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Huibin Li

University of Wollongong, huibin@uow.edu.au

David J. Pinson

Paul Zulli

University of Wollongong, paulz@uow.edu.au

Liming Lu

Raymond Longbottom

University of Wollongong, rayl@uow.edu.au

See next page for additional authors

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Authors

Huibin Li, David J. Pinson, Paul Zulli, Liming Lu, Raymond Longbottom, Sheng J. Chew, Brian J. Monaghan, and Guangqing Zhang

Zinc Removal from Basic Oxygen Steelmaking (BOS)

Filter Cake by Sintering

Huibin LI¹, David J. PINSON², Paul ZULLI¹, Liming LU³, Raymond J. LONGBOTTOM¹, Sheng J. CHEW², Brian J. MONAGHAN¹, Guangqing ZHANG¹

- 1). School of Mechanical Materials Mechatronics and Biomedical Engineering, University of Wollongong, Wollongong, NSW 2500. ARC Research Hub for Australian Steel Manufacturing. Email: hl762@uowmail.edu.au
- 2). BlueScope Steel, Coke and Ironmaking Technology, Port Kembla, NSW 2505. ARC Research Hub for Australian Steel Manufacturing.
- 3). CSIRO Queensland Centre for Advanced Technologies, Brisbane, QLD 4069.

Abstract

Zinc removal from basic oxygen steelmaking filter cake was studied by tablet testing and in a millipot under different conditions. The results from tablet testing show that coke and metallic iron in filter cake play the role of reductants to remove zinc during sintering. Zinc removal increased with increasing temperature and decreasing partial pressure of oxygen. Zinc removal reached 24.6% when a tablet of filter cake without addition of coke was sintered at 1300°C in a nitrogen atmosphere. Addition of 3 to 9 wt% of coke breeze into filter cake enhanced the zinc removal to 60.6 to 91.4%, in an atmosphere with 0.5 vol% oxygen. The results from millipot sintering show that adding filter cake in the form of tablets was effective in removing zinc, especially when additional coke was added into the tableted filter cake. Zinc vapour generated at high temperature in the reducing atmosphere diffused out of the tablets and was carried with flowing gas, and then re-oxidized and deposited on the lower layer of sintering material in the bed. Positioning the filter cake in the form of tablets at the bottom of the sinter bed is therefore suggested as a possibility for zinc removal from filter cake.

KEY WORDS: tablet testing, millipot sintering, recycling, steelmaking dust

1. Introduction

Significant amounts of metallurgical by-products such as sludge, dust and filter cake are generated each day from steelmaking operations – this generation leads to significant environmental and land management issues associated with stockpiling (Mikhail and Turcotte, 1998). Basic oxygen steelmaking (BOS) dust is one of the aforementioned by-products, containing significant amounts of iron as well as varying amounts of zinc present mainly as ZnO and ZnFe₂O₄, due to utilization of galvanized scrap (Oustadakis et al., 2010; Sammut et al., 2008; Veres et al., 2011). At BlueScope, BOS dust is separated from the off gas by a wet scrubbing process and stored in stockpiles in the form of dewatered filter cake (Longbottom et al., 2019). There are two difficulties in recycling the filter cake directly back through the steelmaking processes, such as the blast furnace or sinter plant (BlueScope, 2005; Esezobor and Balogun, 2006; Ma, 2016;): the by product is too fine in particle size, and contains too much zinc for blast furnace or BOS operations. In some industrial practices, small amounts of self-sintered filter cake lumps are added in BOS furnace as a coolant and fine filter cake is added in the sintering process. These measures consume too little amount of these by-products compared with their amounts of generation due to the concerns of zinc accumulation (Doronin and Svyazhin, 2011; Lanzerstorfer et al., 2015).

A number of investigations have been undertaken to develop methods for handling the dust and reclaiming iron and zinc, including leaching and pyro-metallurgical techniques. For leaching processes, various liquid agents have been tested, including inorganic acids, organic acids and bases (ammonium or sodium hydroxide) to selectively remove zinc; some of the tests were conducted using heating, microwave treatment, stirring or high pressure to improve the kinetics of the reaction and the leaching effects. Generally, the leaching processes do not completely remove zinc from the silicates and ferrites commonly present in BOS filter cake (Cantarino et al., 2012; Goksel and Mich, 1973; Kelebek et al. 2004; Shawabkeh, 2010; Wang et al., 2019). For pyro-metallurgical processes, the rotary hearth furnace is one of the key technologies used to treat by-products streams; however, significant capital investment is required and hence, broad adoption of this technology is limited (Oda et al., 2006). There has not been an economically acceptable process developed until now.

