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Characterisation of Steelplant By-Products to Realise the Value of Fe and Zn

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Abstract

Recycling of steel plant by-products is a critical area that needs careful assessment and development if the integrated steel plant is to remain environmentally and economically sustainable into the future. A research program is being embarked upon in the Australian Steel Research Hub with aims to realise the value of the by-products to the Australian Steel industry and minimise volumes being stockpiled. As a first step, key by-product streams (such as blast furnace, BOS and sinter dusts) are being evaluated and characterised so that their potential uses in-plant or elsewhere can be assessed/evaluated. These streams contain components including iron and zinc units which have value on plant and elsewhere. Realising the value in these streams by recycling or other processing will help to minimise emissions and reduce costs by replacement of raw materials and reducing the amount going to stockpile. In this paper, microscopy (SEM and EDS analysis), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of a by-product material are presented and discussed with a view of understanding the behaviour of the material in use and on plant and its limits for further processing.

Keywords

realise, steelplant, value, by-products, fe, zn, characterisation

Disciplines

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CHARACTERISATION OF STEELPLANT BY-PRODUCTS TO REALISE THE VALUE OF FE AND ZN

Abstract

Recycling of steel plant by-products is a critical area that needs careful assessment and development if the integrated steel plant is to remain environmentally and economically sustainable into the future. A research program is being embarked upon in the Australian Steel Research Hub with aims to realise the value of the by-products to the Australian Steel industry and minimise volumes being stockpiled. As a first step, key by-product streams (such as blast furnace, BOS and sinter dusts) are being evaluated and characterised so that their potential uses in-plant or elsewhere can be assessed/evaluated. These streams contain components including iron and zinc units which have value on plant and elsewhere. Realising the value in these streams by recycling or other processing will help to minimise emissions and reduce costs by replacement of raw materials and reducing the amount going to stockpile. In this paper, microscopy (SEM and EDS analysis), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of a by-product material are presented and discussed with a view of understanding the behaviour of the material in use and on plant and its limits for further processing.

Keywords

By-products, BOS dust, recycling, sustainability

1. Introduction

The drive for improved environmental and economic sustainability of the steel industry has resulted in a strong research focus to enable on-plant recycling of by-products [1,2]. In the ARC Research Hub For Australian Steel Manufacturing, a research program has been developed with the principal aims to realise the value in by-products and to minimise the amounts of potential by-products going to stockpiles.

In the basic oxygen steelmaking (BOS) process, oxygen is blown at supersonic velocities. As this gas impacts on the liquid steel and slag it generates significant quantities of dust which is made up of droplets of liquid steel, slag and fine particulates from the added fluxes [1-4]. As steelmaking temperatures are often greater than 1600°C, elements such as zinc or lead can volatilise from the bath, enter the gas stream and condense as or on the dust as the temperature drops. Subsequent recycling of BOS dust can therefore result in a recirculating load of zinc, which may lead to process issues. Knowledge of the form in which the iron and zinc are found within the BOS dust is crucial in understanding where to best recycle the dust or how best to process it for recycling [2,3,5]. This information also has application in understanding and developing novel ways to separate the zinc from the dust [5-9].

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At BlueScope, the BOS dust is separated from the off gas by a wet scrubbing process and the dust, in the form of dewatered filter cake, is stored in stockpiles prior to recycling. Experience has shown that the BOS filter cake stockpiles have a tendency for self-sintering. This self-sintering is likely a result of exothermic oxidation reactions. The sintered material is preferred for recycling as it has better physical properties (higher strength and larger particle size) compared to the original filter cake, which allow it to be directly recycled to the BOS as a coolant, replacing iron ore. Undersize material is currently recycled to the sinter plant at a low rate, limited by the blast furnace zinc load limit for both process stability and occupational health and safety. Enhancing the in situ sintering/oxidation of the BOS dust will allow more material to be recycled to the BOS (further decreasing the need for lump ore) and decrease the proportion being fed to the sinter plant. This should lead to a decrease in production costs while also improving the environmental performance of the plant.

Steel plant by-products are known to have high variability [1]. In the case of BOS dust, the composition and particle size can change from heat to heat, depending on the target and hot metal (and scrap) composition, as well as within a single heat, depending on the blowing conditions and any additions made (fluxes and coolants). This makes these materials difficult to use, for both characterisation at a laboratory scale and for recycling at the steel plant.

Better understanding of the oxidation and sintering behaviour of the BOS filter cake will allow optimisation of this process and improved recyclability via the BOS coolant route. To achieve this, the BOS filter cake from BlueScope's Port Kembla steelworks has been characterised by several techniques, including scanning electron microscopy (SEM), X-ray diffraction (XRD), thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC). Freshly produced BOS filter cake was characterised and compared to samples after processing in the TGA. In addition to characterising the phases present, morphology and oxidation behaviour of the BOS filter cake, a focus was also placed on the representation and repeatability of the characterisation.

