1. Introduction

On-plant utilisation and recycling of by-products will have an important role in achieving both the environmental and economic sustainability of the steel industry. One of the largest by-product streams in an integrated steel plant is dust from the basic oxygen steelmaking (BOS) process, making it an area of particular interest and an opportunity for improving recycling. In the BOS process, oxygen is blown at supersonic velocities to decarburise the steel, resulting in significant amounts of gas and dust being generated. This dust, often agglomerated into a filter cake, is made up of very fine steel and slag droplets, as well as flux fines, and contains valuable elements such as iron and calcium. It is desirable to reuse this filter cake in the BOS process and elsewhere to reclaim these elements.

Unfortunately, recycling of BOS filter cake can be problematic. The high temperatures (well in excess of 1873 K) realised in the BOS process cause the volatilisation of tramp elements (such as zinc) to the gas phase. As the gas phase is cooled in the extraction process, these volatilised metals can condense as separate particles or onto existing dust particles. This zinc can cause processing issues in iron and steelmaking, limiting on-plant recycling. Scaffolds can form in the blast furnace with increasing zinc loads, limiting the amount of BOS filter cake that can be recycled through the blast furnace (typically via a sinter or pellet plant) to a low rate. This makes recycling of the dust back through the BOS favourable, if possible.

BOS dust is often removed from the off-gas using a wet scrubbing process, resulting in a slurry that is usually dewatered to produce a low moisture filter cake that is stockpiled for future recycling. When stored in stockpiles prior to recycling, BlueScope BOS filter cake has been found to...
The self-sintered material is preferred for recycling back through the BOS as it has better handling/transport properties, with higher strength and larger particle size, when compared to the original filter cake. These improved properties offer opportunities for increased BOS filter cake recycling if the self-sintering process can be better understood and optimised. This would improve the environmental performance of the plant and potentially lower production costs through the reclaiming of the valuable iron and calcium units in the filter cake.

In previous work by the current authors, the self-sintering reactions have been studied using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques. The oxidation of the BOS filter cake was found to have a characteristic behaviour that appeared largely independent of sample size, reaction system or heating rate. The characteristic behaviour of the BOS filter cake during heating in air was the result of a complex, multi-step process. The characteristic behaviour was divided into 5 steps. These steps, as identified from TGA and TGA-DSC experimentation, and their typical temperature ranges are:

Step 1. Drying of the sample at $T < 393$ K.
Step 2. Oxidation of the initial metallic iron and wüstite mixture to hematite and zinc ferrite, at $393–403$ K $< T < 873$ K. The oxidation of the metallic iron and wüstite did not occur until after the water has been removed from the sample.
Step 3. Calcination of dolomite at $873–893$ K $< T < 1043$ K.
Step 4. A very small mass gain at $1003–1043$ K $< T < 1173$ K, likely caused by further oxidation of the large iron/iron oxide particles.
Step 5. A very small decrease in sample mass at $T > 1173$ K, possibly caused by calcination of limestone.

While the overall processes that occur in self-sintering have been identified, mechanistic details of the self-sintering and an improved understanding of the oxidation and self-sintering behaviour of the BOS filter cake are required if it is to be optimised. In situ measurement of the phases present during the oxidation of BOS filter cake may help to achieve this goal.

The main objective of this study was to improve the on-plant recycling of the BOS filter cake to the BOS by improving the understanding of the self-sintering process. The specific aim of this study was to use in situ phase analysis during the oxidation of BOS filter cake to help identify specific reactions that occur at each of the steps in the self-sintering process.

To achieve this, unreacted, freshly produced BOS filter cake from the BlueScope steelworks has been characterised in situ during oxidation using high temperature X-ray diffraction (XRD). These results have been compared against results from thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC) of BOS filter cake collected at the same time as the samples used for the in situ measurements.

2. Experimental

The reaction of the BOS filter cake with air was studied non-isothermally by in situ high temperature XRD during heating to 1273 K. The quantitative phase analyses from the in situ XRD were compared against mass change and energy release measured using a TGA-DSC system.