To solve the two difficulties mentioned above, an alternative method of zinc removal from BOS filter cake is proposed. Sintering is a widely used process to agglomerate iron ore fines into sinter lumps as the major raw material for blast furnace ironmaking, which can be used for

the agglomeration of the filter cake. Based on current practice with addition of a very small amount of filter cake into iron ore sinter blend, zinc nearly all enters into sinter. This work is to explore the possibility to remove zinc during sintering process. The benefit of using the sintering process to deal with zinc bearing dust is that it can potentially be achieved without significant changes of the operation or capital investment on an existing plant.

To achieve zinc removal from sinter, zinc oxides need to be reduced into zinc vapour. Two key requirements must be met to reduce zinc oxides: a) sufficient temperature and b) a reducing atmosphere. The sintering temperature can reach 1350°C or higher, which meets the temperature requirement for common reducing agents (C, CO, Fe) and keeps the reduced zinc as vapour. However, since the oxygen partial pressure in sintering can be relatively high (between 0.5 and 21 vol-%), it is necessary to ensure a locally reducing atmosphere around zinc oxide contained in the materials so that reduced zinc vapour may escape from the sinter bed before being re-oxidised. The coke rate in sintering affects not only the sintering temperature, but also the oxygen potential in the high temperature zone and so the capacity of zinc reduction. Furthermore, the oxygen potential in the local zones of sinter bed is highly non-uniform, and briquetting the filter cake with coke breeze helps to maintain a local strong reducing atmosphere for zinc reduction. In this study, the effects of coke content in sinter blend and the use of tablets of filter cake and coke on zinc removal were investigated.

In this study, the effects of sintering temperature and oxygen partial pressure on zinc removal from the BOS filter cake were investigated using tablet sintering tests, while the zinc removal performance under commercial sinter plant conditions was simulated using millipot (a small pilot-scale sinter pot (Li et al., 2018)) sintering tests as mentioned above. The aims were to develop a better understanding of zinc removal mechanisms in the sintering process, and to identify the optimal sintering conditions for zinc removal from filter cake.

2. Experimental

2.1 Materials

BOS filter cake from BlueScope was used. Table 1 shows its chemical composition and Figure 1 presents the XRD pattern of the filter cake. Iron is present as metallic iron, wustite, magnetite and hematite, while zinc is present as zincite (ZnO) and zinc ferrite (ZnFe_2O_4). Small amounts of fluxes (CaCO_3 and MgCO_3), were also present in the sample. The measured carbon content in Table 1 is lower than calculated from the CaO and MgO contents in the sample assuming

both oxides were present as carbonates, meaning that the filter cake contained little elemental and organic carbon. The presence of solid solutions formed from FeO and ZnO and from ZnFe_2O_4 and Fe_3O_4 cannot be excluded.

Table 1. Chemical composition of filter cake, wt%

XRF							Titration				Carbon analysis
TFe	SiO ₂	Al ₂ O ₃	CaO	Mn	MgO	Zn	TFe	Metallic Fe	Fe ²⁺	Fe ³⁺	C*
62.3	1.54	0.066	4.25	0.74	1.86	6.85	61.4	12.0	44.4	5.00	1.15

Figure 1. XRD pattern of the filter cake.

The coke and sinter blend used in the millipot experiments was sourced and collected from BlueScope's sinter plant. The chemical composition of the blend is presented in Table 2. In the table, the ash minerals are also accounted in the composition.

Table 2. Chemical composition of the green feed (dry basis, coke free)

Component	Total Fe	FeO	SiO ₂	Al ₂ O ₃	CaO	MgO	TiO ₂	Zn	P	Mn
Content, wt%	47.8	1.76	5.56	1.51	8.71	1.01	0.09	0.01	0.05	0.31

The tablets for sintering experiments consist of BOS filter cake with addition of 0 - 9 wt% coke. The filter cake – coke mixture was pressed into tablets at 100 MPa. The tablet sintering was carried out using a tube furnace, with the ground mixture pressed into cylindrical tablets of 6 mm diameter and ~5 mm high, and weighing ~0.5 g. In the millipot tests, tablets of 16 mm diameter and ~10 mm high were used, weighing ~7g.