2. Experimental

BOS filter cake samples in the form of dense "biscuits" (Fig. 1a), composed of dewatered BOS dust slurry were obtained prior to stockpiling and contained 13.2 mass% moisture as sampled. The BOS dust was collected using a wet scrubber, and the resulting slurry thickened and then separated using a tube press filter. The dry composition of the BOS dust is given in Table 1.

Table 1 – Composition of BOS dust, as measured by EDS (in mass%).

Total Fe	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	P	Zn	Pb
56.7	2.1	< 1	4.2	1.5	1.1	< 1	13.6	< 1

The BOS filter cake was characterised by a number of techniques. For microscopy, samples were prepared by mounting in epoxy resin, followed by grinding and polishing by hand to a 1 µm finish. These samples were examined using back-scattered electrons in an SEM, equipped with an energy dispersive spectroscopy (EDS) detector for elemental analysis. Samples for XRD were ground in a mortar and pestle. The diffraction patterns were collected using Cu-K α radiation, with a Ni filter at 35 kV and 1 kW of power.

A large scale TGA system, as shown in Fig. 1b, was used to measure weight change during reaction of the BOS filter cake with air while heating to 1000°C. A single BOS filter cake "biscuit" with a nominal mass of 20 g was placed in an alumina crucible hung from the balance. The crucible had twelve 8 mm holes circumferentially around the bottom end of the crucible for gas access. In order to separate the drying and oxidation processes, the sample

was held at 100°C under Ar flowing at 1 L/min for 70 minutes. The system was then heated at 10°C/min to 1000°C under air flowing at 1 L/min. The system was held at 1000°C in the flowing air for a further 30 minutes before cooling under Ar. The gases used were high purity (99.99%) and further purified by passing through drierite and ascarite prior to entering the furnace. The Ar was further cleaned by passing it through Cu turnings at 300°C.

The weight of the sample was logged during heating and the calculated fractional weight change (FWC) used to characterise the extent of oxidation according to Eq. (1),

$$\text{FWC} = (W - W_0) / W_0 \quad (1)$$

where W_0 and W are the initial mass and the mass of a sample at time t , respectively in grams. Reacted samples of BOS filter cake were characterised by XRD and SEM-EDS.

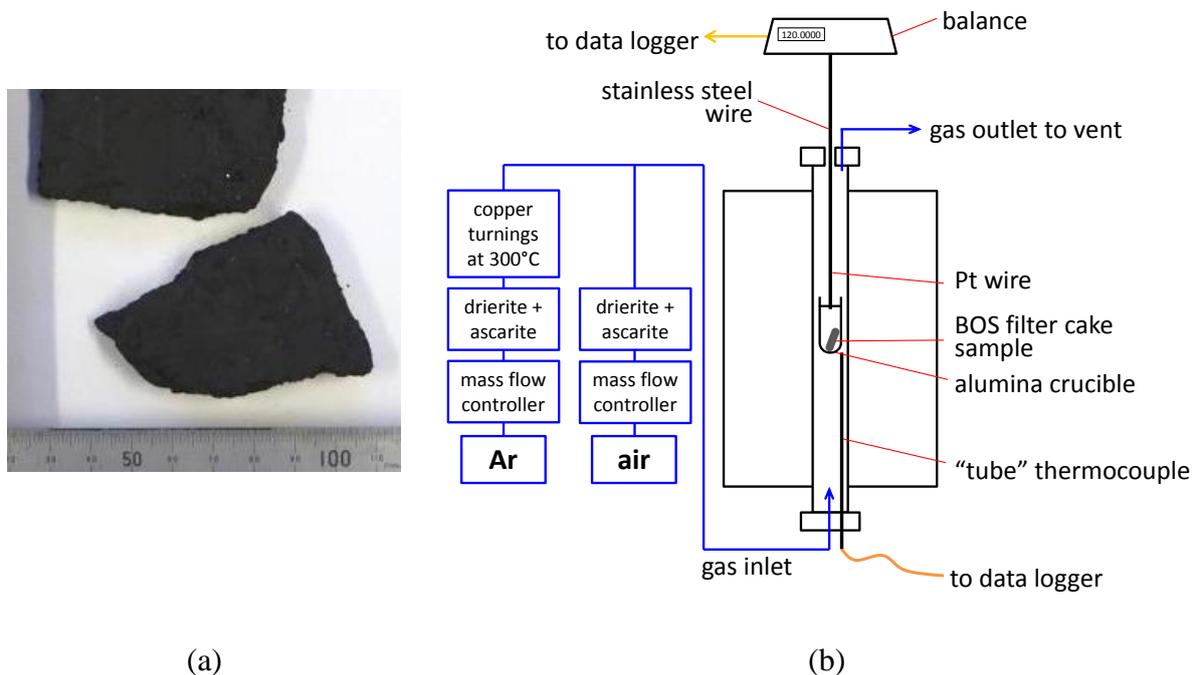


Fig. 1 – (a) BOS filter cake “biscuit”; (b) Schematic of large scale TGA set-up.

