.11 wt% SiO₂ and 21.14 wt% CaO) cooled from 1623 K (1350 °C) to a) 1493 K (1220 °C) at 0.1 K/s, b) 1503 K (1230 °C) at 0.5 K/s and c) 1473 K (1200 °C) at 2 K/s in air (L – Liquid, H- Hematite, C – C₂S, CF₂ – Calcium Diferrite) (BSE micrographs)

The microstructures observed consist of individual CF₂ crystals (IIIa) and a coupled C₂S-CF₂ microstructure (IIIb). The morphologies of these microstructures have been previously reported [7]. The individual CF₂ crystals were observed to form on the hematite and the coupled C₂S-CF₂ microstructure on the individual CF₂ crystals. No measurable dissolution of previously solidified hematite, was observed.

At a cooling rates of 2 K/s, the individual CF₂ crystals (IIIa) were observed to form thin faceted plates, forming an interface with both hematite, liquid and occasionally C₂S. The individual CF₂ crystals were occasionally observed to be curved. At this cooling rate, the coupled C₂S-CF₂ microstructure (IIIb) was only observed in some regions of assemblage III.

At cooling rates of 0.5 K/s and 0.1 K/s, the individual CF₂ crystals were less frequently observed, typically present on the edges of the coupled C₂S-CF₂ microstructure (IIIb) and hematite(I). The individual CF₂ crystals were consistently observed to be faceted and blocky. The individual CF₂ crystals...
formed when cooling at 0.1 K/s and 0.5 K/s were less numerous and thicker (~20μm wide) when compared to those formed at 2 K/s. The length of the crystals appeared to be physically limited by the presence of solids formed in Assemblage I and II.

The coupled microstructure (IIIb) was frequently observed at the cooling rates of 0.5 K/s and 0.1 K/s, typically nucleating on CF₂. The CF₂ formed the continuous phase with C₂S rods, indicating that CF₂ formed a larger volume proportion of this microstructure. With variation in cooling rate, the diameter of the C₂S rods was not observed to noticeably change.

### 3.4 C₂S + CF₂ + CF (Assemblage IV)

The final microstructures to form consisted of individual CF crystals (IVa), coupled C₂S-CF microstructures (IVb) and a coupled C₂S-CF-CF₂ microstructure (IVc) [7]. The general morphologies of these microstructures have been previously reported [7]. This assemblage and the associated three microstructures were observed to form at all three cooling rates (0.1 – 2 K/s); examples of these structures are given in Figure 8.

![Figure 8: Examples of typical microstructures observed in Assemblage IV (L+C₂S+CF₂+CF), liquid (72.74 wt% Fe₂O₃, 6.11 wt% SiO₂ and 21.14 wt% CaO) cooled from 1623 K (1350 °C) to 1453 K (1180 °C) at 0.1 K/s (BSE micrographs)](image)

The C₂S-CF₂-CF coupled microstructure (IVc) and the C₂S-CF coupled (IVb) microstructures were both observed to consist of either rods of C₂S (<1μm) in a CF or CF/CF₂ matrix or as an irregular coupled microstructure. Due to similar morphologies and average composition, the coupled C₂S-CF (IVb) and coupled C₂S-CF-CF₂ (IVc) microstructures were difficult to differentiate based on BSE imaging with FE-SEM. The presence of the two microstructures was confirmed using line analysis with EPMA using the procedure previously outlined [7, 8].

The cooling rate was observed to change the relative volumes of the individual CF crystals and the coupled microstructures. Decreasing the cooling rates from 0.5 K/s to 0.1 K/s resulted in an increase in the mean length of the individual CF crystal (IVa) from around 40 μm to 100 μm. While the diameter of the C₂S rods was not observed to change with cooling rate, decreasing the cooling rates from 0.5 K/s to 0.1 K/s resulted in the increased volume fractions of the coupled microstructures (IVb,c).

### 3.5 Liquid + ‘SFC-I’ (Assemblage V)

The Liquid + ‘SFC-I’ phase assemblage was only observed when cooling a melt at 0.5 K/s to 1518 K (1245 °C). The composition of the individual ‘SFC-I’ crystals, as measured by EPMA, was 83.7 wt% Fe₂O₃, 1.86 wt% SiO₂ and 14.51 wt% CaO, when formed at 0.5 K/s. This composition differs from that measured in crystals formed within the SFC primary phase field at 2 K/s [8], which contained 86 to 87 wt% Fe₂O₃, 0.01 to 0.34 wt% SiO₂ and 12.8 to 13.7 wt% CaO. Despite the difference in composition,
the measured composition is still consistent with the intergrowth of SFC-I and \( \text{Ca}_{7.2}\text{Fe}^{2+}_{0.8}\text{Fe}^{3+}_{30}\text{O}_{53} \) reported in an earlier study of this system [7]. Within the ‘SFC-I’ intergrowth, variations in the proportions of the two phases will lead to variations in the bulk composition. This is a potential cause for the variation in brightness of these crystals. Due to the small proportion of this intergrowth, the phases were unable to be confirmed with XRD. Due to the similarities in composition with that previously observed, it was concluded that these crystals are an intergrowth of SFC-I and \( \text{Ca}_{7.2}\text{Fe}^{2+}_{0.8}\text{Fe}^{3+}_{30}\text{O}_{53} \).

![Figure 9: Microstructures observed in Assemblage V (L+'SFC-I'), liquid (72.74 wt% Fe\(_2\)O\(_3\), 6.11 wt% SiO\(_2\) and 21.14 wt% CaO) cooled from 1623 K (1350°C) to 1518 K (1245°C) at 0.5 K/s in air (BSE micrograph) (S – ‘SFC-I’, L-Liquid)](image)

The phase assemblage was observed to consist of consisting of individual ‘SFC-I’ crystals (V) distributed through the liquid. These ‘SFC-I’ crystals were never observed to be associated with hematite, forming at least 100 μm from this phase. The individual crystals were observed to be approximately 100 μm long and 10 μm wide. The individual ‘SFC-I’ crystals (V) were observed to have side arms, which appear to have formed by nucleation on the existing ‘SFC-I’.

### 3.6 Liquid + C\(_2\)S + ‘SFC-I’ (Assemblage VI)

Assemblage VI (L+C\(_2\)S+'SFC-I') was observed when the liquid (72.74 wt% Fe\(_2\)O\(_3\), 6.11 wt% SiO\(_2\) and 21.14 wt% CaO) was cooled to 1483 K (1210 °C) at 0.1 K/s, and 1488 K and 1483 K (1215 °C and 1210 °C) at 0.5 K/s. This assemblage appeared concurrently with Assemblage II. Figure 10 shows a micrograph of this phase assemblage.
In this phase assemblage, ‘SFC-I’ and C\textsubscript{2}S were observed as a coupled microstructure (VI), identified by line analysis with EPMA. This microstructure was always observed to originate at a distance from the hematite. The coupled microstructure appeared with ‘SFC-I’ as the continuous phase and C\textsubscript{2}S as either rods or as an irregular unfaceted microstructure. All eutectic grains were observed to be less than 1 μm in thickness.

Individual C\textsubscript{2}S crystals (IIa) were also observed to appear in this phase assemblage. The C\textsubscript{2}S was present in the form of unfaceted crystals either isolated (IIb) in the liquid or associated (IV) with the coupled C\textsubscript{2}S-‘SFC-I’ microstructure. Similar to that observed in Assemblage II, the C\textsubscript{2}S appears to be in the form of dendrites. These dendrites appear to have formed in Assemblage II and later transitioned into Assemblage VI.

### 3.7 Liquid composition variation with temperature and cooling rate

In the current study, the compositions of the liquids at selected temperatures were measured with EPMA. The measured liquid compositions are summarised in Figure 11 and given in Tables 1 and 2.
For all cooling rates, 0.1-2 K/s, the same trends in composition with time were observed. During the formation of isolated hematite (Assemblage I), as temperature decreased and solidification progressed, the liquid composition moved from the hematite primary phase field, through the SFC primary phase field into the C$_2$S primary phase field. With faster cooling rates, the liquid composition moved further from the hematite primary phase field. In assemblage II, as the C$_2$S was formed the liquid compositions moved away from the C$_2$S composition and towards the CF$_2$ primary phase field as temperature decreased. At slower cooling rates, the liquid composition was observed to be closer to the equilibrium SFC-C$_2$S or the metastable hematite-C$_2$S boundary line. This solidification of C$_2$S and/or hematite continued until the liquid reached the CF$_2$ primary phase field. At this point, some regions of the sample were observed to exist as assemblage III. With the formation of CF$_2$ the composition of the liquid in assemblage III moved away from the CF$_2$.

The phases formed and the processes observed differed from those predicted under equilibrium cooling, specifically:

- SFC was not formed even though the melt composition moved through the SFC primary phase field.
- Melt undercooling occurred prior to the nucleation of C$_2$S, the extent of undercooling reducing with a decrease in cooling rate.
- Peritectic reactions involving the dissolution and replacement of solids formed at higher temperatures did not take place at any cooling rate.

4.0 Discussion

4.1 Formation of Assemblage I (L+H)

As previously established[7], Assemblage I (L+H) is the first to form. Upon cooling the homogenous liquid, the hematite nucleates, either heterogeneously on the substrate or homogenously within the
liquid. The hematite continues to solidify to form individual hematite crystals (I), with the liquid composition moving through the hematite, SFC and then into the C$_2$S primary phase field as the sample is cooled. No SFC is observed to form during the formation of this phase assemblage, instead progressing directly to form Assemblage II and III. During the last stages of Assemblage I, the liquid is undercooled with respect to SFC, hematite and C$_2$S.

While the crystal shapes were unaffected by differences in cooling rate, faster cooling rates (2 K/s) were associated with the formation of more numerous but smaller individual hematite crystals. This is an indicator that less long range mass transfer is occurring in the melt at faster cooling rates (2 K/s), leading to a greater extent of liquid undercooling prior to nucleation of hematite and in turn the formation of more hematite nuclei. The slower cooling rates (0.5 K/s, 0.1 K/s) resulted in the liquid composition being closer to the SFC-C$_2$S boundary line prior to the formation of Assemblage II, further suggesting that a slower cooling (0.5 K/s, 0.1 K/s) rate leads to less liquid undercooling prior to nucleation. The slower cooling rates also provide more time for mass transfer and crystal growth to occur during cooling.

Based on mass balance calculations between the starting and final melt compositions, the proportion of hematite formed in Assemblage I increased with increasing cooling rate. The lowest temperatures at which assemblage I was observed was the same for all cooling rates investigated.

### 4.2 Formation of Assemblage II (L+C$_2$S+H)

This phase assemblage is additive to Assemblage I. Upon cooling the liquid further, C$_2$S nucleates either heterogeneously on the hematite or in the concentration profile at the hematite-liquid interface within the liquid. Once nucleated, the C$_2$S rapidly solidifies to form a thin C$_2$S layer (IIa) on the hematite followed by individual C$_2$S crystals (IIb). The liquid is initially undercooled with respect to C$_2$S, enabling the rapid solidification of these two microstructures, moving the liquid composition towards the C$_2$S-SFC or in this case the metastable C$_2$S-hematite boundary line (see Figure 12). The coupled C$_2$S-hematite microstructure is subsequently formed, with the liquid composition moving towards the C$_2$S-SFC-CF$_2$ ternary peritectic invariant point. At the final stages of this assemblage, the liquid composition moved into or near the CF$_2$ primary phase field and becomes undercooled with respect to CF$_2$.

With a slower cooling rate (0.5 K/s, 0.1 K/s), the liquid composition approached the C$_2$S-hematite boundary line more closely, as illustrated by Figure 12.

![Figure 12: The change in liquid composition as solidification take place for Assemblages I and II.](image)
The C$_2$S layer (IIa) was observed to form for all cooling rates examined. The individual C$_2$S crystals (IIb) were observed to increase in size and a decrease in number with a decreasing cooling rate, suggesting that more extensive long range mass transfer is occurring at slower cooling rates (0.5 K/s, 0.1 K/s). The thickness of the coupled C$_2$S-hematite microstructure and interlamellar spacing increased with decreasing cooling rate.

Assemblage II was observed to form at higher temperatures at slower cooling rates (0.5 K/s, 0.1 K/s), indicating that nucleation occurred at a higher temperature and lower undercooling with respect to C$_2$S. This is attributed to a slower cooling rate providing more time for C$_2$S nucleation.

The proportion of hematite present in Assemblage I relative to that in assemblage II increases with increasing cooling rate. This is directly related to the melt composition prior to the nucleation of the C$_2$S, the start of Assemblage II.

### 4.3 Formation of Assemblage III (L+C$_2$S+CF$_2$)

Assemblage III (L+C$_2$S+CF$_2$) consists of individual CF$_2$ crystals (IIla) and a coupled C$_2$S-CF$_2$ microstructure (IIlb). The microstructural evidence indicates that the individual CF$_2$ crystals (IIla) are formed through heterogeneous nucleation on the hematite phase in the coupled Hematite+C$_2$S (IIc) microstructure or individual hematite crystals (I). The C$_2$S is already present in the coupled Hematite+C$_2$S microstructure. As the CF$_2$ is formed, the liquid composition moves away from the CF$_2$ composition. On reaching the C$_2$S-CF$_2$ boundary line, the coupled C$_2$S-CF$_2$ microstructure is formed and the liquid composition moved along the C$_2$S-CF$_2$ boundary line and approaches the C$_2$S-CF$_2$-CF eutectic invariant point (See Figure 13).

With slower cooling rates (0.5 K/s, 0.1 K/s), the proportion of the coupled C$_2$S-CF$_2$ microstructure (IIlb) relative to the isolated CF$_2$ increased. From the proportion of CF$_2$ formed during cooling, it is suggested that a slower cooling rate (0.5 K/s, 0.1 K/s) results in less undercooling with respect to CF$_2$ prior to this phase forming and in turn less CF$_2$ forming prior to the solidification of the C$_2$S-CF$_2$ microstructure. From this it is suggested that with slower cooling rates, the formation of the individual CF$_2$ crystals (IIla) occurs over a smaller liquid composition range and the coupled C$_2$S-CF$_2$ microstructure (IIlb) occurs over a wider liquid composition range, as evident in the changing proportion of these two microstructures with cooling rate.

![Figure 13: The change in liquid composition as solidification occurred for Assemblage III.](image-url)
4.4 Formation of Assemblage IV (C$_2$S+CF$_2$+CF)

Based on the microstructures obtained in these experiments it is believed that the first microstructure to form in Assemblage IV (C$_2$S+CF$_2$+CF) is that of the individual crystals of CF (IVa). This microstructure solidified from a liquid undercooled with respect to CF. After the rapid solidification of this phase, the C$_2$S-CF coupled microstructure (IVb) would have formed via a coupled growth mechanism and finally the C$_2$S-CF$_2$-CF coupled ternary microstructure (IVc).

For Assemblage IV, a slower cooling rates resulted in larger individual crystals and interlamellar spacing in the coupled microstructures. This can be attributed to a longer time provided for mass transfer and kinetic processes, allowing for the increase in crystal sizes.

Consistent with the metallographic evidence and the inferred solidification processes, the impact of cooling rate on the liquid composition can be determined. As the liquid enters the CF primary phase field (see Figure 14), the CF nucleates from an undercooled liquid, with the nucleation occurring at higher temperatures for slower cooling rates. The slower cooling rates result in less undercooling and smaller proportions of the individual CF (IVa) crystals. The second stage is the formation of the C$_2$S-CF coupled microstructure (IVb), and the movement of the liquid composition along the C$_2$S-CF boundary line. The final microstructure, C$_2$S-CF-CF$_2$ ternary coupled microstructure (IVc), was observed to be relatively unaffected by the rate of cooling as all phases in this microstructure had previously nucleated.

![Figure 14: The change in liquid composition as solidification occurred for Assemblage IV (C$_2$S+CF$_2$+CF).](image)

4.5 Formation of ‘SFC-I’ (Assemblage V (L+’SFC-I’) and VI (L+’SFC-I’+C$_2$S))

‘SFC-I’ containing microstructures were observed at the slower cooling rates (0.5 and 0.1 K/s) that were investigated, always originating at a distance from the hematite. Based on the observation of the SFC in regions distinct and separate from hematite, it is suggested that the presence of hematite is not conducive for or does not assist in the formation of the SFC phase. No other phases are present in the initial microstructures (see Figure 9). It would appear that the ‘SPC-I’ forms by homogenous nucleation.
4.6 Overall Impacts of Cooling Rate on Kinetics

The present study has demonstrated that the cooling rate of a molten oxide play a significant role in determining the nucleation and subsequent growth of phases, and the microstructures formed during oxide solidification. The phases formed during cooling differ from equilibrium cooling of the melts. The phases that did form were the same for all cooling rates studied. Even at the slowest cooling rate investigated, 0.01 K/s, equilibrium phases and microstructures were not observed. The sizes and shapes of microstructures were observed to vary with cooling rates, with a slower cooling rate typically resulting in coarser coupled microstructures and larger individual crystals. The proportions of microstructures was also observed to vary, with a larger proportion of coupled microstructures observed at slower cooling rates, suggested to result from a lower degree of undercooling prior to the nucleation of new phases.

Adding to the results of previous research [7, 8], the present study further demonstrates that nucleation and growth plays a key role in the formation of the microstructures during liquid cooling. Importantly, the SFC was not formed at any cooling rate. Rather, with a slower cooling rate, SFCA-I and Ca₇₂Fe²⁺₀.₈Fe³⁺₃₀O₅₃ were observed to nucleated homogenously and heterogeneously from the liquid. Peritectic reactions, anticipated from phase equilibria, were not observed under any of the cooling rates investigated.

5.0 Summary

The effects of cooling rate on the phase formation and the product microstructures formed from a liquid within the hematite primary phase field of the ternary "Fe₂O₃"-CaO-SiO₂ system in air have been determined for cooling rates between 2 K/s and 0.1 K/s. The principal phases formed on cooling were determined by EPMA to be Fe₂O₃, SFCA-I, Ca₇₂Fe²⁺₀.₈Fe³⁺₃₀O₅₃, C₂S, CF₂ and CF. The SFCA-I and Ca₇₂Fe²⁺₀.₈Fe³⁺₃₀O₅₃ phases were only formed at slow cooling rates.

The solidification sequence was found to be independent of cooling rate in the range investigated. However, the proportions of the microstructures and the dimensions of individual crystals were observed to vary with thermal history. A slower cooling rate was observed to result in larger and fewer individual crystals, and larger and coarser coupled microstructures. A slower cooling rate was observed to result in the liquid composition during cooling approaching equilibrium conditions more closely. However the SFC phase was not observed to form, with an intergrowth of SFC-I and Ca₇₂Fe³⁺₀.₈Fe³⁺₃₀O₅₃ forming in regions of liquid that were a significant distance from the surrounding hematite crystals.

The study clearly demonstrates the cooling rate of liquids influences the phase assemblages and microstructures formed on solidification of oxide liquids. The absence of equilibrium phases further emphasising that nucleation plays a significant role in the solidification of oxide liquids. This observation is significant in that it provides valuable insight into the key process sets taking place during industrial iron ore sintering, suggesting that the microstructure of industrial sinter can be changed by cooling rate.

6.0 Acknowledgements

The authors would like to thank the Australian Research Council Linkage Program and BHP for financial support to enable this research to be carried out, and to the Centre of Microstructure and Microanalysis (CMM), the University of Queensland for providing electron microscope facilities that enabled the microanalytical measurements to be undertaken. This research was supported by an
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Table 1: Liquid compositions measured by EPMA, formed by cooling a liquid from 1623 K (1350 °C) at 0.5 K/s

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Assemblage I (L+H)</th>
<th>Assemblage II (L+C₂S+H)</th>
<th>Assemblage III (L+C₂S+CF₂)</th>
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<td>CaO</td>
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Table 2: Liquid compositions measured by EPMA, formed by cooling a liquid from 1623 K (1350 °C) at 0.1 K/s

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<th>Temperature °C</th>
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<th>Assemblage II (L+C₂S+H)</th>
<th>Assemblage III (L+C₂S+CF₂)</th>
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References


Appendix D: Effect of Fe$_2$O$_3$ on the Controlled Solidification of “Fe$_2$O$_3$”-CaO-SiO$_2$ Liquidus in Iron Ore Sinter
Effect of the bulk Fe$_2$O$_3$ concentration on the controlled solidification of “Fe$_2$O$_3$”-CaO-SiO$_2$ liquids in air

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Abstract

The solidification of “Fe$_2$O$_3$”-CaO-SiO$_2$ liquids in air at a controlled cooling rate of 2.0 K/s for a range of Fe$_2$O$_3$ concentrations in the bulk was investigated. The bulk compositions investigated were within the hematite primary phase field and had a CaO/SiO$_2$ ratio of 3.46 wt/wt.

Non-equilibrium phase assemblages were formed for all bulk compositions investigated. Specifically, the silico ferrite of calcium (SFC) phase was not formed on cooling. The microstructures and proportions of the phase assemblages formed were found to vary with the Fe$_2$O$_3$ concentration in the bulk.

Keywords: Iron ore sinter; microstructure; solidification; “Fe$_2$O$_3$”-CaO-SiO$_2$, hematite

1.0 Introduction

The local bulk iron oxide concentrations in iron ore sinters can vary as a result of a range of factors; differences in the ore characteristics, such as mineralogy, grade, physical structure and heterogeneity within the packed bed due to granulation practice, distribution of other feeds, fluxes, return sinter and secondary oxides.

An improved understanding of the impact of the bulk iron concentration on the solidification processes taking place during sintering would be beneficial in assessing the impacts of this variability on the sinter phases and microstructures. In turn, this information can be taken into account when designing granulation and operating sintering processes.

The dominant iron oxide phases in sinter, hematite and magnetite, have been observed to form a range of different morphologies and phase associations within a single sinter sample [1]. These oxides have been broadly classified as primary, secondary and multi-component. The primary or relict hematite is the iron oxide material that is not dissolved during sintering, while the secondary hematite is formed on cooling the liquid [1] and oxidation of magnetite during cooling. The primary hematite is typically present as euhedral crystals or is granular in morphology, and the secondary hematite in the presence of liquid forms skeletal and rhombohedral crystals. It has been postulated that the different iron oxide morphologies and phase associations result in different sinter properties[1].

A series of studies have been undertaken to determine the stages and phase assemblages occurring during the solidification of “Fe$_2$O$_3$”-CaO-SiO$_2$ melts [2, 3] and the effects of cooling rate on the phases formed and the resulting microstructures on solidification of these melts [4].

In the present study, a systematic investigation of the effects of changing bulk Fe$_2$O$_3$ concentration, independent of other controllable parameters, on the microstructures and phases formed on cooling “Fe$_2$O$_3$”-CaO-SiO$_2$ melts at conditions relevant to iron ore sintering is described.
2.0 Experimental Technique

Details of the experimental technique used in this study have been reported in a previous publication by the authors[2]. The technique enables each stage of the solidification process to be identified and differentiated from the processes occurring during heating. The ability to rapidly quench the sample and to accurately capture the microstructures and phase compositions present at temperature are critical to the experimental design. The controlled cooling rates achievable with the new experimental technique are within the range of cooling rates measured in industrial iron ore sintering [5].

A pelletised oxide powder mixture (0.1 g, 6 mm diameter) supported on a substrate (70/30 Pt/Rh wire, 0.5 mm diameter) was heated and cooled in air in an electrically heated vertical tube furnace (alumina reaction tube, 38 mm OD 30 mm ID). The sample was vertically suspended within the reaction tube in the furnace from an alumina rod. The vertical position of the alumina rod, and in hence the position of the sample, was controlled with a positioning motor affixed to the top of the furnace. The sample is raised into the hot zone of the furnace, and the sample was held for four minutes at or above 1623 K (1350°C) for melting and homogenisation. After homogenisation, the sample was lowered down through the furnace with the use of a computer controlled motor drive to achieve a constant cooling rate. On reaching the target temperature the sample was quenched into water by releasing the sample, which falls under gravity into the quenching medium.

The quenched samples were characterised initially using optical microscopy for phase and microstructure identification using a reflected light microscope (Olympus Provis AX70TRF) and scanning electron microscopy (SEM) in back scattered electron mode (BSE). Phase compositions were measured by an electron probe X-ray microanalysis (EPMA) technique with wavelength dispersive spectroscopy (WDS) (JEOL 8200L EPMA; Japan Electron Optics Ltd., Tokyo, Japan). The EPMA was operated at a voltage of 15 keV and beam current of 20 nA. Three standards were used for calibration, pure CaSiO$_3$, Fe$_2$O$_3$, and Al$_2$O$_3$ (all standards from the Charles M. Taylor Co., Stanford, CA). The iron concentration in phases were recalculated to Fe$_2$O$_3$ for presentation purposes.

