Mineral Phase Formation and Zinc Removal during Sintering of Filter Cake Wastes

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A large amount of filter cake wastes are produced from the gas cleaning systems of blast furnace (BF) ironmaking and basic oxygen furnace (BOF) steelmaking processes. The filter cake wastes cannot be directly recycled through the ironmaking process due to the high zinc contents and are therefore, predominantly, stockpiled. The storage of filter cake wastes presents a long-term environmental issue but also an opportunity to extract or recover the iron content, motivating a search for processes or technologies to allow their cost-effective recycling. In this study, two filter cake wastes from BlueScope Ltd. were sintered at 1100–1300°C in argon and air to evaluate the effects of temperature, gas atmosphere and carbon content on the mineral phase formation and zinc removal of sintered filter cake specimens. The fine particles in filter cake can be well aggregated by bonding phases (calcium ferrites and silicates) during sintering due to the presence of flux materials, CaO and SiO2, in the filter cake. Carbon and metallic iron in the filter cake reduced ZnO to zinc vapour during sintering, which enhanced the zinc removal of the filter cake in a reducing gas atmosphere.

KEY WORDS: filter cake; sintering; mineral phase formation; zinc removal; recycling.

1. Introduction

Steelmaking plants generate a significant amount of flue dusts. These dusts are removed from the off-gases of blast furnaces (BF), basic oxygen furnaces (BOF) and electric arc furnaces (EAF) either in the form of dry dusts by dry separation methods, or in the form of sludge or filter cake from wet separation methods.1) Typically the off-gases are ducted to scrubbers for cleaning so that the cleaned gas can be reused within the steelworks and the collected dusts can be dewatered for stockpiling (or further processing) in the form of filter cake.

These flue dusts usually contain large amounts of iron as well as varying amounts of zinc. The low vaporization temperature of zinc leads to its accumulation in the dusts in the off-gases from the iron and steelmaking furnaces.2) Mineralogical analyses1) show the presence of zinc in oxide forms, such as zincite (ZnO) and franklinite (ZnFe2O4). Iron is found mostly as hematite (Fe2O3), magnetite (Fe3O4), wustite (FeO), franklinite and metallic iron. Typically, EAF dust contains a higher level of zinc (about 15–30%) compared to BF and BOF dusts (1–5%). The levels of zinc in the flue dusts hinder their direct utilization by iron and steelmaking processes. Zinc in the flue dusts recirculates in the plants, causing refractory failure and scaffold formation.1)

Storage of these dusts presents a long-term environmental concern, motivating the search for processes or technologies to allow their recycling. Attempts have been made by many investigators to recycle the flue dusts generated from the iron and steelmaking processes, however information on the treatment of BF and BOF dusts is limited. Processes investigated include pyrometallurgical,1,3–6) hydrometallurgical7–9) and hybrid processes,10–12) the latter involving a combination of bio-leaching, hydrometallurgical and pyrometallurgical stages. After significant effort in process development, the problem is still not well resolved.6) The majority of the pyrometallurgical processes to remove zinc from the dusts are based on high temperature reduction and volatilisation followed by gas phase recovery. ZnO and ZnFe2O4 in the dust are reduced by C, CO or H2 to Zn vapour. Depending on the process, Zn may be recovered as elemental Zn in liquid form in condensers9) or in solid form as ZnO in baghouses.5,6)

In cases where the Zn concentration is low enough to directly recycle the filter cake via BF or BOF, it is necessary to first agglomerate into a lump product, since the weak filter cake fines cannot be charged directly into the BF or BOF. Attempts to briquette filter cake for recycling were conducted by BlueScope and trial production of briquettes was carried out at pilot plant scale in 2004 and 2005, but these attempts were unsuccessful due to the low strength of the briquettes produced.13) Alternatively, utilisation of the existing iron ore sintering route may be an attractive way to assimilate fine particles of filter cake into the normal sin-
ter. However, little information is available for the mineral phase formation and the behaviour of zinc containing filter cake in the sintering process. This paper investigates the sintering behaviour of the filter cake under different sintering conditions including the zinc removal.

2. Experimental

Two types of filter cake wastes were used in this study. A BOF filter cake sample and a mixture (MIX) filter cake sample. The MIX sample represents a 3:1 blend of both BOF and BF filter cake.

