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Zinc Reduction/Vaporisation Behaviour from Metallurgical Wastes

Timothy Kerry, Alexander Peters, Evangelos Georgakopoulos, Ashkan Hosseini, Erik Offerman and Yongxiang Yang

Abstract The steelmaking industry produces large quantities of zinc-bearing wastes of varying forms that cannot be treated through integrated steelmaking processes. Simultaneously, by-products of the zinc industry containing great amounts of iron and zinc are stored or landfilled. The amount of zinc in these materials is generally below that which is of value to be recycled directly to the zinc smelter, consequently a method of concentration is required. Tata Steel owns and operates the pilot HIsarna ironmaking plant which, due to its high raw materials flexibility, is attractive for the purpose of processing secondary iron sources. Furthermore, it can facilitate the simultaneous recovery of a zinc-enriched flue dust. The high temperature behaviour of various waste materials will be presented with regards to their recyclability in the HIsarna furnace. Blast furnace (BF) sludge and basic oxygen furnace (BOF) sludge from Tata Steel IJmuiden have been studied along with 'goethite' waste produced by Nyrstar. The various input materials have been comprehensively characterised and their reduction/vaporisation behaviour recorded. Mixed samples have been produced and tested in order to define the most appropriate form of delivery of these materials to the HIsarna furnace.

Keywords Recycling · Zinc · Dusts · Self-reduction · HIsarna

Introduction

Zinc is present within iron ore and coal; furthermore, it is widely applied as a protective coating in the production of galvanised steel. Consequently, within steelmaking processes, there is the potential looping and accumulation of zinc. This material can generally be found in the dusts and sludges produced from the high temperature operations taking place on these sites, whether from a sinter plant, blast furnace, electric arc furnace, etc. Moreover, along with concentrated zinc in the flue dusts of these

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plants, there are also valuable quantities of other materials such as iron, flux, and carbon. As such, when it is possible, they are returned to the process. However, at high levels of Zn, operational problems can occur in the integrated steelmaking process. The most detrimental effect is the undermining of the walls of the furnaces through Zn penetration, this can lead to localised oxidation [1]. Consequently, the amount of Zn present in the cycle has to be limited, dusts that contain high concentration of Zn are stored or even landfilled [2, 3].

Zn smelters face fluctuating markets for the procurement of zinc ores and can thus face high prices. This leads to the search for secondary sources of zinc at reasonable prices. The zinc-containing residues from steelmaking have a wide variance in zinc concentrations with the maximum being found in EAF dust (up to 43 wt%) [3]. From the integrated steelmaking process, however, values are much more likely to be a maximum of a few percent with a maximum of 8–10% [4, 5]. In general, from any of these sources, concentration of the zinc is required before it can be used within zinc production. Furthermore, the mineralogical form of zinc is of great importance to the zinc recovery. These dusts most commonly contain zinc in the form of ZnO or $ZnFe_2O_4$ [6–8]. Industrially, the former can be readily treated both through hydro- and pyrometallurgical processes, whereas the latter is much more stable and requires harsher, more costly treatment [9].

Commonly, thermal treatment is applied to these secondary materials with the industry standard being a pyrometallurgical technique, the Waelz process [5]. Here, a carbon-based reducing agent (generally in the form of coal) and temperatures of over 1200 °C are utilised to volatilise the zinc [10], the produced vapour can then be condensed and collected. Despite the prevalence of the Waelz kiln, there are several negatives associated with the process such as high amount of newly generated residues and the potential loss of other valuable material [5]. Consequently, alternative approaches for managing these industrial by-products are required. One potential approach is through recycling within the HIsarna furnace. This is an ironmaking route composed of two units, a cyclone converter furnace (CCF) and smelting reduction vessel (SRV). A pilot scale facility has been operating at Tata Steel Ijmuiden since 2010, in which time it has been shown that the process is highly suited to heavy metal recovery. There is no limit on the quantity of zinc that can be input to HIsarna and indeed the process has extremely high raw materials flexibility [11]. HIsarna is capable of recycling ironmaking waste dusts, galvanised steels scrap, and moreover waste materials from other industries, such as zinc production residues. With Zn concentrations of 50% or more in the HIsarna produced dust, it can be sold directly to Zn smelting operations [12]. Not only does this enable the reuse of a valuable resource and therefore contribute towards a circular economy but it also contributes to a positive environmental impact.