The phases present in the samples were confirmed with X-Ray Powder Diffraction (XRD). To enable these samples to be characterised, repeated experiments, cooling from 1623 K to 1073 K (1350°C to 800 °C) at 2 K/s, with 0.2 g of starting oxides were performed to obtain 1 g of material. The material was crushed and ground with an agate mortar and pestle. The resulting powder was analysed with powder X-Ray Diffraction (XRD) (Bruker D8), with a Cu Kα radiation source at a voltage of 40kV and a current of 40mA.

Three bulk oxide compositions were selected for investigation, 70.3 wt% Fe$_2$O$_3$ 72.7 wt% Fe$_2$O$_3$ [2] and 85.0 wt% Fe$_2$O$_3$, all with a CaO/SiO$_2$ ratio of 3.46 wt/wt; these bulk compositions are marked in Figure 1. The compositions were selected such that all were within the hematite primary phase field and at this CaO/SiO$_2$ ratio, it is anticipated that the silico ferrite of calcium (SFC) phase would form on equilibrium solidification at approximately 1529 K (1256 °C). Two compositions (70.3 wt% Fe$_2$O$_3$, 72.7 wt% Fe$_2$O$_3$) have a liquidus temperature of below 1623 K (1350 °C), while the third (85.0 wt% Fe$_2$O$_3$) has a liquidus temperature of approximately 1660 K (1385 °C). At the peak temperature of 1623 K (1350 °C), the samples containing 85 wt% Fe$_2$O$_3$ in the bulk, from the phase diagram, are estimated to consist of 23 wt% hematite and 77 wt% liquid.

The following sequence of solidification is predicted to occur for all three compositions under Scheil-Gulliver cooling; on cooling to 1529 K (1256 °C) the hematite primary phase is formed, from 1529 K (1256 °C) to 1508 K (1235 °C) SFC solidifies from the melt as the melt moves through the SFC primary phase field, the concurrent SFC and C$_2$S solidification occurs from 1508 K (1235 °C) to 1489 K (1216 °C) with the melt following the SFC-C$_2$S boundary line, the concurrent solidification of CF$_2$ and C$_2$S occurs
from 1489 K (1216 °C) and 1465 K (1192 °C) with the melt following the CF$_2$-C$_2$S boundary line and at 1465 K (1192 °C) the concurrent solidification of CF$_2$, CF and C$_2$S such that below this temperature no liquid remains.

Figure 1: Liquidus surface and bulk oxide compositions investigated (marked X) in the “Fe$_2$O$_3$”-CaO-SiO$_2$ system in air [6]

The experiments were performed in air, as sinter cooling at temperatures above the solidus in industrial processes has been measured to have a $p_{O_2}$ close to 0.21 [5] and phase equilibria data is available for the “Fe$_2$O$_3$”-CaO-SiO$_2$ system in air [6]. Samples were cooled from 1623 K to 1073 K at 2 K/s, with the cooling rate selected as this is typical of that encountered in industrial iron ore sintering processes [5].

### 3.0 Results

Initial experiments were undertaken with the three bulk compositions, cooled at 2 K/s from 1623 K to 1073 K (1350 °C to 800 °C). Within this temperature range and cooling rate range, complete solidification was found to have taken place for all compositions investigated. Examples of the typical phases and microstructures formed under the cooling conditions investigated are given in Figures 2 and 3.
Figure 2: a) Typical example of final solidified structure (1523 K to 1478 K, 2 K/s in air, 72.7 wt% Fe₂O₃ and CaO/SiO₂ ratio of 3.46 wt/wt) cooling in air at 2 K/s. (H - hematite, C₂S - 2CaO·SiO₂, CF₂ – CaO.2Fe₂O₃, CF – CaO.Fe₂O₃), b) detail of a) (Backscattered electron (BSE) micrograph)
Figure 3: Examples of typical microstructures observed in samples having a CaO/SiO$_2$ = 3.46 wt/wt, cooled in air at 2 K/s from 1623 K (1350°C) with a) 70.3 wt% Fe$_2$O$_3$ to 1073 K (800 °C), b) 72.7 wt% Fe$_2$O$_3$ to 1468 K (1195 °C) and c) 85.0 wt% Fe$_2$O$_3$ to 1468 K (1195 °C) (Backscattered Electron (BSE) Micrograph) (H-Hematite)

Using FE-SEM and EPMA measurements, the phases present in the samples were identified. In all samples, hematite (H, Fe$_2$O$_3$), dicalcium silicate (C$_2$S, 2CaO.SiO$_2$), calcium ferrite (CF, CaO.Fe$_2$O$_3$) and calcium diferrite (CF$_2$, CaO.2Fe$_2$O$_3$) were present. In addition, samples with a bulk composition containing 70.3 wt% Fe$_2$O$_3$ were also found to contain both the SFC-I and Ca$_{7.2}$Fe$_{2+0.8}$Fe$_{3+30}$O$_{53}$ phases. For simplicity, the SFC-I and Ca$_{7.2}$Fe$_{2+0.8}$Fe$_{3+30}$O$_{53}$ phases are hereafter referred to as ‘SFC-I’.

The phases present in the solidified samples differ from those anticipated under both equilibrium and Scheil-Gulliver cooling. SFC was not present in any of the microstructures formed. Hematite was present in samples containing 85.0 wt% and 70.3 wt% Fe$_2$O$_3$ in the bulk.

To provide a clear understanding of the sequences of reactions and processes occurring, a series of experiments were performed. These experiments were undertaken with samples cooled in air from the same starting temperature (1623 K) and the same cooling rate (2 K/s); the samples were then quenched from selected temperatures between 1533 K and 1453 K (1250 °C and 1180 °C).

Between the initial state and the final microstructure, the four intermediate stages of solidification were consistently observed for all three bulk compositions. These stages are as follows, liquid+H (Assemblage I), liquid+H+C$_2$S (Assemblage II), liquid+C$_2$S+CF$_2$ (Assemblage III) and finally C$_2$S+CF$_2$+CF (Assemblage IV). With a bulk composition containing 70.3 wt% Fe$_2$O$_3$, two additional phase assemblages were observed, liquid+‘SFC-I’ (Assemblage V) and liquid+‘SFC-I’+C$_2$S /liquid+CF$_2$+C$_2$S (Assemblage VI). In the regions containing ‘SFC-I’, Assemblage IV was observed to form following
Assemblage VI. The phase assemblages containing ‘SFC-I’ formed in regions free of hematite. As such, the formation of assemblage of V and VI is considered independent of assemblages I, II and III. The temperatures at which the different phase assemblages were observed are illustrated in Figure 4.

![Figure 4: Occurrence of assemblages with temperature during liquid solidification of “Fe$_2$O$_3$"-CaO-SiO$_2$ melts in air at 2 K/s (CaO/SiO$_2$ = 3.46 wt/wt).](image)

### 3.1 Liquid composition variation with temperature and bulk Fe$_2$O$_3$ concentration

In the current study, the compositions of the liquids at selected temperatures were measured with EPMA, with the measured liquid compositions shown in Figure 5 and given in Tables 1, 2 and 3. For all bulk Fe$_2$O$_3$ compositions studied, the same trends in liquid composition during cooling were observed.
The initial solidification of isolated hematite (Assemblage I) resulted in the liquid composition moving through the hematite and SFC primary phase fields and into the C$_2$S primary phase field. In regions isolated from hematite, only present when the bulk composition was low in Fe$_2$O$_3$, the SFC-I (Assemblage V) was observed to form part way through the solidification of hematite (Assemblage I). During the formation of ‘SFC-I’, the liquid composition in these regions also moved through the SFC primary phase field and into the C$_2$S primary phase field. At the conclusion of Assemblages I and V, the liquid composition was observed to be within the C$_2$S primary phase field. Once C$_2$S formed, resulting in the occurrence assemblages II (L+H+C$_2$S) and VI (L+C$_2$S +‘SFC-I’ /L+C$_2$S +CF$_2$), the liquid composition moved towards the CF$_2$ primary phase field with decreasing temperature. This solidification of C$_2$S, Hematite and/or ‘SFC-I’ continued until the liquid reached the CF$_2$ primary phase field. With the nucleation of CF$_2$, assemblage III (L+C$_2$S +CF$_2$) is formed. The final phase assemblage, C$_2$S+CF$_2$+CF, formed after assemblages III and VI. The relationship between the sequence of formation of the six phase assemblages is shown in Figure 6.
Figure 6: Observed sequences of phase assemblage formation from \textquotedblleft Fe$_2$O$_3$\textquotedblright\textsuperscript{-}CaO-SiO$_2$ melts in air. note: while two pathways are possible, only under specific situations can both occur concurrently. In this study, two pathways were only observed at 70.3 wt\% Fe$_2$O$_3$.

The phases and microstructures obtained on solidification differed to those predicted under equilibrium and Scheil Gulliver cooling, specifically:

- SFC was not formed in any of the samples investigated
- Liquid undercooling occurred prior to the nucleation of phases
- The peritectic reactions (L+H$\rightarrow$L+SFC, L+SFC$\rightarrow$L+CF$_2$) did not take place
- ‘SFC-I’ was observed to form on solidification of a melt with 70.3 wt\% Fe$_2$O$_3$ in the bulk
- The solidification sequences and microstructures formed are dependent on the pre-existing phases

### 3.2 Liquid + Hematite (Assemblage I)

The formation of hematite, assemblage I (L+H), was the first phase assemblage observed on cooling, for all compositions investigated in the present study. Figure 7 shows micrographs of the typical hematite primary phase microstructures. At a high bulk Fe$_2$O$_3$ composition (85.0 wt\%), Assemblage I was observed to transition to assemblage II at lower temperatures, down to 1478 K (1205 °C), compared to the formation for low (70.3 wt\%) and medium (72.7 wt\%) bulk Fe$_2$O$_3$ compositions.
The hematite was observed to form two types of crystals, faceted dendritic (skeletal) crystals at 70.3 wt% and 72.7 wt% bulk Fe₂O₃ concentrations and individual faceted crystals, typically euhedral equiaxed, at 85.0 wt% Fe₂O₃ in the bulk. At low bulk Fe₂O₃ concentrations, a larger proportion of hematite was observed to be present near the platinum substrate. Note the dendritic side arms are only formed in the 70.3 wt% and 72.7 wt% Fe₂O₃ samples. No side arms were observed to form on the hematite in the 85.0 wt% Fe₂O₃ samples despite cooling under the same conditions.

At 85.0 wt% Fe₂O₃ in the bulk, the hematite was relatively evenly distributed through the liquid. The crystals themselves were approximately 30 μm in width and length. It was confirmed experimentally that these crystals were present at the peak temperature of 1623 K (1350 °C).

At 70.3 wt% and 72.7 wt% Fe₂O₃ in the bulk, the hematite was observed to be in the form of dendritic crystals, heterogeneously distributed throughout the liquid. With a decrease in hematite concentration from 72.7 wt% to 70.3 wt%, the temperature at which hematite nucleated and the proportion of hematite formed decreased. In addition, the length of the hematite crystals and dendrite arm length decreased, from 100 μm to 30 μm and from 10 μm to 4 μm respectively with decreasing from 72.7 wt% to 70.3 wt% Fe₂O₃ in the bulk.
Based on the melt composition along the C2S-SFC boundary line at 1508 K (1235 °C), estimated as the point at which Assemblage I transitions into Assemblage II, the proportion of hematite solidifying at this stage can be predicted. At a high (85.0 wt%) Fe₂O₃ bulk composition, it is estimated that at the end of the formation of Assemblage I the system contains 45.5 wt% liquid and 54.5 wt% hematite. At a 72.7 wt% and 70.3 wt% Fe₂O₃ bulk composition, it is estimated that the system contains 9.6 wt% and 17.4 wt% hematite respectively prior to the formation of Assemblage II.

### 3.3 Liquid + Hematite + C₂S (Assemblage II)

Assemblage II is additive to Assemblage I, occurring with the nucleation and growth of C₂S. Figure 8 shows micrographs typical of this phase assemblage.
Figure 8: Examples of typical microstructures observed in Assemblage II (L+H+C$_2$S), sample cooled from 1623 K (1350 °C) to 1493 K (1220 °C) at 2 K/s and with a CaO/SiO$_2$ = 3.46 wt/wt, containing a) 70.3 wt%, b) 72.7 wt% and c) 85.0 wt% Fe$_2$O$_3$ (L-liquid, H-Hematite, C-C$_2$S) (BSE Micrographs)

For all bulk Fe$_2$O$_3$ compositions investigated, the C$_2$S was observed in three phase assemblages, a thin layer on the primary hematite (IIa), individual C$_2$S dendrites (IIb) and a coupled H-C$_2$S microstructure (IIc) (See Figure 9). The proportions of the three microstructures were observed to vary with bulk Fe$_2$O$_3$ composition. The proportion of the coupled H-C$_2$S microstructure increased with a decreased bulk Fe$_2$O$_3$ concentrations, in agreement with the metastable H-C$_2$S equilibrium and mass balances. The thickness of the thin C$_2$S layer on the primary hematite (IIa) was not observed to vary with the bulk Fe$_2$O$_3$ composition. The fraction of this microstructure type (IIa) was typically proportional to the interfacial area of the hematite exposed to the melt.

At 85.0 wt% Fe$_2$O$_3$ in the bulk, the C$_2$S phase formed in the limited free volume between the hematite crystals. The C$_2$S was observed to form all three microstructures, but due to the small free volume, the size of the C$_2$S crystals was constrained. A larger number of individual C$_2$S crystals (IIb) were observed to form, but of a smaller size, when compared to lower bulk Fe$_2$O$_3$ compositions.
At 70.3 wt% Fe$_2$O$_3$ in the bulk, the coupled H-C$_2$S was either associated with the thin C$_2$S layer (IIa) or individual C$_2$S crystals (IIb), as illustrated by Figure 10. The coupled H-C$_2$S (IIc) microstructure associated with the individual C$_2$S crystals was observed to form in regions free of the individual hematite crystals.
3.4 Liquid + C₂S + CF₂ (Assemblage III)

Phase assemblage III (L+C₂S+CF₂) was observed to form at all bulk Fe₂O₃ compositions, with two microstructures forming, individual CF₂ crystals (IIIa) and the coupled C₂S-CF₂ microstructure (IIIb) (See Figure 13). The temperatures at which this phase assemblage was observed varied with the bulk Fe₂O₃ composition. Figure 12 shows micrographs typical of this phase assemblage.

For all bulk Fe₂O₃ compositions, the individual CF₂ crystals were observed to be associated with the hematite, nucleating heterogeneously on this phase. The coupled C₂S-CF₂ (IIIb) microstructure was consistently observed to form on the individual CF₂ crystals. With a decrease in the bulk Fe₂O₃ composition, the proportion of liquid observed prior to the formation of CF₂ increased along with the proportion of CF₂ forming in assemblage III (see Figures 13 and 14).
As the proportion of Fe$_2$O$_3$ decreased in the bulk, the volume of the liquid phase from which CF$_2$ was able to form increased. This was associated with the observation of longer individual CF$_2$ crystals and a larger volume of coupled C$_2$S-CF$_2$ (IIIb) microstructures. Similarly, the proportion of the coupled C$_2$S-CF$_2$ (IIIb) microstructure, relative to the other C$_2$S containing microstructures, increased with decreasing bulk Fe$_2$O$_3$ concentration.

### 3.5 C$_2$S + CF$_2$ + CF (Assemblage IV)

For all bulk Fe$_2$O$_3$ concentrations, individual CF crystals (IVa), coupled C$_2$S-CF (IVb) and a coupled C$_2$S-CF-CF$_2$ microstructure (IVc), were observed to form in Assemblage IV (see Figure 15). The occurrence of the two CF containing coupled microstructures was confirmed via line analysis with EPMA [2]. Assemblage IV is considered additive to both Assemblage III and Assemblage VI. Typical microstructures of this phase assemblage is shown in Figure 15.
With a decrease in the bulk Fe$_2$O$_3$ concentrations, the proportion of liquid solidifying during the formation of Assemblage IV increased. A higher bulk Fe$_2$O$_3$ concentration resulted in smaller but more numerous crystals forming. The solids formed in this assemblage were constrained in shape and size by the solids that had formed at higher temperatures.

The proportion of CF solidifying as individual crystals was also observed to increase with an increase in the bulk Fe$_2$O$_3$ composition. At high bulk Fe$_2$O$_3$ compositions, the coupled microstructures were a smaller proportion of the solidified material in Assemblage IV.

### 3.6 Liquid + ‘SFC-I’ (Assemblage V)

This phase assemblage was only observed in the samples with a low bulk Fe$_2$O$_3$ concentration (70.3 wt% Fe$_2$O$_3$), forming at temperatures below 1513 K (1230 °C). The ‘SFC-I’ was observed to form concurrently with Assemblage I, originating in regions free of hematite crystals, as illustrated in Figure 16.

The phases present in the ‘SFC-I’ crystals were confirmed using XRD. Samples for XRD were prepared by cooling 0.2 g samples from 1623 K to 1073 K (1350 °C to 800 °C) at 2 K/s to obtain 1.5 g of powder. The XRD pattern obtained between 5° and 15° 2θ were used to identify the phases present by comparison with known XRD patterns for SFCA [7], SFCA-I [8] and Ca$_{7.2}$Fe$_{2.2}^2$Fe$_{0.8}^{3+}$O$_{53}$ [9]. The XRD
pattern, as shown in Figure 16, indicated that the ‘SFC-I’ crystals consisted of both the SFC-I and Ca_{7.2}Fe_{0.8}Fe_{30}O_{53} phases but no SFC was present. Difficulty was experienced in determining the phases present due to the low proportion of these phases present in this material. Further determination based on crystal composition was required for phase identification.

![Figure 17: XRD pattern obtained from material cooled from 1623 K (1350 °C) to 1073 K (800 °C) at 2 K/s with 70.3 wt% Fe_{2}O_{3} and a CaO/SiO_{2} = 3.46 wt/wt in the bulk (Cu Kα).](image)

The ‘SFC-I’ individual crystals were observed to be distributed evenly in areas free of hematite, at least 100 μm from this phase. The ‘SFC-I’ crystals were consistently observed as single crystals, approximately 200 μm long and 10 μm wide, with branching side arms. The composition of the ‘SFC-I’ crystals were measured by EPMA, with the composition measured to be approximately 82.2 wt% Fe_{2}O_{3}, 2.9 wt% SiO_{2} and 14.9 wt% CaO. Compared to that previously reported to form on cooling a liquid at 2 K/s with a CaO/SiO_{2} ratio of 4.0 wt/wt and 69.24 wt% Fe_{2}O_{3} [3], the bulk ‘SFC-I’ composition is higher in SiO_{2} and the SFCA-I XRD peak is higher than the Ca_{7.2}Fe_{0.8}Fe_{30}O_{53} peak. Based on the composition of the ‘SFC-I’ crystals, as measured by EPMA, the proportion of the silica free SFC-I in these crystals is 90% by mass, with the balance Ca_{7.2}Fe^{2+}Fe^{3+}_{30}O_{53}.

### 3.7 Liquid + C_{2}S + ‘SFC-I’/Liquid + C_{2}S + CF_{2}
(Asssemblage VI)

Assemblage VI was observed to form following Assemblage V, concurrently with Assemblage II. The two phase assemblages both required the nucleation and growth of C_{2}S. As previously reported [3], four phase assemblages were observed, individual C_{2}S crystals (VIa), coupled C_{2}S-‘SFC-I’ (VIb) individual CF_{2} crystals (VIc) and coupled C_{2}S-CF_{2} crystals (VId). Figure 18 shows a micrograph illustrating this phase assemblage.
Figure 18: Typical microstructures observed in samples cooled from 1623 K (1350 °C) to 1463 K (1190 °C) at 2 K/s in air with 70.3 wt% Fe$_2$O$_3$ and a CaO/SiO$_2$ = 3.46 wt/wt. (BSE Micrograph)

Using EPMA line analysis, as previously described [3], the presence of the four microstructures was confirmed. The individual C$_2$S crystals (Vla) appear to form on the individual SFC-I crystals or as isolated crystals in the liquid as unfaceted crystals (5 μm width and 30 μm length). The coupled C$_2$S-'SFC-I' microstructure (Vlb) is observed in close association with the individual C$_2$S crystals (Vla) and the individual 'SFC-I' crystals (V). The C$_2$S-CF$_2$ coupled microstructure (Vlc) was isolated from the SFC-I phase by unfaceted individual CF$_2$ crystals (Vld). Based on the occurrence and separation of the two coupled microstructures, the first coupled microstructure to form is the C$_2$S-'SFC-I' coupled microstructure (Vlb), followed by the individual CF$_2$ crystals (Vlc) and lastly the coupled C$_2$S-CF$_2$ microstructure (Vld) in contact with the liquid.

4.0 Discussion

4.1 Formation of Assemblage I (L+H)

This phase assemblage was the first to be observed upon cooling the liquid. As the proportion of Fe$_2$O$_3$ in the bulk is increased, the temperature at which the phase assemblage was first observed increased. Consistent with the liquidus, at high Fe$_2$O$_3$ compositions (85.0 wt% Fe$_2$O$_3$), the hematite was present at the peak temperature 1523K (1350 °C), while for the samples with 70.3 wt% and 72.7 wt% Fe$_2$O$_3$ in the bulk, hematite formed on cooling. Hematite formed on cooling was observed to be dendritic in structure, while that present at temperature was euhedral equiaxed.

At 85.0 wt% Fe$_2$O$_3$ in the bulk, the samples contained hematite at all stages, heating, peak temperature and cooling. As the sample were heated, the fine oxides reacted, melted and dissolved to form a homogenous liquid and hematite crystals. The hematite crystals were evenly distributed through the liquid, initially small in size. At temperature, the hematite crystals would have undergone grain growth via Ostwald ripening to decrease the surface free energy of the system. As such, the hematite crystals grew as individual faceted crystals rather than forming dendrites as observed at lower bulk Fe$_2$O$_3$ concentrations.

For samples heated above the liquidus, the hematite nucleated homogeneously in the liquid or heterogeneously on the platinum wire or at the gas/liquid interface. With lower bulk Fe$_2$O$_3$ concentrations, the temperatures at which hematite nucleated decreased, leading to the initial formation and growth of dendrites occurring at lower temperatures. This in turn results in the formation of finer dendrite branches, due to a decrease in the rates of mass transfer in the liquid phase.
The proportion of hematite present at the conclusion of assemblage I increased with increasing Fe$_2$O$_3$ in the bulk, impacting the formation of subsequent assemblages.

### 4.2 Formation of Assemblage II (L+C$_2$S+H)

Assemblage II is additive to Assemblage I, with new microstructures forming on the existing solids [2]. Analysis of the liquid compositions present in the later stages of Assemblage I shows that the melt is undercooled with respect to C$_2$S. Once nucleated, the C$_2$S rapidly solidifies due to the supercooling, with a C$_2$S layer (IIa) forming on the hematite followed by individual C$_2$S crystals (IIb). Due to the rapid solidification of C$_2$S, the liquid composition moves directly away from the C$_2$S composition and towards the C$_2$S-SFC boundary line. Solidification continues to occur with the formation of the coupled H-C$_2$S microstructure (IIc), developing from the previously formed C$_2$S crystals. The H-C$_2$S structure is metastable since the SFC phase is not formed. At the final stages of this assemblage, the liquid composition has moved into the CF$_2$ primary phase field, becoming undercooled with respect to this phase.

Based on the melt composition at the SFC-CF$_2$-C$_2$S invariant point [6], taken as the point at which Assemblage II transitions into Assemblage III, the proportion of hematite and C$_2$S at the end of the formation of Assemblage III can be predicted. At a high (85.0 wt%) Fe$_2$O$_3$ bulk composition, it is estimated that the system contains 29.4 wt% liquid, 64.3 wt% hematite and 6.3 wt% C$_2$S. At medium (72.7 wt%) and low (70.3 wt%) Fe$_2$O$_3$ bulk compositions, it is estimated that the system contains 35.8 wt% and 29.5 wt% hematite respectively and 11.5 wt% and 12.5 wt% C$_2$S respectively, prior to the formation of Assemblage III.

At high Fe$_2$O$_3$, the C$_2$S was observed to primarily form as individual C$_2$S crystals (IIb). This microstructure is associated with hematite, suggesting that increasing the proportion of hematite increases the probability of C$_2$S nucleation at higher temperatures. The individual C$_2$S crystals were constrained by the existing hematite solids, limiting the length of the dendrites formed. The limited free volume for solidification and the short distance between C$_2$S and hematite, increased the likelihood of the divorced solidification of C$_2$S and hematite rather than the coupled solidification of C$_2$S and hematite.

With a decrease in the bulk Fe$_2$O$_3$ concentrations, the proportion of C$_2$S forming in the initial stages of solidification increased. However, due to the limited solidification of hematite in Assemblage I, there was a decrease in the surfaces on which C$_2$S was able to nucleate in association with. Both of these factors were potential contributors to the formation of C$_2$S dendrites in the liquid. At low bulk Fe$_2$O$_3$ concentrations, the proportion of the coupled C$_2$S-hematite microstructure (IIc) increased.