The thermal behaviour of the BOS dust was also characterised using a Mettler Toledo Star^e TGA-DSC1. A BOS filter cake “biscuit” was crushed, and a nominal 100 mg sample was placed in an alumina crucible. This was reacted with flowing air during heating from room temperature to 1000°C at 10°C/min. The weight and temperature of the sample, and energy flow to the sample were logged at a 1 s frequency.

For both the large scale TGA and the TGA-DSC, samples were characterised at least three times in order to help evaluate repeatability and sampling representation.

3. Results

Phase analysis by XRD (Fig. 2) shows that the fresh (unreacted) BOS filter cake predominantly contains metallic iron (Fe) and wüstite (FeO). Other components include smaller amounts of zinc ferrite (ZnFe₂O₄) or magnetite (Fe₃O₄), zincite (ZnO), fluxes (calcite, CaCO₃) and some graphite. It can be difficult to distinguish between magnetite and zinc

ferrite by XRD as they have the same crystal structure and similar lattice parameters [10], and can form a mutual solid solution.

Micrographs of the fresh BOS filter cake are shown in Fig. 3, with elemental mapping by EDS shown in Fig. 4. The sample contained a matrix of fine metallic iron and iron oxides holding together larger particles of metallic iron, iron oxides, flux materials and some remnant slag droplets. The matrix of metallic iron and iron oxides was made up of very fine particles, typically 1 μm or smaller (Fig. 3(b)). The larger particles were unevenly dispersed through the matrix. Remnant lime/limestone particles were typically smaller (5-10 μm) than the dolomite particles. Zinc was generally evenly distributed through the matrix material. This well distributed zinc likely corresponds with ZnFe₂O₄. Some distinctly zinc rich particles, of a size approximately 1-2 μm can be seen in the Zn map in Fig. 4. These zinc-rich particles likely correspond to the small amount of ZnO identified in the XRD patterns.

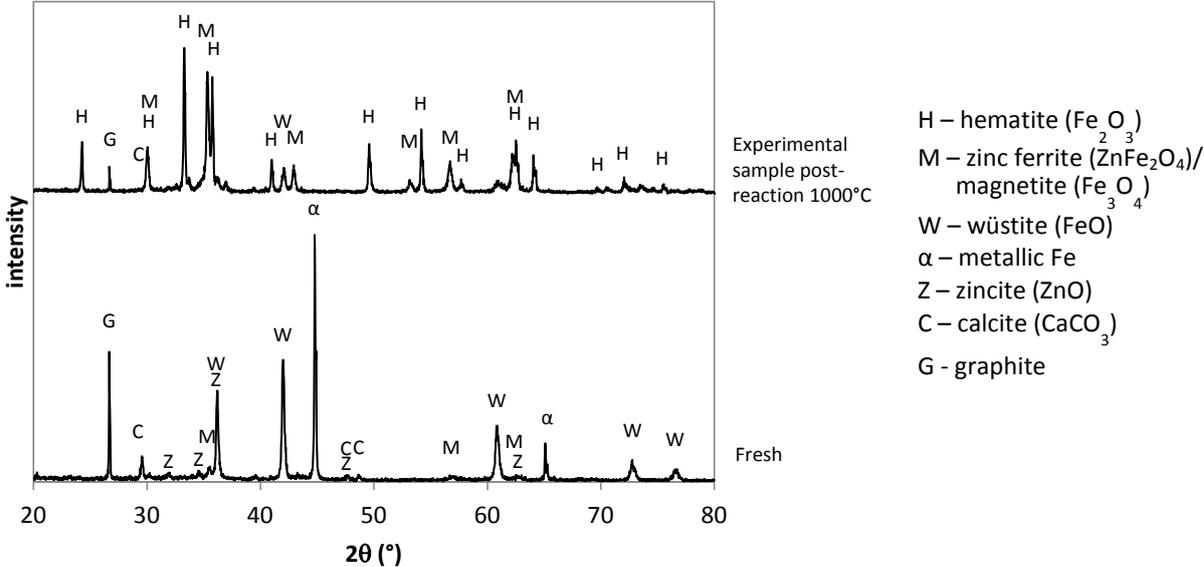


Fig. 2 – XRD patterns for BOS filter cake before and after oxidation during heating to 1000°C in air. The key for the peak labels is given on the right.