These filter cake samples were dried in an oven at 110°C for 48 hours before being crushed and screened to < 200 μm. After drying they were then pressed at 20 kN for 2 minutes into ~1.0 g cylindrical tablets of 8 mm diameter and ~10 mm height for sintering experiments.

Sintering of the filter cake samples was carried out under an argon atmosphere in a vertical tube furnace and in air in a muffle furnace in the temperature range of 1 100–1 300°C (50°C increments) for 5 minutes typical for iron ore sintering. A schematic of the vertical tube furnace has been described in detail elsewhere.41 The internal diameter of the working tube was 55 mm. The furnace was preheated to a designated temperature, and then purged with argon for at least 20 minutes prior to hanging a crucible containing the sinter tablet in the hot zone of the furnace. After sintering for 5 minutes, the samples were rapidly cooled by raising the crucible to the cold top end of the furnace tube. In the muffle furnace, a sample was placed on an alumina plate and sintered in a static air atmosphere for 5 minutes.

The sintered tablets were mounted in epoxy resin, cut perpendicular to the top surface and then polished for optical microscopy (Leica DM6000) and field – emission scanning electron microscopy (FESEM, JEOL JSM – 7001F) analysis.

The original filter cakes and sintered samples were analysed by X-ray diffraction (XRD, MMA, GBC Scientific Equipment, Braeside, Australia). The carbon content in sintered samples was measured by LECO analysis (SC-444 DR Carbon/Sulphur Determinator). The zinc content of samples was analysed by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES). About 0.1 g of crushed sintered sample was digested into a solution consisting of 6 mL HCl, 2 mL HNO3 and 2 mL H2O2. After filtration through 0.1 μm glass fibre filter, the solution was then diluted to an appropriate concentration for analysis.

3. Results

3.1. Characterisation of Filter Cake Samples

The chemical composition of the two filter cake samples measured by X-Ray Fluorescence spectroscopy (XRF) is given in Table 1. Quite similar chemical compositions can be found for these two samples; both contain 53–56 wt% iron and about 2 wt% of zinc. The contents of other impurities, CaO, MgO, SiO2, and Al2O3 are also similar. A major difference between the two samples is in their carbon content. It is significantly higher in the MIX filter cake (3.14 wt%) compared with the BOF filter cake (0.85 wt%). This increased carbon level results from the presence of coke dust from the coke used in the BF process.

Figure 1 shows the XRD patterns of the two filter cake samples. The main mineral phases present were similar, including hematite Fe2O3, magnetite Fe3O4, wustite FeO, metallic iron Fe, limestone CaCO3 and carbon C. Based on relative intensity of the peaks, it is noted that carbon content of the MIX sample was higher than that in the BOF sample, which is consistent with the XRF results. A further difference in the filter cake samples is that the MIX sample contained more metallic iron than the BOF filter cake.

3.2. Sintering of Filter Cake Samples

The XRD patterns of the MIX samples sintered in static air in the temperature range of 1 100–1 300°C (50°C increments) for 5 minutes are presented in Fig. 2. No metallic iron, carbon or limestone was detected by XRD in the sintered samples; the major phases identified were magnetite and wustite in all of the sintered samples. Hematite was detected in the sample sintered at 1 100°C; its peaks became very weak after sintering at 1 150°C and disappeared when sintered at 1 200°C and higher temperatures. A small amount of silico-ferrite of calcium and aluminium (SFCA) can be identified among all the XRD patterns of the sintered MIX samples.

Figure 3 represents the morphology of the MIX samples calcined at 1 100–1 300°C for 5 minutes in the muffle furnace. The sintering extent of the MIX samples increased gradually with increasing sintering temperature. The pressed tablets changed their shape and expanded when sintered at higher temperatures, causing an increase in porosity. The tablets heated at 1 250 and 1 300°C all fractured into several pieces during sintering.