### 4.3 Formation of Assemblage III (L+C$_2$S+CF$_2$)

Assemblage III consisted of individual CF$_2$ crystals (IIIa) and a coupled C$_2$S-CF$_2$ microstructure (IIIB), with formation occurring in that order. The individual CF$_2$ crystals (IIIa) heterogeneously nucleated on hematite, occurring in a liquid undercooled with respect to CF$_2$. The C$_2$S-CF$_2$ coupled microstructure (IIIB) subsequently formed, with solidification of this coupled microstructure moving the liquid composition along the C$_2$S-CF$_2$ boundary line and towards the ternary C$_2$S-CF$_2$-CF eutectic invariant point.

With the variation of Fe$_2$O$_3$ in the bulk, the proportion of material solidifying in Assemblage III and the resulting microstructures are changed. Assuming that the melt composition at the end of the formation of Assemblage II coincided with the SFC-C$_2$S-CF$_2$ ternary invariant point (1215 °C, 1488 K) and the end of the formation of Assemblage III coincided with the C$_2$S-CF$_2$-CF ternary invariant point (1192 °C, 1465 K), the proportion of melt solidifying can be calculated. At a bulk Fe$_2$O$_3$ concentration
of 85.0 wt%, the liquid present decreased from 29.4 wt% to 19.3 wt% of the bulk as a result of the formation of Assemblage III. Similarly, the proportion of liquid present in samples with 70.3 wt% and 72.7 wt% Fe$_2$O$_3$ in the bulk decreased from 53.1 wt% to 34.8 wt% and 58.0 wt% to 38.0 wt% respectively between the two invariant points.

With an increase in Fe$_2$O$_3$ in the bulk from 70.25 wt% to 85.0 wt%, the proportion of material solidified in Assemblage III decreased from 20 wt% to 10 wt%. This resulted in a decrease in the size of the CF$_2$ crystals and the proportion of the coupled C$_2$S-CF$_2$ (IIIb) microstructure. The CF$_2$ crystals were constrained by the previously solidified material, reducing the size to which they could grow.

With a decrease in the bulk Fe$_2$O$_3$ concentration, the proportion of coupled C$_2$S-CF$_2$ (IIIb) relative to individual CF$_2$ (IIIa) crystals increased. This indicates that under these conditions the divorced solidification of C$_2$S and CF$_2$ was less favourable than coupled solidification. This is potentially a result of the long distances over which diffusion was required for solidification to occur.

### 4.4 Formation of Assemblage IV (C$_2$S+CF$_2$+CF)

The formation of Assemblage IV is considered additive to both assemblage III and VI. The formation of Assemblage IV comprises of three steps. Individual crystals of CF (IVa) formed first, solidifying from a liquid undercooled with respect to CF. This was followed by the formation of the C$_2$S-CF$_2$ coupled microstructure (IVb), which forms via a coupled growth mechanism. Finally the C$_2$S-CF$_2$-CF coupled microstructure (IVc) occurs, solidifying the remaining liquid as a ternary eutectic.

As with Assemblage III, the variation of Fe$_2$O$_3$ in the bulk resulted in a change in the proportion of material solidifying in this phase assemblage. An increase in Fe$_2$O$_3$ in the bulk resulted in the decrease in the proportion of material solidifying in Assemblage IV. This led to a decrease in the size of the CF crystals and the proportion of the coupled C$_2$S-CF (IVb) and C$_2$S-CF$_2$-CF (IVc) microstructures relative to the total.

### 4.5 Formation of Assemblage V (L+‘SFC-I’)

During the solidification of hematite at a low (70.3 wt%) bulk Fe$_2$O$_3$ concentration, ‘SFC-I’ was observed to nucleate homogenously in regions free of hematite. This resulted in the occurrence and formation of Assemblage V. These crystals formed during the solidification of hematite in Assemblage I, with the two assemblages (I and V) forming in separate regions of the samples and following different solidification pathways as illustrated in Figure 6. As previously reported[3], the individual ‘SFC-I’ crystals appear to form through heterogeneous nucleation on the platinum substrate and at the liquid-gas interface and later homogenously in the liquid. Once nucleated, the ‘SFC-I’ crystals grow as the temperature is decreased, with the number of ‘SFC-I’ crystals increasing with decreasing temperature through subdivision and heterogeneous nucleation on existing ‘SFC-I’ crystals. The individual ‘SFC-I’ crystals appear to be in the form of intergrowths of SFC-I and Ca$_{7.2}$Fe$_2$Fe$_{0.8}$Fe$_{30}$O$_{53}$. The ‘SFC-I’ continued to solidify until the liquid was undercooled with respect to C$_2$S

Based on the concurrent formation of two separate Assemblages in separate regions, it appears that the heterogenous homogenous nucleation of the ‘SFC-I’ is unlikely to occur in close proximity to hematite. The two phases, hematite and ‘SFC-I’, are both in a metastable state yet continue to form on cooling under the same conditions.

### 4.6 Formation of Assemblage VI (L+C$_2$S+’SFC-I’/L+C$_2$S+CF$_2$)
Assemblage VI was only observed in the samples with a low (70.3 wt%) bulk Fe₂O₃ concentration. The formation of this phase assemblage is dependent on the prior formation of Assemblage V. As such, the proportion of Assemblage VI will increase under conditions that favour the formation of Assemblage V.

This phase assemblage is considered additive to Assemblage V and independent of Assemblage I, II and III. It suggested that this phase assemblage formed in two stages, first C₃S-SFC-I solidification and second C₃S-CF₂ solidification.

4.7 Overall impacts of the bulk Fe₂O₃ compositions on solidification

The results of the current study have demonstrated that the proportion of Fe₂O₃ in the bulk has a significant impact on the phases, assemblages and microstructures present when oxide liquids are solidified. While the process conditions were identical for the three bulk Fe₂O₃ compositions examined, the proportion and appearance of the phase assemblages varied. Consistent with previous research [2, 3], the phase assemblages formed are significantly differs from those formed under equilibrium and Scheill-Gulliver cooling.

In the system investigated, it has been demonstrated that the bulk Fe₂O₃ composition influenced the morphology and proportion of the hematite phase formed during the initial stages of solidification. When hematite is present at the peak temperature, the crystals were observed to be euhedral equiaxed, as opposed to forming dendritic structures when formed on cooling. With an increase in the bulk Fe₂O₃ concentration, the proportion of hematite crystals present in the microstructures increased as did the size and number of crystals.

The hematite phase, which is retained as a metastable phase on cooling, was also observed to influence the solidification of subsequent microstructures. Increasing the concentration of hematite in the bulk resulted in an increase in the proportion of hematite present and a decrease in the volume of the liquid phase from which subsequent microstructures were formed. This led to a decrease in the proportion of coupled microstructures compared to the individual crystals.

A decrease in the volume fraction of hematite formed during cooling was associated with the formation of SFC-I and Ca₇.₂Fe₀.₈Fe₃₀O₅₃ in regions free of hematite. Based on this observation, it is suggested that the nucleation of SFCA-I and SFCA in industrial sinter is unlikely occur in close proximity to hematite. This observation provides a valuable insight into the impact of Fe₂O₃ variation, both within the bulk material and due to the heterogeneity of the sintered material, on the microstructures formed.

5.0 Summary

The effects of changes to the bulk Fe₂O₃ concentration on the solidification processes and microstructures formed on cooling liquids in the “Fe₂O₃”-CaO-SiO₂ system in air have been determined in the high Fe₂O₃ region of this system.

This is the first study that shows that the proportion of iron present in sinter influences the microstructures formed in sinter. This suggests that there is the potential for an optimal iron content to maximise the sinter strength and properties.
Samples of a bulk composition with a CaO/SiO$_2$ ratio of 3.46 and 70.3 wt%, 72.7 wt% and 85.0 wt% Fe$_2$O$_3$ were cooled at 2 K/s from 1623 K (1350 °C) to 1453 K (1180 °C). The phases formed and processes occurring during cooling were identified and have been shown to differ from those predicted under equilibrium cooling. The phases formed were, in order of formation, hematite (Fe$_2$O$_3$), dicalcium silicate (Ca$_2$SiO$_4$), calcium diferrite (CaFe$_4$O$_7$) and calcium ferrite (CaFe$_2$O$_4$). At low bulk Fe$_2$O$_3$ compositions (70.3 wt%), SFC-I and Ca$_7.2$Fe$_{2+0.8}$Fe$_{3+0.2}$O$_{53}$ were also observed to form at selected conditions. The SFC phase did not form on cooling these materials.

The proportion of Fe$_2$O$_3$ in the bulk melt is shown to influence the proportion of hematite in the final structure and the morphology of the hematite phase formed on cooling. The changes in the proportion of metastable hematite formed changes the proportion of liquid present at any temperature, the proportion of other phases present and the microstructures present in the final material. With a decrease of the bulk Fe$_2$O$_3$ concentration, the proportion of hematite formed on cooling decreased and the proportion of coupled microstructures relative to individual crystals increased. At low bulk Fe$_2$O$_3$ compositions, the SFC-I and Ca$_{7.2}$Fe$_{2+0.8}$Fe$_{3+0.2}$O$_{53}$ phases were observed to form in regions free of hematite.

### 6.0 Acknowledgements

The authors would like to thank the Australian Research Council Linkage grant scheme and BHP for financial support to enable this research to be carried out, and to the Centre of Microstructure and Microanalysis (CMM), the University of Queensland for providing electron microscope facilities that enabled the microanalytical measurements to be undertaken. This research was supported by an Education Endowment Fund (EEF) scholarship from the Australasian Institute of Mining and Metallurgy (AusIMM) and an Australian Government Research Training Program (RTP) Scholarship.

**Table 1:** Liquid compositions in microstructures containing Hematite, as measured by EPMA, formed by cooling a liquid with 70.3 wt% Fe$_2$O$_3$ from 1623 K at 2 K/s

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<tr>
<th>Temperature (°C)</th>
<th>Assemblage I (L+H)</th>
<th>Assemblage II (L+H+C$_2$S)</th>
<th>Assemblage III (L+C$_2$S+CF$_2$)</th>
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Table 2: Liquid compositions in microstructures containing Hematite, as measured by EPMA, formed by cooling a liquid with 85.0 wt% Fe$_2$O$_3$ from 1623 K at 2 K/s

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<tr>
<th>Temperature (°C)</th>
<th>Assemblage I (L+H)</th>
<th>Assemblage II (L+H+C$_2$S)</th>
<th>Assemblage III (L+C$_2$S+CF$_2$)</th>
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Table 3: Liquid compositions in microstructures containing ‘SFC-I’, as measured by EPMA, formed by cooling a liquid with 70.3 wt% Fe$_2$O$_3$ from 1623 K at 2 K/s

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Assemblage V (L+‘SFC-I’)</th>
<th>Assemblage VI (L+‘SFC-I’/CF$_2$+C$_2$S)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe$_2$O$_3$ (wt%)</td>
<td>SiO$_2$ (wt%)</td>
</tr>
<tr>
<td>1240</td>
<td>62.0</td>
<td>9.1</td>
</tr>
<tr>
<td>1235</td>
<td>60.9</td>
<td>9.5</td>
</tr>
<tr>
<td>1230</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1225</td>
<td>65.5</td>
<td>7.8</td>
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<tr>
<td>1220</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1215</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1210</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1205</td>
<td>63.7</td>
<td>8.7</td>
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<tr>
<td>1200</td>
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<tr>
<td>1195</td>
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<td>-</td>
</tr>
<tr>
<td>1190</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1185</td>
<td>64.4</td>
<td>8.1</td>
</tr>
</tbody>
</table>
References

3. Nicol, S., E. Jak, and P. Hayes, Controlled solidification of liquids within the SFC primary phase field of the \( \text{Fe}_2\text{O}_3\)-\( \text{CaO-SiO}_2 \) system in air. Met. Trans. B, 2019, in press.
4. Nicol, S., E. Jak, and P. Hayes, Effect of cooling rate on the controlled solidification of \( \text{Fe}_2\text{O}_3\)-\( \text{CaO-SiO}_2 \) liquids in synthetic iron ore sinter. ISIJ Int., 2019, in press.
8. Mumme, W., J. Clout, and R. Gable, The crystal structure of SFCa-I, \( \text{Ca}_{3.18}\text{Fe}_{3+14.66}\text{Al}_{1.34}\text{Fe}_{2+0.82}\text{O}_{20} \) a homologue of the aenigmatite structure type, and new crystal structure refinements of \( \beta\)-CFF, \( \text{Ca}_{2.99}\text{Fe}_{3+14.30}\text{Fe}_{2+0.55}\text{O}_{25} \) and Mg-free SFCa, \( \text{Ca}_{2.45}\text{Fe}_{3+9.04}\text{Al}_{1.74}\text{Si}_{0.6}\text{O}_{20} \). Neues Jahrb. Mineral., Abh., 1998: p. 93-117.
Appendix E: Effect of CaO/SiO$_2$ Ratio on the Controlled Solidification of “Fe$_2$O$_3$”-CaO-SiO$_2$ Liquidus in Iron Ore Sinter
Effect of the CaO/SiO\textsubscript{2} ratio on the controlled solidification of “Fe\textsubscript{2}O\textsubscript{3}”-CaO-SiO\textsubscript{2} liquids in air

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Abstract

The solidification of liquids having bulk compositions in the high iron region of the “Fe\textsubscript{2}O\textsubscript{3}”-CaO-SiO\textsubscript{2} system having selected CaO/SiO\textsubscript{2} ratios has been investigated. The compositions investigated were selected such that the bulk compositions were within the hematite primary phase field, fully liquid at temperature (1573 K, 1350 °C) and pass through the SFC primary phase field on cooling. Specifically, three CaO/SiO\textsubscript{2} ratios (wt/wt) were investigated, 2.78, 3.46[1] and 4.75 with bulk compositions comprising 69.23, 72.74 and 74.94 wt% Fe\textsubscript{2}O\textsubscript{3} respectively. The phases present and their composition was determined with electron probe microanalysis (EPMA) and X-ray diffraction (XRD). During cooling, four stages of solidification were observed at all three CaO/SiO\textsubscript{2} ratios, and an additional two stages at the highest CaO/SiO\textsubscript{2} ratio. Non-equilibrium phase and liquidus compositions were observed. The phases formed were hematite, dicalcium silicate (C\textsubscript{2}S), calcium diferrite (CF\textsubscript{2}), calcium ferrite (CF), silico ferrite of calcium I (SFC-I) and Ca\textsubscript{7.2}Fe\textsuperscript{2+}\textsubscript{0.8}Fe\textsuperscript{3+}\textsubscript{30}O\textsubscript{53}.

Significantly, the silico ferrite of calcium phase (SFC) was not observed in any of the samples, although the formation of this phase was anticipated from phase equilibrium considerations.

Keywords: Iron ore sinter; microstructure; “Fe\textsubscript{2}O\textsubscript{3}”-CaO-SiO\textsubscript{2}, solidification, SFC

1.0 Introduction

Iron ore sinter is the principal feed material to the blast furnace, from which approximately a billion tonnes of iron are currently produced annually. To produce the iron oxide sinter, iron oxide rich fines are blended with fluxes, predominantly CaO containing materials. This blended material is subsequently processed using the Dwight-Lloyd sintering process to produce a coarse competent feed for the blast furnace. The CaO added reacts with the other chemical components in the feed, predominantly SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3} and Fe\textsubscript{2}O\textsubscript{3}, to form new phases and microstructures [2, 3]. It has been shown that the CaO/SiO\textsubscript{2} ratio influences the sinter properties and the performance of the blast furnace [3, 4].

The addition of CaO to iron oxide sintering operations has been observed to lead to the formation of a variety of calcium ferrite phases, including silico ferrites of calcium and aluminium. Previous research has shown that these phases are able to form through solid state reactions and by solidification from the liquid oxide on cooling [5].

A series of studies have been undertaken to determine the processes occurring during the solidification of “Fe\textsubscript{2}O\textsubscript{3}”-CaO-SiO\textsubscript{2} melts in air [1, 6] and to examine the effects of cooling rate [7] and bulk Fe\textsubscript{2}O\textsubscript{3} concentration [8] on the phases formed and the resulting microstructures on solidification of these melts.

In the present study of the “Fe\textsubscript{2}O\textsubscript{3}”-CaO-SiO\textsubscript{2} system in air, a systematic investigation of the effects of the bulk CaO/SiO\textsubscript{2} ratio on the microstructures and phases formed on cooling at conditions relevant to iron ore sintering is reported.
2.0 Experimental Technique

Details of the experimental technique used in this study have been reported in a previous publication by the authors [1]. The technique enables each stage of the solidification process to be identified and differentiated from the processes occurring during heating. The ability to rapidly quench the sample and to accurately capture the microstructures and phase compositions present at temperature are critical to the experimental design. The controlled cooling rates achievable with the new experimental technique are within the range of cooling rates measured in industrial iron ore sintering processes [9].

A pelleted oxide powder mixture (0.1 g, 6 mm ø) supported on a substrate (70/30 Pt/Rh wire, 0.5mm ø) was heated and cooled in air in an electrically heated vertical tube furnace (alumina reaction tube, 38mm OD 30mm ID). The sample was vertically suspended within the reaction tube in the furnace from an alumina rod. The vertical position of the alumina rod, and hence the position of the sample, was controlled with a positioning motor affixed to the top of the furnace. The sample was raised into the hot zone of the furnace, and the sample was held for four minutes at or above 1623 K (1350 °C) for melting and homogenisation. After homogenisation, the sample was lowered down through the furnace with the use of a computer controlled motor drive to achieve a constant cooling rate. On reaching the target temperature the sample was quenched into water by releasing the sample, which falls under gravity into the quenching medium.

The quenched samples were characterised initially using optical microscopy for phase and microstructure identification using a reflected light microscope (Olympus Provis AX70TRF) and scanning electron microscopy (SEM) in back scattered electron mode (BSE). Phase compositions were measured by an electron probe X-ray microanalysis (EPMA) technique with wavelength dispersive spectroscopy (WDS) (JEOL 8200L EPMA; Japan Electron Optics Ltd., Tokyo, Japan). The EPMA was operated at a voltage of 15 keV and beam current of 20 nA. Three standards were used for calibration, pure CaSiO$_3$, Fe$_2$O$_3$, and Al$_2$O$_3$ (all standards from the Charles M. Taylor Co., Stanford, CA). The iron concentration in phases were recalculated to Fe$_2$O$_3$ for presentation purposes.

The phases present in the samples were confirmed using X-Ray powder diffraction XRD. To enable these samples to be characterised, repeated experiments, cooling from 1623 K to 1073 K (1350 °C to 800 °C) at 2 K/s, with 0.2 g of starting oxides were performed to obtain 1g of material. The material was crushed and ground with an agate mortar and pestle. The resulting powder was analysed with powder X-ray diffraction (XRD) (Bruker D8), with a Cu Kα radiation source at a voltage of 40 kV and a current of 40 mA.

Three bulk compositions were selected, based on phase equilibria and liquidus data available for the “Fe$_2$O$_3$”-CaO-SiO$_2$ system in air [10], for investigation, with a CaO/SiO$_2$ ratio (wt/wt) of 2.78, 3.46 [1] and 4.75; these compositions contained 69.23, 72.74 and 74.94 wt% Fe$_2$O$_3$ respectively. The three compositions were selected based on the assumption that the same phases form on equilibrium cooling. The Fe$_2$O$_3$ concentrations were selected such that the same proportion of hematite, approximate 10 wt%, would form prior to SFC formation under equilibrium cooling. The tests were performed in air, as the atmosphere present during cooling in industrial sintering processes has been measured to have a $p_{O_2}$ close to 0.21 atm [9]. A constant cooling rate of 2 K/s was selected as this is typical of the cooling rate in industrial processes [9].
3.0 Equilibrium Cooling

Equilibrium cooling provides a reference against which actual processes can be compared. Equilibrium cooling assumes infinitely fast mass transfer and reaction kinetics, resulting in the occurrence of equilibrium phases and phase compositions at all stages during the cooling processes. Under equilibrium cooling, for all three compositions studied, five stages of solidification are predicted to occur. The equilibrium cooling for the bulk composition with a CaO/SiO$_2$ ratio of 3.46 wt/wt is illustrated in Figure 1.

![Detailed Schematic](image)

Figure 1: Predicted liquid compositions on equilibrium cooling of mixtures of bulk composition X in the “Fe$_2$O$_3$”-CaO-SiO$_2$ system in air [10].

On cooling from 1623 K (1350 °C), no solids are observed until the liquidus temperature is reached (A). On further cooling, hematite solidifies from the liquid as the primary phase until the Hematite-SFC boundary line is reached (B). At this point (B), the liquid and hematite start to react to form SFC (H + L \(\rightarrow\) SFC + L), and this reaction progresses with the liquid composition traversing along the peritectic line until hematite no longer remains in the system at point (C). Further cooling results in SFC solidification from the liquid until the SFC-C$_2$S boundary line is reached (D). From this point, C$_2$S and SFC simultaneously solidify from the liquid with decreasing temperature. The solidification of the two phases progresses until the liquid composition reaches the ternary SFC-C$_2$S-CF$_2$ peritectic invariant point (E). At this point, the SFC and liquid react to form CF$_2$ and C$_2$S. There is insufficient liquid for the complete removal of SFC through the peritectic reaction, resulting in the complete reaction of the remaining liquid to form CF$_2$, C$_2$S and SFC in the final product.

With a change in the CaO/SiO$_2$ ratio, the compositions represented by points A through D in Figure 1 [10] also change. The liquidus temperature (A) changes with both the CaO/SiO$_2$ ratio and the bulk.
Fe$_2$O$_3$ concentration. The bulk Fe$_2$O$_3$ concentrations of the three compositions were selected such that the proportion of hematite in the system prior to the formation of SFC was constant, approximately 10 wt%. From the liquidus of the system shown in Figure 1, the liquidus temperatures (A) was observed at a CaO/SiO$_2$ ratio of 3.46 wt/wt to be 1559 K (1286 °C), at a CaO/SiO$_2$ ratio of 2.78 wt/wt to be 1588 K (1285°C) and at a CaO/SiO$_2$ ratio of 4.75 wt/wt to be 1544 K (1271 °C). The temperatures at which SFC is in equilibrium with Hematite (B, C) also changes with changes in the bulk composition. The SFC-Fe$_2$O$_3$ boundary line has a local maximum at 1257°C, with the liquid at this point containing 68.5 wt% Fe$_2$O$_3$ and a CaO/SiO$_2$ ratio of 3.14. The SFC/hematite equilibrium temperature (B, C) at a CaO/SiO$_2$ ratio of 3.46 is approximately 1529 K (1256 °C), at a CaO/SiO$_2$ ratio of 2.78 is approximately 1529 K, 1256 °C) and at a CaO/SiO$_2$ ratio of 4.75 is approximately 1518 K (1245 °C). Similarly, the highest temperature at which liquid, SFC and C$_2$S are in equilibrium (D) varies with the CaO/SiO$_2$ ratio, decreasing from approximately 1525 K (1252 °C) at 2.78 to 1511 K (1238 °C) at 3.46 and 1493 K (1220 °C) at 4.75. The temperatures along SFC-C$_2$S boundary line (D) decrease with an increase in the liquid CaO/SiO$_2$ ratio.

4.0 Results

Initial experiments were undertaken with the selected compositions, cooled at 2 K/s from fully liquid conditions at 1623 K to 1073 K (1350 °C to 800 °C). The microstructures and phases formed were found to depend on the bulk composition. Micrographs illustrating the typical microstructures formed under these conditions are given in Figure 2 and the phases observed are given in Figure 3.
Using SEM imaging and EPMA measurements, the phases present and microstructures formed from the liquids containing different CaO/SiO$_2$ ratios were identified. At all bulk compositions investigated, hematite (Fe$_2$O$_3$), dicalcium silicate (C$_2$S, 2CaO.SiO$_2$), calcium ferrite (CF, CaO.Fe$_2$O$_3$) and calcium diferrite (CF$_2$, CaO.2Fe$_2$O$_3$) were observed to form. At a high CaO/SiO$_2$ ratio of 4.75 wt/wt (Figure 2d), the SFCA-I and Ca$_{7.2}$Fe$^{2+}_{0.8}$Fe$^{3+}_{3.6}$O$_{5.3}$ phases were additionally observed. These two phases were
observed to form as an intergrowth [6], hereafter referred to as simply ‘SFC-I’. The phases observed, the temperatures at which they formed and their proportions varied with the CaO/SiO$_2$ ratio.

To provide a clear understanding of the formation sequence of the phases and microstructures formed at the CaO/SiO$_2$ ratios investigated, a series of experiments were performed with samples cooled at same cooling rate (2 K/s) and quenched at 5 K intervals between 1533 K and 1453 K (1250 °C and 1180 °C).