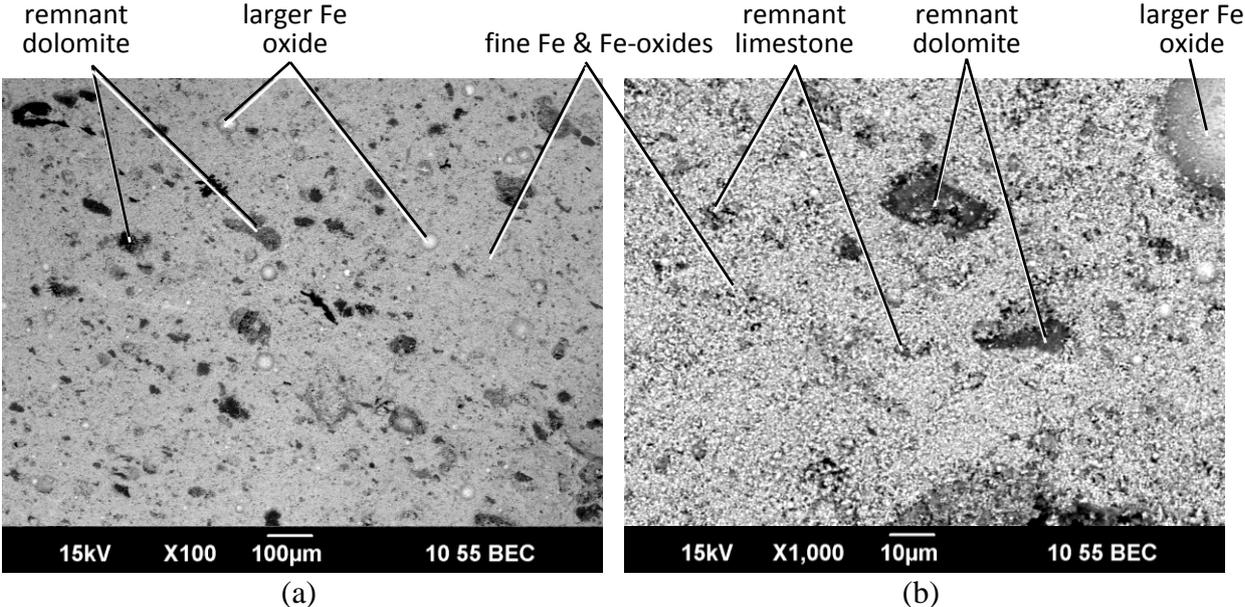


Fig. 3 – Back scattered electron micrographs of fresh BOS filter cake. (a) low magnification; and (b) high magnification.

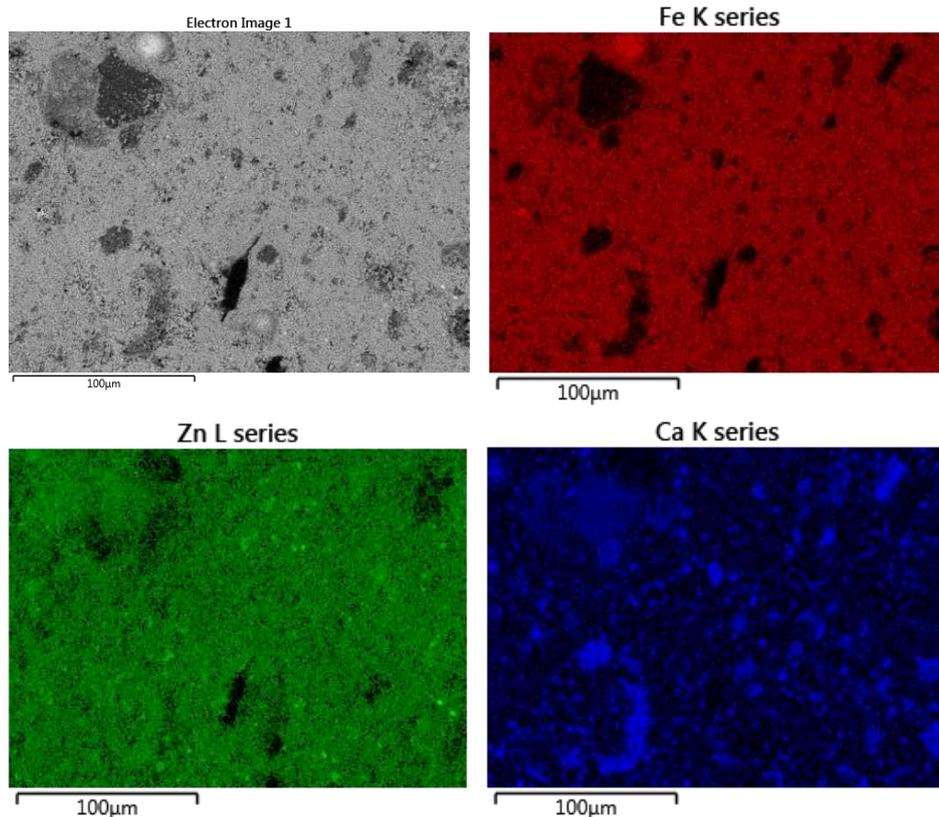


Fig. 4 – Elemental maps of Fe, Zn, and Ca for a fresh BOS dust measured using SEM-EDS.

Typical FWC curves for the reaction of the BOS filter cake with air during heating to 1000°C are shown in Fig. 5, for both the large scale TGA (Fig. 5(a)) and the smaller scale TGA-DSC (Fig. 5(b)). These curves show similar weight change characteristics, indicating similar oxidation behaviour of the BOS filter cake in both techniques. This is despite the large difference in sample size and consequent thermal response of the two techniques.

