Phase Equilibria and Slag Formation in the Magnetite Core of Fluxed Iron Ore Pellets

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Distinctly different morphologies of pellet microstructure develop in the oxidised hematite shell and the reduced magnetite core during induration. Individual pellet induration experiments in an air atmosphere showed that slag formed at lower temperatures in the magnetite core, with molten slag forming between 1 100 and 1 150°C compared to 1 200°C in the oxidised outer rim. The amounts of slag formed were not large enough for accurate compositions to be determined, however. Experiments were then conducted with pellet sized magnetite compacts, held at a temperature between 1 075 and 1 225°C for 20 min in a nitrogen atmosphere containing 0.5 % oxygen (P O2 = 0.005 atm). The aim was to retain magnetite as the stable iron oxide and to generate larger pools of molten slag. These tests showed that a eutectic iron calcium silicate melt can form within the silica particles at temperatures as low as 1 100°C. Surrounding these silica particles, a melt-like morphology appears, although the remaining slag has a wollastonite (CaSiO3) composition. As wollastonite is not molten at the temperatures studied the iron oxide from the slag would have been absorbed by the surrounding magnetite. Above 1 175°C, the molten eutectic slag can be observed to fill in gaps between the magnetite particles after dissolving nearly all the calcium and silicon. This behaviour suggests that the oxygen partial pressure varies greatly within the magnetite core of iron ore pellets and has a strong influence on slag formation. Formation of slag in iron ore pellets is important as sufficient slag must be formed to bond the pellet, but not so much that the core becomes too heavily sintered, pulling away from the shell and reducing pellet strength.

KEY WORDS: iron ore pelletising; pellet mineralogy; thermodynamics; phase equilibria.

1. Introduction

Over the last 30 years, fluxed iron ore pellets have been slowly taking over from acid pellets as the primary burden of blast furnaces in North America and direct reduced iron (DR) furnaces around the world.¹) In fluxed pellets limestone, and sometimes dolomite, are added to the magnetite or hematite concentrate, which already contains silica gangue. By adding calcium (and magnesium) through the pellet burden, the blast furnace or DR furnace removes the need to charge limestone directly to the furnace and can more precisely control the distribution of slag forming components in the burden. One of the primary strength forming mechanisms in iron ore pellets is the formation at high temperatures of liquid bridges between the iron oxide particles. Adding calcium flux to iron ore pellets changes the chemistry of these liquid bridges from iron silicates to iron calcium silicates.²)

In pellets produced from magnetite, the magnetite is oxidised to hematite during the firing process in a diffusion controlled “shrinking core” reaction through the pellet. For most pellets in the process, there is still a significant magnetite core when firing temperatures, above 1 200°C, are reached and liquid slag phases form. As the oxygen is consumed at the reaction front between hematite and magnetite, the gas atmosphere in the core of the pellet is more reducing in nature compared to the outer hematite shell. This causes different microstructures to form in the core of the pellet compared to the outer regions.² ⁵) In extreme cases, the core of pellet can become more sintered than the outer shell and pull away from it, leaving concentric and radial cracking. This causes the pellet compressive strength to drop rapidly and is generally interpreted by plant operators as over-firing. It follows that much of the microstructure difference is due to the higher amount of slag formed in the core compared to the outer zone of pellets. More slag forms in the core of pellets as the reducing atmosphere allows the liquid phase to form at lower temperatures. While it is understood that the slag formed in the core of iron ore pellets is different to that formed in the shell, the formation process of this slag has not been categorised. It is the aim of this study to quantify the slag formation process in the core of iron ore pellets.