Table 1. Chemical compositions of two filter cake waste materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>CaO</th>
<th>Mn</th>
<th>MgO</th>
<th>TiO2</th>
<th>Zn</th>
<th>Free C</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOF</td>
<td>55.70</td>
<td>1.46</td>
<td>0.16</td>
<td>6.31</td>
<td>0.80</td>
<td>2.79</td>
<td>0.04</td>
<td>2.28</td>
<td>0.85</td>
</tr>
<tr>
<td>MIX</td>
<td>53.70</td>
<td>1.84</td>
<td>0.40</td>
<td>6.28</td>
<td>0.72</td>
<td>2.79</td>
<td>0.06</td>
<td>2.01</td>
<td>3.14</td>
</tr>
</tbody>
</table>
In each case a “shell” layer formed around the boundary of each tablet in which the mineral phases present differed from those in the sample interior. This layer (visible by its different colour from the interior) was about 500 μm thick for the sample sintered at 1100°C (see Fig. 3(a)) and became thinner when the sintering temperature was increased. In the shell of samples sintered at 1100°C and 1150°C (Figs. 3(a) and 3(b)), the assimilation of oxide materials was not complete, leaving a large proportion of only partially reacted filter cake particles. In comparison, most of the fine particles of filter cake in the interior were aggregated resulting in the formation of large pores inside the samples. As shown in Figs. 3(c), 3(d) and 3(e), the shell layers of samples sintered at 1200, 1250 and 1300°C were thinner but denser, and the aggregation of particles in them was complete, resulting in almost no discrete filter cake particles remaining.

The mineral phases in different regions of sintered tablets were further analysed by SEM/EDS. Figures 4(a) and 4(b) show the back-scattered electron (BSE) images of the exterior and interior of a MIX sample sintered at 1250°C for 5 minutes in a muffle furnace, respectively. The compositions at different points in Fig. 4, as analysed by energy dispersive X-ray spectroscopy (EDS), are listed in Table 2. It should be noted that when an elemental content is less than 1 wt%, the number is only indicative due to the accuracy limits of EDS analysis. A large number of iron oxide particles associated with columnar SFCA were present in the shell of this sample, as shown in Fig. 4(a). The phase associated with points 1 and 2 containing about 64 wt% iron and 7 wt% zinc represented a solid solution of zinc ferrite (ZnFe$_2$O$_4$) and magnetite (Fe$_3$O$_4$). These oxide particles were bonded by columnar SFCA (points 3 and 4). In comparison, as shown in Fig. 4(b), well aggregated iron oxide particles (points 5

![Fig. 2. XRD patterns of MIX samples sintered in the temperature range of 1100–1300°C for 5 minutes in a muffle furnace.](image)

![Fig. 3. Optical microscope images of MIX samples sintered in the temperature range of 1100–1300°C for 5 minutes in a muffle furnace. (a) 1100°C; (b) 1150°C; (c) 1200°C; (d) 1250°C; (e) 1300°C.](image)
and 6) were present in the interior of the sample associated with dicalcium silicate (points 7 and 8) as well as a small amount of dicalcium ferrite (points 9 and 10). A very low concentration of zinc (about 0.35 wt%) was found in these iron oxide phases which were identified as magnetite and wustite by XRD analysis (Fig. 2).

To examine the effect of gas atmosphere on the sintering behaviour of the filter cake samples, the MIX samples were heated at 1 250°C for 5 minutes in a muffle furnace. (a) Exterior; (b) Interior.

![Back-scattered electron (BSE) images of mineral phases in MIX samples sintered at 1250°C for 5 minutes in a muffle furnace](image1)

**Table 2.** Elemental composition (wt%) of grains marked in Fig. 4 and corresponding phases.

<table>
<thead>
<tr>
<th>Point no.</th>
<th>Fe</th>
<th>Ca</th>
<th>Si</th>
<th>Al</th>
<th>Mg</th>
<th>Zn</th>
<th>Phase identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>63.4</td>
<td>3.7</td>
<td>0.08</td>
<td>0.2</td>
<td>2.0</td>
<td>7.1</td>
<td>Zn-rich iron oxides</td>
</tr>
<tr>
<td>2</td>
<td>64.4</td>
<td>3.6</td>
<td>0.02</td>
<td>0.2</td>
<td>2.3</td>
<td>6.5</td>
<td>Zn-rich iron oxides</td>
</tr>
<tr>
<td>3</td>
<td>59.3</td>
<td>14.5</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td>1.5</td>
<td>SFCA</td>
</tr>
<tr>
<td>4</td>
<td>59.6</td>
<td>14.0</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
<td>1.6</td>
<td>SFCA</td>
</tr>
<tr>
<td>5</td>
<td>73.2</td>
<td>2.0</td>
<td>0.07</td>
<td>0.3</td>
<td>2.6</td>
<td>0.4</td>
<td>Zn-poor iron oxides</td>
</tr>
<tr>
<td>6</td>
<td>72.7</td>
<td>2.5</td>
<td>0.2</td>
<td>0.3</td>
<td>2.6</td>
<td>0.4</td>
<td>Zn-poor iron oxides</td>
</tr>
<tr>
<td>7</td>
<td>4.9</td>
<td>40.1</td>
<td>20.3</td>
<td>0.01</td>
<td>0.1</td>
<td>0.2</td>
<td>Dicalcium silicate</td>
</tr>
<tr>
<td>8</td>
<td>2.1</td>
<td>48.0</td>
<td>18.4</td>
<td>0.04</td>
<td>0.05</td>
<td>0.4</td>
<td>Dicalcium silicate</td>
</tr>
<tr>
<td>9</td>
<td>36.2</td>
<td>33.2</td>
<td>1.0</td>
<td>3.5</td>
<td>0.07</td>
<td>0.3</td>
<td>Dicalcium ferrite</td>
</tr>
<tr>
<td>10</td>
<td>36.2</td>
<td>32.8</td>
<td>0.9</td>
<td>3.9</td>
<td>0.05</td>
<td>0.5</td>
<td>Dicalcium ferrite</td>
</tr>
</tbody>
</table>