Between a fully homogenous liquid and the final microstructure, the four intermediate stages of solidification were consistently observed for all three CaO/SiO$_2$ ratios investigated. These stages were, in the order of formation, liquid+hematite (Assemblage I), liquid+hematite+C$_2$S (Assemblage II), liquid+C$_2$S+CF$_2$ (Assemblage III) and finally C$_2$S+CF$_2$+CF (Assemblage IV). The Assemblages and microstructures are considered additive, with later Assemblages influenced by the microstructures formed at earlier stages.

With a high CaO/SiO$_2$ ratio (4.75 wt/wt), two additional phase assemblages were observed, liquid+‘SFC-I’ (Assemblage V) and liquid+‘SFC-I’/liquid+CF$_2$+C$_2$S (Assemblage VI). In the regions containing ‘SFC-I’, Assemblage VI was observed to be additive to Assemblage V. The phaseAssemblages containing ‘SFC-I’ formed in regions free of hematite. As such the formation of Assemblage of V and VI is considered independent of assemblages I, II and III. These reaction sequences are shown in Figure 4.

![Figure 4](image)

Figure 4: Observed sequences of phase assemblage formation. Typically, only one path is followed for a specific solidification condition. Only some solidification conditions leading to the observation of both paths simultaneously within a single sample. RHS: High basicity cases only

Although the resultant total phase assemblages are additive, consisting of all microstructures that formed in previous stages, for ease of description of the solidification phenomena, the sequence of phase assemblages are presented as occurring in isolation. The temperatures at which the different phase assemblages were observed are illustrated in Figure 5.
Figure 5: Occurrence of phase assemblages with temperature and CaO/SiO$_2$ ratio during liquid solidification at 2K/s in the “Fe$_2$O$_3$”-CaO-SiO$_2$ system in air.

4.1 Liquid composition variation with temperature

In the current study, the compositions of the liquids at selected temperatures were measured with EPMA. The measured liquid compositions are shown in Figure 6 and given in Tables 1, 2 and 3.

The same trends in liquid composition were observed with all samples. During the formation of isolated hematite (I), as temperature decreased and solidification progressed, the liquid composition moved from the hematite primary phase field, through the SFC primary phase field into the C$_2$S primary phase field.

Figure 6: Measured liquid compositions for oxide samples, with CaO/SiO$_2$ ratios (wt/wt) of 2.78 and 4.75 in the bulk system, cooled from 1623 K (1350°C) at 2 K/s in comparison to the equilibrium liquidus for the “Fe$_2$O$_3$”-CaO-SiO$_2$ system in air [10].
In regions isolated from hematite, only observed in the sample with the high CaO/SiO$_2$ ratio (4.75 wt/wt), ‘SFC-I’ was observed to form in the temperature range in which solidification of hematite in Assemblage I occurred, forming Assemblage V in these regions. At the conclusion of Assemblage I and V, the liquid composition was observed to be within the C$_2$S primary phase field. Once the C$_2$S phase is formed, Assemblages II (L+H+C$_2$S) and VI (L+SFC-I+C$_2$S/L+CF$_2$+C$_2$S) occur, with the liquid composition moving away from C$_2$S and towards the CF$_2$ primary phase field as the temperature decreased. The formation of C$_2$S and/or hematite continued until the liquid reached the CF$_2$ primary phase field. With the CF$_2$ nucleated, Assemblage III (L+CF$_2$+C$_2$S) formed. Solidification was complete with Assemblage IV (C$_2$S+CF$_2$+CF).

### 4.2 Liquid + Hematite (Assemblage I)

As previously reported [1] Assemblage I, involving the formation of hematite crystals, was the first phase assemblage observed to form during cooling for CaO/SiO$_2$ ratios investigated. Figure 7 shows a micrograph illustrating the typical hematite primary phase and microstructure.

![Figure 7: Examples of typical microstructures observed in Assemblage I, sample cooled from 1623 K to 1523 K (1350 °C to 1250 °C) at 2 K/s, with a CaO/SiO$_2$ ratio of a) 2.78 wt/wt b) 3.46 wt/wt and c) 4.75 wt/wt (H-Hematite, L-Liquid) (BSE micrograph)](image)

The equilibrium predictions aligned with the observation that Assemblage I transformed into Assemblage II at higher temperatures with a decreasing CaO/SiO$_2$. The temperature range over which solidification occurred and the proportion of liquid solidifying potentially impacted the hematite solidification processes.
The hematite was observed to form faceted dendritic (skeletal) crystals at all three CaO/SiO$_2$ ratios. The hematite was distributed throughout the liquid, occurring more frequently in association with the platinum substrate and the liquid-gas interface. As previously observed and reported[6], concentration profiles within the liquid were observed in this assemblage and attributed to mass transfer during quenching. The liquid distant from the liquid-hematite interface was observed to be most representative to the bulk liquid composition at temperature.

The hematite crystals decreased in size from approximately 300 μm in length and 50 μm in width at a CaO/SiO$_2$ ratio of 4.75 to 200 μm in length 40 μm in width at a CaO/SiO$_2$ ratio of 3.46 and finally 300 μm in length and 25 μm in width at a CaO/SiO$_2$ ratio of 2.78. The dendrite branches similarly decreased in length from approximately 10 μm through to 7.5 μm as the CaO/SiO$_2$ ratio decreased from 4.75 to 2.78 wt/wt.

### 4.3 Liquid + Hematite + C$_2$S (Assemblage II)

As previously reported[1, 7, 8], after hematite solidification from a liquid within the hematite primary phase field, the second phase for form is C$_2$S. The liquid+hematite+C$_2$S phase assemblage, assemblage II is considered to be additive to Assemblage I. Figure 8 shows micrographs illustrating this phase assemblage.

![Micrographs](image)

Figure 8: Examples of typical microstructures observed in Assemblage II, sample cooled from 1623 K to 1493 K (1350 °C to 1220 °C) at 2 K/s, with a CaO/SiO$_2$ ratio of a) 2.78 wt/wt b) 3.46 wt/wt and c) 4.75 wt/wt (H-hematite, C$_2$S – CaO.2SiO$_2$) (BSE micrograph)
At all CaO/SiO$_2$ ratios investigated, three microstructures were observed to form in Assemblage II (see Figure 8). In order of formation, and as previously reported [1], these were a thin C$_2$S layer on the primary hematite (IIa), individual C$_2$S crystals (IIb) and a coupled hematite+C$_2$S microstructure (IIc). The proportions and sizes of the microstructures were observed to vary with the CaO/SiO$_2$ ratio. At all compositions investigated, the forming solids were not constrained by the solids formed in prior phase assemblages.

The thin C$_2$S layer (IIa) was observed to be of a consistent thickness (~2 μm) with a variation in CaO/SiO$_2$ ratio. The formation of this phase was associated with hematite, with the quantity formed increasing proportionally with hematite surface areas. As such, a larger proportion of the thin C$_2$S layer was observed at a higher CaO/SiO$_2$ ratio.

At a CaO/SiO$_2$ ratio of 4.75, only a small proportion of the liquid solidified in Assemblage II. The microstructures present are shown in Figure 9. The individual C$_2$S crystals were observed to form short dendrites, less than 20 μm long and 5 μm wide, originating at the liquid-hematite interface. These dendrites were not observed to branch significantly. The coupled C$_2$S-hematite layer was observed to be relatively thin, less than 15μm thick and coarse relative to the other CaO/SiO$_2$ ratios investigated.

![Figure 9: Examples of typical microstructures observed in Assemblage II, formed from a liquid with a CaO/SiO$_2$ ratio of 4.75 wt/wt. Sample cooled from 1623 K to 1483 K (1350 °C to 1210 °C) at 2 K/s. (H-hematite, C$_2$S – CaO.2SiO$_2$) (BSE micrograph) (BSE micrograph)](image)

At the CaO/SiO$_2$ ratio of 2.78 wt/wt, a significant proportion of the liquid solidified to form Assemblage II (See Figure 10). The coupled Hematite-C$_2$S microstructure (IIc) was the largest contributor to the solidified material, forming in both association with the hematite formed in Assemblage I and associated with individual C$_2$S (IIb) in the liquid. The coupled microstructure was significantly finer than that observed at higher CaO/SiO$_2$ ratios and thicker, up to 40 μm in thickness.
Figure 10: Examples of typical microstructures observed in Assemblage II, formed from a liquid with a CaO/SiO$_2$ ratio of 2.78 wt/wt. Sample cooled from 1623 K to 1463 K (1350 °C to 1190 °C) at 2 K/s (H-hematite, C$_2$S – CaO.2SiO$_2$) (BSE micrograph)

4.4 Liquid + C$_2$S + CF$_2$ (Assemblage III)

Phase assemblage III was observed to be additive to Assemblage II, forming at all CaO/SiO$_2$ ratios investigated. Two microstructures are formed in Assemblage III, individual CF$_2$ (IIIa) and coupled C$_2$S-CF$_2$ (IIIb). The proportions of material solidified during the formation of this Assemblage vary with the CaO/SiO$_2$ ratio. The microstructures formed in Assemblage III are illustrated in Figure 11 and the phases observed in Figure 12.
Figure 11: Examples of typical microstructures observed in Assemblage III, sample cooled from 1623 K to 1468 K (1350 °C to 1195 °C) at 2 K/s, with a CaO/SiO$_2$ ratio of a) 2.78 wt/wt b) 3.46 wt/wt and c) 4.75 wt/wt (mixed Assemblage III and VI) (H-Hematite, S – 'SFC-I' L-Liquid) (BSE micrograph)

Figure 12: Micrograph showing phases and microstructures observed in Assemblage III, sample cooled from 1623 K (1350 °C) to 1468 K (1195 °C) at 2 K/s, with a CaO/SiO$_2$ ratio of 4.75 wt/wt (H-Hematite, C$_2$S – CaO.2SiO$_2$, CF$_2$ – CaO.2Fe$_2$O$_3$) (BSE micrograph)
At all CaO/SiO$_2$ ratios, both microstructures (IIIa,b) were observed, with the individual CF$_2$ crystals (IIIa) forming in association with hematite, and the coupled C$_2$S-CF$_2$ microstructure (IIIb) with the individual CF$_2$ crystals. The sizes and shapes of the two microstructures (IIIa and IIIb) were not sensitive to variations in the CaO/SiO$_2$ ratio.

### 4.5 C$_2$S + CF$_2$ + CF (Assemblage IV)

Assemblage IV, C$_2$S+CF$_2$+CF is considered additive to both Assemblage III and VI, forming once CF nucleates. Three microstructures, individual CF crystals (IVa), coupled C$_2$S-CF microstructures (IVb) and coupled C$_2$S-CF$_2$-CF microstructure (IVc), were observed and confirmed via EPMA line analysis. Micrographs illustrating the microstructures observed in this phase assemblage are shown in Figure 2 and Figure 13.

![Microstructures observed in Assemblage IV, samples cooled from 1468 K (1350 °C) to 1073 K (800 °C) at 2 K/s in air with a CaO/SiO$_2$ ratio of 2.78 wt/wt. (BSE micrograph)](image)

The coupled microstructures, C$_2$S-CF (IVb) and C$_2$S-CF$_2$-CF (IVc), were observed to be of a similar morphology for all compositions investigated. The coupled microstructures consist of fine rods of C$_2$S (<1μm) in a matrix of CF or CF$_2$-CF. The size of the individual CF crystals increase with a decreasing CaO/SiO$_2$ ratio. The size of both the individual crystals and coupled microstructures were observed to be constrained by the previously solidified material.

The proportion of coupled microstructures relative to individual crystals was observed to decrease with a decreasing CaO/SiO$_2$ ratio. The fine scale and complexity of these structures made it impossible to accurately estimate the volume fraction of the phases present from the micrographs.

### 4.6 Liquid + ‘SFC-I’ (Assemblage V)

This phase assemblage was only observed in the samples with a high CaO/SiO$_2$ ratio (4.75 wt/wt) in the bulk, forming in regions free of hematite. Assemblage V was observed to form concurrently with Assemblage I and II, forming at temperatures lower than first occurrence Assemblage I. The microstructure of the crystals formed in this assemblage is illustrated in Figure 14. The phases present in the ‘SFC-I’ individual crystals were confirmed by XRD analysis of 0.2g of material cooled from 1623 K to 1073 K (1350 °C to 800 °C) at 2 K/s, as shown in Figure 15. The XRD pattern was compared to known XRD patterns for SFCA [11], SFCA-I [12] and Ca$_{7.2}$Fe$_{2+\theta}$Fe$_{30-\theta}$O$_{53}$[13]. Based on the XRD pattern observed between 5 and 15 2θ, both SFCA-I and Ca$_{7.2}$Fe$_{6.8}$Fe$_{30.0}$O$_{53}$ were identified; this evidence indicates that the ‘SFC-I’ crystals are intergrowths of these two phases.
Figure 14: Microstructures observed in Assemblage V, samples cooled from 1468 K (1350°C) to 1508 K (1235°C) at 2 K/s in air with a CaO/SiO$_2$ ratio of 4.75 wt/wt. (L- Liquid, S-‘SFC-I’) (BSE micrograph)

Figure 15: XRD pattern obtained from material cooled from 1623 K to 1073 K (1350 °C to 800 °C) at 2 K/s with a CaO/SiO$_2$ ratio of 4.75. (Cu Kα)

The ‘SFC-I’ individual crystals were distributed throughout the regions free of hematite. The ‘SFC-I’ crystals were consistently observed as individual crystals, approximately 300 μm long and 20 μm wide. The composition of the ‘SFC-I’ crystal was measured by EPMA, with the composition measured to be approximately 87.9 wt% Fe$_2$O$_3$, 0.04 wt% SiO$_2$ and 12.04 wt% CaO. Based on a mass balance, it was calculated that this composition corresponds to an intergrowth with approximately 86 wt% SFCA-I and 14 wt% Ca$_{7.2}$Fe$_{0.8}$Fe$_{30}$O$_{53}$.

4.7 Liquid + C$_2$S + ‘SFC-I’/ Liquid + C$_2$S + CF$_2$

(Assemblage VI)

Assemblage VI was observed in the samples with a CaO/SiO$_2$ ratio of 4.75 wt/wt, forming additively to Assemblage V and appearing concurrently with Assemblage II and III. Both Assemblage II and VI require the nucleation and growth of C$_2$S. Four phase microstructures were observed in this assemblage, individual C$_2$S crystals (VIa), coupled C$_2$S-SFC-I (VIb), individual CF$_2$ crystals (VIc) and coupled C$_2$S-CF$_2$ crystals (VId). A micrograph illustrating this phase assemblage is given in Figure 16.
It was not possible to differentiate the SFC-I and CF$_2$ phases based on SEM imaging[6]. EPMA line analysis was used to confirm the presence of the four microstructure assemblages.

Figure 16: Microstructures observed in Assemblage VI, samples cooled from 1623 K (1350 °C) to 1473 K (1200 °C) at 2 K/s in air with a CaO/SiO$_2$ ratio of 4.75 wt/wt. (S-'SFC-I', C$_2$S-CaO.2SiO$_2$, CF$_2$-CaFe$_4$O$_7$) (BSE micrograph)

5.0 Discussion

5.1 Formation of Assemblage I (L+H)

At all CaO/SiO$_2$ ratios investigated, and in agreement with equilibrium cooling, this phase assemblage was the first observed upon cooling of a homogenous liquid. With a variation in the CaO/SiO$_2$ ratio, the temperature at which hematite formed and the hematite microstructures varied. The formation of these microstructures is influenced by both thermodynamics and kinetics.

The initial nucleation of hematite requires undercooling below the liquidus temperature. Liquids with a high CaO/SiO$_2$ ratio nucleate with a lower undercooling due to a higher diffusivity and lower viscosity of the melt. With a decrease in the CaO/SiO$_2$ ratio, the number of hematite crystals increased and the size of the hematite crystals were observed to decrease.

5.2 Formation of Assemblage II (L+C$_2$S+H)

Assemblage II forms additivity to Assemblage I. During the formation of Assemblage I, the Fe$_2$O$_3$ concentration of the liquid decreases and the liquid composition moves into the C$_2$S primary phase field. The C$_2$S phase nucleates from this undercooled liquid, forming of a thin C$_2$S layer on the hematite (IIa). The C$_2$S subsequently forms individual crystals (IIb), with the solidification of these crystals moving the liquid composition towards equilibrium conditions, away from C$_2$S. With further decreases in temperature, the C$_2$S-hematite coupled microstructure (IIc) is observed to solidify, with the liquid composition moving along the metastable C$_2$S-hematite boundary line. The liquid composition moves from the C$_2$S primary phase field towards the H-C$_2$S- CF$_2$ invariant point as a result of the solidification of this microstructure. The liquid composition on cooling is illustrated schematically in Figure 17.
Based on a mass balance, assuming that the Assemblage II transitions into Assemblage III when the liquid composition is at the equilibrium C$_2$S-SFC-CF$_2$ peritectic (1489 K, 1216 °C), the proportions of liquid and solids present during the formation of Assemblage II can be calculated. At the highest CaO/SiO$_2$ ratio (4.75 wt/wt), only a small proportion of the liquid solidified, with 3.1 wt% C$_2$S and 22.3 wt% hematite in the system at the end of Assemblage II. At a CaO/SiO$_2$ ratio of 2.78 wt/wt, the proportion of the solids increased to 17.8 wt% C$_2$S and 38.6 wt% hematite. This is in qualitative agreement with the samples analysed (see Figure 8).

Based on the measured liquid compositions and the liquidus temperature[10], it is estimated that prior to C$_2$S nucleation, the proportion of hematite in the bulk was a minimum of 13.4 wt% at a CaO/SiO$_2$ ratio of 2.78, 24.1 wt% at 3.46 and 24.7 wt% at 4.75. The liquidus temperature and C$_2$S supercooling at this minimum was estimated to be 1553 K (1210 °C) and 70 K at 2.78 wt/wt, 1593 K (1225 °C) and 95 K at 3.46 wt/wt and 1573 K (1195 °C) and 105 K at 4.75 wt/wt. This suggests that the nucleation of C$_2$S was more favourable at higher SiO$_2$ concentrations in the bulk.

![Diagram](image)

**Figure 17:** The changes in liquid composition as solidification occurred for Assemblages I and II.

The proportion of the liquid solidifying to form the coupled C$_2$S-hematite microstructure increased with decreasing CaO/SiO$_2$ ratio, larger individual crystals and coupled microstructures. With a decrease in the CaO/SiO$_2$ ratio, the liquid composition at the conclusion of Assemblage I was further from the C$_2$S-H-CF$_2$ ternary invariant point. Based on the liquid composition prior to C$_2$S nucleation and the composition of the C$_2$S-H-CF$_2$ ternary invariant point, the liquid present in the samples were estimated to decrease from 46 wt% to 13 wt% at a CaO/SiO$_2$ ratio of 2.78, 60 wt% to 24 wt% at 3.46 and 77 wt% to 25 wt% at 4.75 during solidification of assemblage II.

The total amount of C$_2$S in the thin C$_2$S layer on the hematite increases proportionally with an increase in the surface area of hematite in the system. The thickness of this layer is not observed to change with the CaO/SiO$_2$ ratio. Individual C$_2$S crystals were observed to form on the thin C$_2$S layer and grow into the surrounding liquid to form dendrites. With a decrease in the CaO/SiO$_2$ ratio, the proportion and size of the dendrites decreases. With an increase in the CaO/SiO$_2$ ratio, the coupled microstructure was observed to be coarser. This may partially due to an increase in liquid diffusivity with an increase in the CaO/SiO$_2$ ratio.

### 5.3 Formation of Assemblage III (L+C$_2$S+CF$_2$)

Assemblage III formed additively to Assemblage II, with the microstructures formed in Assemblage II influencing the formation of Assemblage III. For all liquid compositions investigated, the liquid
composition prior to the formation of Assemblage III is approximately the same as the composition of the ternary $\text{C}_2\text{S}$-SFC-CF$_2$ invariant.

With an increase in the CaO/SiO$_2$ ratio, the proportion of material solidifying during the formation of Assemblage III decreased. Equilibrium calculations indicated that the change in liquid composition during the formation of Assemblage III for all three compositions investigated was identical. The proportion of liquid solidifying during Assemblage III is proportional to liquid in the system prior to the transformation of this structure, increasing with the bulk CaO/SiO$_2$ ratio. Based on equilibrium cooling, it is estimated that the liquid present decreased during the formation of Assemblage III from 45 wt% to 34 wt% at a CaO/SiO$_2$ ratio of 2.78 wt/wt, 59 wt% to 44 wt% at a CaO/SiO$_2$ ratio of 3.46 and 76 wt% to 57 wt% at a CaO/SiO$_2$ ratio of 4.75. This represents a 11 wt%, 15 wt% and 19 wt% change respectively.

The proportion of liquid solidifying during the formation of Assemblage III increases with increasing CaO/SiO$_2$. Based on the liquid composition at the $\text{C}_2\text{S}$-SFC-CF$_2$ invariant point and the $\text{C}_2\text{S}$-CF$_2$-CF invariant point, the change in the proportion of the liquid in the sample can be estimated. At a CaO/SiO$_2$ ratio of 2.78 wt/wt, the liquid present in the sample is estimated to decrease from 45.6 wt% to 33.5 wt%, at a ratio of 3.46 wt/wt to decrease from 59.7 wt% to 43.9 wt% and at a ratio of 4.75 wt/wt to decrease from 77 wt% to 56.6 wt%. This represents a net change of 12.1 wt%, 15.8 wt% and 20.4 wt% liquid respectively; that is with an increase in the CaO/SiO$_2$ ratio, a larger quantity of CF$_2$ and $\text{C}_2\text{S}$ to solidifies in Assemblage III.

It was previously observed that the solids formed prior to Assemblage III were able to influence the size and proportion of the individual CF$_2$ crystals (IIIa) and the coupled $\text{C}_2\text{S}$-CF$_2$ microstructure (IIIb)[8]. However, within the compositional range investigated, this was not observed. The solidified material was not constrained by the previously formed material, the volume of the new microstructures formed are smaller than the free volume available.

### 5.4 Formation of Assemblage IV ($\text{C}_2\text{S}+\text{CF}_2+\text{CF}$)

Assemblage IV was the final assemblage to form, being additive to Assemblage VI and III. The size and proportion of the microstructures formed in Assemblage IV was observed to vary with the bulk CaO/SiO$_2$ ratio. The proportion of liquid and free volume between previously solidified material found to vary between the compositions investigated and this impacted the formation assemblage IV.

For all compositions investigated, the liquid composition prior to the formation of this assemblage is similar, that is close to the $\text{C}_2\text{S}$-CF$_2$-CF ternary eutectic. However, the proportion of liquid present increases with increases in the CaO/SiO$_2$ ratio. Based on equilibrium cooling, it is estimated that the liquid solidifying in Assemblage IV represented 34 wt%, 44 wt% and 57 wt% of the bulk for a CaO/SiO$_2$ ratio of 2.78, 3.46 and 4.75 wt/wt respectively.

Three microstructures were observed to form in this Assemblage, individual CF (IVa), coupled $\text{C}_2\text{S}$-CF (IVb) and coupled $\text{C}_2\text{S}$-CF$_2$-CF (IVc). As previously established for this reaction [1], the individual CF crystals formed first, from the liquid undercooled with respect to CF. The initial solidification of CF moves the liquid composition from within the CF primary phase field and to the CF-$\text{C}_2\text{S}$ invariant line. This lead to the growth of a coupled $\text{C}_2\text{S}$-CF microstructure, moving the liquid composition towards the ternary eutectic point. Final solidification occurs with the solidification of the remaining liquid to form the coupled $\text{C}_2\text{S}$-CF$_2$-CF (IVc) microstructure.

With an increase in the bulk CaO/SiO$_2$ ratio, the volume and proportion of the microstructures formed in Assemblage IV was observed to increase. The microstructures formed in Assemblage IV were
constrained in size by the previously formed solids. With an increase in the proportion of liquid present, a larger amount of material solidified, increasing the proportions of all three microstructures (IVa,b,c) present when solidification is complete.

**5.5 Formation of ‘SFC-I’ (Assemblages V and VI)**

Assemblages V and VI were observed in regions free of hematite, were only observed at the highest CaO/SiO$_2$ ratio investigated. This is consistent with previous research [8], which suggests that the ‘SFC-I’ forms homogenously from the melt rather than heterogeneously on the hematite. Compared to previous research [6], the ‘SFC-I’ contained a higher proportion of SFC-I. A higher CaO/SiO$_2$ ratio is associated with a larger proportion of SFC-I forming relative to Ca$_7$Fe$_2^{3+}$Fe$_{0.8}^{5+}$O$_{30}$.

Four microstructures were observe to form. Initially, the ‘SFC-I’ was observed to nucleate homogenously within regions free of hematite, forming long individual ‘SFC-I’ crystals (V). The nucleation and growth of this phase results in the movement of the liquid composition into the C$_2$S primary phase field. The undercooling with respect to C$_2$S leads to the formation and growth of C$_2$S individual crystals. This is followed by the formation of a coupled ‘SFC-I’-C$_2$S microstructure (VIa), forming on the individual C$_2$S crystals and the individual ‘SFC-I’ crystals. The growth of this microstructure moves the liquid composition from the C$_2$S primary phase field to the SFC-C$_2$S boundary line and then into the CF$_2$ primary phase field. This leads to the formation of individual CF$_2$ crystals (IVc) and then the formation of the coupled C$_2$S-CF$_2$ microstructure (VId).