2.2 Sintering Procedures

2.2.1 Tablet Sintering in Tube Furnace

The effects of carbon content, temperature and oxygen partial pressure on the reduction of zinc oxides from filter cake were examined using tablet tests in a tube furnace with controlled atmospheres. The knowledge developed from these outcomes helps better understanding of the zinc removal mechanism and performance in the millipot sintering process and industrial sinter plants. Figure 2(a) shows the schematic diagram of the vertical tube furnace used for testing zinc removal from the filter cake tablets (Li et al., 2018). The furnace was preheated to the required temperature. A gas mixture of air and nitrogen of controlled oxygen content was used to flush the furnace tube for 15 minutes to ensure the accurate atmosphere in the furnace. A basket with a filter cake tablet was then allocated in the hot zone of the furnace. After sintering for 4 minutes, the tablet was lifted to the top of the furnace tube to allow cooling before taken out of the furnace. Sintering temperature was predetermined by calibration carried out by inserting a type R thermocouple into the furnace tube, with the thermocouple tip at the location of a sintered tablet. The sintering was conducted in the ranges of 800 - 1300°C and oxygen partial pressure 0 - 21 kPa.

Figure 2. Sintering equipment. (a) Vertical tube furnace; (b) Millipot set-up

2.2.2 Millipot Sintering

The millipot (a small-scale sinter pot as presented in Figure 2(b)), was used to simulate commercial sinter plant conditions. The sinter tube is a stainless steel column (53 mm internal diameter, 490 mm high) surrounded by 50 mm of thermal insulation material. Six ports on the side of the column allow for insertion of thermocouples to monitor the sintering temperature.

Two extra ports are available at the bottom extended section (T7 and P) for the measurement of off-gas temperature and the suction pressure applied to the sinter bed.

The sintering process was initiated using an LPG burner located at the top of the millipot. The air suction system included a water ring vacuum pump and a buffer container, used as a wind box to stabilize the system suction pressure. The wind box was half filled with water so that the flue gas generated during sintering could be cooled down and cleaned. The suction pressure was controlled using a bypass valve (Li et al., 2017). Temperature and pressure data were logged using LabVIEW.

The coke rate (CR) for the base sinter blend (green feed) was adjusted to 7.43 wt% in order to satisfy millipot sintering requirements, i.e. a higher coke rate than industrial sintering was used to compensate for higher heat losses from the furnace wall (Li et al., 2017). This base blend was used to load the millipot tube, in the sections where no filter cake was present. The filter cake was mixed with green feed in the following two ways: (1) green feed and filter cake in a 1:1 ratio, with extra coke added to obtain mixtures with a coke rate set at 5.43, 7.43 and 9.43 wt% respectively (dry and total solid weight basis); the mixture was then placed at specific positions along the millipot tube; (2) filter cake-coke tablets were placed in the middle position of the millipot tube. The tablets were prepared from 115.7 g filter cake and mixed with coke breeze (3, 7 and 11 wt%, dry and total solid basis). The tablets were then loaded into the millipot with a further 7.43 wt% of coke breeze mixed to maintain the coke rate with the other parts.

The operating parameters of the millipot were: ignition at 1200 °C for 90 s, with suction pressure 5.3 kPa; after ignition, suction pressure was adjusted to 10.7 kPa. After sintering, sintered columns were carefully removed from the millipot tube and sampled by sectioning from centre and edges.

2.3 Sample Characterization

Bulk chemical composition of the filter cake sample and the zinc content in the sintered samples were analysed by X-ray fluorescence spectroscopy (XRF). To avoid loss of zinc due to the reduction by carbon residue during melting to prepare the XRF discs, the samples were preheated to 800 °C at 2 °C/min in oxygen to remove carbon before XRF analysis. Powder X-ray diffraction (XRD) data were collected using a Philips X'Pert diffractometer Data were

collected in steps of 0.02°, with a counting time of 5 s at each step. Qualitative phase analysis was carried out using HighScore Plus (Version 3.0.5, PANalytical Australia).