The composition of fresh, unreacted BOS filter cake as measured by X-ray fluorescence (XRF) spectroscopy is given in Table 1. Samples for XRF spectroscopy were oxidised before analysis by heating to 1273 K in air at 10 K/min. In Table 1, all iron is reported as Fe$_2$O$_3$ and all sulphur is reported as SO$_3$. These do not represent speciation, but rather total iron and total sulphur content in the sample. Moisture was determined by heating a sample of BOS filter cake to 393 K for 18 hours and measuring the weight change.

### 2.1. XRD Measurements

Initial XRD characterisation of the unreacted BOS filter cake was conducted ex situ using a Panalytical Empyrean instrument using a Co long-fine-focus X-ray tube at 40 kV and 40 mA. The step size was a nominal 0.03°, with each scan from 0–90° 2θ lasting for 1 hour. Samples were prepared by light hand grinding using a mortar and pestle. Samples were back pressed into the sample holder to prepare a randomly oriented, flat surface to the X-ray beam. The samples were rotated at 15 rpm during the measurement. Three sub-samples were analysed from each of four different pieces of BOS filter cake and an average value reported. These pieces of BOS filter cake corresponded to those used in the in situ measurements.

The in situ high temperature XRD was carried out in an INEL diffractometer, using a Co tube at 40 kV and 35 mA. The diffraction patterns were collected using a CPS120 position sensitive detector, which collected 120° 2θ of diffraction data simultaneously. Datasets were collected in 60 second increments during heating and cooling. The samples were held in an Anton Paar HTK16N high temperature chamber, which used a Pt strip heater. A slurry of the BOS filter cake and acetone was prepared and placed within the sample well ($20 \times 7 \times 0.2$ mm) on the Pt strip heater. A separate piece of BOS filter cake was sampled for each experiment. Flowing air was passed through the chamber at $\sim 580$ mL/min during the measurements.

Samples were heated at 5 K/min, 10 K/min and 20 K/min to 1273 K in flowing air. All samples were cooled at 20°/min. Different heating rates were used to examine any possible changes in the temperatures of the onset of the phase changes. The test was repeated at a heating rate of 10 K/min.

<table>
<thead>
<tr>
<th>Component</th>
<th>mass%</th>
<th>Component</th>
<th>mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>1.9 ± 0.1</td>
<td>CaO</td>
<td>4.7 ± 0.1</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>&lt;0.5</td>
<td>TiO$_2$</td>
<td>0</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>2.3 ± 0.8</td>
<td>MnO</td>
<td>0.7 ± 0.03</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>&lt;0.5</td>
<td>Fe$_2$O$_3$</td>
<td>72.7 ± 2.1</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>&lt;0.5</td>
<td>ZnO</td>
<td>16.7 ± 2.9</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>&lt;0.5</td>
<td>moisture</td>
<td>15.4 ± 0.5</td>
</tr>
</tbody>
</table>

The composition of fresh, unreacted BOS filter cake, as measured by XRF. Moisture was determined by drying at 393 K. The variability is indicated by the scatter between the analyses of two samples.
K/min to help better understand the repeatability. Diffraction patterns were collected during both heating and cooling. The temperature reported for each pattern was that at the beginning of acquisition. The error in the reported temperature value has been estimated to be ±10 K.\(^{10}\)

Qualitative phase analysis of the XRD data was performed using Panalytical Highscore Plus software (version 4.5). Quantitative phase analysis was carried out using the Rietveld method using Topas software (version 6). The amorphous (or non-bulk crystalline) content of the sample was estimated (\textit{ex situ}) using the internal standard method, using a crystalline corundum (Al\(_2\)O\(_3\)) sample as the internal standard. The crystal structure data of Lager et al.,\(^{11}\) Maslen et al.,\(^{12}\) Hamilton,\(^{13}\) Fjellvåg et al.,\(^{14}\) Owen and Yates,\(^{15}\) Abrahams and Bernstein,\(^{16}\) Jacobs et al.,\(^{17}\) Brown et al.,\(^{18}\) Blake et al.\(^{19}\) and Ofteda\(^{20}\) were used as the initial input for quartz, calcite, spinel, wüstite, α-Fe, zincite, Zn(OH)\(_2\), corundum, hematite and lime, respectively. In addition to the background (four coefficient Chebychev function) and specimen displacement correction parameters, the unit cell, peak profile and Rietveld scale factor parameters for each of the phases were refined simultaneously to achieve the best fit of the calculated pattern to the experimental data.