While this work refers mainly to pellets produced from magnetite concentrates, the conclusions can also be applied to pellets produced from hematite concentrates with high levels of internal carbon addition. This is due to the reducing conditions in the core of the pellet due to incomplete carbon combustion causing the hematite to be reduced to secondary magnetite.⁶ ⁷) This leads to a similar microstruc-
tural evolution for hematite and magnetite pellets of a similar chemistry.\textsuperscript{8,9}

Interpretation of the formation process and composition for the slag in iron ore pellets is difficult for a couple of reasons. Firstly, because the areas of slag are so small, particularly in samples fired at low temperatures or for short times, good results from electron probe micro-analysis (EPMA) free from the interference of the surrounding iron oxide particles are nearly impossible to obtain. Secondly, while the FeO–CaO–SiO\textsubscript{2} system has been rigorously investigated in equilibrium with air (Fe\textsubscript{2}O\textsubscript{3})\textsuperscript{10} and with molten iron (FeO),\textsuperscript{10} the system in the core of pellets is in equilibrium with magnetite at an intermediate oxygen partial pressure (5×10\textsuperscript{-3} atm being used in this study as the external oxygen partial pressure). This system has not been studied rigorously and the data that is available\textsuperscript{11–13} is restricted to the temperature range 1240–1400°C, well above the minimum slag eutectic temperature of around 1200°C in air.\textsuperscript{11} This study will focus on the same oxygen partial pressure of 5×10\textsuperscript{-3} atm, but at temperatures where liquid slag is beginning to form, between 1000 and 1225°C. The aim of the investigation was to find the eutectic temperature for slag in the core of iron ore pellets as this is the absolute minimum temperature required for bonding to occur.

2. Method

2.1. Single Pellet Tests

For the initial single pellet tests, a 20 kg batch of green balls was prepared from an industrial magnetite concentrate, with added limestone and dolomite fluxes and 0.07% bentonite used as the binder. The magnetite concentrate and the fluxes were ground to 85–90% –38 μm and mixed together in a batch balling drum. The target chemical analysis of the fluxed pellets (calcined) was 65.3% total Fe, 2.4% SiO\textsubscript{2}, 2.4% CaO, 1.4% MgO and 0.14% Al\textsubscript{2}O\textsubscript{3}.

After being dried in an oven at 105°C for 16 h, the individual green balls were heated using a QHC-E44 VHT infra-red image furnace produced by Ulvac-Riko Inc. (Fig. 1). The furnace uses gold-plated parabolic mirrors to focus infra-red radiation on the hot zone, allowing close control and rapid changes in temperature. The atmosphere of the furnace was controlled at an air composition (79% N\textsubscript{2} and 21% O\textsubscript{2}), slightly higher than normal gas composition during firing but useful due to the large amount of thermodynamic data available at this oxygen concentration. Rapid quenching of the samples was performed using a high flowrate of nitrogen gas. The test method used here was originally developed by Firth\textsuperscript{15} for the evaluation of firing profiles for pellets produced from Australian magnetite concentrates.

Single green balls of a suitable size, about 12.5 mm in diameter, were placed in a nickel foil crucible before being placed in the furnace with an R type thermocouple (platinum–platinum–10% rhodium) used to measure the surface temperature of the pellet. Once the pellet was in place, its temperature and phase transformations to be linked to a specific method allows local equilibrium of the pellet microstructure, with confidence that the determined composition was not affected by surrounding phases. Probe analysis, however, suggested that the slag formed in the unoxidised portion appeared to differ from that in the oxidised area.

To increase the size of the slag pools that formed, it was decided to produce cylindrical compacts of a similar size to pellets with higher limestone and silica contents than would normally be used (5 and 10% SiO\textsubscript{2}). The concentrate used for the compacts was very high in grade (70.1% Fe\textsubscript{total}, 20.2% Fe\textsuperscript{2+}, 1.45% SiO\textsubscript{2}, 0.33% MgO, 0.03% Al\textsubscript{2}O\textsubscript{3}). Reagent grade silica and high purity limestone were used to simplify the reaction system, excluding aluminium and magnesium as much as possible beyond the content of the concentrate. Three basicity (CaO/SiO\textsubscript{2}) levels were chosen furnace,\textsuperscript{15} although the ramp to the preheat temperature is also similar to that experienced by pellets on their way to firing temperatures in straight grate furnaces.\textsuperscript{16} While holding the individual pellet at a specific temperature does not correlate directly to the pellet induration process, this method allows local equilibrium of the pellet microstructure and phase transformations to be linked to a specific temperature range. After 3 min at the desired temperature (1000, 1050, 1100, 1150 and 1200°C), the run was terminated and the pellet was quenched immediately in nitrogen.