Fractured and the original as-pressed shape of the tablets persisted. From the XRD patterns of these sintered samples presented in Fig. 5, it is noted that the sintered MIX samples in argon were dominated by a wustite phase; a small amount of metallic iron was also present within samples sintered at higher temperatures (1 200–1 300°C). A weak carbon peak was only detected in the sample sintered at 1150°C; a small amount of dicalcium silicate (Ca2S) was identified by XRD in all the samples. Optical microscope and SEM analysis show that these mineral phases were uniformly distributed in these sintered samples. Figure 6 shows a typical BSE image of the MIX samples sintered in argon at 1300°C for 5 minutes. This figure shows the dispersed metallic iron in the wustite matrix and the dicalcium silicate phase.

To examine the influence of carbon content on the sintering behaviour of filter cake samples, the BOF filter cake samples (containing less carbon, Table 1) were heated in air (muffle furnace) and in argon with a flow rate of 1.5 L/min (vertical furnace) in the temperature range of 1100–1300°C for 5 minutes. None of the BOF tablets sintered in air fractured and the original as-pressed shape remained. Compared with the MIX filter cake, a similar but thicker shell structure was identified in the BOF tablets sintered in air. The mineral phases of these sintered BOF samples were examined by XRD analysis (Fig. 7(a)). It can be seen that the BOF samples sintered in air at 1100 and 1150°C were dominated by magnetite, hematite and SFCA but no wustite which was present in a significant amount in the MIX samples sintered under the same conditions. As the sintering temperature increased, the content of magnetite increased gradually with a corresponding decrease in the contents of hematite and SFCA.

No shell structure was observed in BOF filter cake samples sintered in argon, and the distribution of mineral phases within these samples was relatively uniform. The XRD analysis (Fig. 7(b)) showed that magnetite and wustite were the dominant phases in the BOF samples sintered in argon. The CaFe₂O₅ phase peak intensity, though not pronounced, appeared to decrease with increasing sintering temperature.
sintered BOF filter cake, as the high carbon concentration levels in the MIX samples provided a more reducing atmosphere than that of the BOF samples.

3.3. Zinc Removal from Filter Cake Samples

The zinc contents of filter cake samples sintered under different conditions were analysed by ICP-OES. The effects of temperature, gas atmosphere and carbon content on the zinc removal of sintered filter cake sample are shown in Fig. 8.

In general, increasing the sintering temperature improved the zinc removal rate of sintered filter cake samples except for the BOF filter cake samples sintered in air where the effect of temperature on zinc removal was negligible. At 1150°C, the zinc removal of MIX sample sintered in Ar was less than 20%. It increased to 55% at 1250°C and achieved 62% at 1300°C.

For each filter cake sample sintered in the temperature interval of 1100–1300°C, removal of zinc in argon was higher than in air. The zinc removal of the MIX sample sintered in air at 1300°C was only 22%, which is 40% lower than that achieved in argon. For BOF filter cake, the zinc removal after sintering in argon and in air at 1300°C was 13% and 3%, respectively.