2.2. TGA-DSC Testing

The results from the \textit{in situ} XRD analyses were compared against results from TGA-DSC testing, using a Netzsch STA449 F5 Jupiter. Samples of fresh BOS filter cake were heated at 5 K/min, 10 K/min and 20 K/min to 1723 K under air flowing at 120 mL/min. The measured data were analysed using the Netzsch Proteus Analysis software (version 6.1). The sample size was a nominal 100 mg, and the samples were contained within Pt-Rh crucibles with a thin alumina liner.

The TGA mass change data were normalised against the sample mass to give a dimensionless fractional weight change (FWC, as calculated from Eq. (1)) to allow comparison between samples,

\[
\text{FWC} = \frac{W_t - W_0}{W_0} \quad \text{.................. (1)}
\]

where \(W_0\) and \(W_t\) are the mass after drying and the mass of a sample at time \(t\), respectively in grams. This is slightly different to the normal definition of FWC, with the initial sample mass replaced with the mass after drying. This was used as a common base for the comparison with the quantitative XRD data.

2.3. Conversion of Phase Mass\% Data to FWC

To compare weight change data from the TGA with the quantitative XRD results, the proportions of phases were converted to a mass change. Only phases reported in the \textit{in situ} XRD analyses were considered in this calculation. Assuming that there was 100 g of sample, the mass\% of each phase at each time step was converted into moles, as given in Eq. (2),

\[
n_i = \frac{m_i}{M_i} \times \left(\frac{\text{mass}\%}{M_i}\right) \quad \text{.................. (2)}
\]

where \(n_i\) is the number of moles of species \(i\), \(m_i\) is the mass of species \(i\) (equal to mass\% if we assume 100 g sample), and \(M_i\) is the molar mass of species \(i\). The number of moles in the sample was then normalised to a total of one mole of Fe bearing species, and then converted back into a mass of each species,

\[
n_i^* = \frac{n_i}{\left(n_Fe + 3 \cdot n_{FeO} + 2 \cdot n_{Fe_2O_3}\right)} \quad \text{.................. (3)}
\]

\[
m_i^* = n_i^* \times M_i \quad \text{.................. (4)}
\]

Equations (2) and (3) were used for all species (metallic Fe, FeO, Fe\(_2\)O\(_3\), Fe\(_3\)O\(_4\) and CaCO\(_3\)) except for CaO. The mass of CaO was instead based on a molar balance of the reaction given in Eq. (5). The \(n_{CaO}\) calculated from Eq. (6) was then used to calculate the \(m_{CaO}\) as in Eq. (4),

\[
\text{CaCO}_3 = \text{CaO} + \text{CO}_2(g) \quad \text{.................. (5)}
\]

\[
n_{CaO}^* = \Delta n_{\text{CaCO}_3}^* \quad \text{.................. (6)}
\]

The apparent total mass of the sample was then calculated (Eq. (7)), and FWC calculated using this total mass as given in Eq. (1).

\[
m_{\text{total}}^* = m_{Fe}^* + m_{FeO}^* + m_{Fe_2O_3}^* + m_{Fe_3O_4}^* + m_{CaO}^* + m_{CaCO_3}^* \quad \text{.................. (7)}
\]

Zinc oxide was ignored in this calculation as it was assumed that it played no role in the mass change of the sample.

3. Results and Discussion

\textit{In situ} phase analysis by quantitative high temperature XRD was used to study the phase changes that occur in BOS filter cake during self-sintering.