Four pellets were fired at the same conditions, mounted in epoxy resin, sectioned at the approximate centre-line of the pellets, and then polished flat to a surface finish of 1 μm. These pellets were then analysed microscopically under reflected light at a variety of magnifications. Selected samples were also assessed by electron probe microanalysis (EPMA) with both point compositions and element maps being collected. Quantitative analysis of the composition of the slag generated during preheat was difficult as the pools of slag were very small and the composition given by EPMA was influenced by the nearby iron oxide phase.

2.2. Compact Tests in a Low Oxygen Atmosphere

For the single pellet tests described above, only very small pools of slag were formed which could not be probed with confidence that the determined composition was not affected by surrounding phases. Probe analysis, however, suggested that the slag formed in the unoxidised portion appeared to differ from that in the oxidised area.

To increase the size of the slag pools that formed, it was decided to produce cylindrical compacts of a similar size to pellets with higher limestone and silica contents than would normally be used (5 and 10% SiO\textsubscript{2}). The concentrate used for the compacts was very high in grade (70.1% Fe\textsubscript{total}, 20.2% Fe\textsuperscript{2+}, 1.45% SiO\textsubscript{2}, 0.33% MgO, 0.03% Al\textsubscript{2}O\textsubscript{3}). Reagent grade silica and high purity limestone were used to simplify the reaction system, excluding aluminium and magnesium as much as possible beyond the content of the concentrate. Three basicity (CaO/SiO\textsubscript{2}) levels were chosen...
for study: 0.6, 1.2 and 2.0. A basicity of 1.2 is typical for fluxed blast furnace pellets while, a basicity of 2.0 would be more typical of fluxed iron ore sinter and is included for comparison only. The basicity of 0.6 was included as analysis of available phase diagrams suggest that different phase equilibria would occur below a basicity of 1.0.

As slag formation in the core of the pellet was the focus of our study, a purchased air mixture of 0.5% oxygen in nitrogen was used ($p_{O_2}$=5×10^{-3} atm). This gas atmosphere has been used extensively by CSIRO Minerals for its work into melt formation at the flame front in iron ore sintering. At this oxygen partial pressure, magnetite is the stable iron oxide phase. The compacts were heated in an infrared image furnace using the same ramp profile as the single pellet tests (4 min to 240°C, then 3 min to maximum temperature). They were held at the maximum temperature for 20 min to ensure good local equilibrium between the materials and form large areas of slag for EPMA composition analysis, though not so long as to achieve full equilibrium as in normal phase diagram testwork. Qualitative equilibrium results in terms of phases present can be interpreted from these tests but experiments at a smaller scale with longer equilibration times would be required for proper quantitative phase diagram development. The methodology is to determine the phase compositions that would be tended towards in the firing of real iron ore pellets.

3. Results

3.1. Single Pellet Tests

A series of single pellet firing experiments with normal blast furnace fluxed pellets (CaO/SiO$_2$=1.0) were conducted. While the pellets were made from magnetite concentrate, the microstructures observed would be valid for hematite pellets with high carbon addition typical of current Brazilian and Canadian practice. The pellets were held at the preheat temperature for 3 min, a time that is insufficient to oxidise all the magnetite resulting in the remaining core.

At 1 000°C, it was observed that the silicon and calcium had only just started to react. A small amount of calcium had reacted with the iron oxides to form dicalcium ferrite (Ca$_2$Fe$_2$O$_5$), predominantly in the re-oxidised secondary hematite zone as calcium is partially soluble in the magnetite.