To help better determine the temperature ranges at which the different processes occurred, the rate of the weight change was plotted against temperature. These curves were also used to help evaluate the repeatability of the test and representation of the samples. The rate against temperature plots for four repeats in the large scale TGA are given in Fig. 6. It can be seen that the oxidation of the BOS filter cake during heating follows a very characteristic behaviour. There are two sharp increases in the rate at 120-130°C and 730-770°C. In between these ranges, the rate of weight change decreases with temperature, crossing from weight gain to weight loss at 600-620°C. These results demonstrate good repeatability between the larger ~20 g samples used in the large scale TGA. Similar repeatability was found for the smaller (~100 mg) samples used in the TGA-DSC.

From the behaviour seen in Figs. 5 and 6, this characteristic behaviour of the BOS filter cake during heating can be separated into several distinct segments:

1. Drying of the sample at temperatures below ~110°C. This is represented by the large weight decrease.
2. Oxidation of the sample, beginning at ~120-130°C and complete at ~600°C, represented by the increase in the sample weight.
3. A slight decrease in sample weight between ~600-620°C and ~750°C.
4. A slight further weight gain caused by oxidation at temperatures between ~730-770°C and ~900°C.

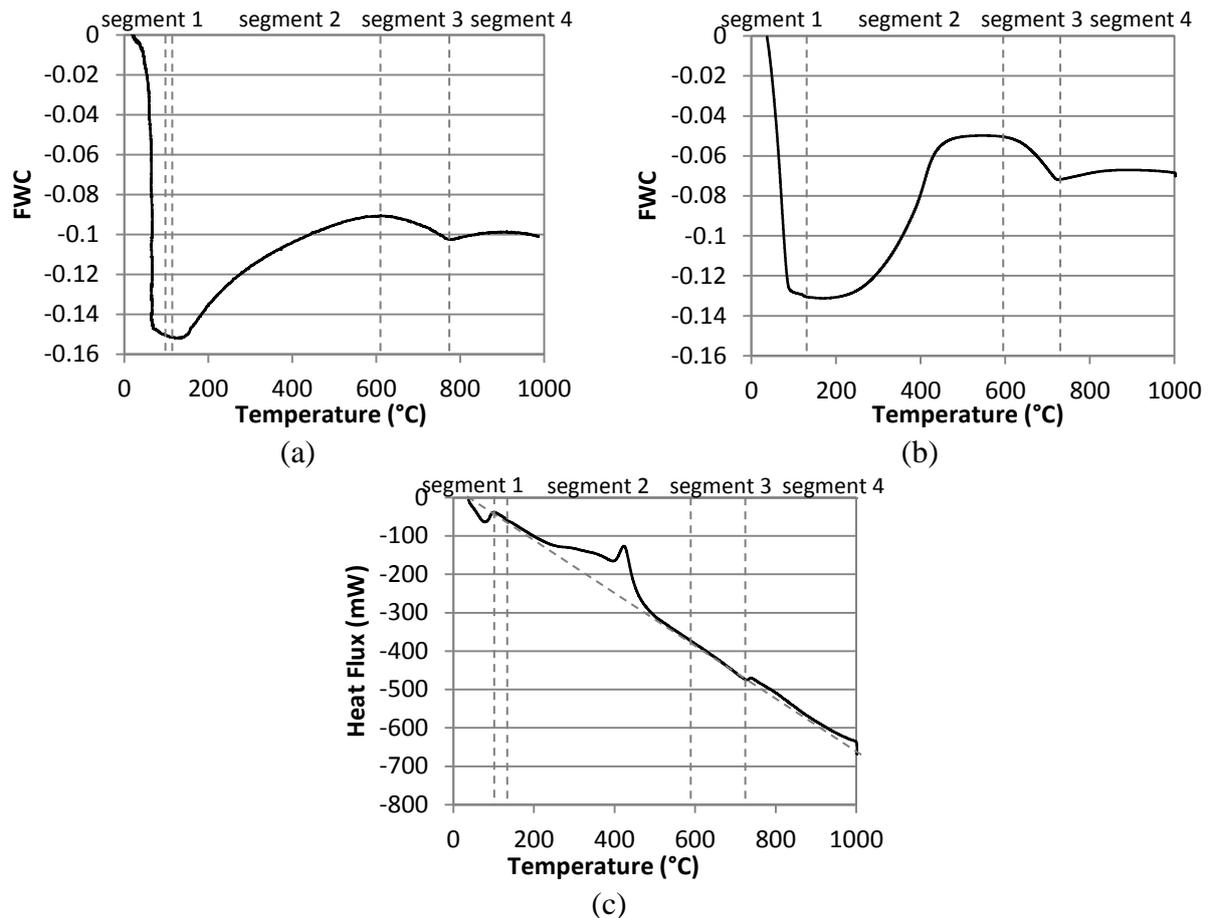


Fig. 5 – FWC curves for BOS filter cake oxidation in (a) the large scale TGA (20 g samples); (b) the TGA-DSC (100 mg samples); and (c) heat flow curve from the TGA-DSC.