3.1. Characterisation of Unreacted BOS Filter Cake

The phases present within the unreacted BOS filter cake samples were analysed by XRD. A typical diffraction pattern is given in Fig. 1. Three samples were taken from each of the four original BOS filter cake pieces, with the average results from the quantitative XRD given in Table 2. The main crystalline phases in each sample were iron bearing, with wüstite having the largest content, followed by metallic iron and spinel. The spinel phase could be either magnetite or zinc ferrite, but was most likely a solid solution of the two. The presence of zinc ferrite or a zinc-containing spinel within the sample has been noted in other steel plant by-products that contain iron and zinc oxides.\(^{21-24}\)

It should be acknowledged that there were not enough of the zinc bearing phases (zincite and spinel, with a trace amount of zinc hydroxide detected) to account for all of the ZnO content as measured by XRF (Table 1). This “missing” zinc is most likely one of the components of the non-bulk crystalline proportion of the sample. MgO is another component that is difficult to quantify by XRD in these samples. It is expected that MgO in the BOS filter cake is in the form of dolomite. There are several possible reasons for MgO being difficult to measure by XRD. The amount of MgO in the sample is small (~2 mass\%, Table 1), so it can be difficult to detect. Further, MgO has solubility within the spinel phase and limited solubility in calcite\(^{25}\) and, so at least some MgO may be present within the spinel and/or
calcite that was observed in the XRD patterns. This would most likely present as a peak shift in the XRD pattern. Given the amount of MgO, this shift would be small and difficult to differentiate from other effects. It may also be possible that MgO may be contained within the ~30 mass% non-crystalline content within the BOS filter cake.

It would be helpful to be able to better characterise the non-crystalline content of the BOS filter cake. Previous SEM characterisation of the BOS filter cake has shown that it is largely an agglomeration of extremely fine particles, with particle sizes significantly less than 1 μm. This fine particulate nature of the material makes simple microscopy of the BOS filter cake to characterise the components of the non-crystalline content difficult. Identification of the components of the non-crystalline content within the BOS filter cake is an area that warrants further study.

As shown in Table 2, there was some variation between the samples. The high variability of steel plant by-products is a well-known issue. For BOS filter cake, it is possible for the composition, phase content and particle size to change from heat to heat as well as within a single heat. These variations depend on the target steel grade and charge materials (hot metal and scrap composition), blowing conditions and any additions made (fluxes and coolants). This variability in material makes both a thorough characterisation of the BOS filter cake and acknowledgment of the limitations of the characterisation important. The latter is often neglected in the literature.

The variation between the samples here was noted but not extensively studied. The largest difference was in the measured non-bulk crystalline content of the BOS filter cake samples. The crystalline phases which had the largest variation between the samples were ZnO and CaCO₃ (with one standard deviation being 8–9% of the average value). On the other hand, the variation in the iron bearing phases was smaller.

### 3.2. In situ Characterisation of BOS Filter Cake during Oxidation at High Temperatures

The change in the proportions of the crystalline phases during heating in air, as measured in situ by XRD is shown in Fig. 2. Changes in the iron bearing phases present in the BOS filter cake begin to occur at temperatures well below 473 K. The wüstite content appears to decrease at temperatures of approximately 273 K, with a corresponding increase in the magnetite-zinc ferrite spinel solid solution phase. Metallic iron began to react at higher temperatures (~523–573 K), with a sharper drop off. Both phases have largely disappeared by 773–873 K, where the magnetite-zinc ferrite spinel reaches an initial maximum. Between 773 K and 923–973 K, the fraction of magnetite-zinc ferrite spinel...
then decreases slightly with increasing temperature, before increasing again at temperatures above 973 K. Hematite begins to appear at approximately 573 K, reaching a maximum or plateau at ~973 K. The appearance of hematite possibly correlates with the onset of oxidation of metallic iron. While there is a correlation between the onset of iron oxidation and hematite formation, a definitive link cannot be made with the current data, due to the overlapping reactions/processes that are occurring. Further data would be required to confirm this correlation. The maximum in the hematite content corresponds with the intermediate minimum in the magnetite-zinc ferrite spinel. Hematite then decreases as temperature increases above 1 173 K.