At 1 050°C, the observations are similar to 1 000°C except that the dicalcium ferrite is now more widespread and calcium has dissolved in the magnetite up to a concentration of 2%, mainly in the regions around ex-flux particles. Silica particles do not appear to have reacted with the calcium as yet, except directly next to flux particles. The distributions of the main elements are shown in Fig. 2.

At 1 100°C, especially in the unoxidised core of the pellet, there is evidence of significant reaction between calcium and silica, and most likely with the iron oxides as well. This is most abundant in the magnetite core of the pellet. In particular, there is evidence of dissolution of parts of the large silica grains into a calcium- and silicon-rich phase.

At 1 150°C, the areas containing both silica and lime have become more numerous compared to 1 100°C, although they are still quite small. Some small areas of slag also appear to have been trapped within hematite grains as the oxidation front has passed through. These trapped slag regions often appear to have a lower calcium to silicon ratio compared to slag in other areas. Due to the small size of the slag grains however, it is difficult to measure the compositions of the various slag morphologies. These trapped slag regions are common in pellets produced industrially from both hematite and magnetite concentrates.

At 1 200°C, an iron calcium silicate melt has formed in both the oxidised hematite shell and unoxidised magnetite core of the pellet. While it has previously been suggested that the composition of the melt might vary between oxidising and reducing atmospheres, this is difficult to determine in practice. The fields of slag are typically very small and quantitative point analysis by EPMA invariably has some interference by the nearby iron oxide, increasing the apparent iron content.

3.2. Compact Tests in a Low Oxygen Atmosphere

The microstructures observed from this investigation can essentially be divided into three broad types. It must be remembered that the samples were only held at temperature for 20 min hence the microstructure will reflect local equilibrium conditions much more than total equilibrium.

3.2.1. 1 100 to 1 150°C

At temperatures of between 1 100 and 1 150°C, the microstructure followed the element map shown in Fig. 4. Essentially all phases, except for the end members of lime and silica, are in contact with magnetite. In between the lime and silica, however, there are several phases that can form depending on the local chemistry. Typical EPMA point analyses for the phases can be found in Table 1. Nearest to the lime formed after the calcination of the limestone is dicalcium ferrite (Ca$_2$Fe$_2$O$_5$), marked on the figure as C$_2$F. The amount of calcium ferrite formed in the magnetite core of the pellets is less substantial than in the hematite shell. This is in part due to the higher solubility of calcium in magnetite compared to hematite. Some of the divalent iron also dissolves into the lime.

At 1 075°C, the wollastonite phase between the magnetite grains and the eutectic melt phase inside the silica grains were not observed, illustrating a transition temperature occurs between 1 075 and 1 100°C. Some physical breakdown of the silica grains was observed, however, consistent with the phase transition of quartz to tridymite above 965°C.

Iron diffusing into the silica from contact with magnetite grains, along with the small amount of calcium that has diffused into the magnetite (around 1% at 1 100°C) appears to be responsible for the eutectic melt that has formed inside the silica particles. The diffusion and melt formation processes have been assisted by the breakdown of the silica structure from the quartz-tridymite transition at 965°C. The composition of the melt (Table 1) is close to the melting composition in the FeO$_x$–CaO–SiO$_2$ system at low oxygen partial pressures of about 10^{-9} atmospheres. Thermodynamic simulations and experimental data from studies at low oxygen partial pressures suggest that this melt could form at about 1 100°C, as observed, if the oxygen po-
potential at the locations where melt formed had a sufficiently low oxygen potential. The long hold time of 20 min at temperatures below the typical firing temperatures of pellets resulted in a silica particle structure mottled with such eutectic melt. Aiding this structure developing would be the decomposition of the quartz crystal structure of the silica. Eutectic melts contained in silica grains are not usually seen in