The thermal behaviour of the BOS filter cake during oxidation was characterised by DSC with a typical heat flux curve given in Fig. 5(c). Endothermic or exothermic behaviour can be seen as occurring below or above the fitted baseline, respectively. The thermal behaviour of the sample matches well with the events seen in the weight change curves. Endothermic drying of the sample occurs at low temperatures (<100°C) (segment 1). A large exothermic peak between ~150 and ~500°C corresponds to the oxidation of the BOS filter cake (segment 2). A much smaller exotherm can be seen above 710°C, which appears to correspond to segment 4 above.

After oxidation in the large scale TGA, the samples were characterised by XRD and SEM-EDS. A typical XRD pattern of a sample after oxidation was given in Fig. 2. It can be seen that during reaction the sample was oxidised from predominantly metallic iron and wüstite to hematite and magnetite-zinc ferrite. As the sample appears to be predominantly hematite and zinc ferrite (both containing Fe^{3+}) the sample has been nearly fully oxidised during heating to 1000°C in air.

The micrographs of the samples after reaction are shown in Fig. 7. The microstructures have changed significantly from the fresh samples. At low magnification, densification of the structure can be seen, along with some interaction between matrix and the remnant flux and slag particles. Most obvious is the formation of a dense layer towards, but not at, the outer surface of the sample. EDS analysis showed that this dense layer was Zn rich. At higher magnifications, the matrix has sintered from discrete particles into a spongy structure reminiscent of porous refractories. There is little evidence remaining of the flux particles. Magnesium oxides were found in solution in the zinc ferrite. Calcium oxides were not found in the zinc ferrite phase, but rather as separate calcium ferrites.

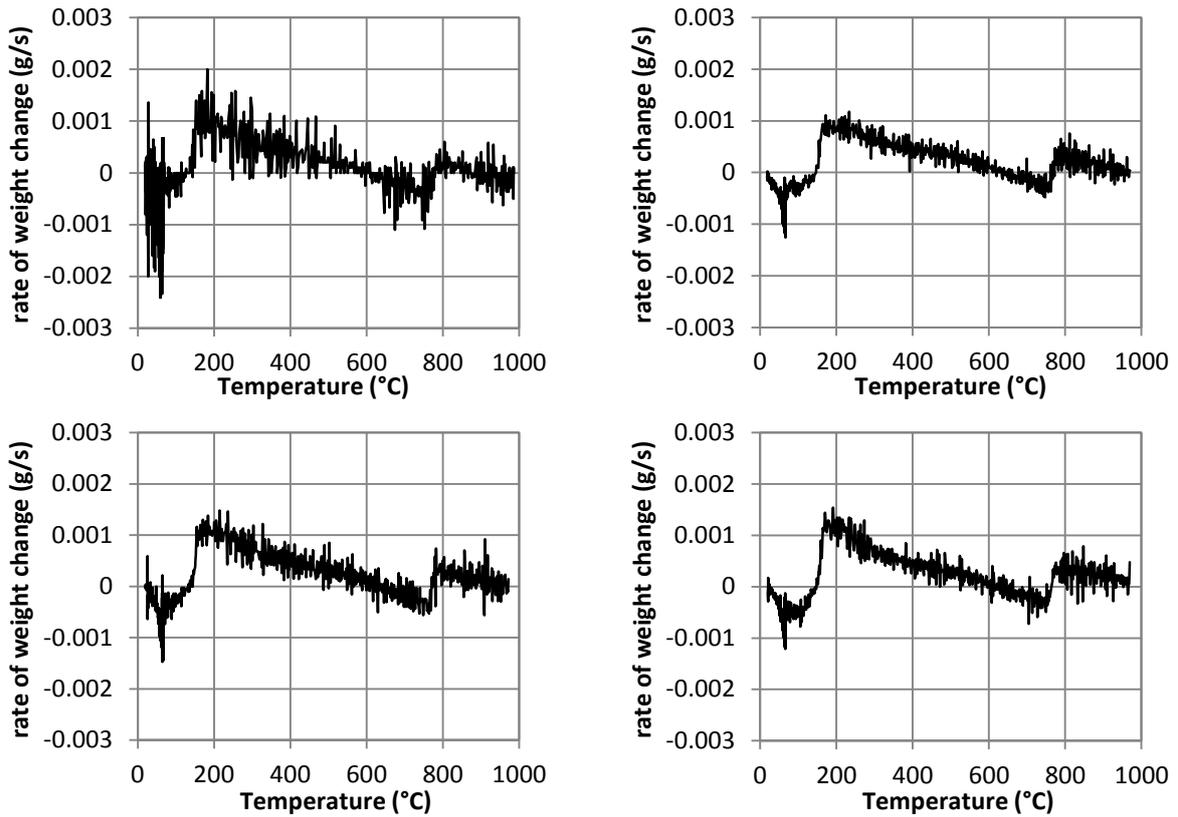


Fig. 6 – Rate of weight change plotted against temperature for BOS filter cake during oxidation during heating to 1000°C for four repeats in the large scale TGA.