The morphology and phase composition of the sintered samples were examined by Leica DM6000 Optical Microscope and scanning electron microscopy – energy-dispersive X-ray spectroscopy (SEM-EDS, JEOL JSM – 6490LV). The mounted samples in epoxy resin were polished to a 1 µm finish for optical microscopy and SEM-EDS analyses.

The total carbon content of filter cake was determined by combusting at 800°C and measuring the CO and CO₂ released using an infrared absorption gas analyzer (Ultramat 23, Siemens, Germany).

3. Results

3.1 Zinc Removal from Tablets Sintered in Tube Furnace

Zinc removal (R_{Zn}), as defined in Eq. (1), from filter cake tablets was examined by sintering tablets, with and without the addition of carbon, under different oxygen partial pressures. Figure 3(a) shows the effects of oxygen partial pressure and temperature on zinc removal from these tablets, without the addition of coke. Zinc removal was very low at 800 °C but for all atmospheres used, increased with increasing temperature. It also increased as the oxygen partial pressure decreased. For example, the zinc removal in a 100% nitrogen atmosphere increased dramatically with an increase in temperature almost linearly until 1200 °C. Zinc removal was more markedly affected by the oxygen partial pressure at temperatures below 1100 °C; above 1100 °C, the effect was less significant. At 1300 °C, the zinc removal reached 24.6% in nitrogen and 22.0% in air.

$$R_{Zn} = \left(1 - \frac{m'_{Zn}}{m_{Zn}}\right) \times 100\% \quad (1)$$

where R_{Zn} is zinc removal; m'_{Zn} and m_{Zn} are zinc mass in sample after and before sintering.

Figure 3. (a) The relationship between zinc removal without coke addition and sintering temperature under various atmospheres. (b) The relationship between zinc content of filter cake tablet and coke content in the tablet at 1300°C.

To study the influence of locally reducing conditions, coke was added to the filter cake tablets to enhance zinc removal. Figure 3(b) presents the effect of coke addition on zinc removal in 0.5 vol% O₂ at 1300 °C. Addition of 3 wt% of coke had a significant effect by increasing zinc removal to 60.6%. Further increasing coke content in filter cake tablets to 9 wt% increased zinc removal to 91.4%. Previous work by Shen et al. (2006) achieved almost 100% zinc removal from tablets of manganese furnace dust containing 1.5 wt% zinc and 19.5 wt% carbon at temperatures above 1100 °C. The high zinc removal was due to excellent contact between zinc oxides and the carbonaceous material (tar) deposited in dust collection process. Furthermore, exploratory work by Wang et al. (2016) showed that more zinc was removed from tablets of a blast furnace filter cake-BOS filter cake mixture than those of the pure BOS filter cake, because more carbonaceous materials were present in blast furnace filter cake. Therefore, providing sufficient carbonaceous materials to improve the reducing atmosphere is critical for zinc removal. In commercial sinter plant, the coke rate is limited by a maximum temperature to avoid potential damage of the grate supporting the sintering bed.

3.2 Zinc Removal in Millipot Sintering

In order to investigate zinc removal performance in the actual sintering process, a millipot was employed to simulate industrial sintering conditions. In the first series of experiments, the sinter blends consisting of filter cake, additional coke breeze and green feed were mixed without tableting, and loaded into one of three different layers (location A, B or C in Figure 5) of the millipot. The major conditions and results are shown in Table 3. The zinc content in the originally loaded sintering material in the filter cake containing layers (carbon free) was 3.62

wt%. In general, there were different extents of zinc removal from the layers in all sintering experiments; the removed zinc, however, deposited in the layer immediately below the filter cake containing layer.

Table 3. A summary of millipot sintering experiments, showing zinc removal under different conditions

Experiment No.	11	12	13	14	15	16	17	18
Filter cake layer position	C	B	A	B	B	B	B	B
Filter cake type	← Untableted →					← Tableted →		
Coke rate, wt%	7.43	7.43	7.43	5.43	9.43	7.43	7.43	7.43
Extra coke pressed in tablet, wt%	-	-	-	-	-	3	7	11
Zn content before sintering, wt%	3.62	3.62	3.62	3.62	3.62	6.85	6.85	6.85
Zn content after sintering, wt%	2.88	2.65	2.63	2.90	1.10	6.18	4.54	2.28
Zn removal, %	20.4	26.8	27.3	19.9	69.6	9.8	33.7	66.7

Figure 4 provides examples of the temperature profiles at different locations along the millipot column (Experiments 16 and 18). The peak temperatures measured at the centre of the millipot column showed an increasing trend overall along the depth of the millipot due to the accumulation of heat during sintering.