**5.6 Overall Impacts of CaO/SiO$_2$ ratio on microstructure formation**

The bulk CaO/SiO$_2$ ratio has been demonstrated to influence the phases, phase assemblages and the microstructures formed on the solidification of ‘Fe$_2$O$_3$’-CaO-SiO$_2$ liquids. These changes to the bulk composition result in changes in both the thermodynamic driving force for phase formation and the kinetic processes taking place. Consistent with previous research on this topic, solidification was observed to differ from both equilibrium and Sheil-Gulliver cooling with the variation in the CaO/SiO$_2$ ratio [1, 6-8].

Metastable solid phase assemblages were formed for the bulk compositions investigated. Notable was the absence of the SFC phase, a phase that was anticipated to form following the primary hematite phase. The change in bulk compositions of the melts resulted in the same phase assemblages for three CaO/SiO$_2$ ratios investigated, however the relative proportions of the phases and the phase assemblages were changed.

The change in liquid viscosity and diffusivity, associated with a change in the bulk CaO/SiO$_2$ ratio is suggested to have led to a change in size of the initial microstructures that formed (i.e. Assemblage I and II). For the compositions investigated, an increase in the proportion of material solidifying at any stage was associated with larger microstructures and a larger proportion of coupled microstructures.

**6.0 Summary**

The effects of the CaO/SiO$_2$ ratio on the phases and microstructures formed on solidification of liquid in the “Fe$_2$O$_3$”-CaO-SiO$_2$ system in air have been studied. The phases formed on cooling samples with CaO/SiO$_2$ ratio (wt/wt) of 2.78, 3.46 and 4.75, containing 69.23, 72.7 and 74.94 wt% Fe$_2$O$_3$ respectively. The phases formed were, hematite (Fe$_3$O$_4$), dicalcium silicate (Ca$_2$SiO$_4$), calcium diferrite (CaFe$_2$O$_4$) and
calcium ferrite (CaFe₂O₄). In addition, at a high CaO/SiO₂ ratio (wt/wt), SFCA-I and Ca₇₂Fe²⁺₀.₈Fe³⁺₃₀O₅₃ were observed to form a complex intergrowth. The CaO/SiO₂ ratio influenced the kinetic processes occurring and the proportions and morphology of the microstructures formed. The change in ratio resulted in a change in the equilibrium cooling path and the proportions of phases that formed at different stages of solidification. Additionally, the CaO/SiO₂ ratio changes the melt composition at early stages of solidification, influencing the kinetic processes that are occurring. These observations provide a valuable insight into the impact of the CaO/SiO₂ ratio on industrial iron ore sintering processes, emphasising the importance in controlling this parameters. The CaO/SiO₂ influences the phases and microstructures in the sinter, and in turn the sinter properties.

### 7.0 Acknowledgements

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| Table 1: Liquid compositions in microstructures containing Hematite, as measured by EPMA, formed by cooling a liquid with a CaO/SiO₂ ratio of 4.75 from 1623 K at 2 K/s |
| --- | --- | --- | --- | --- |
| Temperature (°C) | Assemblage I (L+H) | Assemblage II (L+H+C₂S) | Assemblage III (L+C₂S+CF₂) |
| | Fe₂O₃ (wt%) | SiO₂ (wt%) | CaO (wt%) | Fe₂O₃ (wt%) | SiO₂ (wt%) | CaO (wt%) | Fe₂O₃ (wt%) | SiO₂ (wt%) | CaO (wt%) |
| 1260 | 74.6 | 4.8 | 20.7 | - | - | - | - | - | - |
| 1255 | 73.9 | 4.7 | 21.4 | - | - | - | - | - | - |
| 1250 | 74.2 | 4.8 | 21.0 | - | - | - | - | - | - |
| 1245 | 74.3 | 4.7 | 21.1 | - | - | - | - | - | - |
| 1240 | 70.4 | 5.2 | 24.4 | - | - | - | - | - | - |
| 1235 | 70.5 | 5.0 | 24.6 | - | - | - | - | - | - |
| 1230 | 69.1 | 5.7 | 25.2 | - | - | - | - | - | - |
| 1225 | 70.7 | 4.7 | 24.6 | 70.4 | 4.5 | 25.2 | - | - | - |
| 1220 | 69.9 | 5.1 | 25.0 | 69.4 | 4.8 | 25.8 | - | - | - |
| 1215 | 67.7 | 6.1 | 26.3 | 65.9 | 6.8 | 27.3 | - | - | - |
| 1210 | 66.8 | 6.8 | 26.4 | 71.0 | 4.8 | 24.2 | - | - | - |
| 1205 | 66.7 | 6.2 | 27.1 | 68.3 | 4.8 | 26.9 | - | - | - |
| 1195 | 67.2 | 6.4 | 26.4 | 70.4 | 3.3 | 26.3 | 70.2 | 3.7 | 26.1 |
| 1190 | - | - | - | 68.7 | 5.2 | 26.1 | - | - | - |

| Table 2: Liquid compositions in microstructures containing Hematite, as measured by EPMA, formed by cooling a liquid with a CaO/SiO₂ ratio of 2.78 from 1623 K at 2 K/s |
| --- | --- | --- | --- | --- |
| Temperature (°C) | Assemblage I (L+H) | Assemblage II (L+H+C₂S) | Assemblage III (L+C₂S+CF₂) |
| | Fe₂O₃ (wt%) | SiO₂ (wt%) | CaO (wt%) | Fe₂O₃ (wt%) | SiO₂ (wt%) | CaO (wt%) | Fe₂O₃ (wt%) | SiO₂ (wt%) | CaO (wt%) |
| 1260 | 68.9 | 8.4 | 22.8 | - | - | - | - | - | - |
| 1255 | 67.7 | 8.8 | 23.5 | - | - | - | - | - | - |
| 1250 | 68.1 | 8.6 | 23.4 | - | - | - | - | - | - |
| 1245 | 66.2 | 9.0 | 24.7 | - | - | - | - | - | - |
Table 3: Liquid compositions in microstructures containing 'SFC-I', as measured by EPMA, formed by cooling a liquid with a CaO/SiO$_2$ ratio of 4.75 from 1623 K at 2 K/s

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Assemblage V (L+S)</th>
<th>Assemblage III (L+S/CF$_2$+$C_2$S)</th>
</tr>
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<tr>
<td></td>
<td>Fe$_2$O$_3$ (wt%)</td>
<td>SiO$_2$ (wt%)</td>
</tr>
<tr>
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<td>70.0</td>
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<tr>
<td>1190</td>
<td>65.8</td>
<td>6.7</td>
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</tbody>
</table>
References


8. Nicol, S, Jak, E, and Hayes, P, Effects of the bulk \(^{\text{Fe}_2\text{O}_3}\) concentration on the controlled solidification of \(^{\text{Fe}_2\text{O}_3}\)-CaO-SiO\(_2\) liquids. ISIJ int., 2019 in press.


12. Mumme, W., J. Clout, and R. Gable, The crystal structure of SFCA-I, Ca\(_{2}\).3\(_{8}\)Fe\(_{3+14.66}\)Al\(_{1}\).\(_{3}\)Fe\(_{2+9.82}\)O\(_{38}\), a homologue of the aenigmatite structure type, and new crystal structure refinements of \(^{\beta}\)CFF, Ca\(_{2}\)\(_{98}\)Fe\(_{3+14.30}\)Fe\(_{2+0.55}\)O\(_{25}\) and Mg-free SFCA, Ca\(_{2}\)\(_{45}\)Fe\(_{3+9.04}\)Al\(_{1}\).\(_{74}\)Fe\(_{2+0.16}\).\(_{6}\)Si\(_{0.6}\)O\(_{20}\). Neues Jahrb. Mineral., Abh., 1998: p. 93-117.

Appendix F: Measurement of Process Conditions Present in Pilot Iron Ore Sintering
Measurement of Process Conditions Present in Pilot Scale Iron Ore Sintering

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Abstract

An improved experimental technique has been developed to measure, concurrently, the oxygen partial pressures and temperatures within a pilot scale iron ore sinter pot as a function of time. The measurements and thermodynamic calculations have demonstrated that the oxygen partial pressure at peak bed temperature and during cooling can be oxidising or reducing relative to hematite. Examples of typical microstructures and phase assemblages observed in product sinters are presented. Potential mechanisms of hematite and magnetite formation at sub-liquidus and sub-solidus conditions are demonstrated.

The relative impacts of changes to coke rate and draft pressure drop on the process conditions and proportions of the phases formed in the sinter have been measured. Increasing coke rate was shown to result in a faster sinter heating rates, higher peak bed temperatures and times at peak temperature. Higher draft pressures across the sinter bed resulted in faster sinter heating rates and shorter times at peak temperature.

Keywords: Iron ore sintering; temperature; oxygen partial pressure; processes, hematite, magnetite

1. Introduction

Iron ore sintering is undertaken at steelworks to produce coarse and competent feed for the iron blast furnace from iron ore fines and secondary iron oxide sources. In the sintering process, a blend of iron oxide fines (<6 mm) is mixed and agglomerated with the addition of fluxes, return sinter and coke breeze. The agglomerated material is loaded as a packed bed onto a continuous downdraft sinter strand and the surface of the bed is ignited using a secondary heat source. Air is continuously drawn down through the bed, resulting in the movement of a heat front down through the charge. At a critical temperature the coke ignites, providing additional thermal energy, and creating CO and CO2 gases in the bed. The gaseous combustion products pass through the bed, heating the solids, enabling further reactions to occur and the partial melting of the charge. On cooling, solidification of the melt occurs, resulting in the formation of strong sinter lumps. The sintering conditions and the microstructures formed influence the final sinter properties and performance in the iron blast furnace.

The general thermal history of sinter, namely rapid heating, peak bed temperature and cooling, has been well established through measurement of temperature profiles in the bed [1]. From the temperature profiles and the analysis of the phases present within a sinter bed at different stages of sintering, a number discrete regions or reaction zones have been identified in the sinter bed, as illustrated by Figure 1. These are, in the order in which they occur, from the bottom of the sinter bed to the top, the wet zone, dry zone, calcination and dehydration zone, combustion zone, sinter and cooling zone [2, 3]. In the wet zone, green sinter agglomerates are heated by moist air, with water
condensing from the air. Further heating of the wet sinter with the hot and dry air, removes all the physically entrained water in the sinter, creating the dry zone. The dry sinter is rapidly heated in the dehydration and calcination zone, with the dehydroxylation of hydrates and decarbonation of carbonates occurring in this zone. After dehydration and calcination on further heating the coke breeze is ignited and is combusted, rapidly heating the gas stream and sinter to the peak bed temperature. After achievement of the peak bed temperature, the sinter is cooled by the air drawn down through the sinter bed.

Despite the widespread industrial use of this process, relatively few measurements of the oxygen partial pressure (p$_{O_2}$) within the sinter bed during sintering have been carried out [4, 5]. The p$_{O_2}$ measurements by Sugiwara et al. [5] indicated that the lowest oxygen pressure, p$_{O_2}$ of ~10$^{-8}$ atm, occurred at the peak bed temperature of approximately 1400 °C. The position and method of introducing the probe into the sinter bed was not described in the paper. During heating, the p$_{O_2}$ was reported to be lower than 0.21 atm.; on cooling, the measured oxygen partial pressure was close to 0.21 atm. Research by Van den Berg et al.[4] indicated that the most reducing conditions, a p$_{O_2}$ of ~10$^{-2}$ atm, occurred prior to the peak bed temperature. To perform the p$_{O_2}$ and temperature measurements, an oxygen probe and a thermocouple were inserted from the top of the sinter bed, into the centre of the sinter pot. On heating, the p$_{O_2}$ was between 10$^{-1.5}$ and 10$^{-1}$ atm at 750 °C, this decreased to 10$^{-2}$ to 10$^{-1.5}$ atm at approximately 950 °C and subsequently increasing to approximately 10$^{-1}$ atm at the peak bed temperature of approximately 1250 °C. On cooling, oxygen partial pressures between 10$^{-1}$ and 0.21 atm was recorded.

Mathematical models of the sintering process [6-9] have been used to predict the temperature profiles within a sinter pot and the associated off gas composition with reasonable agreement to those measured in sinter pot tests. The models replicate the rapid heating, attainment of the peak bed temperature and the sinter cooling measured in these down draught sinter processes. The sinter off gas compositions have been simulated and in agreement with gas composition measurements on sinter pots, both CO and CO$_2$ was observed. However, the p$_{O_2}$ within the sinter bed and its relationship to the temperature profile was not determined [8].
A number of process parameters can be used to influence the sinter microstructures and resulting properties. The temperature and thermal history of sinter can be controlled with the addition of coke breeze and adjustment of the sinter draft pressure [1]. Previous modelling and sinter pot tests have demonstrated that, with an increase in coke rate there is an increase in the sinter peak bed temperature and time at temperature [10], and with an increase in the draft pressure, there is a decrease in the sinter peak bed temperature and time at temperature.

The focus of the present study is on the measurement of the temperature profiles and $p_{O_2}$ in sintering. In addition, the effects of coke rate and sinter draft on the temperature profiles and the phases formed during sintering are determined.

2. Methodology

2.1 Pilot Scale Sinter pot tests

Previous studies of the iron ore sinter process have established that the process conditions, temperature, gas composition vary with time and position in the bed [3]. The thermal profile changes as it moves down through the bed [7]. A single probe inserted in the bed measures the sum of multiple local sub processes taking place within the bed. There are uncertainties associated with the heterogeneity of the system and the measurement techniques used to characterise this system;

- Local differences in phase and particle distribution. These are directly related to the materials used in the feed, particle size distribution, and methods of granulation. The differences in local chemical composition and phase assemblage result in differences in enthalpy of reaction, enthalpy of fusion. The combustion of coke provides a local heat source.
- Partial melting. Whilst the initial sinter charge resembles a randomly packed bed of solids during sintering, partial melting of the bed takes place resulting in channelling of the gas and changes to bed porosity. These changes result in changes to the local rates of heat transfer from gas to condensed phases.
- Bed shrinkage. The partial melting of the burden leads to an increase in bulk density and shrinkage of the bed. The interaction of the sinter bed and the probes during sintering can lead to the creation of voids and changes to the local voidage around the probe. This can be minimised by inserting the measuring devices from the top of the bed rather than from the side, enabling the probe to move with the bed and reduce the hold-up of the bed by the probe. However, it is recognised that the bed has moved relative to the thermocouple during the measurement. The extent of the movement depends on the initial position of the thermocouple and the overall change in bed height during sintering, typically 13-15 vol%.
- Thermocouple type. To protect the metal thermocouples, prevent the thermocouple wires from breaking during bed shrinkage, provide stiffness for insertion into the bed and prevent a junction forming from crossed thermocouple wires, the thermocouple wires are inserted into an aluminium oxide sheath. The material and mass of the oxide sheath has the potential to influence the local thermal profile and response time, particularly if the thermocouple tip is enclosed by the sheath.
- Probe type. A range of materials and designs can be used in solid state oxygen probes. The materials and dimensions of the sensor tip can influence the response time and sensitivity of the probe to changes in temperature and oxygen potential in the gas phase with time. To determine the oxygen partial pressure, separate or combined measurement of temperature and electromotive force (EMF), $\Delta E$ across a solid electrolyte may be undertaken. The calculated oxygen partial pressure, $(\Delta E = RT/nF \ln(p_{O_2, \text{unknown}}/p_{O_2, \text{reference}}))$ is a function of both
the measured temperature (T) and the measured electrical potential difference (∆E). As such, the difference if any between the measured temperature and that at the tip of the solid electrolyte is required in order to accurately determine the actual $p_{O2}$.

- The rate of response of the oxygen probe to changes in oxygen pressure is dependent on temperature. At high temperatures the response times are rapid and the EMF measurement provide accurate measurement of the $p_{O2}$. At low temperatures in rapidly changing systems the EMF measured is limited by the rates of ionic transfer in the solid state probes, and measurements should be treated with caution as these may not accurately reflect the $p_{O2}$ at the time of measurement.

- The rate of response to changes in the oxygen partial pressure of the system is dependent on mass transfer from the system to the outer surface of the probe. The mass transfer is fastest when the oxygen probe is in contact with the gas phase. If, during the sinter process, the sensor tip is partially or fully covered with liquid and/or solids, again the EMF recorded may not accurately reflect the gas partial pressure at the time of measurement.

In the present study, pilot scale sinter pot tests were performed at Baosteel Shanghai using the existing equipment onsite. The feed materials for the tests were collected from the sinter plant iron ore blend. The materials used included; iron ore fines, limestone, dolomite, coke breeze, and sinter returns. The feed materials were blended such that there was 1.2 wt% MgO and 1.5 wt% Al$_2$O$_3$ in the sinter product, and the bulk CaO/SiO$_2$ ratio was approximately 1.7 wt/wt. Coke was blended into the feed, with a base case of 36 kg/t of feed, and 33 kg/t and 39 kg/t of feed for the low and high coke addition tests respectively. The mean compositions of the sinters, as measured by XRF after sintering, and the sintering conditions investigated are summarised in Table 1.

<table>
<thead>
<tr>
<th>Draft Pressure drop (kPa)</th>
<th>Base Case</th>
<th>Low Coke</th>
<th>High Coke</th>
<th>Low Draft</th>
<th>High Draft</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coke (kg/t feed)</td>
<td>36</td>
<td>33</td>
<td>39</td>
<td>36</td>
<td>33</td>
</tr>
<tr>
<td>Coke breeze size (mm)</td>
<td>1.5-1.8</td>
<td>1.5-1.8</td>
<td>1.5-1.8</td>
<td>1.5-1.8</td>
<td>1.5-1.8</td>
</tr>
<tr>
<td>Sinter Returns (wt%)</td>
<td>18.0</td>
<td>18.0</td>
<td>18.0</td>
<td>18.0</td>
<td>18.0</td>
</tr>
<tr>
<td>Moisture (wt%)</td>
<td>7.2</td>
<td>7.2</td>
<td>7.2</td>
<td>7.1</td>
<td>7.2</td>
</tr>
<tr>
<td>Sinter Feed Size (mm)</td>
<td>2.6</td>
<td>2.6</td>
<td>2.8</td>
<td>2.7</td>
<td>2.6</td>
</tr>
<tr>
<td>Goethite in feed (wt%)</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Hematite in feed (wt%)</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>40</td>
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<tr>
<td>Magnetite in feed (wt%)</td>
<td>6-8</td>
<td>6-8</td>
<td>6-8</td>
<td>6-8</td>
<td>6-8</td>
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<tr>
<td>Flame Front Speed (mm/min)</td>
<td>23.9</td>
<td>18.5</td>
<td>22.8</td>
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<td>24.2</td>
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<td>4.6</td>
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<td>4.5</td>
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<tr>
<td>Al$_2$O$_3$ (wt%)</td>
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<td>1.7</td>
<td>1.8</td>
<td>1.6</td>
<td>1.6</td>
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<tr>
<td>CaO (wt%)</td>
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<td>7.9</td>
<td>7.9</td>
<td>8.2</td>
<td>7.9</td>
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<td>MgO (wt%)</td>
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<td>1.3</td>
<td>1.3</td>
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<tr>
<td>FeO (wt%)</td>
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<td>8.1</td>
<td>10.3</td>
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<tr>
<td>Total Fe (wt%)</td>
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<td>59.6</td>
<td>59.6</td>
<td>59.5</td>
<td>59.9</td>
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<tr>
<td>CaO/SiO$_2$ (wt/wt)</td>
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<td>1.70</td>
<td>1.65</td>
<td>1.75</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>O$_2$ (vol%)</td>
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<td>11.51</td>
<td>11.55</td>
<td>13.70</td>
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<td>CO (vol%)</td>
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<td>0.51</td>
<td>0.59</td>
<td>0.35</td>
<td>0.30</td>
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<tr>
<td>CO$_2$ (vol%)</td>
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<td>4.51</td>
<td>4.50</td>
<td>3.59</td>
<td>2.47</td>
</tr>
<tr>
<td>H$_2$O (vol%)</td>
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<td>20.00</td>
<td>20.00</td>
<td>17.13</td>
<td>20.00</td>
</tr>
<tr>
<td>CO/CO$_2$ (vol/vol)</td>
<td>0.10</td>
<td>0.11</td>
<td>0.13</td>
<td>0.10</td>
<td>0.12</td>
</tr>
</tbody>
</table>
The feed material to be sintered was initially blended and mixed in an agglomeration drum. Both a dry and wet stage of agglomeration was performed, providing homogenisation and agglomeration of the charge. The product from agglomeration, green pellets approximately 2.6 mm diameter, was loaded into the sinter pot. The sinter pot used was 300 mm ID and 750 mm high, holding approximately 53 L of material.

Oxygen probes and thermocouples were used to measure the $p_{O_2}$ and temperature during sintering. The oxygen probes, CP-500-0-NS C700, were supplied by Australian Oxytrol Systems. These probes utilised a SIRO$^1$ C700 sensor, with a zirconia based solid electrolyte located at the tip of the alumina tube. The oxygen probe specifications indicate the dynamic operating range of the instrument is from pure oxygen to a $p_{O_2}$ of $10^{-24}$ atm and temperatures from 500 °C to 1700 °C. Above 600 °C the sensitivity is better than 2 mV, below 600 °C, the response may be slower and the error may increase to 3 mV. Separate B-type thermocouples (70%Pt/30%Rh-94%Pt/6%Rh) were used to measure the temperature within the sinter pots. In the experiments performed, the reference $p_{O_2}$ was that of the surrounding atmosphere. The thermocouple tips were exposed directly to the sinter, with the wires shielded by an alumina sheath. These thermocouples are suited to temperatures up to 1800 °C.

A schematic of the sinter pot and the positions of these probes in the sinter bed prior to sintering are shown in Figure 2. The oxygen probes and thermocouples were inserted from the top of and along the central axis of the sinter bed, with the tips of the sensors located in the middle of the sinter pot (375 mm depth). The tips were positioned such that the two probes were measuring the conditions at the same point in the sinter bed. A computer was used to log the temperatures and voltages measured by the thermocouple and oxygen probe respectively.

The surface of the sinter bed was ignited with a flame at 880 °C for 120s, with a draft pressure drop of 8.8 kPa across the bed. After ignition, sintering was commenced by drawing air down through the packed bed, moving the combustion front from the top to the bottom of the sinter pot. To achieve this, during sintering a draft pressure drops of 14.7 kPa (base case), 16.7 kPa (high draft) or 12.7 kPa (low draft) across the bed were applied. After the flame front had passed through the sinter bed the sinter was cooled using a draft pressure drop of 7.8 kPa across the bed. Once cooled, the resulting sinter was crushed and separated into fine (-2mm) and coarse (+2mm) sizes, designated as the sinter returns and sinter product respectively.
The proportions of the phases present in the sinter product and fines were determined by semi-quantitative XRD. The sinter product and fines were separately ground in a ring mill. The resulting powders were analysed with powder X-Ray Diffraction (XRD) (Bruker D8), with a Cu Kα radiation source at a voltage of 40 kV and a current of 40 mA. Semi-quantitative phase analysis was performed with DriffracEVA by Bruker, with the proportion of each phase determined by the relative peak intensity between that measured and the XRD patterns from the International Centre for Diffraction Data Powder Diffraction Files.

2.2 Laboratory Scale Tests

In the controlled cooling experiments, oxide pellets (0.1 g) are heated and cooled in air in an electrically heated vertical tube furnace (alumina reaction tube, 38 mm OD 30 mm ID). The oxide sample supported on Pt wire is vertically suspended by a 70/30 Pt-Rh wire within the reaction tube in the furnace, with the wire held by an alumina rod. The vertical position of the alumina rod, and in turn the sample, is controlled with a positioning motor affixed to the top of the furnace. The sample is raised into the hot zone of the furnace and held at the target temperature for homogenisation at for 480 s. After homogenisation, the sample is lowered using a computer controlled motor drive to achieve a constant cooling rate. On reaching the target temperature the sample is released and falls under gravity into water, the quenching medium. Further details of the experimental apparatus are provided elsewhere [11].