The crystalline ZnO content of the sample is largely constant up to approximately 573 K. It then slowly decreases with increasing temperature without completely disappearing. There is no simple correspondence of changes in the ZnO with changes in the magnetite-zinc ferrite spinel. Hematite then decreases as temperature increases above 1 173 K.

Calcium carbonate is largely constant up to approximately 873 K, when it decomposes, corresponding well with an increase in the CaO content. The amount of the CaO phase increased to a maximum at approximately 973 K. Further heating resulted in a decrease in the CaO content. This decrease in the CaO content does seem to correlate with the increase in the magnetite-zinc ferrite spinel solution at higher temperatures.

For the magnetite-zinc ferrite spinel solution, there were a local maximum in its proportion (at T ≈ 773 K) and local minimum (at T ≈ 923–973 K). These are likely due to the changing rates of their production and consumption. It is unlikely that there was a cessation in either the production or consumption of the spinel at these points. This argument may also be applied to the maximum in the proportion of hematite, where it is possible that it may still be forming at T > 973 K. On the other hand, for CaO, the maximum in its proportion is more likely a result of the mostly complete conversion of CaCO₃ at T ≈ 973 K.

The behaviour of the BOS filter cake was largely similar at each heating rate, with similar shapes of the curves. There was a little variation in the intermediate maximum (at T ≈ 773 K) and final values reached for the magnetite-zinc ferrite spinel solution (and also in the hematite). This
difference may be related to either the variability between samples, or changes in the non-bulk crystalline content of the sample. It is also likely that some of the non-bulk crystalline material may become more crystalline during heating and/or reaction. As the non-bulk crystalline content was not assessed in the in situ measurements, it would not be possible to distinguish this effect from the current data.

The similarity between the different heating rates can also be seen clearly when the rate of change of the phases is examined. The rate of change of the proportions of the iron bearing species with temperature for all heating rates is shown in Fig. 3. The denominator in the rate term used here is temperature rather than time to make comparison between the different heating rates simpler. The rate curves for each phase largely overlap each other, indicating that both the values for rate of change with temperature, and the temperatures that they occur, are similar at each heating rate. Differences in the curves may be caused by resolution of the measurement. Diffraction data were collected over a one minute span, such that each point relates to a different temperature span for each heating rate.

3.3. Comparison with TGA and DSC Experiments

The comparison between the mass change measured by TGA and that calculated from the in situ phase analysis data at each heating rate is shown in Fig. 4. While the weight change curves from the two technique were similar, there were slight differences between them. These slight differences in the curves may be expected, due to differences in the sample mass and physical set-up of the two experiments. In the in situ XRD measurements the sample consisted of a thin layer placed directly onto the heat source, while in the TGA-DSC the sample was held in a crucible and was approximately 1 mm thick, and heated by being placed within a tube furnace. These differences in the experimental set-ups would be expected to cause differences in heat and mass transfer during the measurements, in turn leading to slightly difference weight change curves. Slight differences would also be expected to be caused by the heterogeneous nature of the BOS filter cake. Despite this, the mea-
Sured and calculated weight change curves had common features. One feature not present in the in situ measurements is the large drying stage seen in the TGA curves at T < 373 K. As the moisture content of the sample is not measured by XRD, this step is not present in the curves calculated from the in situ measurements.

The large increase in mass begins at similar temperatures, with a significant mass increase beginning above 473 K. The finish of the large mass increase was slightly higher for the calculated mass change from the in situ phase analysis than for the measured mass change. In Eqs. (2)–(7), it may be considered that, for a fixed amount of total iron in a sample, an increase in mass can be caused by an increase in the proportions of magnetite and hematite. As the initial BOS filter cake was primarily composed of wüstite and metallic iron, the similarity between the curves indicates that the increase in mass is caused by the oxidation of wüstite and metallic iron to magnetite and hematite. It should be noted that a simplification made in these calculations was that the magnetite-zinc ferrite solid solution was considered to be pure magnetite.