4. Discussion

The phases present in the reacted BOS filter cake samples clearly show that the final sample is more oxidised than the initial material (Fig. 2), as would be expected for a mixture of metallic iron and wüstite heated in air. This oxidation of the sample correlates with the increase in weight seen in the TGA curves and the exothermic peak seen in the DSC curve, indicating that the oxidation of the BOS dust appears to begin at low temperatures (~150°C). The micrographs show that the majority of the fresh BOS filter cake constituents are tightly packed, very fine particles of metallic iron and wüstite. Sub-micron particles of metallic iron would be expected to be highly reactive and susceptible to reaction at low temperatures. The processes occurring at higher temperatures (segments 3 and 4) have not yet been analysed, and will be the subject of future study.

Examining what phases are present in the BOS filter cake before and after reaction, several reactions can be proposed (eq. 2-4) to represent the overall changes occurring during the heating of the BOS filter cake in air. Using FactSage [11], each of these reactions was found to be exothermic between 100-1000°C, matching what was seen in the DSC curves where only exothermic peaks were found. While reactions (2) to (4) represent the overall changes occurring, they likely do not represent the mechanism of oxidation of the BOS filter cake.



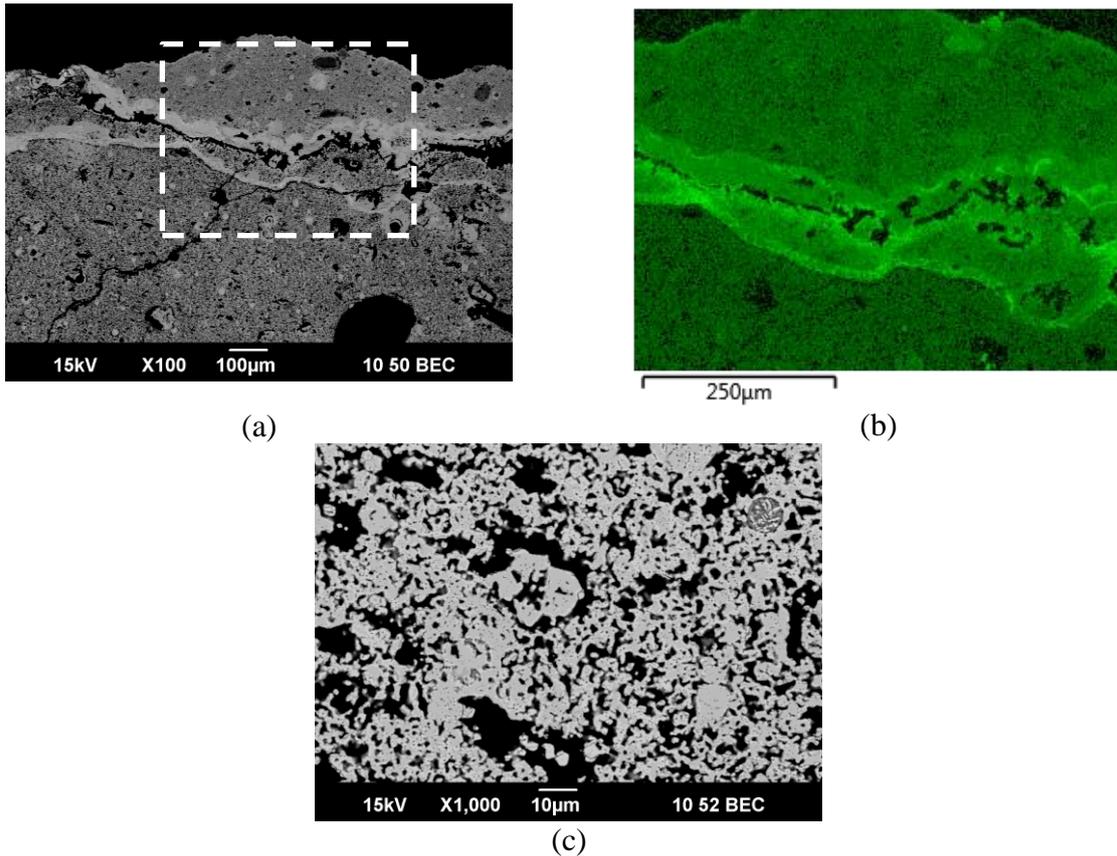


Fig. 7 – Back-scattered electron SEM micrographs of BOS filter cake after reaction in air during heating to 1000°C. (a) Low magnification image; (b) EDS map for Zn for the area shown on the micrograph in (a); and (c) higher magnification image.