Figure 4. Temperature profiles at different locations along the millipot column (Experiment 16 and 18). (T1, T3, T4, T5, T6: at the centre of the column; T2: at the wall; T7: off gas temperature).

Figure 5(a) compares the zinc removal from the blend of filter cake and green feed with 7.43 wt% of coke, placed at different sections i.e. top (position A), middle (position B) and bottom (position C) (Experiments 11-13). Zinc removal was evaluated by removal of samples along the length of the sintered column for bulk analysis. Samples were taken above, below and at the bottom of the original filter cake layer location. The results show that zinc removal slightly decreased as the distance of the filter cake layer from the bed top increased (Position A to C). The zinc removal ranged from 20.4 to 27.3% (Table 3), calculated by the zinc content in each section sampled from the sinter product column in the middle of each filter cake layer. The zinc content was generally higher in the sample taken from the lower part because of the re-oxidation and deposition of zinc vapour from upper part of the layer. It was considered as a more representative value for the case when zinc was originally distributed throughout the column. In Experiment 13, the sinter sample taken from the upper part of section A (-60mm) contained approximately 40% of the original zinc, showing that zinc was partly removed from the layer during sintering. The sample taken from the lower part (-100mm) had significantly lower zinc removal due to the deposition of zinc from the layer above the sampling height. The zinc contents of sample below the filter cake layer in Experiment 13 and the hearth layer in Experiment 11 contained 0.4% and 0.15%, respectively, which are significant in comparison with negligible zinc content in iron ore blend. The hearth layer particles appeared coated with white substance. Figure 6 presents the BSE image of the cross section of a particle from the hearth layer in Experiment 11, and the EDS mapping of zinc distribution on the cross section. From the zinc mapping and the EDS results, the white coating on the hearth layer particles is zinc oxide, which confirms re-oxidation and deposition of zinc vapour generated from the reduction of ZnO in the filter cake layer.

Figure 5. Zinc removal in the millipot. Zinc distributions after sintering in millipot (a) when the same blends with 7.43% CR of filter cake, green feed were not tableted and loaded at positions A, B and C; (b) when blends with CR of 5.43, 7.43 and 9.43%, respectively, of filter cake and green feed were not tableted and loaded at position B; (c) when filter cake was tableted with varying coke amounts. (dotted lines are used to aid identification; Position A: -60mm – -120mm, Position B: -210mm – -270mm, Position C: -340mm – -400mm, Position B': -230mm – -270mm).

Figure 6. The BSE image of the cross section of a particle from the hearth layer in Experiment 11 and the Zn mapping of zinc distribution on the cross section.

Zinc removal had a slight decreasing trend down the sinter bed from top to bottom (Experiments 11-13), because the re-oxidation and deposition of zinc vapour was sensitive to both temperature and oxygen content in the atmosphere. This can be explained by the following - although the slight increase in the sintering temperature as the flame front moved downward (Figure 4) favoured zinc vapour removal from the layer, the improved permeability of the sinter bed with the progress of sintering increased the air flow rate and oxygen level in the gas (Mou and Morrison, 2016), which promoted the reoxidation and deposition of zinc vapour.

The effect of coke content on zinc removal was examined when the filter cake blend layer was placed in position B (Figure 5(b)). Zinc removal increased with increasing coke rate from 5.43 to 7.43 wt%. Further increasing the coke rate to 9.43 wt% significantly increased zinc removal to 69.6%. Figure 5(b) also shows that zinc was more extensively distributed downwards for a coke rate of 9.43 wt%. Notably, in Experiments 11 and 12 (Figure 5(a)), zinc was detected in the hearth layer (0.11%), which indicated convective transport of zinc vapour and its deposition on the hearth layer.