The decreases in mass at temperatures above 873 K are also similar. The magnitude of the decrease in mass is similar, although it appears to occur slightly earlier in the in situ measurements than in the TGA experiments. Using a similar consideration to the mass gains, the decomposition of CaCO3 to CaO, which appears to occur sharply at these temperatures will lead to a decrease in mass of the BOS filter cake. This indicates that the decrease in mass at these temperatures is likely caused by this decomposition. Under equilibrium conditions, CaCO3 is stable up to ~1167 K, considering the reaction given in Eq. (8). However, if non-equilibrium conditions were considered, with pCO2 < 1 atm, such as under a flowing stream of air, then the reaction becomes thermodynamically favourable at much lower temperatures, down to the range considered here (~873 K to ~1023 K), where pCO2 = 0.01 atm or more.

\[
\text{CaCO}_3(s) = \text{CaO}(s) + \text{CO}_2(g) \quad (8)
\]

In previous considerations based on the TGA-DSC results, this decrease in mass was considered to be caused by the decomposition of dolomite or hydrated fluxes (Ca(OH)2 or Mg(OH)2). The current results have allowed the flux species reacting in this temperature range to be correctly identified.

At temperatures above 1073 K, another smaller mass decrease is caused in these calculations by the reaction of hematite with zinc oxide to form zinc ferrite, with the reaction given in Eq. (9).

\[
\text{Fe}_2\text{O}_3(s) + \text{ZnO}(s) = \text{ZnFe}_2\text{O}_4(s) \quad (9)
\]
While the reactions in Eqs. (9)–(11) do not lead to a mass loss, in Eqs. (2)–(7), zinc ferrite has been treated as magnetite. In effect, this means that the reaction in Eqs. (9)–(11) is treated as though the reaction given in Eq. (9) was occurring, leading to an apparent mass loss.

\[
3 \cdot \text{Fe}_2\text{O}_3(s) = 2 \cdot \text{Fe}_3\text{O}_4(s) + \frac{3}{2} \text{O}_2(g) \tag{12}
\]

Although it coincides with a slight decrease in mass in the TGA measurements, this apparent mass loss is an artefact of the simplifications made in the calculation. Under the oxidising conditions used it is unlikely that the decrease in mass in the TGA curves is caused by a reduction of hematite to magnetite (Eq. (12)). At this temperature range, 1 073 to 1 273 K, thermal decomposition of hematite to magnetite would also be unlikely. While zinc is volatile at these temperatures, any zinc in the sample is likely to have oxidised to ZnO, making this an unlikely cause of weight loss. Further flux decomposition, as proposed previously, is a more likely explanation for the any decrease in mass at these temperatures.\textsuperscript{6,7} While there is no endothermic peak shown in Fig. 5, any weight change above 1 073 K is very small and spread over a large temperature range, an endothermic peak may not be expected.

The in situ phase analysis also appears broadly consistent with energy changes and transition temperatures observed in the DSC measurements (see Figs. 5 and 6).
exothermic peak beginning at temperatures just below 473 K correlates very well with the decrease in wüstite and metallic iron. It may also be possible to distinguish between the larger, broader exothermic peak (~453 < T < ~773 K) and the sharper, higher peak (~633 < T < ~873 K). In Fig. 6, the DSC curve is compared against the rate of change of the iron bearing phases. The decrease in the wüstite content appears to begin at a lower temperature range, while the decrease in the metallic iron content appears to occur at higher temperatures. The increase in hematite was noted to appear to correlate to the onset of the oxidation of metallic iron.

The large exotherm may be resolved into a large, broad, exothermic peak related to the oxidation of wüstite, overlapped with a sharper, higher peak related to the oxidation of metallic iron.

The finding that wüstite reacted at lower temperatures than metallic iron is surprising. The high reactivity of the BOS filter cake has been attributed to its very fine particle size.\(^6,7\) However, both wüstite and metallic iron have the fine particle size of significantly less than 1 μm, which would be expected to lead to a high reactivity for both. Although the metallic iron has such a fine particle size, it may be possible for it to be passivated by a dense oxide (magnetite) layer. A dense oxide layer may hinder mass transfer of oxygen to an iron-oxide interface, and would not have to be very thick as the solid state diffusivity of oxygen at these temperatures would be low.