Investigations have been taking place into the pyrometallurgical behaviour of some of these industrial by-products. Blast furnace (BF) dust and basic oxygen furnace (BOF) dust along with ‘goethite’ waste from the zinc industry have all been studied. Through an understanding of how to maximise the zinc vaporisation efficiency, the concentration of zinc in the HIsarna off-gas system can be increased. Furthermore, secondary material that is also rich in iron can be added to the process and from this its reduction behaviour can be investigated. Consequently, the behaviour of individual dusts and also proposed mixtures have been studied to optimise the delivery of the zinc-containing material to the furnace cyclone.

Experimental

Blast furnace dust and basic oxygen furnace dust were received from Tata Steel Europe and goethite from Nyrstar (Fig. 1). The material was dried overnight in a furnace at 120 °C. The elemental compositions of these starting materials were determined using an Axios Max WD-XRF (in oxides mode) and LECO C/S 744 analysis, the results are displayed in Table 1. X-ray diffraction studies were conducted using a Bruker D8 Advance diffractometer for investigating mineralogy of the samples.

Experiments were conducted in a Carbolite STF 16/50/450 horizontal furnace. A flow (2 SLPM) of inert gas (N_2 or Ar) was maintained across the reaction tube. Dust samples were introduced to the furnace in alumina boat crucibles. These could be held in a water-cooled flange prior to introduction to the hot zone at appropriate temperature. After the desired retention time (ranging from 1 to 60 min) had been completed samples could be quenched through pushing the crucible back into the water-cooled flange. Weight measurements were recorded before and after heating. Off-gas analysis was conducted using a Hiden Analytical HPR-20 R&D mass spectrometer.

Fig. 1 As-received material in the wet form, from left-to-right BF dust, BOF dust, and goethite

Table 1 Initial composition of received dusts after drying. C and S calculated with LECO, rest with XRF

Sample	Wt%													
	C	S	Fe_2O_3	ZnO	SiO_2	CaO	MgO	Al_2O_3	MnO	P_2O_5	PbO	K_2O	CdO	As_2O_3
BF dust	41.3	2.32	33.3	4.8	5.3	2.3	0.9	2.8	0.1	0.2	1.1	0.9	0.029	–
BOF dust	2.4	0.09	84.1	0.6	1.3	8.5	1.4	0.1	0.9	0.1	–	–	–	–
Goethite	0.21	12.06	52.1	9.4	4.1	9.3	–	2	0.7	–	3.3	0.1	0.043	0.6

Results and Discussion

Weight loss measurements for the individual dusts were measured over an hour-long residence time at 1000 °C in inert atmosphere (Fig. 2). In the case of BOF dust and goethite, a stable mass was achieved after 5 min indicating that no further reactions were taking place. This reduction equated to 7 and 22% loss of initial mass, respectively. In the case of BF dust, the loss was observed to be higher (30%) and achieved after a 30-min time period (Fig. 2). It can be seen that these values are all much higher than the contained quantity of zinc in the materials, consequently other components must also be lost at this temperature. Off-gas analysis shows the release of carbon monoxide and carbon dioxide from each material and in the case of goethite, an additional release of sulphates. This indicates the desulphurisation from compounds within the goethite sample. In the case of the carbon oxides it shows the reaction of carbon (which makes up 41.3% of BF dust) as a reductant of other material within the sample whilst being oxidised itself.

Over longer retention times, sintering of the BOF dust and goethite was observed leading to the production of strong agglomerates. Blast furnace dust appeared to remain in a similar form throughout the tests, the minimal sintering can be explained through reduced quantities of CaO and iron oxides. The colour of the materials was also noted to become much darker, particularly in the case of goethite. This change from a lighter red/orange colour to a darker brown suggests the reduction of iron to lower oxidation states.