Figure 5(c) shows the results for filter cake tablets with coke breeze (3.0, 7.0, and 11.0 wt% in Experiments 16-18, respectively). The original zinc content in the tablets was 6.85wt%. When the tablets were loaded into the middle layer of the millipot with an additional 7.43 wt% of blended coke breeze (based on tablet weight), a higher coke content in the tablets significantly increased zinc removal. With the coke addition in tablets at 3.0, 7.0 and 11.0 wt%, the zinc content in the sintered tablets was decreased to 6.18, 4.54 and 2.28 wt%, corresponding to zinc removal of 9.78, 33.7 and 66.7%, respectively.

It should be noted that the sampling methods were different for tableted and untableted filter cake. In order to collect sinter samples unaffected by wall effects, only the centre part of the sinter column was collected from the untableted filter cake (Experiments 11-15). However, in the sintering of the tableted filter cake (Experiments 16-18), whole tablets were collected due to the limited number of tablets used. In the case of tableted filter cake, the concentration of zinc at locations close to the wall made the zinc removal data lower than those reached at the center of the column.

4. Discussion

4.1 Zinc Vapour Formation from Reduction of Zinc Containing Compounds

Zinc in BOS filter cake is present mainly as ZnO and ZnFe₂O₄ (Sammur et al., 2008; Veres and Lovas, 2011). The removal of zinc from filter cake relies on the reduction of these compounds to form zinc vapour at high temperatures, where the potential reductants are carbon, metallic iron or CO gas. It should be noted that the content of metallic iron in filter cake was 12.0 wt% (Table 1).

Chemical reactions during sintering are complex, involving zinc and iron-containing mineral phases, coke and other carbonaceous materials, amongst others. The occurrence and extent of these reactions are affected by the temperature and gas atmosphere during sintering. In the presence of a reductant, some of the reactions listed below show that at sintering temperatures, ZnO and ZnFe₂O₄ may form zinc vapour.

CO used for Reactions (6) and (7) is from that generated from Reactions (2) and (3), or formed by the oxidation of carbon (e.g. coke). Due to the presence of carbon in the sintering systems investigated, the localised partial pressure of CO₂ can be maintained at very low levels through

its conversion to CO via the Boudouard reaction. Reactions (6) and (7) represent the indirect reduction reactions of zinc-containing minerals and are important for zinc removal because carbon and iron are not always in direct contact with the zinc-containing minerals during sintering, and CO provides a route for gas phase mass transfer.

Based on the results in Figure 3(a), a small fraction of zinc, up to approximately 25%, was removed due to metallic iron existing in the filter cake. Figure 3(b) shows that with the addition of coke in the tablets, a much greater fraction of the zinc could be removed. In this case, normal size (<7 mm) coke breeze was mixed in the blend, which means that the added reductant was not finely and evenly distributed in the tablet. While contact between filter cake and coke particles was limited, indirect reduction via carbon monoxide, Reactions (6) and (7), could proceed at high temperatures.

As shown in Figure 3, zinc removal increased with increasing temperature and decreasing oxygen partial pressure. In the sintering of tablets in a furnace, with the change of sintering atmosphere to less oxidative at a high temperature, coke played a more significant role as reductant instead of being combusted with oxygen, which favored the formation of a strong reducing atmosphere lasting a longer time. This is supported by the presence of residual carbon in the sintered tablets, as observed by optical microscopy. Higher temperature and lower oxygen partial pressure promote zinc removal. Increasing the coke content in tablets (Figure 3(b)) increased the reducing atmosphere in the tablet and improved zinc removal conditions.

4.2 Zinc Migration in Tablets

The migration of zinc in tablets were examined using a filter cake tablet with 7.0 wt% coke, sintered in a 0.5% O₂ atmosphere at 1300 °C for 4 minutes. Overall appearance (by optical micrograph) and BSE images and EDS elemental mapping analyses for two representative local zones within the sample (in the centre of tablet close to coke and on the edge of tablet). The presence of magnetite (as the major phase, by Reaction (8)), metallic iron and coke particles in the sintered sample indicates that a local reducing atmosphere existed in the tablets, providing favourable conditions for zinc removal. Residual zinc was concentrated on the external surface of the tablet, including the surface of large pores and cracks; very low zinc content was detected within the tablet bulk. This was totally different from the original relatively uniform zinc distribution in the green tablet, which suggests that zinc was initially reduced and vaporized, but a fraction of the zinc vapour was re-oxidized and deposited on the

surface of materials close to the crack and edge of tablet where the partial pressure of oxygen was likely higher (Reactions (9) and (10)). A ZnO shell was formed, in which the zinc content reached as high as ~75 %. Detailed information on the sample analyses is presented in **Supplementary Materials 1**.