![Fig. 2. Map generated by EPMA of a pellet heated at 1050°C for 3 min in air. The maps were taken in the magnetite zone near the oxidation front in the pellet. Calcium concentration is shown in blue, silicon concentration in green and iron concentration in red. \( \delta \)-ratio gives the mass percent of the element with the scale bars at right indicating their relative concentration for the intensity of colour. Mixed colours indicate a mixture of the elements, for instance purple represents calcium ferrites.](image1)

![Fig. 3. Map generated by EPMA of a pellet heated at 1150°C for 3 min in air. The maps were taken in the magnetite zone near the oxidation front in the pellet. Calcium concentration is shown in blue, silicon concentration in green and iron concentration in red. \( \delta \)-ratio gives the mass percent of the element with the scale bars at right indicating their relative concentration for the intensity of colour. Mixed colours indicate a mixture of the elements with purple representing calcium ferrites and cyan representing calcium silicates, often with minor dissolved iron.](image2)

![Fig. 4. Element map using EPMA showing the possible phase equilibria of a section of a pressed tablet containing 10% SiO₂ and 12% CaO (1.2 basicity), the remainder being magnetite, heated to 1100°C for 20 min at \( p_{O_2} = 0.005 \) atm. P=pore, S=silica, Sl=eutectic slag, CS=wollastonite, C₂S=lamnite, C₂F=dicalcium ferrite, Mt=magnetite, Per=ferroan periclase [(Mg, Fe)O].](image3)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Fe (mass %)</th>
<th>Si (mass %)</th>
<th>Ca (mass %)</th>
<th>O (mass %)</th>
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<tr>
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<tr>
<td>Magnetite</td>
<td>70.3</td>
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<td>0.3</td>
<td>28.6</td>
</tr>
</tbody>
</table>

Table 1. Typical point analyses of the phases present at 1100°C.
pellets as they are not usually held at temperatures around 1100°C but transition through this temperature rapidly to firing temperatures above 1230°C.

The eutectic melt is not observed beyond the silica particles at 1100 or 1125°C. The likely reason for this is that the eutectic melt came into contact with magnetite in equilibrium with the higher oxygen potential (5×10⁻⁷ atm) in the pores of the compact. Upon contact with the higher oxygen potential, phase separation of the melt into magneteite and wollastonite (CaSiO₃ with 1–2% Fe) occurred, with the magneteite crystallizing on the existing magneteite matrix. This is the most likely interpretation for the melt-like morphology of the wollastonite, occurring interstitially between magnetite particles and appearing to assist the formation of solid bridges between them. Wollastonite with the composition found by point analysis would not produce liquid until 1280°C²⁰ and not melt completely until 1500°C. While slag fields are much smaller in real pellets and usually defy quantitative probing, it is possible that a wollastonite phase could appear in pellets, especially as trapped slag bubbles within iron oxide particles agglomerates after sintering of the magneteite particles followed by the oxidation front moving through, but between 1100 and 1200°C where some liquid slag forms but not enough to support substantial “wet” oxidation.¹⁹

In areas of high basicity near lime particles with rims of dicalcium ferrite, there is also an outer rim of larnite (Ca₂SiO₄). This appears to be sensible according to thermodynamics as in the sub-solidus region of the FeO–CaO–SiO₂ system, lime and dicalcium ferrite are in the same equilibrium triangle with larnite.¹⁰ For the 2.0 basicity samples, the areas of dicalcium ferrite formation were more extensive, as were the existence of larnite rims. The phase morphology was similar, however, to that observed in the lower basicity cases.

3.2.2. Above 1150°C, Low Basicity

Between 1150 and 1175°C, the interstitial phase between the magneteite grains changes from one of “solid” wollastonite to an olivine melt phase (Fig. 5), similar to that present in the silica grains at lower temperatures. Typical point analyses from EPMA are given in Table 2.