Elemental investigations of the dusts showed minimal reduction in zinc concentration within the goethite sample (Table 2). Conversely, in the BF and BOF dusts, a majority of the zinc was removed. In the latter case, this was from a very low starting point (0.6 wt%). However, it was deemed valuable to study the general BOF dust behaviour as other sources will contain appreciable zinc levels. Focusing on the case of the BF dust, it can be seen that a substantial amount of carbon was also

Fig. 2 Weight loss of industrial waste dusts after incremental residence times at 1000 °C under an inert atmosphere

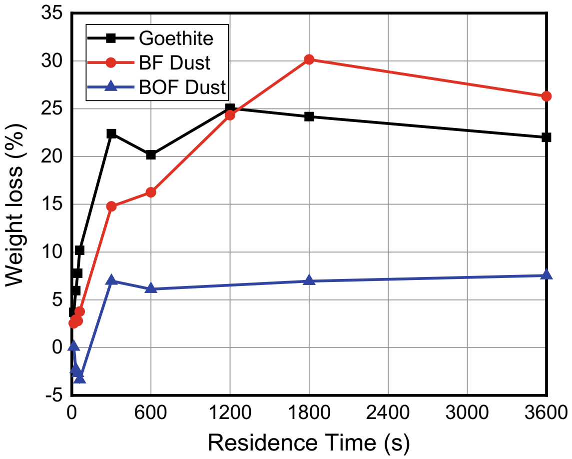

Table 2 Weight loss of zinc and carbon from individual dust samples

		Goethite		BF dust		BOF dust	
Element	Residence time (min)	Mass of element (g)	Weight loss (%)	Mass of element (g)	Weight loss (%)	Mass of element (g)	Weight loss (%)
Zn	0	0.12	8.33	0.06	96.67	0.007	71.43
	30	0.11		0.002		0.002	
C	0	0.0007	57.14	0.4	27.5	0.023	95.65
	30	0.0003		0.29		0.001	

lost in this time indicating the self-reducing behaviour of the dust. On the contrary, in goethite, there is extremely low quantity of carbon to facilitate the zinc reduction reaction. Zinc will be present in the varying industrial waste dusts in different mineralogical forms but primarily as zinc oxide (ZnO) and franklinite ($ZnFe_2O_4$) [6–8]. These compounds will undergo simultaneous reduction and vaporisation at the temperatures studied in the presence of a reducing agent [8].

The reduction of ZnO primarily takes place through the mechanism described by reactions 1–3. The overall mechanism is given by 1 which is mediated by reactions 2 and 3 [13].

$$\mathrm{ZnO(s) + C(s) \leftrightarrow CO(g) + Zn(g)} \tag{1}$$

$$\mathrm{C(s) + CO_2(g) \leftrightarrow 2CO(g)} \tag{2}$$

$$\mathrm{ZnO(s) + CO(g) \leftrightarrow CO_2(g) + Zn(g)} \tag{3}$$

In the case of franklinite, it has been shown that at 1000 °C franklinite decomposes into zinc oxide and hematite through reaction 4 [14]. Concurrently, direct reaction with carbon can lead to the release of zinc vapour (reaction 5 as mediated by reaction 2) [14].

$$\mathrm{ZnFe_2O_4(s) \leftrightarrow ZnO(s) + Fe_2O_3(s)} \tag{4}$$

$$\mathrm{3ZnFe_2O_4(s) + 4C(s) \leftrightarrow 3Zn(g) + 2Fe_3O_4(s) + 4CO(g)} \tag{5}$$

In the case of reaction 4, this is obviously followed by the previously described reduction process given by reactions 1–3. It can be seen that by increasing the carbon content of the material the reduction and hence, vaporisation of zinc can be realised and kinetics increased. However, excess carbon should be accounted for when looking at the carbon balance of the process.

The reducing behaviour of carbon also has an impact on the oxidation states of iron found in the various materials. XRD analysis has shown the starting and final mineralogy (Table 3) indicating the reactions taking place. It has been shown that there is enough carbon present in the BF dust to fully reduce the iron from hematite to the metallic form. Similarly, in BOF dust, the magnetite present has been reduced leaving metallic iron and wüstite. It is apparent that there was insufficient carbon within the sample to fully reduce the iron. In the case of goethite, limited reduction has been observed with some hematite being formed, this is due to the minimal carbon within the sample. The ability of the material to undergo self-reduction is of interest as it can potentially minimise use of virgin carbon sources within the process.