$$\Delta G^\circ = 479433 - 293.6T \quad (J) \quad (8)$$

$$\Delta G^\circ = -410422 + 200.64T \quad (J) \quad (9)$$

$$\Delta G^\circ = -431599 + 202.85T \quad (J) \quad (10)$$

4.3 Zn Migration in a Sintered Column with Untableted Filtercake

The BSE images and EDS mapping of a sintered sample (**Supplementary Materials 2**) show that zinc oxide is distributed on the surface of a large pore, where the local gas atmosphere can be changed easily by the overall sintering atmosphere due to better void space connectivity. This suggests that zinc oxide and zinc ferrite in the filter cake were reduced in local reducing gas atmosphere in carbon enriched areas, and then the zinc vapour diffused into big pores where it was partially re-oxidized and deposited on the surface of solid minerals while the rest diffused and was blown downward. Zinc content of the deposit zone ranged from 9.00 – 12.4 at%, supporting zinc vapour re-oxidation and deposition resulting from a local change of atmosphere. Therefore, maintaining a reducing atmosphere during reduction of zinc-bearing materials and diffusion of zinc vapour was critical. The move downwards of zinc by re-oxidation and deposition was also observed by Shen et al. in normal sinter pot testing of manganese ore sintering with additional manganese furnace dust (Shen et al., 2007).

4.4 Zn Migration in a Sintered Column with Tableted Filter Cake

Optical microscopy and BSE observations and EDS zinc mapping were applied to the analyses of sintered column across its cross-section, and the detailed information was presented in **Supplementary Material 3**. The results indicate that ZnO and ZnFe₂O₄ in the tablets were

reduced and zinc vapour diffused outward, but some zinc vapour was re-oxidized and deposited on the surface of tablets where oxygen potential was high. Inherent reductants in the filter cake and added coke reduced ZnO and ZnFe_2O_4 to zinc vapour, generating gas species flowing outward through the tablets. This process favoured the maintenance of a reducing atmosphere to avoid zinc vapour re-oxidation and deposition within tablets and removal of zinc from them. However, during sintering at high temperature, some cracks gradually appeared with thermal shrinkage and melting phase formation. The formed cracks allowed the diffusion of oxygen into the tablets and so some zinc vapour was oxidized into deposited ZnO on the crack surfaces.

Tableting of the filter cake material with coke ensures effective reduction of ZnO and ZnFe_2O_4 within tablets, thus a lower proportion of zinc vapour was re-oxidized and deposited on the pore surface or tablet edge. High zinc removal could be achieved in the part not affected by millipot wall. However, the peak temperature close to millipot wall was low (e.g. Thermocouple T2 on port 2 only reached 548°C), and below the boiling temperature of zinc, 907°C . At this low temperature, reduction of ZnO and ZnFe_2O_4 was not effective. Instead, zinc vapour from centre of millipot diffused to and condensed on surface of solid materials at low temperature, and then was re-oxidized to form the observed ZnO -rich layer. This wall effect played a negative role in zinc removal from filter cake in millipot sintering, but would be negligible in a commercial sinter plant.

4.5 Overall Behaviour

In millipot sintering Experiments 11, 12 and 13, zinc removal of filter cake was limited. In comparison, a more significant difference was observed in Experiments 12, 14 and 15. A higher coke rate in the filter cake blend removed more zinc from the layer, since higher temperatures were reached for a longer time.

Good results were obtained with sintering of filter cake in the form of pressed tablets in millipot. The coke pressed into these tablets assisted in creating a more reducing atmosphere within tablets, thereby enhancing reduction of ZnO and ZnFe_2O_4 to zinc vapour. This vapour then diffused out from tablets. The pressed tablets guaranteed the reducing atmosphere promoted by the carbonaceous material was disturbed to the minimum extent, which created an excellent atmosphere for zinc reduction and removal. The large size of the tablets, relative to the column diameter, may have retarded the heating of the tablets to a temperature sufficient for ZnO reduction and decreased the reduction time, both of which negatively affected zinc removal.