Reheating experiments were performed to examine magnetite formation and oxidation, with samples containing 94.33 wt% Fe₂O₃ and a CaO/SiO₂ ratio of 5.32 wt/wt. Samples were held in air at 1400 °C for four minutes, prior to quenching in water. The quenched samples were dried, rapidly heated and held for four minutes at 1200 °C, 1100 °C and 1000 °C in air, followed by quenching in water. In addition, using the composition investigated in reheating experiments, separate samples were prepared by controlled cooling in air from 1400 °C to 800°C at 2 °C/s.
The samples were characterised initially using optical microscopy for phase and microstructure identification using a reflected light microscope (Olympus Provis AX70TRF). The compositions of the phases were measured using an electron probe X-ray microanalysis (EPMA) technique with wavelength dispersive spectroscopy (WDS) (JEOL 8200L EPMA; Japan Electron Optics Ltd., Tokyo, Japan) at a voltage of 15 keV and current of 20 nA. Three standards were used for calibration, pure CaSiO$_3$, Fe$_2$O$_3$ and Al$_2$O$_3$ (all standards from the Charles M. Taylor Co., Stanford, CA). Iron concentrations in phases were recalculated to Fe$_2$O$_3$ for presentation purposes.

3. Results

3.1 Base Case Temperature and $p_{O_2}$

The base case sinter pot test was performed using 14.7 kPa draft pressure drop and 36 kg$_{coke}$/t$_{feed}$. The apparent $p_{O_2}$ and temperature measurements as a function of time are shown in Figure 3. The term apparent oxygen pressure is used as the calculated $p_{O_2}$ assumes that the tip temperature of the probe and the external thermocouple are identical.

![Figure 3: Temperature and $p_{O_2}$ profile measured for the base case sinter pot test (14.7 kPa draft pressure, 36 kg$_{coke}$/t$_{feed}$)](image)

The changes in temperature of the sample can be described in terms of three stages, heating, peak temperature and cooling. During heating, the temperature was initially relatively constant at approximately 110 °C to 120 °C, followed by rapid heating to the peak temperature of approximately 1350 °C. The average heating rate between 200 °C and 1250 °C was 5.6 °C/s. The heating rate was a maximum of 15 °C/s at 860 °C. The total time for which the temperature exceeded 1200 °C, which is approximately the solidus temperature in the iron ore sinter [12], was 450s. During sinter cooling, between 1280 °C and 1200°C, the cooling rate was relatively constant, with an average cooling rate of 0.7 °C/s. The maximum of 2 °C/s was at 900 °C. The cooling rate in this critical period is observed to be significantly slower than the heating rate.

The measured $p_{O_2}$ during heating was observed to have a single low $p_{O_2}$ peak of $10^{-7.52}$ atm occurring at approximately 780 °C. Above 1200 °C, two small reducing peaks were observed, both occurring at 1340 °C one with a $p_{O_2}$ of $10^{-1.64}$ atm and the other with a $p_{O_2}$ of $10^{-1.85}$ atm. A single reducing $p_{O_2}$ peak was observed on cooling from 1200 °C to 200 °C, occurring at approximately 370 °C with a $p_{O_2}$ of $10^{-8.2}$ atm.
3.2 Effects of coke addition on temperature and $p_{O2}$

To determine the effect of coke addition on the temperature and $p_{O2}$ in sintering, two additional sinter pot tests, at high coke addition (3.9 kg/t$_{feed}$) and low coke addition (3.3 kg/t$_{feed}$) were undertaken. The $p_{O2}$ and temperature measurements for the two tests are shown in Figure 4.

![Figure 4: Temperature and $p_{O2}$ profiles measured for a) low coke (14.7 kPa draft pressure, 33 kg$_{coke}$/t$_{feed}$) and b) high coke (14.7 kPa draft pressure, 39 kg$_{coke}$/t$_{feed}$) additions](Image)

With a variation in the coke addition, both the temperature and $p_{O2}$ profiles were observed to change. On heating, in both the low (33 kg/t$_{feed}$) coke and high (39 kg/t$_{feed}$) coke tests relatively rapid heating took place, with a peak heating rates of 10.8 °C/s at 940°C and 21.0 °C/s at 890°C respectively. The average heating rate between 200°C and 1250°C was 4.3 °C/s at both a low coke addition rate and a high coke addition rate. The peak bed temperatures increased from 1370°C to 1450°C with an increase in coke addition from 33 kg/t$_{feed}$ and 39 kg/t$_{feed}$. The time at which the bed temperature was greater than 1200°C increased from 190 s to 1100 s on increasing the coke rate from 33 kg/t$_{feed}$ to 39 kg/t$_{feed}$. On cooling, a maximum cooling rate of 1.64 °C/s at 1200°C and 1.25 °C/s at 1000°C was observed for low and high coke addition rates respectively. At a low coke addition, the cooling rate was relatively constant at 1.1 °C/s from 1280°C to 1200°C. At a high coke addition, the cooling rate was relatively constant at 1.1 °C/s from 1280°C to 1200°C.

For both coke additions, two reducing peaks were observed on heating. For 33 kg/t$_{feed}$, a minimum oxygen partial pressure of $10^{11.21}$ atm was observed at 845°C and $10^{3.15}$ atm at 980°C. For 39 kg/t$_{feed}$, a minimum oxygen pressure of $10^{10.15}$ atm was observed at 310°C and $10^{8.85}$ atm at 915°C. At 39 kg/t$_{feed}$ above 1200°C, the oxygen partial pressure was measured to be between $10^{1}$ atm and $10^{2}$ atm. During cooling, a single reducing peak was observed for both coke additions investigated. For 33 kg/t$_{feed}$, a $p_{O2}$ of $10^{2.02}$ atm was observed at 380°C and for 39 kg/t$_{feed}$ a $p_{O2}$ of $10^{5.02}$ atm was observed at 840°C.
3.3 Effects of draft pressure on temperature and $p_{O2}$

To determine the impact of sinter draft pressure on the temperature and $p_{O2}$ in sintering, two additional sinter pot tests were undertaken at 12.7 kPa and 16.7 kPa draft pressure respectively. The $p_{O2}$ and temperature measurements for the two tests are shown in Figure 5.

![Graphs showing temperature and $p_{O2}$ profiles with draft pressure](image)

**Figure 5**: Temperature and $p_{O2}$ profile measured for (a) low draft pressure (12.7 kPa draft pressure, 36 kg coke/feed) and (b) high draft pressure (16.7 kPa draft pressure, 36 kg coke/feed)

With a variation in the draft pressure, both the temperature and $p_{O2}$ profiles were observed to change. On heating, a peak heating rate of 12.4 °C/s at 810 °C was observed at 12.7 kPa, and 10.9 °C/s at 1025 °C at 16.7 kPa. The average heating rates between 200 °C and 1250 °C for both conditions were approximately 4.0 to 4.3 °C/s. With an increase in draft pressure, the peak bed temperature decreased from 1370 °C to 1340 °C. The time at which the bed temperature was greater than 1200 °C decreased from 671 s to 260 s with an increase in draft pressure from 12.7 kPa to 16.7 kPa. On cooling, maximum cooling rates were between 1.0 to 1.3 °C/s at approximately 980 °C for both low and high draft pressures.

For both draft pressures, a single low oxygen pressure peak was observed on heating and a single reducing peak was observed on cooling. At 12.7 kPa, an oxygen pressure of $10^{-12.28}$ atm was observed at 200 °C and 16.7 kPa, an oxygen pressure of $10^{-13.18}$ atm was observed at 380 °C. Above 1200 °C, unlike the base case, no $p_{O2}$ peaks were observed and the $p_{O2}$ was relatively constant at an oxygen pressure of $10^{-1}$ atm. On cooling, at 12.7 kPa, oxygen pressure of $10^{-3.96}$ atm was observed at 760 °C and at 16.7 kPa oxygen pressure of $10^{-3.01}$ atm was observed at 480 °C.

3.4 Proportions of phases in sinter products and fines

The proportions of the major sinter phases in the product material obtained from the present sinter pot tests, excluding amorphous material, were determined by semi-quantitative XRD. The proportions
of the phases, calculated for the sinter product are shown in Figure 6 and the sinter fines are shown in Figure 7. Some minor variations in the proportions of the phases were observed in all tests. The variation were attributed to uncertainties in sampling and measurement technique; these are estimated to be in the order of +/−20% of the measured values.

![Figure 6: Proportions of phases in the sinter product as determined by semi-quantitative XRD.](image)

![Figure 7: Proportions of phases in the sinter fines as determined by semi-quantitative XRD.](image)

The sinter product was observed to consist of predominantly hematite (Fe₂O₃) (~30 wt%), magnetite (Fe₃O₄) (~25 wt%) and silico ferrite of calcium and aluminium (SFCA) (~20 wt%), and minor quantities of dicalcium silicate (Ca₂SiO₄, C₂S) (~10%). The sinter fines was observed to contain a significant quantity of hematite (~50%), and minor quantities of the other components. In addition, the sinter fines were observed to contain significantly larger quantities of silica than the sinter product. Both the product and fines contained larger proportions of magnetite than present in the sinter feed.

The increase in coke rate to sintering was observed to increase the proportion of magnetite in both the sinter product and fines. The variation in sinter draft pressure did not significantly influence the proportions of the phases formed in either the sinter fines or product.

### 3.5 Microstructures formed in sinter products

Samples of iron ore sinter product were taken from the Baosteel Shanghai Sinter Plant no. 3 for microstructural analysis. Examples of porous and dense sinter lump are shown in Figures 8a) and 8b) respectively. The sinter samples exhibit an irregular shape and porous structure with pore diameters ranging from 0.1 to 5mm.
Polished cross sections of the sinter product were examined by optical microscopy, scanning electron microscopy (SEM) and electron probe micro X-ray analysis (EPMA) to determine the phases and microstructures present, and the phase compositions. Figure 9 shows the overall scale of the microstructures within the sinter, illustrating the presence of undissolved hematite ore in a matrix of fine crystals (which from XRD data appear to be SFCA-I) and gas pores.

The hematite and magnetite are present in different forms and microstructures, as can be seen in Figures 10 to 12. In Figure 10, a fine grained porous hematite (detail shown in Figure 10b) is present with larger grained dense magnetite. The porous hematite is believed to result from the decomposition of goethite. The rounded magnetite grains (details shown in Figure 10a) appear to have
formed following reaction with the surrounding liquid phase at temperature. Hematite has also been observed to form equiaxed hematite and large angular dendrites. The equiaxed hematite crystals were observed to be present in a glassy high silica matrix (liquid at temperature), shown in Figure 11a. Hematite in the form of large angular dendrites surrounded by a partially crystallised matrix is shown in Figure 11b.

![Figure 10: Examples iron oxide structures in industrial sinter lumps, a) a mixed hematite-magnetite microstructure, b) fine grained hematite. (H-Hematite, M-Magnetite) (Back scattered electron images(BSE) )](image1)

![Figure 11 Microstructures of the hematite phase associations, a) equiaxed hematite in a glassy low Ca/SiO$_2$ matrix, b) angular hematite dendrites surrounded by a partially crystallised matrix. (BSE) (H-Hematite, L-Liquid, C-C$_2$S)](image2)

Plate-like (Figure 12a) and blocky (Figure 12b) SFCA phase was typically found to be associated with magnetite crystals. There are subtle differences in the magnetite structure between these two cases, for platy SFCA, the magnetite/SFCA interface is irregular (Figure 12a), whilst for the blocky SFCA, the magnetite/SFCA interface is smooth and the crystals have a more equiaxed appearance (Figure 12b).
A single sinter lump typically consists of multiple microstructures. The boundaries between these regions vary from well defined to diffuse. An example of a diffuse boundary between regions containing SFCA and magnetite and primary hematite is shown in Figure 13. EPMA analysis of the continuous liquid phase present in this transition structure demonstrates a variation in the chemical composition, indicating the penetration of high calcia liquid into the matrix surrounding the primary hematite structures. Examples of well defined transitions are shown in Figure 14a and b. In Figure 14a) there is a well defined transition between the platy SFCA and magnetite structure present in the bulk of the sinter sample, and the dendritic hematite and liquid phase assemblage present adjacent to the gas pore. This type of transition structure is observed to be typically present as a layer several hundred microns thick where clearly open or connected pores were present in the sinter macrostructure. In Figure 14b) magnetite is present in both structures but in the one case associated with platy SFCA, in the other a partially crystallised liquid matrix. This is indicative of materials with very different thermal histories. In this case potentially SFCA present in return sinter is in contact with liquid and newly produced equiaxed magnetite that has formed in the melt.
Figure 14: Examples of the heterogeneous structure of the sinter materials, a) hematite present close to the pore or surface, and b) interface between regions containing (SFCA+magnetite+liquid) and (magnetite+liquid). (S-SFCA, M- Magnetite, H-Hematite) (BSE images)

The compositions of the phases present in the sinter were measured by EPMA, with a random selection of the measurements made summarised in Table 2. It was found that the hematite contained between 0.0 to 0.7 wt% CaO and 0.5 to 2 wt% Al$_2$O$_3$. Magnetite was found to contain between 0.9 to 2.8 wt% CaO and 0.7 to 2.0 wt% Al$_2$O$_3$. The liquid was found to contain appreciable concentrations of silica (35.7 to 39.9 wt% SiO$_2$), lime (37.4 to 44.3 wt% CaO) and iron (16.0 to 18.7 wt% ‘Fe$_2$O$_3$’). The composition of the SFCA phase was variable, however once normalised to the ternary ‘Fe$_2$O$_3$’-CaO-SiO$_2$ system with the Mg$^{2+} \rightarrow$ Ca$^{2+}$ and Al$^{3+} \rightarrow$ Fe$^{3+}$ cation exchange reactions, as illustrated in Figure 15, the compositional changes are consistent with the CF$_3$-C$_2$S$_3$ solid solution[13].

Table 2: Measured composition of phases present in industrial sinter(EPMA)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition (wt%)</th>
<th>'Fe$_2$O$_3$'</th>
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<th>CaO</th>
<th>Al$_2$O$_3$</th>
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<th>MnO</th>
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4. Discussion

4.1 Hematite and magnetite in sinter

4.1.1 Hematite and magnetite stability

Both hematite and magnetite are observed to be present in industrial iron ore sinters. The two phases are able to achieve equilibrium with oxygen gas, as represented by the reversible reaction;

\[ 3\text{Fe}_2\text{O}_3(s) \leftrightarrow 2\text{Fe}_3\text{O}_4(s) + 0.5\text{O}_2(g) \]

The \( p_{O_2} \) at which hematite, magnetite and oxygen are at equilibrium varies with temperature and the composition of hematite and magnetite. With increasing temperature, the equilibrium \( p_{O_2} \) increases. In air (0.21 atm \( O_2 \)), pure magnetite is able to form from pure hematite if the temperature is at or above 1380 °C.

Based on the measured \( p_{O_2} \) and temperature within the sinter pots, the calculated Gibbs free energy of reaction for the reduction of pure hematite to pure magnetite is shown in Figure 16. At a high coke rate, the reduction of hematite to magnetite in air (0.21 atm \( O_2 \)) is observed to be spontaneous at the peak bed temperature. At all other conditions investigated, the reaction was not observed to be spontaneous for any significant period of time, but closely approached conditions at which the reduction of pure hematite to pure magnetite is spontaneous.

On heating, reducing \( p_{O_2} \) peaks were observed to occur, however, the predictions indicate that the reduction of pure hematite to form pure magnetite at the measured temperature and \( p_{O_2} \) is not favoured.
The impact of the composition of hematite and magnetite on the spontaneity of the hematite reduction at temperature can be predicted knowing the thermodynamic data for the phases. The $p_{O2}$ for hematite and magnetite equilibrium was calculated between 1300 °C and 1400 °C using FactSage and an internal thermodynamic database, summarised in Figure 17. As observed in industrial sinters (Table 2), hematite typically contains $Al_2O_3$ and magnetite contains $Al_2O_3$, MgO and CaO. The industrial hematite and magnetite compositions used in the calculations represent the average compositions in the industrial sinter (see Table 2). It can be seen that the presence of $Al_2O_3$, MgO and CaO in solid solution in magnetite decreased the temperature at which hematite is reduced to magnetite in air. The presence of $Al_2O_3$ in hematite was observed to increase the temperature at which the hematite is reduced to magnetite in air.
Figure 17: The calculated oxygen pressures for equilibrium between hematite to magnetite phases at selected compositions. Lines show the hematite/magnetite equilibrium conditions, with pure phases the base case.

Based on the measured composition of the hematite and magnetite, it is estimated that the reduction of hematite to form magnetite is spontaneous in air (0.21 atm O\textsubscript{2}) at approximately 1330 °C. The peak bed temperature at all conditions investigated in the present study exceeded 1330 °C, indicating that the reduction of hematite to magnetite is spontaneous at the peak bed temperature in all sinter pot tests.

The proportions of phases present in the sinter at the peak bed temperature were also calculated using FactSage and a private database, assuming equilibrium is achieved at an oxygen partial pressure of 0.21 atm. The results of the calculations are summarised in Figure 18. The proportion of liquid present is shown to be significant and sensitive to the peak bed temperature. An increase in peak bed temperature from 1300 °C to 1400 °C increases the proportion of liquid present from 28 wt% to 50 wt%. As a result of the solid solutions both hematite and magnetite are predicted to co-exist below 1380 °C. The composition of the liquid is summarised in Figure 19. The CaO/SiO\textsubscript{2} ratio is observed to decrease with reduction of hematite to magnetite, due to the inclusion of CaO in the spinel crystal structure. On melting of the magnetite, the CaO/SiO\textsubscript{2} ratio of the melt is observed to increase.

If during the sintering processing the bed material is not heated above the liquidus, some of the primary iron ore will not be dissolved. It is well recognised that this primary iron ore contains inclusions of silica. If the iron oxides are not dissolved then the associated silica is not released into the liquid phase and the CaO/SiO\textsubscript{2} in the liquid is increased relative to that of the bulk.
4.1.2 Targeted laboratory scale experiments

The measurements of oxygen partial pressures during the sintering process show that the gas atmosphere favours the formation of magnetite only at the peak bed temperature, with hematite favoured at all other conditions during sintering. However, in the sinter pot products, both magnetite and hematite are present. This indicates the sinter charge does not attain chemical equilibrium on cooling. In the present study targeted laboratory experiments were undertaken to examine the mechanisms by which magnetite is oxidised to form hematite during sintering. To simulate industrial sintering, and to ensure that magnetite is present at the peak temperature, samples with a bulk composition of 88.0 wt% Fe$_2$O$_3$ and a CaO/SiO$_2$ ratio of 3.46 wt/wt were cooled from 1400 °C to 800 °C in air at 2 K/s. The resulting microstructure was found to contain both hematite and magnetite; three individual hematite microstructures, dense, fine and lath hematite, and a dense magnetite microstructure. Examples of these microstructures are shown in Figure 20.
The oxygen required for the oxidation of magnetite to hematite can be transferred directly by reaction with the gas phase or through a solid or liquid carrier phase. To assist in identifying the oxidation processes taking place, experiments were performed by first heating samples in air for 240 s at 1400 °C to form magnetite, followed by quenching in water and reheating for 240 s at 1200 °C, 1100 °C and 1000 °C in air and quenched in water. The magnetite structure formed by heating at 1400 °C is shown in Figure 21. The magnetite was observed to be anhedral and irregular in shape, with grains formed in the order of 50-100 μm. The magnetite analysed using EPMA and found to contain approximately 2.50 wt% CaO.

Reheating of this magnetite in air at 1200 °C resulted in the complete oxidation of the magnetite to form dense hematite, as shown in Figure 22. The composition of the hematite formed was measured by EPMA and found to contain 0.01 wt% CaO. The dense hematite was approximately 20 μm in size, smaller than the magnetite present at 1400 °C. With the oxidation of magnetite to hematite, an increased porosity of the sample was observed. The dense hematite appears to be surrounded by a matrix of high CaO-containing material. The phase diagram for the CaO-Fe₂O₃-SiO₂ system in air [14] indicates that liquid can form at this temperature.
Figure 22: Example of dense hematite and associated microstructures observed from magnetite formed at 1400 °C and reheated in air at 1200 °C for 4 minutes (94.33 wt% Fe₂O₃ and a CaO/SiO₂ ratio of 5.32 wt/wt).

(BSE Micrograph)

On reheating of the magnetite for 240s at a temperature of 1100 °C and 1000 °C, both magnetite and hematite phases were observed. A micrograph illustrating these microstructures is shown in Figure 23. The hematite was observed to be present in two forms, i) as a fine grained (<1 μm) two phase structure with an unidentified phase, and ii) as laths (~ 2 μm in width) within the magnetite grains. The hematite is observed to form on the exterior surfaces of the magnetite crystals, and in association with cracks and porosity. The cracks and porosity can provide pathways for the transfer of oxygen from the gas into the sample.

The unknown phase present in the fine grained two phase structure appears to have formed as a result of the compositional difference between the magnetite (2.50 wt% CaO) at 1400 °C and the hematite (0.01 wt% CaO). Due to the small size of the unknown calcium ferrite crystals, the phase could not be positively identified by EPMA but are assumed to be calcium ferrite crystals. Based on the composition difference between the hematite and magnetite, calcium is rejected to a second phase, with potential candidates including SFC, SFC-I, CF₂, CF and Ca₇₂Fe²⁺₀.₈Fe³⁺₃₀O₅₇ [15].
4.1.3 Mechanisms of formation of hematite and magnetite

When simulating magnetite oxidation occurring on the cooling of sinter, three distinct hematite morphologies were observed to form, dense hematite, hematite laths and fine hematite. These two phases were observed to form as a result of magnetite oxidation. The magnetite formed at the peak temperature contained approximately 2.5 wt% CaO, while both dense and fine hematite was found to contain minimal CaO. The oxidation of magnetite must be accompanied by the transfer of the CaO into a second phase.

Dense hematite was observed to form at high temperatures in the presence of a liquid. In systems in which the iron is present in the melt, oxygen is transferred from the gas/melt interface to the liquid in the ionic state via a redox reaction. In these iron oxide containing systems the electrons are provided by the Fe$^{3+}$/Fe$^{2+}$ ions, which are oxidised from the Fe$^{2+}$ to the Fe$^{3+}$ state. The transfer of ferric ions through the melt takes place through an electron hopping mechanism rather than by ionic diffusion.

To form the dense hematite in the presence of a liquid, the hematite would have either originated as homogenous nuclei or formed on the surface of the magnetite. This suggests that there are four potential mechanisms for hematite formation, i) as a dense product layer on the magnetite with the diffusion of Ca$^{2+}$ ions from the magnetite/hematite interface into the melt via solid state diffusion in hematite, ii) as a porous product layer on the magnetite with the diffusion of the Ca$^{2+}$ from the magnetite/hematite interface to the bulk melt via the liquid filled pores, iii) by the formation of separate hematite and magnetite phases with the melt facilitating the mass transfer of the chemical components or iv) as a dense product layer on magnetite with the diffusion of Ca$^{2+}$ ions from the
hematite/magnetite interface into the magnetite phase. These reaction mechanisms are illustrated schematically in Figure 24.

Figure 24: Schematic of liquid-facilitated magnetite oxidation a) dense hematite on magnetite with calcium rejection into the melt, b) porous hematite on magnetite, c) isolated hematite and magnetite and d) dense hematite on magnetite with calcium rejection into the magnetite.

With the rejection of the Ca\(^{2+}\) into the magnetite phase during oxidation, the calcium accumulates in the magnetite, leading to the potential formation of calcium ferrite phases in the centre of the hematite. In Figure 22 the dense hematite appeared to be free of inclusions, suggesting that the CaO in the magnetite is rejected into the surrounding liquid rather than a second solid phase. The mechanisms by which calcium is rejected from the magnetite into the surrounding liquid requires further investigation.

Fine hematite was observed to form in the absence of a liquid, i.e. at temperatures below the solidus. The fine hematite was observed to form on the surface of the magnetite with the morphology of the original magnetite retained. The unknown calcium ferrite appears to form throughout the secondary hematite. These observations indicate that the magnetite oxidation occurred through a gas-solid reaction process. The volume of the calcium ferrite formed is smaller than the hematite. The phases formed either through i) a coupled growth mechanism or ii) the rejection of Ca\(^{2+}\) into the magnetite phase and ultimately the formation of the calcium ferrite at the centre of the secondary hematite. These two mechanisms are illustrated in Figure 25.
The third form of hematite observed was in narrow (approximately 2 μm in width) laths in the magnetite. This microstructure, formed at sub solidus temperatures, is consistent with that observed in earlier studies involving the high temperature oxidation of magnetite crystals [16]. In this study it was demonstrated that these lath structures form by a military transformation propagated through the magnetite along the close packed oxygen planes common to both hematite and magnetite. The hematite phase does not support the presence of Ca$^{2+}$ ions, and as such, in order for the growth of the hematite phase to occur the calcium in the magnetite must be rejected locally into the surrounding magnetite matrix at the crystal lath tip or a second calcium rich phase, preventing the further formation of laths.

Based on the observed oxidation mechanisms of magnetite, it is demonstrated here that the forensic EPMA measurement of the minor element concentrations present in the feed and product phases provides a method of determining the origin of the phases. If the feed material does not react with the liquid, the concentrations of elements present in solid solution are expected to be the same as in the original material. In contrast, if the same phase is present in the sinter product but formed from a secondary reaction; this material would be expected to be of a different chemical composition.