In parts of the melt, it can be seen that another, richer in calcium phase is trying to precipitate out. This phase is almost certainly larnite co-precipitating with magneteite that is too fine to see on the element map. Particularly at higher temperatures, as can be seen in the reflected light image in Fig. 6, the slight imperfection in the quenching process, reducing the cooling rate, forces a combination of larnite and magneteite to precipitate from the melt as its composition deviates from the olivine eutectic melt.

Some large relict flux particles were observed, although they had mainly decomposed into a mass of calcium ferrites. Surrounding these calcium ferrites was a large amorphous region of larnite, much larger than at lower temperatures, with a distinct interface with the eutectic melt (Fig. 7). As the temperature increases above 1175°C, the amount of melt increases, mainly due to increasing iron content. The amount of magneteite precipitated during cooling was also observed to increase, usually with larnite precipitating in the same region. This was due to imperfect quenching at the centre of the compact samples, indicating that the molten slag present at that temperature (1200°C) was rich in calcium and iron in comparison to molten slag at lower temperatures.

3.2.3. Above 1150°C, High Basicity

With a basicity of 2.0 in the starting composition, there were some differences in the phase mix after the olivine melt became the abundant interstitial phase. Due to the higher basicity, more larnite formed in the regions surrounding flux particles. Calcium and silicon in larnite were solidified and no longer mobile, limiting the penetration of the olivine melt. Also near the larnite in regions of high basicity, interstitial regions with compositions similar to monocalcium ferrite (CaFe₂O₄), can be found. These probably precipitated on cooling from a calcium ferrite rich melt as they occur interstitially between magneteite particles remote from large pores at temperatures around 1175°C. This phase assemblage can be seen in Fig. 8.

4. Discussion

The coexisting phases found in these experiments largely match those found at 1240°C in a study of the same oxide system and oxygen partial pressure by Pownceby and Clout.¹¹ The primary difference between the current results and experimental results from Pownceby and Clout,¹¹ Henao et al.,¹² Nikolic et al.,¹³ and Kimura et al.¹⁴ was the presence of melt-like structures at 1100°C. The results also appear to contradict the thermodynamic modelling results of Kongoli and Yazawa²¹ who suggest that the eutectic melting temperature is approximately 1200°C at 10⁻⁵ atm O₂ and 1125°C at 10⁻⁸ atm O₂. There did not appear to be any wüstite forming the compact, however, suggesting that the pore spaces retained an oxygen partial pressure of at least 10⁻⁸ atm. Notably, the location of the eutectic melt below 1150°C was entirely within the original silica particles. Inside the silica particles, it appears that there is no contact with the oxygen in the gas phase, allowing the lower melting point. Once the eutectic melt travels out of the silica particle, however, it appears to be influenced by the oxygen in the atmosphere of the pore space as the molten slag transforms into solid wollastonite with most of the contained iron in the slag being precipitated on the surface of magneteite particles.

A comparison can be made between the results presented here and the work of Fitton and Goldring,²² who investigated the amount of assimilation and microstructure of fluxed magneteite pellets fired at fixed temperatures with rapid heating and cooling. The temperature profile was achieved by inserting the pellets into a tube furnace, then removing them rapidly. The assimilation results obtained by Fitting and Goldring for pellets produced from Sydvaranger concentrate can be found in Fig. 9. The raw pellets were primarily composed of magneteite with 7.6% SiO₂ and 9.4% CaO as the other significant minerals. Fitton and Goldring²² found that initial assimilation of the pellets, which would be concurrent with liquid slag formation, occurred just below 1100°C. They also found that full assimilation of the pellet occurred when heated above 1175°C, with the extent of assimilation relatively independent of
time after 5 min at firing temperature. While the experiments were conducted in an air atmosphere and oxidation proceeded fairly rapidly at these low temperatures, the extremely rapid heating rate would have ensured that most of the slag formed before the oxidation front had moved through.