In millipot sintering, the zinc vapour removed from filter cake was observed to have been re-oxidized and deposited below the initial filter cake position. Loading the filter cake at the bottom of sinter bed (above hearth layer) is expected to be the most favourable for effective zinc removal from sinter product.

Based on the above analysis on the zinc reduction and migration in BOS filter cake sintering process, the schematic diagram of zinc removal mechanism from filter cake unit during sintering is presented in Figure 7. When flame front reaches the filter cake layer, coke combustion heats the materials to high temperature and generates local reducing atmosphere where reductants (C, CO and metallic iron) reduce ZnO and ZnFe_2O_4 to zinc vapour (Eqs. (2) – (7)). The zinc vapour diffuses out of the local zones with relatively reducing atmosphere and partly enters into the gas flow by which it is blown downwards. The remaining vapour is either: a) re-oxidized to ZnO and ZnFe_2O_4 by oxygen and deposited on the surface of solid materials or b) dissolved into molten phase, and then forms some mineral phases in the final sinter product. The part of zinc vapour blown to the lower layer of sinter bed is either liquefied to zinc on the solid particle surface at low temperature and then re-oxidized to ZnO , or directly reoxidized and deposited as solid oxides. The local reducing atmosphere during sintering guarantees ZnO and ZnFe_2O_4 in the original filter cake could be reduced to zinc vapour, but the overall oxidizing atmosphere caused by air suctioned from the top of sinter bed reoxidised the zinc vapour again, which is the problem of traditional sintering process and the reason why zinc removal does not work in current sinter plant. Loading filter cake at the bottom of sinter bed favours zinc removal by reducing reoxidation and deposition of zinc on sinter. Increasing coke rate and briquetting adopted in this study enhance the local reducing atmosphere and extend the duration of the atmosphere, which helps more zinc migration out of the sinter bed.

Figure 7. Schematic of the mechanism of zinc removal from filter cake (the numbers in brackets refer to Reactions (2)-(10))

5. Conclusions

Zinc removal by sintering of a filter cake generated in basic oxygen steelmaking was examined in tablet testing and millipot sintering under simulated commercial sinter plant conditions. According to the outcomes of this investigation, it is feasible to recycle zinc bearing dusts by sintering. The major findings are summarized below:

Coke and metallic iron in filter cake play the role of reductant in zinc removal during sintering. Zinc removal from the filter cake tablets increased with an increase in temperature and decrease in oxygen partial pressure. In a nitrogen atmosphere at 1300°C, zinc removal from a tablet reached 24.6%. Addition of coke breeze into the filter cake tablets in the range of 3 to 9 wt% increased zinc removal from 60.6% to 91.4% at 1300 °C in an atmosphere of 0.5 vol% oxygen.

In millipot sintering, when loading a filter cake blend with a coke rate of 7.43 wt%, zinc removal was very low (~21%). Increasing the coke rate to 9.43 wt% enhanced local zinc removal to 69.6%, and zinc was moved downward farther in the sintering bed.

When the filter cake was loaded into the millipot in the form of tablets, addition of coke in the tablets improved zinc removal. Zinc removal from the tablets reached 66.7% with a coke rate of 11 wt% in the filter cake.

The proposed mechanism of zinc removal from filter cake during sintering is as follows. Reductants such as carbon and CO reduce ZnO and ZnFe_2O_4 to zinc vapour during the sintering process. Some of the zinc vapour which diffuses out from the filter cake particle is convected away, while the remaining vapour is either re-oxidized (to ZnO and ZnFe_2O_4) and deposited on the surface of solid materials or dissolved into molten phase or liquefied to zinc on the particle surface at low temperature and then re-oxidized to ZnO.

Zinc removal from the filter cake in millipot sintering was affected by the deposition of zinc oxide on the materials close to the wall with lower temperature. However, this negative effect (wall effect) would be negligible in a commercial sinter plant. It is suggested that filter cake be loaded at the bottom of a commercial sinter bed so as to minimize the deposition of zinc within the bed and maximize the removal of zinc.

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