### 4.2 Analysis of Process Conditions

The present study has provided detailed information on the process conditions within the sinter bed. Before using these data the following comments and observations on the precision and accuracy of the measurements obtained are provided.

The response rate of the oxygen probe at low temperatures, below 500 °C, is slow since this is directly related to the rate of solid state diffusion through the partially stabilised zirconia at these conditions. This factor should be taken into consideration when interpreting data during the rapid initial heating at these low temperatures.

The measured temperatures and oxygen partial pressures can be influenced by the properties of the sinter. If the sinter is porous, as shown in Figure 8a, the high porosity and thin sections of solid material enables rapid heat transfer between the gas and solid such that the thermocouple reading closely reflects the local temperature of the gas. If there is a dense sinter structure, resembling that shown in Figure 8b, there is limited gas/solid contact and the temperature measured may more closely reflect that of the condensed phases than the gas phase. A large thermal mass of the sinter surrounding the thermocouple and the relatively low heat transfer rate will result in significant temperature differences between the inner and the outer surfaces of the particles. The measured cooling rate is
then dependent on the position of the thermocouple within the condensed phase, the local geometry of the condensed phase and the gas temperature. In this case, there will be a difference in the thermal history of the solid/liquid mixture between the interior and exterior of the fused section.

On heating, the oxygen probe is in contact with gas passing down through the bed. In practice, the oxygen probe is measuring the $p_{O_2}$ of the material above the probe tip, rather than that at the tip. In addition, it has been assumed that the local temperature at the oxygen probe tip is the same as that measured by the thermocouple. The position of the thermocouple junction relative to the oxygen probe tip and the temperature difference arising from this difference should be taken into account.

### 4.2.1 Relationship between process conditions and microstructure

Variations in the measured oxygen pressures at the peak bed temperature provide clear evidence of heterogeneity in the local process conditions. The combustion of coke particles will lead to local variation in temperature and oxygen partial pressure within the sinter. The magnitudes of these variations will depend on the initial particle size, and dispersion of both coke and the oxides in the sinter granules.

The anomalous $p_{O_2}$ on cooling, the oxidation of magnetite, appears to take place when the probe covered with solidified material. The bulk gas at this stage, which has a composition close to air, has a higher $p_{O_2}$ (~0.21 atm) than that measured. In this event, as demonstrated in Section 3.2, due to the reactions taking place at the probe tip, the effective $p_{O_2}$ approaches the Fe$_2$O$_3$/Fe$_3$O$_4$ equilibrium at these lower temperatures.

Examples of sinter microstructure observed in product and return sinter have been given in Figures 10 to 14. Caution should be taken when making direct correlations between microstructure and probe results, since the samples in the industrial sized sinter process may be subjected to different process conditions to those in the sinter pot tests.

In the present study the position of the thermocouple and probe are approximately half way down the bed at the start of the sinter process. As demonstrated previously [7], the thermal history at this position will differ to other regions within the sinter bed. The variation in thermal history will be reflected in a variation in product microstructures. A potential solution to this would be to in future studies examine sinter samples from the regions surrounding the probe tips, rather than sampling the bulk sinter.

The origin and thermal history of different phases can potentially be determined from their composition, morphology and associated phases. The determination of the minor element compositions of hematite/magnetite crystals by EPMA microanalysis can help to determine whether the crystals originate from primary or secondary hematite/magnetite.

### 4.2.2 Comparison with previous studies

The present study has shown that accurate and repeatable measurements of temperature and oxygen partial pressure in the sinter bed can be obtained as a function of time. In the present study, the main
reduction peak was observed, in all cases, to occur on heating. Small, short term variations in $p_{O_2}$ were observed during heating and at peak bed temperature. At the peak bed temperature, oxidising conditions were observed, with the $p_{O_2}$ measured to be greater than 0.01 atm.

The $p_{O_2}$ measured during sintering, and the corresponding temperature, differed significantly from that previously measured [4, 5]. Multiple reducing peaks were observed, both before and after the peak bed temperature, while only a single peak was previously observed either before [4] or at the peak bed temperature [5]. The $p_{O_2}$ peaks were more reducing than that previously observed [4, 5], with a variation in the peaks observed between sinter pot tests.

The effect of variation in the coke additions and the draft pressures on the temperature profile in the sinter bed in agreement with prior sinter modelling research [8]. Specifically, the peak bed temperature and time at temperature were observed to increase with increasing coke addition and the time at peak bed temperature was observed to increase with decreasing draft pressure.

4.3 Processes taking place during sintering

4.3.1 Heating: Calcination, dehydration and combustion

Rapid heating of the charge takes place between approximately 100 °C and 1200 °C. For all the conditions investigated, low oxygen partial pressures, $p_{O_2}$ between $10^{-3.15}$ and $10^{-13.18}$ atm were observed on heating between approximately 200 °C and 1000 °C. The heating rates are observed to increase with increase in high draft pressure and coke addition rates. A higher coke addition increases the heat generation per unit mass of sinter. A higher draft results in a higher gas flow, increased the convective heat transfer between the gas and condensed phases.

No thermal arrests were observed at the goethite dehydroxylation (290 °C to 330 °C) and the calcite decarbonation temperatures (895 °C) [17]. The temperatures at which these processes occur vary with the composition and the degree of crystallinity of these phases [17]. A thermal arrest associated with the dehydroxylation and decarbonation of these minerals is unobservable with the current technique. The generation of $H_2O(g)$ and $CO_2(g)$ as a result of dehydroxylation and decarbonation will dilute the oxygen in the gas phase, decreasing the $p_{O_2}$.

The coke ignition temperature has been shown to depend on coke composition, gas composition and coke size [18] and occurs at temperatures below 525 °C [19]. Coke combustion therefore occurs well before the attainment of the peak bed temperature. The combustion of coke particles results in the localised generation of $CO(g)$ and $CO_2(g)$, and the formation hot spots and low oxygen partial pressure locations within the sinter. Due to the formation of individual channels, the coke is combusted as individual particles, as opposed to simultaneous combustion. The localised $CO(g)$, once generated, is diluted and reacts as it is drawn down through the sinter bed by the draft pressure. As the $CO(g)$ passes down through the bed, it reacts with the excess oxygen, however on cooling the final gas mixture is not at thermodynamic equilibrium.

From the observed temperature and $p_{O_2}$ profiles, it is apparent that there are two stages to the sinter heating process. The first occurs with the transfer of heat from the gas to the condensed material. At the conclusion of the first stage, the coke reaches conditions at which it is able to ignite and combust. After the rapid combustion of the coke, the materials in contact with and close to the combustion are heated to temperatures higher than the surrounding material. The second stage of heating occurs with the transfer of heat from these hot reducing spots to the surrounding cooler material.
4.3.2 Peak bed temperature

In the present study, the oxygen partial pressures measured at peak bed temperatures and within 100 °C of the peak temperatures were all greater than 0.01 atm, in contrast to ~10^-6 atm previously reported by [5].

It is suggested that the gas and condensed phases do not reach equilibrium in sintering, with the average $p_{O_2}$ in the condensed phases lower than the gas phase. In addition, due to the heterogeneous heating, it is further suggested that the $p_{O_2}$ within the sinter is variable with distance from the coke combustion.

The proportion of magnetite in the sinter fines was lower than that observed in the sinter product, and marginally greater than in the sinter feed. The formation of magnetite occurs under reducing conditions at high temperatures. In addition, the proportion of silica phases in the sinter fines is shown to be greater than in the product. Both observations suggest that the sinter fines originate predominantly from regions that experienced lower peak bed temperatures.

In agreement with previous research [20], the length of time at the peak bed temperature was observed to increase with decreasing draft pressure. However, in contrast to that previously reported[20], the peak bed temperatures do not appear to be greatly influenced by changes in draft pressure.

Increasing the coke addition rate was observed to increase the peak bed temperature and time at temperature, consistent with past observations [10]. The increase in coke rate results in increases in the heat generated. For an identical rate of heat loss to the gas, this results in increased bed temperature and increased liquid fraction in the charge, which results in an increased agglomeration of the ore. The increased agglomeration means that the rate of heat loss to the gas passing through the bed is also reduced and the solid/liquid mixture is maintained at the peak bed temperature for longer periods of time.

With increased temperatures and increased time at temperature, a larger proportion of hematite will be reduced to magnetite, as observed by the semi-quantitative XRD.

4.3.3 Cooling

The cooling rates of the sinter were observed to be largely independent of the draft and coke addition rate. The cooling rate was observed to vary from approximately 1 °C/s to 2 °C/s. Due to the heterogeneity of the coke combustion and the generation of a heterogeneous temperature profile with respect to horizontal position, it is proposed that a relationship between these variables is present but unable to be measured with the techniques used. The cooling rate within the sinter is influenced by extent of agglomeration. With a more extensive agglomeration, associated with greater sinter melting, the rate of heat transfer from the solids to the gas decreases, decreasing the rate of sinter cooling.

At all conditions investigated, the oxygen probe registered low oxygen pressures on cooling in the temperature range of 1000 °C to 300 °C, despite the fact that the bulk gas passing through the bed contains a high $p_{O_2}$, approaching that of air. This indicates the low oxygen pressure measurements are related to reactions taking place adjacent to the probe sensor. As observed in laboratory scale experiments (see Sections 4.1.2 and 4.1.3), the oxidation of magnetite in this temperature range can occur through gas-solid reactions. As the gas-solid oxidation of magnetite is able to occur slowly in the temperature range at which the peak was observed, this reaction is proposed to be the cause for this peak. As the peak varies in width, $p_{O_2}$ and occurrence temperature, the oxidation is likely to be caused by the formation of cracks within the sinter. The formation of these cracks, as a result of phase changes
or differences in thermal expansion, would expose the previously enclosed magnetite to air, enabling oxidation to occur. During the oxidation of the magnetite, the average $p_{O_2}$ in the condensed material increases and the $p_{O_2}$ of the gas phase decreases.

### 4.4 Stages of sintering

The stages of sintering identified in previous studies (Figure 1) have focused on particular reaction steps that occur during the process. However, these stages do little to define the process conditions that are present during the sinter process and their potential impact on sinter microstructure, which ultimately determine the properties of the sinter product. It has been shown in the present and previous studies [4, 5] that temperature and oxygen partial pressure are key process variables. Analysis of the results obtained in the present study show that both equilibrium and non-equilibrium phases can be formed depending on these conditions and the thermal history. To more clearly understand the reasons for the formation of these phases the heating, peak bed and cooling stages of the process are more clearly defined, as follows

1a. Heating solids under high/low oxygen pressures
1b. Heating solid/liquid mixtures under high/low oxygen pressures
2. Peak bed temperature under high/low oxygen pressures with solid/liquid mixtures
3. Cooling in solid/liquid mixtures under high oxygen pressures
4. Cooling solid mixtures under high oxygen pressures

In stage 1a, the granular sinter is heated up in high oxygen pressure conditions, with the dehydroxylation and decarbonation of minerals occurring as the temperature is rapidly increased. The extent of reactions between solid components is limited due to the limited point contact between solids and the relatively low rates of mass transfer in the solid state.

In stage 1b, ignition and combustion of the coke results in the generation of locally reducing conditions. This leads to two extremes of process conditions within the sinter, high oxygen pressures approaching that in the gas that is being drawn through the bed; low oxygen partial pressures associated with coke combustion and high CO/CO$_2$ ratios. At this stage, liquid can appear in selected regions of the charge dependent on temperature and oxygen pressure; the liquid phase facilitates rapid reaction between the phases. The proportion of liquid present increases with increasing temperature.

In stage 2, at the local peak bed temperatures encountered in iron ore sintering, liquid/solid mixtures are present, and the mixtures move towards isothermal chemical equilibrium in these sub-liquidus conditions. The local process conditions may be oxidising or reducing with respect to magnetite and are sensitive to peak bed temperature and chemical composition of the charge materials.

In stage 3, as the mixture is cooled, precipitation of selected chemical components from the liquid onto existing solids takes place, and new phases and microstructures are formed. The solidification occurs under conditions that are oxidising relative to the magnetite phase.

In stage 4 all the metal oxides are in the solid state. During cooling the air drawn down through the sinter ensures that the gas phase maintained oxidising conditions relative to magnetite and secondary hematite is formed.

### 5. Summary

Instrumented pilot scale iron ore sinter tests have been undertaken to determine the temperatures and oxygen partial pressures present in the charge during sintering, and the impact of coke rate and draft pressure on the process conditions and sinter products. Repeatable trends and relationships
between the $p_{O_2}$ and temperature profile during sintering were obtained using this experimental design and procedure. The increase in the coke addition led to an increased heating rate, a higher peak bed temperature and longer time at peak temperature. An increase in the draft pressure was observed to result in increased heating rate and shorter times at peak temperature. The sintering stages have been classified in terms of the process conditions present during sintering to enable the influence of these variables on the resulting microstructure to be more clearly identified.

Thermodynamic and microstructural analysis have provided further information on the processes taking place during sintering, and the relationships between key process variables and product structures.

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References


Appendix G: Silico Ferrite of Calcium (SFC) Formation in the “Fe₂O₃”-CaO-SiO₂ System
Silico Ferrite of Calcium (SFC) Formation in the “Fe₂O₃”-CaO-SiO₂ system

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Abstract
The silico ferrite of calcium (SFC) phase is anticipated based on phase equilibria to form from the solidification of high iron oxide melts in the “Fe₂O₃”-CaO-SiO₂ system in air at CaO/SiO₂ molar ratios greater than 2. Experimental studies undertaken for a range of compositions and cooling rates have demonstrated that this is not generally the case. The SFC phase is expected to form on cooling following the formation of hematite, but was not observed in any experiments. Kinetic factors associated with the nucleation of this phase appear to play an important part in its formation.

The isostructural phase SFCA-I has been observed to form directly from melts by homogeneous nucleation and by heterogeneous nucleation on the surfaces of magnetite. The results of the experiments to date suggest that the difficulties in SFC nucleation are related to the complex crystal structure of this phase. The SFCA phase is observed in industrial sinters in association with the magnetite phase. The presence of magnetite, or spinel, and the increased stability of the SFCA phase as the result of the incorporation of Al₂O₃ in the crystal structure, may account for the formation of this phase in industrial sinters from the melt on cooling.

Keywords: Iron ore sinter; microstructure, SFC, SFC-I, SFCA; solidification, “Fe₂O₃”-CaO-SiO₂

1.0 Introduction
The Silico Ferrite of Calcium and Aluminium (SFCA) group minerals form a significant proportion of the material in iron ore sinters, along with hematite (Fe₂O₃), magnetite (Fe₃O₄), dicalcium silicate (2CaO·SiO₂, C₂S), and glass.¹ The silico ferrite of calcium (SFC) phase, which has crystal structure identical to the SFCA phase, is a member of the polysomatic SFCA group. This phase can exist over a range of chemical compositions. Three related SFCA phases have been identified through the use of X-Ray Diffraction (XRD), SFCA², SFCA-I³ and SFCA-II⁴, with their compositions determined by Electron Probe X-Ray Micro Analysis (EPMA). The SFCA group of minerals consists of polysomes of pyroxene <Py> and spinel <Sp>, with the crystal structure formed from repeating sequences of these polysomes.⁵ The crystal structure of SFCA shown in Figure 1⁶, illustrates the arrangement of the pyroxene and spinel polysomes. The spinel polysomes are modules of the spinel structure, oriented normal to the close packed oxygen plane, consisting of one tetrahedral and one octahedral unit. The pyroxene polysome is a module, again normal to the close packed oxygen plane, consisting of one silicate chain of the pyroxene structure with both tetrahedral and octahedral units. The crystal structure of the SFCA phase consists of alternating <Sp> and <Py> polysomes, <SpPy>⁷, while the SFCA-I structure comprises of a repeat pattern of two <Sp> polysomes and one <Py> polysome, <SpSpPy>³.⁹ The SFCA-II phase is believed to be a micro intergrowth of SFCA and SFCA-I, <SpPySpSpPy>⁴.
The focus of the present research is to determine the conditions under which the SFC group minerals are formed at process conditions relevant to iron ore sintering.

2.0 Phase Equilibria

The phase equilibria in the reaction system defines a number of potential chemical reactions that could occur on sintering. The relevant phase diagrams to sintering are defined by the composition, temperature and oxygen partial pressure of the system. As indicated in the previous section, a range of process conditions are present in the sinter bed. In particular, the temperature oxygen partial pressures change with time and position in the bed.

Considering the potential chemical reactions that can occur between the components within the sinter feed, the relevant chemical systems are described by a range of binary, ternary and higher order systems, with a focus on the “Fe$_2$O$_3$”-CaO-SiO$_2$ system. Additionally, phase equilibria in the parent binary “Fe$_2$O$_3$”-CaO$^{[10]}$ system is relevant to the process. There are limited experimentally determined phase equilibria data available in the FeO-Fe$_2$O$_3$-CaO-SiO$_2$ quaternary.

Whilst the general characteristics of all the binary and ternary subsystems in the quaternary have been well established, some ambiguity and inconsistencies have been identified, particularly in the liquidus of some systems. Additionally, whilst the SFC phase has been observed to be an equilibrium phase under specific conditions, the SFC-I phase has not been observed under equilibrium conditions.

The liquidus of the “Fe$_2$O$_3$”-CaO-SiO$_2$ system in air has been reported$^{[11]}$. In this system, a number of calcium ferrites were observed, calcium diferrite (CF$_2$), calcium ferrite (CF) and dicalcium ferrite (C$_2$F). These researchers did not detect the SFC phase in the high iron corner of the phase diagram.

Isothermal phase equilibrium measurements on the “Fe$_2$O$_3$”-CaO-SiO$_2$ system in air have been performed$^{[12]}$, with the liquidus isotherms reported. These measurements were for the high Fe$_2$O$_3$ region of the phase diagram at 1573 K (1300 °C), 1543 K (1270 °C), 1528 K (1255 °C) and 1513 K (1240 °C) (see Figure 2). The SFC phase was found to form below 1528 K (1255 °C) and to be stable over a range of chemical compositions. The phase has been shown to form a solid solution on CF$_2$-Ca$_2$Si$_3$ section. The range of compositions observed is described by the substitution reaction $2Fe^{3+} \rightarrow Si^{4+} + Ca^{2+}^{[12]}$. 

Figure 1: The crystal structure of SFCA, detailing the arrangement of the spinel (Sp) and pyroxene (Py) polysomes$^{[6]}$. 

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[10]: Parent binary system refers to the system containing the elements of the quaternary system in a different order or proportion.

[11]: The temperature and composition of these measurements are specific to the condition of the experiment.

[12]: The substitution reaction describes the transformation of iron ions in the crystal structure of the phases.
Further experimental study of the \( \text{Fe}_2\text{O}_3 \)-CaO-SiO\(_2\) system in air was undertaken\[^{[12]}\] to determine the phase equilibria and liquidus of the system. From the results obtained on the solid and liquid compositions, the liquidus of the iron rich corner was determined for temperatures between 1473 K (1200 °C) and 1533 K (1260 °C) and the extent of the SFC primary phase field was established. The liquidus for this system, selected liquidus isotherms and the compositional limits of SFC in air at 1473 K (1200 °C) are shown in Figure 3\[^{[11]}\]
The SFC primary phase field is located between the C2S, CF2, and hematite primary phase fields. Three ternary invariant points and one saddle point exists for the SFC phase. Two ternary invariant points are associated with the formation of SFC through the peritectic reactions, L+Hematite $\rightarrow$ L+SFC+C2S at 1529 K (1256°C) and L+H $\rightarrow$ L+SFC+CF2 at 1498 K (1225°C) and one with the consumption of SFC through a peritectic reaction, L+SFC+C2S $\rightarrow$ L+C2S+CF2 at 1489 K (1216°C). The SFC saddle point occurs along the SFC- Hematite boundary line at 1530 K (1257°C). The projected compositions of the liquids in equilibrium with SFC between 1530 K (1257°C) and 1489 K (1216°C) are given in Figure 4. The 1573 K, 1543 K, 1528 K and 1513 K (1300 °C, 1270 °C, 1255 °C and 1240 °C) isothermal sections for the “Fe2O3”-CaO-SiO2 system at a P02 of 0.005 atm have also been determined \textsuperscript{[13]}, the phase boundaries in these isothermal sections are shown in Figure 5.
Figure 5: Isothermal sections of the phase diagram “Fe$_2$O$_3$”-CaO-SiO$_2$ at a P$_{O_2}$ of 0.005 atm$^{[12]}$.

The liquidus in the “Fe$_2$O$_3$”-CaO-SiO$_2$ system at 1 atm CO$_2$ in the high iron region has been determined experimentally between 1473 K and 1503 K (1200 °C and 1230 °C)$^{[14]}$. Under these conditions, the P$_{O_2}$ varied with the temperature, increasing from $10^{-3.9}$ atm at 1473 K (1200 °C) to $10^{-3.7}$ atm at 1503 K (1230 °C), and the SFC phase was not observed at any of the conditions examined. The absence of SFC was attributed to a decrease in the stability of this phase under reducing conditions.

The solidification pathways on cooling of these oxide melts depend critically on the local bulk composition. In the “Fe$_2$O$_3$”-CaO-SiO$_2$ system in air, the equilibrium cooling of high iron oxide melts can result in three different eutectic systems. For CaO/SiO$_2$ mol ratios below 1, the final liquid undergoes the reaction L$\rightarrow$ CS + H + S. For CaO/SiO$_2$ mol ratios between 1 and 2, the final liquid undergoes the reaction L$\rightarrow$ CS + C$_3$S$_2$ + H. For CaO/SiO$_2$ mol ratios greater than 2, which corresponds to the Fe$_2$O$_3$-Ca$_2$SiO$_4$ join, the final liquid undergoes the reaction L$\rightarrow$ CF + CF$_2$ + C$_3$S.

In the “Fe$_2$O$_3$”-CaO-SiO$_2$ system in air the SFC phase can only form from cooling of melts with CaO/SiO$_2$ mol ratios greater than 2$^{[12]}$. As illustrated in the simplified schematic given in Figure 6, the formation of SFC from bulk compositions within the hematite primary phase field takes place through a peritectic reaction of the form L + H $\rightarrow$ SFC. For bulk compositions within the SFC primary phase field, the SFC is formed directly from the melt through the reaction L $\rightarrow$ SFC. For bulk compositions within the magnetite primary phase, if the temperature exceeds the magnetite/hematite equilibrium temperature, oxidation of magnetite, $4\text{Fe}_3\text{O}_4(s) + \text{O}_2(g) \rightarrow 6\text{Fe}_2\text{O}_3(s)$, occurs on cooling.
Figure 6: Schematic pseudo-binary section the "Fe$_2$O$_3$"-CaO-SiO$_2$ system in air through the SFC primary phase field, illustrating the peritectic (incongruent melting of SFC) reaction.

At high Fe$_2$O$_3$ bulk concentrations and CaO/SiO$_2$ mol ratios greater than 2, the SFC phase forms through a number of different pathways, as determined by the Alkemade Triangles shown in Figure 7. The solidification pathways occurring between 1623 K (1350°C) and 1423 K (1150°C) are illustrated in Figure 8. If the starting temperature for solidification exceeds 1653 K (1380°C), in addition to the solidification of an iron oxide, the oxidation of magnetite occurs on cooling in air to form hematite.

Figure 7: Schematic diagram showing the Alkemade triangles for the ternary "Fe$_2$O$_3$"-CaO-SiO$_2$ system in air

Figure 8: Predicted equilibrium solidification pathways for the ternary "Fe$_2$O$_3$"-CaO-SiO$_2$ system in air, in particular melts relevant to iron ore sintering in air, high iron, low in silica and with CaO/SiO$_2$ >2 mol/mol.
Based on these phase equilibria considerations, it is demonstrated that the formation of the SFC phase can only form under specific ranges of bulk melt compositions. The SFC phase forms at high CaO/SiO\(_2\) ratios (>2 mol/mol) and at high Fe\(_2\)O\(_3\) concentrations.

### 3.0 Process Conditions During Iron Ore Sintering

In the iron ore sintering process, the charge experiences a range of process conditions that change with time. A typical example of the change in temperature and oxygen partial pressure taken from a pilot scale test using a sinter pot is shown in Figure 9\textsuperscript{15}. From the p\(_{O_2}\) and temperature measured during the sintering process, four stages of sintering have been observed. The stages and the corresponding conditions experienced by the charge are as follows;

1. Heating solids under high/low oxygen pressures
2. Heating solid/liquid mixtures under high/low oxygen pressures
3. Peak bed temperature under high/low oxygen pressures with solid/liquid mixtures
4. Cooling solid mixtures under high oxygen pressures.

The terms “high” and “low oxygen” pressures used here are relative to the hematite/magnetite equilibrium. A high oxygen pressure is one at which hematite is stable. A low oxygen pressure is when the formation of magnetite is favoured. These conditions may also be referred to as “oxidising” and “reducing” respectively relative to this equilibrium.