4. Discussion

4.1. Mineral Phase Formation

The mineral phases present in the sintered filter cake tablets are summarised in Table 3. It can be seen that the predominant phases of the sintered samples are very different although the starting materials had very similar metal oxide compositions. These variations are mainly attributed to the differences in carbon and metallic iron contents in the original filter cake samples and the sintering environment for the inner and outer areas of the tablet in addition to the sintering temperature used.

When the MIX filter cake tablets were sintered in air, the combustion of carbon and decomposition of calcium carbonate took place by reactions (1) and (2), respectively:

\[
\begin{align*}
C(s) + \frac{1}{2}O_2(g) &= CO_2(g), \Delta G^\circ = -394.597 - 1.226T (J) \tag{1} \\
CaCO_3(s) &= CaO(s) + CO_2(g), \Delta G^\circ = 161.621 - 138.5T (J) \tag{2}
\end{align*}
\]
The standard Gibbs free energy changes of the reactions in this paper were calculated using available data\textsuperscript{15) in the range of 773 K to 1 773 K (500°C to 1 500°C). The Bou-
douard reaction (3) is highly favoured thermodynamically
within the temperature range of sintering experiments in
this investigation.
\[
C(s) + CO_2(g) = 2CO(g), \Delta G^\circ = 168 284 - 172.9T \text{ (J)} \ldots (3)
\]

Reaction (2) and other reactions in argon atmospheres
generated a small amount of gases, which escaped from the
MIX tablets easily without damaging the tablets. As a result,
the MIX tablets sintered in argon showed only shrinkage.
The MIX tablets sintered in air swelled or even broke due
to rapid release of gas from the combustion of carbon, Reaction (1). Figure 9 presents the carbon loss in the MIX and
BOF filter cakes after sintering in air and argon. It is noted
that when sintered at temperatures below 1 250°C, carbon
was consumed at a much higher rate in air than in argon.

A more reducing atmosphere in the interior of the tablets
can be inferred due to the fact that the reducing gas pro-
duced from carbon combustion (a combination of reactions
(1) and (3)) diffused outwards. As shown in Fig. 3, a higher
extent of aggregation of particles was likely achieved in the
interior of sintered tablets, probably since the heat released
from the carbon combustion was accumulated internally,
leading to a higher interior temperature than the exterior.

The MIX samples sintered in air showed different phases
in the interior and exterior of the tablets. When sintered in
air, combustion of carbon by reaction (1) caused diffusion
of oxygen inwards, while heat released from the reaction
transferred towards the surface of the tablets. These pro-
cesses resulted in higher temperature and a more reduc-
ing atmosphere in the interior which prevented iron from
oxidising to hematite. Only wustite and magnetite were
observed in the interior. In comparison, the shell of sintered
MIX tablets mainly consisted of magnetite associated with
SFCA, as shown in Figs. 3 and 4. SFCA phases (including
SFCA-I) are key bonding materials of industrial iron ore
sinter. CaFe$_2$O$_4$ (CF) can be formed as the precursor phase of SFCA through solid state reaction:
\[
CaO(s) + Fe_2O_3(s) = CaFe_2O_4(s),
\Delta G^\circ = -29 519 - 9.929T \text{ (J)} \ldots (4)
\]

where calcium from the flux initially reacts with hematite
to form the new phase, CF. Formation of Ca$_2$Fe$_2$O$_5$ (C$_2$F) is also possible when enough lime is available. Impurities such as silica and alumina reacted with these early formed ferrites to form SFCA phases.

No formation of SFCA was observed in the interior of
tables sintered in air. Although a small amount of hematite
was present in the original filter cake, the high temperature
and low pO$_2$ conditions in the interior of the tablets led to
the reduction of hematite into magnetite (Reaction (5)) and
correspondingly suppressed the formation of SFCA.
\[
6Fe_2O_3(s) = 4FeO_4(s) + O_2(g),
\Delta G^\circ = 479 433 - 293.6T \text{ (J)} \ldots (5)
\]

During iron ore sintering, the mass ratio of CaO to SiO$_2$
of the sinter blend is known to be a key factor governing
mineral phase formation and sinter microstructure. A ratio
greater than 1.8 to 2.0 favours the formation of SFCA phases, while a lower ratio favours the formation of calcium
silicate and glassy phases.\textsuperscript{16–18) The BOF and MIX filter
cakes used in this investigation have ratio between 3.41 and
4.32, therefore the formation of SFCA phases observed in
the sintered filter cake samples was highly favoured.