A comparison can also be made between observations made at different temperatures in this investigation and phase relationships in both the CaO–FeO–SiO\(_2\) system,\(^{10}\) nominally at iron saturation, and the CaO–FeO\(_2\),\(^{23}\) and FeO\(_2\)–SiO\(_2\),\(^{24}\) systems at intermediate iron oxidation levels. The minimum eutectic temperature for the iron saturation system is 1093°C, just below the 1100°C used at the minimum temperature for the testwork. This eutectic is between wollastonite and olivine-fayalite, both phases with large

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**Table 2.** Typical point analyses of the phases present 1175°C.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Fe (mass %)</th>
<th>Si (mass %)</th>
<th>Ca (mass %)</th>
<th>O (mass %)</th>
</tr>
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<tbody>
<tr>
<td>Melt</td>
<td>13.3</td>
<td>18.7</td>
<td>29.6</td>
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<tr>
<td>Magnetite</td>
<td>71.8</td>
<td>0.1</td>
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</table>
reaches the wollastonite solid solution line. It is notable that no wollastonite was observed in the compact samples at temperatures where magnetite is stable in equilibrium with CaO and SiO$_2$, although thermodynamic modelling and experiments examining the size of the liquid field at 1250°C suggest that the minimum eutectic temperature is likely to be just below 1100°C. Likewise, both investigations found that sufficient melt formation for full assimilation in the magnetite core of pellets does not occur until a temperature of around 1170°C. These findings were similar for the wide range of calcium to silicon ratios investigated here (0.6, 1.2 and 2.0), and are valid for systems without significant quantities (>0.5%) of alumina where stabilisation of the silico-ferrite of calcium and aluminium (SFCA) phase occurs.

5. Implications for Pelletising Performance and Quality

Practically, it would be difficult to exploit the lower slag formation temperature in the core of pellets to improve assimilation at low temperatures due to the mixture of hematite and magnetite zones in iron ore pellets during firing. The higher solidus temperatures for slags in contact with hematite are around 1200°C. This difference in slag forming potential at different oxygen partial pressures in different zones in the same pellet causes problems with the more highly sintered core pulling away from the shell. This can lead to internal stresses and cracking of the pellet, manifesting itself in a reduced pellet compressive strength.

To improve pelletising productivity while maintaining pellet properties, further understanding of the variation in oxygen potential inside pellets is required. As measurement of oxygen potential inside pellets during induration, and even within the same zones of the pellets, is required. As measurement of oxygen potential inside pellets is difficult, comparing observed pellet microstructures from carefully controlled compact experiments with mathematical modelling of pellet induration and thermodynamic modelling of slag formation is required to understand where further optimisation of the firing process can be achieved.
6. Conclusions

This investigation has shown that the formation temperature of liquid calcium silicate slag in the magnetite core of iron ore pellets is around 1 100°C, much lower than 1 200°C, which is the slag solidus in the hematite shell of the pellets. The temperature of 1 100°C was lower than expected for the oxygen partial pressure studied of $5/3H_1100^3/10^2 atm$. The location of first liquid slag formation was also unusual as it occurred within the silica grains. The composition of the slag formed at 1 100°C (21.3% Fe, 25.4% Si, 9.5% Ca, 42.7% O by mass) was close in composition to the eutectic melt between olivine and wollastonite in the CaO–FeO–SiO$_2$ equilibrium at iron saturation. These features suggest that the oxygen partial pressure within pellets and within the particles in the pellets can vary widely, allowing lower liquid slag formation temperatures.

This investigation also suggested that the liquid slag would not migrate significantly from the silica particles due to the higher oxygen partial pressure in the void space of the pellet. Such slag would then transform into solid wollastonite and magnetite, though some diffusional bonding through the liquid may occur during its brief existence.

Further work is required to properly assess the variation of oxygen partial pressure within pellets during induration as this has a significant influence on strength development within iron ore pellets. In particular, an investigation into the minimum slag formation temperature in the presence of an oxidising atmosphere (15–21% O$_2$), where hematite is the stable iron oxide phase, should be performed to complement the current investigation.

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