FactSage [11] was used to predict the phases present at equilibrium at 100 to 1000°C in air for a simplified Fe-Zn-O system with a composition corresponding to the unreacted BOS filter cake. At all temperatures, hematite (Fe_2O_3) and a spinel with a composition close to that for stoichiometric zinc ferrite (ZnFe_2O_4) were the only phases predicted. The results of the thermodynamic analysis show, as would be expected, that oxidation of the BOS filter cake is possible at low temperatures. The thermodynamic analysis predicts that all iron should be Fe^{3+} . The phases identified by XRD (Fig. 2) largely agree with this. However, a small amount of wüstite was identified in the reacted samples, while it is also possible that some magnetite was also present (in solution with zinc ferrite). The presence of these Fe^{2+} containing phases is an indication that the sample was not at equilibrium and the oxidation of the BOS filter cake being kinetically limited. This is not surprising considering the short reaction times, and the large, dense samples used in the large scale TGA.

Zinc showed some mobility through the BOS dust sample, as seen by the formation of dense Zn-rich layers in Fig. 7. All the zinc within the oxidised sample appeared to be in the form of zinc ferrite, with any zincite (ZnO) identified in the initial sample no longer present. Similar mobility of zinc was found by Wang et al. [12] who proposed a reduction-oxidation-nucleation based mechanism for this mobility.

While the weight change results from the two different scale TGA systems showed similar features, there were some differences (Fig. 5). These differences could be caused by two main factors. The thermal response of the two furnaces and the two different sample sizes cannot be expected to be the same. In the large scale TGA with the 20 g sample, it is also quite possible that temperature gradients are formed across the sample during heating. It is

also probable that the mass transport of oxygen through the sample plays a larger role in determining the kinetics in the dense “biscuits” used in the large scale TGA than in the crushed samples used in the small scale TGA.

These represent some of the disadvantages of the large scale TGA. However, the 20 g sample size has the advantage of likely being more representative than the 100 mg samples used in the TGA-DSC. Fig. 3(a) shows just how variable the BOS dust samples can be, even within a small cross-section of a single “biscuit”. While there will always be a question of whether the samples are representative of the bulk BOS filter cake stockpile, the 20 g samples, being two orders of magnitude larger than the 100 mg samples, will likely better represent the BOS filter cake.

With steel plant by-product materials like the BOS filter cake, there are significant concerns about sample representation and variability [1]. However, despite these concerns, it has been found that the results of the small scale TGA-DSC and especially the large scale TGA were consistent and repeatable (Fig. 6). This gives confidence that the characteristic oxidation behaviour of the samples in the TGA tests reasonably represents the behaviour of the BOS filter cake during heating in air.

The behaviour of the BOS filter cake in the TGA tests can be used to help better understand the self-sintering behaviour of the BOS filter cake in the on-plant stockpiles. The onset of the reaction of BOS filter cake with air occurs once moisture has been removed from the sample. From Fig. 6, it can be seen that the onset of weight gain (oxidation) occurs at temperatures as low as 120-130°C. This seemingly indicates that reaction of the BOS filter cake with air occurs in these experiments only after the moisture is removed. The BOS filter cake is stockpiled hot, at 50-70°C, which may provide enough heat to assist in locally drying the BOS filter cake. As the oxidation of wüstite and especially metallic iron in air are exothermic, any reaction occurring within the stockpile will serve to increase the temperature, further driving oxidation and increases in temperature.

Having identified the characteristic weight changes that occur during oxidation of the BOS filter cake this work represents an incomplete analysis of the processes occurring. Fully understanding these processes, and what initiates reaction below 100°C and elevates the temperature of the BOS filter cake to the onset temperature for reaction with air at 120-130°C will be the topic for further studies.

Hence, likely factors that may possibly be controlled to promote self-sintering (and recycling) include the temperature of the BOS filter cake during stockpiling, the moisture level of the BOS dust and possibly the amount of metallic iron in the dust. While it cannot be controlled, the fine particulate nature of the metallic iron and wüstite in the BOS filter cake gives it the high reactivity required for the low temperature oxidation. Increasing the initial temperature, and decreasing the moisture content may promote the self-sintering of the BOS filter cake in the stockpiles, allowing more of the BOS dust by-product to be recycled back to the BOS as coolant.

5. Conclusions

BOS filter cake from BlueScope’s Port Kembla steelworks has been characterised in terms of its phases and morphology, as well as its behaviour during heating in air.

The BOS filter cake predominately consisted of very fine (< 1 µm) particles of metallic iron and wüstite. The fine particulate nature of the BOS filter cake leads to it being highly reactive, even at low temperatures. After reaction with air at 1000°C, the BOS filter cake had predominantly transformed to hematite and zinc ferrite. The fine particles in the unreacted filter cake had transformed to a porous, spongy morphology.

Characteristic behaviour of the BOS filter cake was identified as being a complex, multi-step process, involving sequential drying and oxidation of the metallic iron and wüstite, as well as the formation of zinc ferrite and reaction with fluxes. The onset of oxidation occurred after the moisture was removed from the BOS filter cake, at temperatures as low as 120-130°C.

Factors that were presumed as being important, based on the results of this study, for the promotion of BOS self-sintering in stockpiles were the elevated temperature at which the BOS filter cake is stockpiled, the fine particulate nature of the BOS dust and the level of moisture within the BOS filter cake.

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