It has been shown that for ternary “Fe\(_2\)O\(_3\)”-CaO-SiO\(_2\) system in air, the lowest solidus temperature at 1465 K (1192°C) associated with the pseudo-ternary eutectic reaction \(L \rightarrow C_2S + CF – CF_2\)\textsuperscript{11}. This temperature has been included in Figure 9 to demonstrate the minimum temperature that must be achieved to obtain liquid and liquid phase assisted reactions in the sintering process.

![Figure 9: A typical temperature and p\(_{O_2}\) profile experienced by the sinter charge as measured in a sinter pot \textsuperscript{15} and the stages of sintering that have been observed.](image-url)
During sintering in this case, the charge is initially heated slowly to approximately 373 K (100 °C) under an oxygen partial pressure approaching that of air. The sinter is subsequently rapidly heated from 373 K (100 °C) to the peak bed temperature, in this case at average heating rate of 5.6 K/s\[^{15}]. On heating a single period of low p\(_{O_2}\) conditions, of between 10\(^{-3.15}\) and 10\(^{-13.18}\) atm is observed between 573 K (200 °C) and 1373 K (1000 °C). This observation can be attributed to the combustion of coke particles, which on heating leads to locally low oxygen partial pressures and high local temperatures. The peak bed temperature was observed in this test was 1625 K (1352 °C), and the time at between 1473 K (1200 °C) and the peak bed temperature was approximately 450s. After the peak bed temperature was reached, the sinter was observed to cool in this case at an average rate of 0.7 K/s. The low oxygen partial pressure recorded between 1073 K (1000 °C) and 573 K (300 °C), that is below the solidus temperature, has been shown to be associated with the oxidation of magnetite to hematite. A range of p\(_{O_2}\)'s and temperatures are experienced by the sinter bed. The actual values will depend on a range of factors, including the raw materials and their proportions used in the sinter feed, agglomeration practice, position within the sinter bed and the process conditions used in industrial practice.

### 4.0 Sinter Heating (stage 1)

Experimental studies of the phase formation and reactions taking place in the Fe\(_2\)O\(_3\)-SiO\(_2\)-CaO system relevant to iron ore sintering\[^{16}\], pure oxides were mixed and heated in a DTA furnace open to air. The DTA analysis of two samples (CaO/SiO\(_2\) of 1.2 and 3 wt/wt) showed that there were three reactions occurring on heating, Ca(OH)\(_2\) dehydroxylation, CaCO\(_3\) decarbonation, and melting of the oxides.

In the same research\[^{16}\], samples were rapidly heated in an electric furnace, cooled in air and subsequently analysed with XRD and EPMA. It was observed that in the range of approximately 1223 K (950 °C) to 1273 K (1000 °C) calcium ferrite, CF formed from CaO and iron oxide. As the temperature increased to approximately 1473 K (1200 °C), the CF, SiO\(_2\) and Fe\(_2\)O\(_3\) reacted to form a melt at low basicities, CF and glass at intermediate basicities, and CF and C\(_2\)S at high basicities. At higher temperatures (approximately 1593 K, 1320 °C), the hematite was found to be reduced to form magnetite. This research, whilst identifying the formation of calcium ferrites, did not identify the different ferrite phases present; the SFCA group phases were not reported as present.

In situ XRD has been used to determine the processes occurring when heating synthetic iron ore sinters in air\[^{17}\] using Al\(_2\)O\(_3\)-free and Al\(_2\)O\(_3\)-containing mixtures. The Al\(_2\)O\(_3\)-free mixture of high purity CaO, Fe\(_2\)O\(_3\) and SiO\(_2\) oxide powders (<2 μm diameter), with 14.08 wt% CaO and a CaO/SiO\(_2\) ratio of 3.95 wt/wt was heated in air at a rate of 5 K/min from 298 K (25 °C) to 1473 K (1200 °C) and the phases present at temperature were determined. The particle size of the powders were finer than that encountered in industrial sintering, however, this enabled intimate contact and an even distribution of material throughout the samples to be achieved. The decomposition of calcite was shown to occur under these conditions at approximately 873K (600 °C). The presence of dicalcium ferrite, C\(_2\)F was first detected at approximately 973K (700 °C). The concentration of C\(_2\)F in the mixture decreased rapidly as the temperatures were raised above approximately 1173K (900 °C) and is not present above 1050°C. Monocalcium ferrite, CF, is the major calcium-containing phase between 1023K (950°C) and 1423K (1150°C). SFCA, which corresponds to SFC in the alumina free system, was first detected on heating at approximately 1373 K (1100 °C) and SFCA-I, i.e. SFC-I, was found to form on heating at approximately 1373 K (1100 °C) with a simultaneous decrease in the concentrations of CF, Fe\(_2\)O\(_3\), and SiO\(_2\) in the system.
In-situ XRD measurements on the formation of phases on heating \( \text{Fe}_2\text{O}_3 \)-CaO-SiO\(_2\) mixtures under reducing conditions have not been reported.

### 5.0 Peak Bed Temperature (Stage 2)

The phases present at the peak bed temperature (stage 2) are determined by the bulk composition, temperature, oxygen partial pressure and time. The phase diagrams for the system \( \text{Fe}_2\text{O}_3 \)-CaO-SiO\(_2\) in air given in Figures 4 and 7 shows that, at the peak bed temperatures encountered in industrial sintering practice, the phase assemblage can consist of fully liquid melt, liquid + hematite and liquid + magnetite. The presence of Al\(_2\)O\(_3\) in the system may also result in the stabilisation of SFCA at these temperatures\cite{18}.

The equilibrium morphology of SFC in the \( \text{Fe}_2\text{O}_3 \)-CaO-SiO\(_2\) system in air equilibrated in air for 2 hours, is shown in Figure 11.\cite{11} The SFC is in the form of plates, varying in size with the liquid composition, temperature and time at temperature, typically in the order of 150 \( \mu \)m in length and 20 \( \mu \)m in width. The equilibrium morphology of the crystals is determined by the minimum surface free energy of the system. The facetted SFC crystals reflect differences in the surface energies of the different crystal planes in contact with the melt.
Figure 11: Examples of equilibrium SFC in the “Fe₂O₃”-CaO-SiO₂ system in air at 1240 °C (1513 K) 2h. (SFC - SFC, L – Liquid, H - Hematite) (BSE micrograph) [11]

To identify the morphology and composition of the SFC formed at the peak bed temperature and the impact on the microstructures formed on cooling, controlled cooling tests were undertaken. Samples of a bulk composition of CaO/SiO₂ = 3.46 wt/wt and 72.7 wt% Fe₂O₃ were heated to 1503 K (1230 °C) and held for four minutes, prior to cooling at 2 K/s. Figure 12 shows the microstructure present at 1498 K (1225 °C).

Figure 12: Example of typical microstructures observed when SFC is present as a result of heating in the SFC primary phase field to temperatures below the liquidus temperature. Sample cooled at 2 K/s from 1503 K to 1498 K (1230 °C to 1225 °C) with a CaO/SiO₂ = 3.46 wt/wt and 72.7 wt% Fe₂O₃ (S-SFC, L-Liquid) (BSE micrograph)

At 1498 K (1225 °C), individual crystals were present as small plates, approximately 30 μm long and 2 μm thick. The plates themselves were homogenously distributed throughout the sample. Due to the small sizes of the plates, it was not possible to determine using the EPMA if the compositions within the crystals were uniform or if they varied. It was not possible to determine whether or not changes in composition of the phase took place during formation, which would result in coring during cooling.
Using EPMA analysis the bulk composition of these crystals were found to contain 81.94 wt% “Fe₂O₃”, 3.50 wt% SiO₂ and 14.57 wt% CaO. The phases present were confirmed by XRD analysis of 0.2 g of material cooled from 1623 K to 1073 K (1230 °C to 800 °C) at 2 K/s, as shown in Figure 13. Based on the XRD pattern observed between 5 and 15 2θ, the presence of SFC, an endmember of the SFCA solid solution series, was confirmed with other potential phases either not present or at concentrations below the detection limit of the technique. The peaks of the SFC were at a lower 2θ to that of the reference material. This indicates that the unit cell dimensions are larger than that of the reference material.

Figure 13: XRD pattern obtained from material cooled from 1503 K to 1073 K (1230 °C to 800 °C) at 2 K/s with 72.7 wt% Fe₂O₃ and a CaO/SiO₂ = 3.46 wt/wt in the bulk showing the presence of SFC, an end-member of the SFCA solid solution series (Cu Kα).

On cooling at 2 K/s to 1073 K (800°C) until solidification was complete, the SFC was retained in the final product. The SFC phase did not decompose or dissolve as a result of peritectic reactions as anticipated by equilibrium cooling. This experiment demonstrates that SFC formation and retention is possible for melts held at peak bed temperatures within the SFC primary phase field.

6.0 Melt Cooling (Stage 3)

6.1 “Oxidising” conditions

At stage 3, cooling under “oxiding” conditions, in the Fe₂O₃-CaO-SiO₂ system in air, hematite is the stable iron oxide phase at temperatures below 1653 K (1380 °C)[19]. According to the phase equilibrium studies[14] melts having CaO/SiO₂ mol ratios in excess of approximately 4 and compositions intersecting the SFC primary phase field, on cooling should decompose completely according to the peritectic reaction L + H→ L + SFC, as illustrated schematically in Figure 7. Previous research[20-22] has shown that, on continuous cooling from fully liquid materials, this reaction does not necessarily take place. The sequence of reactions and solidification pathways are dependent on the cooling rate of the system and the bulk composition of the mixture. It has been shown that a metastable hematite phase is retained in the fully solidified product at faster cooling rates.

For compositions for which it was predicted SFC would form under both equilibrium and Scheil-Gulliver cooling, in the hematite containing regions, the hematite, C₃S, CF₂ and CF phases were
observed to form. That is, the SFC phase was not obtained at the conditions investigated (i.e. cooling rates between 2 K/s to 0.1 K/s).

In the hematite-free regions, ‘SFC-I’, C_{2}S, CF_{2} and CF were observed in the final solid products. Here ‘SFC-I’ refers to a composite material that has been shown to be an intergrowth of SFC-I and Ca_{7.2}Fe^{2+}_{0.8}Fe^{3+}_{3.0}O_{57}. The intergrowth (‘SFC-I’) does not readily form on or in close proximity to hematite.[20-21]

The presence of the SFC-I/ Ca_{7.2}Fe^{2+}_{0.8}Fe^{3+}_{3.0}O_{57} intergrowth was confirmed with a combination of Electron Probe X-Ray Micro Analysis (EPMA) and X-Ray Diffraction (XRD). The intergrowth was observed to nucleate homogenously from the melt with a bulk composition within the SFC primary phase field. The formation of this intergrowth homogenously within the melt is shown by the microstructure in Figure 14.

![Figure 14: Homogenous nucleation of the SFC-I/ Ca_{7.2}Fe^{2+}_{0.8}Fe^{3+}_{3.0}O_{57} intergrowth, samples cooled from 1623 K to 1468 K (1350 °C to 1195 °C) at 2 K/s in air with a CaO/SiO_{2} ratio of 4.75 wt/wt.](image)

The intergrowth was seen to form individual crystals, varying in size and length with the cooling rate and melt composition. The individual crystals formed needle-like shapes varying in length from 100 μm to 300 μm and in width from 10 μm to 20 μm. Following the formation of the individual crystals, C_{2}S was observed to nucleate from the liquid at the ‘SFC-I’-liquid interface. Once nucleated, the C_{2}S formed as individual crystals and as a coupled microstructure with ‘SFC-I’.

From the EPMA and XRD measurements (see Figure 15) it can be concluded that the ‘SFC-I’ intergrowths consist primarily of CaO and Fe_{2}O_{3}, with small concentrations of FeO and SiO_{2}. The compositions of the ‘SFC-I’ phase were found to vary with both cooling rate and melt composition. The proportions of SFC-I in the intergrowths in these studies were found to vary from approximately 50 wt% to 90 wt%. In contrast to previous research on this phase[20, 22] the SFC-I in this intergrowth was free of alumina.
6.2 “Reducing” conditions

During stage 3, cooling under “reducing” conditions, can result in the formation of magnetite rather than hematite is present. The conditions for magnetite formation depend on temperature, oxygen partial pressure and the compositions of the condensed phases. The magnetite phase is stable at lower oxygen partial pressures.

Both SFC and SFC-I share common features in their crystal structure with magnetite. Specifically, all three phases can be considered to contain spinel polysomes, with magnetite consisting of solely spinel polysomes and SFC and SFC-I consisting of both spinel and pyroxene polysomes [5]. Controlled cooling tests were performed to examine the nucleation and growth of SFC or SFC-I in the presence of magnetite crystals.

Samples with a bulk composition of 88 wt% Fe₂O₃ and a CaO/SiO₂ ratio of 3.46 wt/wt were heated to 1673 K (1400 °C) in air, at these conditions, both a magnetite and a liquid are present. The sample was then cooled at 2 K/s. Heating the high iron samples at 1673 K (1400 °C) enabled the formation of magnetite, which is stable in air at temperatures above 1653 K (1380 °C) [19].

On cooling to 1073 K (800 °C), two major regions were observed in the samples. In the centre, or core, of the sample the iron oxide was present in the form of magnetite. EPMA analysis demonstrated that this magnetite contained 3.74 wt% CaO. A micrograph showing the phase assemblages within this core is shown in Figure 16.

Figure 15: XRD pattern obtained from material cooled from 1623 K to 1073 K at 2 K/s 70.3 wt% Fe₂O₃ and a CaO/SiO₂ = 3.46 wt/wt in the bulk showing the presence of the SFCA-I and Ca₇.₂Fe₀.₈Fe₃₀O₅₃ phases (Cu Kα) [20].
A “calcium ferrite” phase was observed to form on the magnetite. Micro-XRD (Rigaku SmartLab) and EPMA was performed to identify this phase. The Micro-XRD technique was not successfully able to identify this phase as it was only a small contributor to the overall sample mass and volume and the spatial resolution of the instrument was limited by the optical microscope used to locate the region of interest.

Based on EMPA measurements, the composition of the “calcium ferrite” phase was found to be 88.67 wt% “Fe$_2$O$_3$” and 11.33 wt% CaO. This composition aligns with the theoretical composition of an alumina and silica free SFCA-I ($\text{Ca}_3\text{Fe}_{17}\text{O}_{28}$, 88.97 wt% “Fe$_2$O$_3$” and 11.03 wt% CaO) $[^3]$. Unlike the SFC-I crystals formed homogenously, the composition indicates that these crystals do not contain any $\text{Ca}_7\text{Fe}^{3+}_{2.5}\text{Fe}^{2+}_{0.8}\text{O}_{5.7}$ as an intergrowth.

The individual SFC-I crystals were also observed to form on the magnetite, forming faceted interfaces with the surrounding microstructures. The SFC-I crystals were observed to form on all magnetite crystals faces as a 5 μm thick layer, effectively isolating magnetite from the surrounding microstructure. Occasionally, the SFC-I was observed to extend (~20 μm) from the magnetite interface and form faceted plates. The size of the crystals strongly indicates that the SFC-I phase was formed from the melt through heterogeneous nucleation on the surfaces of the pre-existing magnetite crystals on cooling of the sample.

In addition to the individual SFC-I crystals, based on EPMA line analysis, C$_2$S, CF$_2$ and CF phases are confirmed to be present in the surrounding matrix material present in the region of the magnetite core. The fine scale eutectic microstructures of these materials indicate these have formed from the liquid phase on cooling $[^{20-22}]$.

In industrial sinters, the SFCA and SFCA-I crystals have also been found to be associated with the magnetite phase. Both the plate-like SFCA and blocky SFCA are observed to preferentially form interfaces with the magnetite phase over other phases. Examples of these structures in industrial sinters are given in Figure 17 $[^{15}]$. 

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Figure 16: SFC-I and associated phases and microstructures when a liquid associated with magnetite is cooled in air from 1673 K to 1073 K at 2 K/s in air (88 wt% Fe$_2$O$_3$ and a CaO/SiO$_2$ ratio of 3.46 wt/wt) (BSE Micrograph)
7.0 Cooling of Solid Mixtures (Stage 4)

From the research that has been undertaken to date there is no microstructural or analytical evidence of SFC or SFC-I formation on cooling below the solidus temperatures. The only reactions observed under these conditions were the oxidation of residual magnetite. In the region adjacent to the sample surface, that is in contact with the air, the iron oxide phase is present as hematite, indicating this material was formed by oxidation of the magnetite originally present. Neither SFC nor SFC-I was present in this oxidised layer of material. EPMA analysis of the hematite was observed to contain 0.05 wt% CaO. This indicates that rejection of CaO into a second phase takes place during magnetite oxidation to hematite. The microstructures of this secondary hematite and the mechanisms of formation of the coarse hematite (<50 μm) and fine hematite (<10 μm) structures have been discussed elsewhere.

8.0 SFC/SFC-I Formation Mechanisms

Experiments undertaken under controlled laboratory conditions have shown on heating that SFC, SFCA and SFCA-I phases can form at temperatures below the solidus, i.e. through solid state reactions. The in situ XRD experiments that CF phase is formed preferentially below 1100 °C (1373 K). It has been shown that the SFC phase can form at sub-liquidus conditions in the SFC primary phase field.

However for the “Fe₂O₃”-CaO-SiO₂ system in air, melts having a range of compositions and cooled over a wide range of cooling rates, have not been observed to result in the formation of SFC on cooling. The hematite, dicalcium silicate, calcium diferrite and calcium ferrite phases all having primary phase fields in this system, have been observed to form on cooling. On cooling, at conditions at which SFC is expected to form, the SFC-I phase formed by nucleation directly from the melt in air and by heterogeneous nucleation on magnetite.

Analysis of the microstructures and phase assemblages formed at different temperatures during these cooling sequences indicate that prior to the nucleation of a new phase, the melts become noticeably undercooled with respect to the new phase. The undercoolings resulted in the formation of individual crystals of the respective phases prior to the formation of a coupled microstructure.
These observations indicate that there are features associated with the crystal structures of the SFCA group of phases and the nucleation processes that are determining the conditions under which they form.

Based on the X-ray powder diffraction data, the crystal structures and site occupancies within the SFC group phases have been determined for \( \text{Ca}_{2.90}\text{Mg}_{0.95}\text{Fe}_{10.11}\text{Al}_{5.99}\text{O}_{28} \) (SFCA-I)\(^9\), \( \text{Ca}_{2.1}\text{Mg}_{1.2}\text{Fe}_{5.55}\text{Si}_{1.50}\text{Al}_{3.65}\text{O}_{20} \) (SFCA) and \( \text{Ca}_{2}\text{Mg}_{2}\text{Fe}_{4.45}\text{Si}_{2.15}\text{Al}_{3.4}\text{O}_{20} \) (SFCA)\(^6\). The cations are found to be distributed across both spinel \(<\text{Sp}>\) and pyroxene \(<\text{Py}>\) polysomes. Within these structures, Fe is observed to preferentially occupy sites in the spinel polysome, \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) the pyroxene octahedral sites, \( \text{Si}^{4+} \) and \( \text{Al}^{3+} \) the pyroxene tetrahedral sites\(^6,9\). The pyroxene polysome is analogous to the \((\text{Ca},\text{Mg})_2\text{SiO}_4\) pyroxene crystal, with the \( \text{Mg}^{2+} \) and \( \text{Ca}^{2+} \) occupying the octahedral sites and the \( \text{Si}^{4+} \) the tetrahedral sites, with the silica tetrahedral forming a chain of coordination polyhedra. The spinel polysome is analogous to the \( \text{Fe}_3\text{O}_4 \) magnetite crystal, within the spinel polysome both tetrahedral and octahedral sites exist with \( \text{Fe}^{3+} \) preferentially occupying the octahedral sites and the tetrahedral sites fully occupied by \( \text{Fe}^{3+}\)\(^{23}\). To achieve the observed phase compositions, cation substitution is required.

It has been demonstrated that the SFC and SFCA phases form solid solutions with notional end members \( \text{CF}_3 \) and \( \text{C}_4\text{S}_3 \), and \( \text{CF}_3 \) and \( \text{CA}_3 \) and \( \text{C}_4\text{S}_3 \) respectively, although these endmembers are not themselves thermodynamically stable at 1atm pressure \(^{11}\). Based on the compositional range of the SFC and SFCA phases, the compositional range is explained substitution reaction; \( 2(\text{Fe}^{3+},\text{Al}^{3+}) = \text{Ca}^{2+} + \text{Si}^{4+} \).

The distribution of cations between the pyroxene and spinel polysomes suggests that the SFCA and SFCA-I phases can be stabilised by the addition of specific cations. In particular, it is suggested that the addition of \( \text{Al}^{3+} \) and \( \text{Mg}^{2+} \) stabilises the pyroxene polysome, and in turn the SFCA and SFCA-I phases. The preferred growth of the SFCA phases in the form of plates may be the result of the higher bond strength and directionality of the pyroxene polysome within the crystal structure.

The nucleation of the SFC phases was observed to occur heterogeneously on magnetite (Figures 16 and 17) and homogenously within the melt. In addition, it was observed \(^{20-22}\) that SFC phases did not heterogeneously nucleate upon hematite. This is observed under laboratory conditions, under both controlled cooling conditions (Figure 14) and equilibrium (Figure 11).

The results of the controlled cooling experiments (Figures 14 and 16) suggest that the SFC-I crystals share a structural relationship with magnetite but not with hematite. The SFC group phases contains both spinel and pyroxene modules, normal to the close packed oxygen plane. It is argued that these spinel modules, identical to the magnetite crystal structure, enable the SFC group to form at surface or points where the [001] planes are exposed to the melt. Hematite and magnetite share crystal structure similarities, in that they both contain close packed oxygen planes. However, this close packed oxygen plane is not present in the SFCA group phases. It may be that for this reason the nucleation of the SFC-I or SFC on the hematite phase is not favoured.

The heterogeneous nucleation of \( \text{CF}_2 \) on hematite has been observed \(^{20}\) during the solidification of melts with the “\( \text{Fe}_2\text{O}_3 \)-CaO-SiO\(_2\)" system. Unlike the SFC group, \( \text{CF}_2 \) shares a similarity with the hematite crystal structure. The \( \text{CF}_2 \) crystal contains polysomes, spinel and 'Motif-F'\(^{24}\). Unlike the SFC groups, the spinel polysomes in the \( \text{CF}_2 \) crystal contain the close packed oxygen plane. This suggests that the \( \text{CF}_2 \) crystals nucleate preferentially on the close packed oxygen plane in hematite.

The ‘SFC-I’ crystals have been shown to be a complex intergrowth of SFC-I and \( \text{Ca}_{7.2}\text{Fe}_2^{3+}\text{Fe}_3^{3+}\text{Si}_{30}\text{O}_{53} \). The bulk composition of the intergrowth varies with the relative proportions of the phases present.
The formation of the ‘SFC-I’ intergrowth at conditions in which SFC is expected indicates that the phases formed in sinter are potentially meta-stable.

8.0 Summary

Silico ferrite of calcium (SFC) is an incongruently melting compound that can exist over a range of compositions. The liquidus surface the “\( \text{Fe}_2\text{O}_3 \)-CaO-SiO\(_2\)” system in air including the limits of the primary phase field for SFC have been established. This has enabled the necessary conditions for SFC formation on cooling of oxide melts in this system to be identified. Targeted experimental investigations have shown however, that whilst this is a necessary it is not sufficient condition for SFC formation – the formation of this phase is dependent on a number of kinetic factors.

SFC can form on heating at sub solidus conditions through solid state reactions. The extent of these reactions depends on the particle size, temperature and time at temperature. Whilst this has been shown to take place in laboratory conditions using fine powders, the rates of heating employed in these studies are much lower than those experienced in industrial iron ore sintering. It is therefore suggested that the formation of SFC from solids is not a major contributor to the SFC formation in industrial practice.

The current series of studies by the authors has shown that the formation of SFC during cooling of melts in the “\( \text{Fe}_2\text{O}_3 \)-CaO-SiO\(_2\)” system in air is also problematical. SFC was only obtained by heating mixtures at subliquidus conditions in the SFC primary phase field. SFC was not formed on the cooling of melts having a wide range of compositions and over a range of cooling rates, despite the fact that the formation of this phase was anticipated based on the phase equilibrium information available. The SFC phase should occur on cooling following the formation of hematite- but this was not observed in any experiments.

The related phase SFC-I has been observed to form directly from melts by homogeneous nucleation and by heterogeneous nucleation on the surfaces of magnetite. The results of the experiments to date suggest that the difficulties in SFC nucleation are related to the complex crystal structure of this phase. The SFCA phase is observed in alumina containing industrial sinters in association with the magnetite phase. The presence of magnetite, or spinel structure, and the increased stability of the SFCA phase as the result of the incorporation of Al\(_2\)O\(_3\) in the crystal structure, may account for the formation of this phase from the melt on cooling.

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References

10. X. Liu, (The University of Queensland, School of Chemical Engineering: 2013).