When the MIX filter cake tablets were sintered in argon,
the carbon and metallic iron in the filter cake created a more
reducing sintering atmosphere. Wustite was the main phase
and an amount of metallic iron was produced when the
samples were sintered at temperatures higher than 1 200°C. The formation of wustite and iron can mainly be shown in
Reactions (6)–(8).
\[
3Fe_2O_3(s) + C(s) = 2FeO_4(s) + CO(g), \Delta G^\circ = 126 343 - 233.7T \text{ (J)} \ldots (6)
\]

\[
Fe_2O_4(s) + C(s) = 3FeO(s) + CO(g), \quad \Delta G^\circ = 186 429 - 190.9T \text{ (J)} \ldots (7)
\]
FeO(s) + C(s) = Fe(s) + CO(g), \Delta G^\circ = 150.265 - 151.67T(J)

Under this reducing atmosphere, although calcium ferrites were not formed, the MIX filter cake was also well sintered.

Compared to the MIX filter cake, the BOF filter cake contained less carbon reductant, so less reduction took place when the BOF samples were sintered in both air and argon. Similar to the MIX filter cake, a shell structure was identified in the BOF tablets sintered in air, with more hematite and SFCA present in the shell layers after sintering at and below 1 200°C. The interior was mainly magnetite; wustite that dominated within the air-sintered MIX samples was not detected in the interior of air-sintered BOF samples. This is because sufficiently strong reducing conditions could not be generated from the low carbon and metallic iron contents.

In terms of the BOF samples sintered in argon, the dominant phases were magnetite and wustite, and no metallic iron was present. It is noted that CaFe2O4 phase identified by XRD analysis was distributed around iron oxide particles as a bonding phase in these samples. In general, CaFe2O4 is not a common phase identified in iron ore sinter but could be generated with the reaction between Fe2O3 and CaO.19

4.2. Zinc Removal

During sintering of filter cake samples, carbon within the samples acted as a reductant. Zinc oxide in filter cake was reduced to zinc vapour (Zn(g)) by Reaction (9).

\[ \text{ZnO(s) + C(s) = CO(g) + Zn(g)} \]
\[ \Delta G^\circ = 356.434 - 291.2T(J) \]

Like carbothermal reduction of other metal oxides,20-22 the above reaction proceeds via the gas phase. CO reacts with ZnO to form Zn vapour and CO2, and the latter, further reacts with carbon to regenerate CO (Boudouard reaction (3)).

Zinc oxide could also be reduced by metallic iron by Reaction (10)

\[ \text{ZnO(s) + Fe(s) = Zn(g) + FeO(s)} \]
\[ \Delta G^\circ = 206.170 - 139.67T(J) \]

Figure 10 presents the partial pressure of zinc vapour in equilibrium with ZnO and CO calculated from Reaction (9) at various CO pressures and temperatures. The equilibrium partial pressure of zinc vapour following Reaction (10) and the saturation vapour pressure of liquid zinc are also shown in the figure. Both Reactions (9) and (10) are thermodynamically favoured in a wide range of reaction conditions. For instance, at 1 000°C and CO partial pressure of 10 kPa, equilibrium zinc vapour pressure in Reactions (9) and (10) reaches approximately 400 kPa and 10 kPa, respectively.

The experimental results show that the gas atmosphere has an important influence on the potential for zinc removal. For experiments in argon, the reduced zinc vapour diffused out of tablets and was removed from the filter cakes. In the experiments in air, zinc vapour generated in the tablet interior diffused outwards. In the exterior of the tablets, zinc vapour was oxidised as follows.

\[ \text{Zn(g) + \frac{1}{2} O_2 = ZnO, \Delta G^\circ = -469.808 + 204.4T(J)} \]
\[ \text{Zn(g) + \frac{1}{2} O_2(g) + Fe_2O_3 = ZnFe_2O_4,} \]
\[ \Delta G^\circ = -483.479 + 193.1T(J) \]

Figure 11 presents the partial pressure of zinc vapour in equilibrium with ZnO or ZnFe2O4 calculated from reactions (11) and (12) under different oxygen partial pressures at different temperatures. The equilibrium zinc vapour pressure decreases significantly with decreasing temperature and increasing oxygen partial pressure. Both Reactions (11) and (12) are thermodynamically favoured over a fairly wide range of reaction conditions. For Reaction (11), a pO2 of 1 kPa suppresses the equilibrium zinc vapour pressure to the order of 10-4 to 10-2 kPa in the sintering temperature range of this work; the equilibrium zinc pressure is an order of magnitude lower for Reaction (12).