Wüstite is metastable at temperatures below 843 K.\(^32\) It may be possible that the metastable nature of wüstite at these temperatures leads to a higher reactivity with air than metallic iron. However, proposing a mechanism for the oxidation of wüstite to magnetite (or the magnetite-zinc ferrite spinel solution), or why it the wüstite is more reactive than the metallic iron, is not possible using the current data. Extensive further characterisation of unreacted material to determine if there is a variation in size distribution between metallic iron and wüstite, and characterisation of samples partially reacted at temperatures below 633 K and quenched may provide further information about both the metallic iron and wüstite particles. This characterisation will not be simple due to the fine particulate nature of the sample, and may have to be carried out at very high resolution, or with advanced techniques. However, such characterisation may provide a way to clarify why wüstite reacts before metallic iron.

At higher temperatures, the decrease in the CaCO\(_3\) (and corresponding increase in CaO) correlates well with the small endotherm in the DSC curve between ~873 K and ~1 023 K. The further small exotherm at temperatures above 1 023 K does not seem to correlate particularly well with any change in content of any of the phases. However, it is possible that the different processes overlap one another, for instance the exothermic process may overlap the endothermic CaCO\(_3\) decomposition. If this is the case, the exotherm may be related to the increase in the magnetite-zinc ferrite spinel solution which can be seen to begin at temperatures ~973 K.

### 3.4. Identification of Reactions during Oxidation of BOS Filter Cake

In a previous study using mass change and DSC experiments, the oxidation of the BOS filter cake had a characteristic behaviour that appeared to be mostly independent of sample size, reaction system or heating rate.\(^6,7\) This characteristic nature of the oxidation of BOS filter cake is also evident in the results from the \textit{in situ} phase analysis, as shown in the comparison of the mass change in Fig. 4. While this characteristic behaviour of the BOS filter cake during heating in air was a complex, multi-step process it has been divided into 5 steps.\(^6,7\) Using both the existing mass change and DSC data, and relating it to the new \textit{in situ} phase analysis, the steps may be confirmed or updated.

Step 1. Drying of the sample at T < ~393 K.
Step 2a. Oxidation of wüstite in the BOS filter cake at ~453 < T < ~773 K. It is possible that the product of wüstite oxidation in this step is the magnetite-zinc ferrite solution phase.

\[
\text{FeO}_6(s) + \frac{1}{2} \text{O}_2(g) = \frac{1}{2} \text{Fe}_2\text{O}_4(s) \quad \text{(13)}
\]

Step 2b. Oxidation of metallic iron in the BOS filter cake at ~633 < T < ~873 K. It is possible that metallic iron is oxidised through to hematite in this step.

\[
\text{Fe}_6(s) + \frac{1}{4} \text{O}_2(g) = \frac{1}{2} \text{Fe}_2\text{O}_4(s) \quad \text{(14)}
\]

Step 3. Calcination of the fluxes, including CaCO\(_3\), at temperatures between ~873 K and ~1 023 K.

\[
\text{CaCO}_3(s) = \text{CaO}_6(s) + \text{CO}_2(g) \quad \text{(8)}
\]

Step 4. Very small weight gain at ~1 003–1 043 K < T < ~1 173 K, likely caused by further oxidation of the large iron/iron oxide particles. Also in this temperature range, hematite reacts with ZnO, CaO or MgO, resulting in more of the magnetite-zinc ferrite-(calcium ferrite-magnesio ferrite) spinel solution phase.

\[
\text{Fe}_2\text{O}_3(s) + \text{ZnO}_6(s) = \text{ZnFe}_2\text{O}_4(s) \quad \text{(9)}
\]

\[
\text{Fe}_2\text{O}_3(s) + \text{CaO}_6(s) = \text{CaFe}_2\text{O}_4(s) \quad \text{(10)}
\]

\[
\text{Fe}_2\text{O}_3(s) + \text{MgO}_6(s) = \text{MgFe}_2\text{O}_4(s) \quad \text{(11)}
\]

Step 5. Very small decrease in sample weight at T > 1 173 K, possibly related to further calcination of CaCO\(_3\).

Reactions 8 to 11 and 13 to 14 are a simplified reaction scheme, only representing the major phases identified by the \textit{in situ} high temperature XRD, and ignoring solution phases.

Steps 4 and 5 were not readily observed in the \textit{in situ} phase analysis results. There are three likely reasons for this. Variations in these smaller changes are likely a result of the variability of the BOS filter cake, and the small sample size used for the \textit{in situ} phase analysis. It is also possible that these small changes are likely related to relatively few particles within the sample, and may be below the resolution of the \textit{in situ} XRD phase analysis. A final possible reason for the difference in behaviour at high temperatures may be due to the differences in experimental set-up. Steps 4 and 5 were most visible in large scale TGA experiments (~20
g sample size). It is known that temperature gradients and/or mass transfer through the sample played a role in the kinetics of these experiments.\(^6,7\) These gradients are almost certainly not present within the thin layer of sample used for the \textit{in situ} high temperature XRD experiments, so that slight differences in the behaviour observed at high temperatures may be expected.

A further limitation to the current analysis may be caused by changes in the non-bulk crystalline content of the sample. As discussed previously, it is likely that at least a proportion of the non-bulk crystalline material may become more crystalline during heating or by reaction with the gas phase or with other solid phases. The non-bulk crystalline content was assessed using an internal standard in the \textit{ex situ} measurements. To prevent any reactions between the sample and standard at elevated temperature, no internal standard was used in the \textit{in situ} measurements, so any changes in its proportion cannot be estimated. It would not be possible to distinguish any increase in crystallinity of the sample from the current data.

Despite these limitations, being able to resolve Step 2 into two separate reactions, Step 2a: oxidation of wüstite, and Step 2b: oxidation of metallic iron, as well as the finding that Step 3 involves the calcination of all fluxes represents an advancement in the understanding of the self-sintering of BOS filter cake. As the temperature ranges for Step 2a and Step 2b overlap over a broad range, it was previously not possible to resolve the two reactions using the TGA or DSC data. The finding that wüstite is the first component of the BOS filter cake to react may lead to a better understanding of the initiation of self-sintering. This in turn will lead to enhancements to the self-sintering process, leading to a greater self-sintered proportion of the BOS filter cake in the stockpiles, and consequently more material that is available for recycling back to the BOS.

4. Conclusions

Self-sintering of BOS filter cake has been studied through \textit{in situ} phase analysis during oxidation to 1273 K. The specific aim of this study was to use the \textit{in situ} analyses to better identify specific reactions that occur at each of the steps in the oxidation of BOS filter cake.

The change in the proportion of the phases translates well to the characteristic nature of the BOS filter cake oxidation observed previously. However, the \textit{in situ} phase analyses have given further insights into what reactions/processes are occurring at each temperature range.

Wüstite was found to be the first component of the BOS filter cake to react, oxidising (at least initially) to a magnetite-zinc ferrite spinel solid solution, beginning at very low temperatures (slightly higher than 373 K) and finishing at approximately 773 K.

Metallic iron reacted at higher temperatures than the wüstite, beginning at ~633 K and finishing at ~873 K.

At temperatures above 873 K, calcination of limestone and other fluxes took place, leading to a mass loss. At higher temperatures, starting at approximately 1 073 K, hematite reacts with ZnO, CaO and/or MgO to form a spinel solution phase.

Resolving step 2 (the main exothermic reaction step in the self-sintering process) into two separate oxidation reactions of wüstite and metallic iron is an improvement in the understanding of the self-sintering of BOS filter cake, and possibly of the initiation of self-sintering. Such improvements in the understanding of the self-sintering process should lead to an enhancement in self-sintering and to more material that can be recycled back to the BOS.

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REFERENCES

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