It has been demonstrated that the oxidation of zinc vapour cannot occur in the gas phase due to the lack of crystallisation sites. In an investigation on the reduction of zinc oxide from manganese furnace dust, Shen et al.23 observed that oxidation of zinc only took place on the crucible wall or contained materials rather than in the gas phase. Weidenkaff et al.24 concluded that oxidation of zinc vapour by oxygen is heterogeneous and, in the absence of nucleation sites, zinc vapour and oxygen gas coexist in a metastable state.

In the present investigation, zinc vapour formed by reduction of zinc oxide in tablets diffused outwards and was removed from the tablets when sintered in argon. When
sintered in air, an oxidising atmosphere was present at the exterior of tablets due to the inward diffusion of \( \text{O}_2 \), and zinc vapour was oxidised and doped in the magnetite substrate forming a zinc ferrite-magnetite solid solution. Particularly during sintering at higher temperatures (1 250 and 1 300°C), the fracturing of samples provided more opportunities with zinc vapour to react with \( \text{O}_2 \) and consequently form the zinc ferrite-magnetite solid solution. This resulted in migration of zinc vapours to the exterior of tablets as observed in Figs. 3 and 4. As shown by the thermodynamics of reactions (11) and (12), the combination of \( \text{ZnO} \) with iron oxide phases stabilises \( \text{ZnO} \) and makes it less prone to reduction reactions.

The significant difference in zinc removal from two filter cake samples shown in Fig. 8 can be attributed to their difference in carbon and metallic iron contents. The removal of zinc in MIX filter cake was more complete than that in BOF filter cake, since the MIX filter cake had higher carbon and metallic iron contents which were available as reductants for \( \text{ZnO} \) reduction. Argon was more beneficial to zinc removal than air by maintaining a more reducing atmosphere. The zinc removal from the MIX sample sintered in air was still higher than that of the BOF sample sintered in argon, which demonstrates the critical importance of a reductant such as carbon in the sample. Also, it is worthwhile to note that the filter cake samples used in this investigation contained significantly lower content of metallic iron than when freshly generated from steelmaking processes. Further investigation on the sintering behaviour of the filter cakes containing more metallic iron and with added carbon is in progress.

5. Conclusions

A mixture of blast furnace filter cake and basic oxygen steelmaking filter cake (MIX filter cake) and a pure basic oxygen steelmaking filter cake (BOF filter cake) were sintered at different temperatures (100–1 300°C) in argon and in air to evaluate the effects of temperature, gas atmosphere and carbon content on the mineral phase formation and zinc removal of sintered filter cake specimens.

The sintering extent of both filter cake samples increased with increasing sintering temperature. When sintered in air, filter cake particles showed greater aggregation in the interior than in the exterior of sintered tablets, because the heat released from the combustion of carbon in the filter cake likely led to a higher temperature in the interior. SFCA and \( \text{ZnO} \) containing magnetite phases were formed in the external layer of the tablets, while internal phases were magnetite and wustite.

When sintered in argon, mineral phases were evenly distributed in the samples due to the absence of carbon combustion. The dominant phases were magnetite, wustite, metallic iron and silicates. Although SFCA was not present in the filter cake samples sintered in argon due to the relatively reducing sintering conditions, the particles in filter cake can be well aggregated.

Removal of zinc was observed during the sintering of filter cake samples, which was enhanced by increasing the contents of carbon and metallic iron as well as using a reducing gas atmosphere. Zinc oxide in filter cake was reduced to zinc vapour by carbon or metallic iron in filter cake. During sintering in argon, the reduced zinc vapour diffused out of the tablets and was removed from the filter cake. In comparison, when sintered in air, the zinc vapour formed in the interior diffused to the exterior of tablets where it was oxidised and doped in the magnetite substrate forming a zinc ferrite-magnetite solid solution.

In conclusion, the particles of the two filter cake samples were well aggregated in both oxidizing and reducing gas atmospheres, but the removal of zinc in the filter cake samples was enhanced in a reducing atmosphere. Therefore, to recycle the filter cake by steelmaking processes, a reducing atmosphere is more desirable during sintering the filter cake.

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