In order to volatilise the remaining zinc and investigate the reducing effect on iron within the sample, it was decided to mix materials. Goethite and BOF dust were both mixed in 60:40 ratios with BF dust, a material rich in carbon (41.3 wt%). The ratio was chosen to allow enough carbon for the theoretical complete reduction of Zn and Fe. The accentuated effect of the reductant on the sample weight loss is shown in Fig. 3. After 30 min, there is roughly an extra 10 and 20% weight loss in the BOF/BF dust and goethite/BF dust mixtures, respectively, when compared to a calculated cumulative value of the two individual dusts. This can be accounted for by reduction of iron and zinc and loss of zinc vapour and carbon oxides. Table 4 shows the loss of carbon and zinc from the material. It can be seen that in both mixtures, the zinc vaporisation is mostly complete. Similarly, a large proportion of the carbon present has also been lost from the sample through reduction reactions.

Table 3 Fe-bearing phases present in industrial waste dusts before and after heating in inert atmosphere at 1000 °C

	Initial Fe-bearing phases	30 min Fe-bearing phases
Goethite	FeOOH	Fe_3O_4, Fe_2O_3
BF dust	Fe_2O_3	Fe
BOF dust	Fe, FeO, Fe_3O_4	Fe, FeO

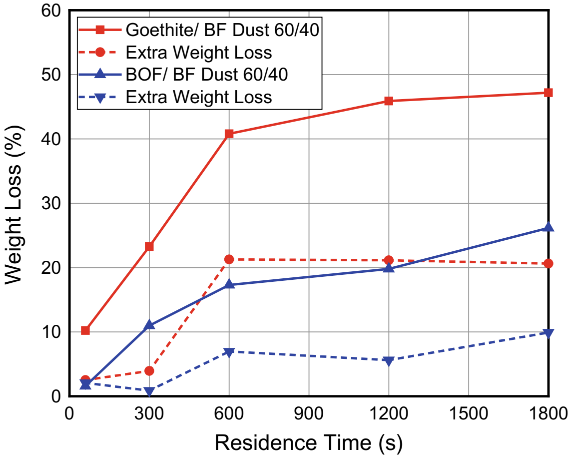

Fig. 3 Weight loss of mixed dusts and the extra weight loss calculated compared to the behaviour of individual dusts

Table 4 Weight loss of Zn and C from mixed dust samples

		Goethite/BF dust (60:40)		BOF/BF dust (60:40)	
Element	Residence time (min)	Mass of element (g)	Weight loss (%)	Mass of element (g)	Weight loss (%)
Zn	0	0.1	90.00	0.04	97.50
	30	0.01		0.001	
C	0	0.18	61.11	0.18	44.44
	30	0.07		0.1	

Table 5 Fe-bearing phases present in mixed waste dusts before and after heating in inert atmosphere at 1000 °C

	Initial Fe-bearing phases	30 min Fe-bearing phases
Goethite/BF dust (60:40)	FeOOH, Fe_2O_3	Fe
BOF/BF dust (60:40)	Fe, FeO, Fe_2O_3, Fe_3O_4	Fe

Once again, over the longer time periods of the experiment, a darker colour could be observed. However, compared to the individual BOF dust and goethite samples, the mixed material showed little sign of sintering. XRD analysis was used to investigate the reduction of iron within the mixed dusts and in both cases, it was seen that the only phase remaining was metallic iron (Table 5). This is indicative of the fact that there is sufficient carbon within the sample to reduce both the iron and zinc. In fact, it is in great excess based on the residual carbon in the mixed dusts (Table 4). The morphology of this material is comparable to that of direct reduced iron (DRI) and allows both resource recovery and reduction of coal usage [15].

By mixing industrial waste dusts with carbon-rich blast furnace dust, it has been shown that both reduction/vaporisation of zinc and complete reduction of iron can be achieved. This confirms their appeal for usage with the HIsarna furnace as a means of resource recovery. It is clear that carbon is in considerable excess in the 60:40 ratios tested in this study, consequently work needs to be made on finding optimal concentration. Furthermore, studies of briquette/-pellet formulation should be undertaken to define the most appropriate composition.

Conclusions

The behaviour of industrial waste dusts at 1000 °C in inert atmosphere has been undertaken. The potential of BF dust, BOF dust, and goethite for recycling within the HIsarna furnace has been considered with respect to contained iron and zinc. It was found that by mixing the latter two materials with BF dust in a 60:40 ratio produced a mixture that showed very promising behaviour for zinc recovery and iron reduction. Whilst almost all of the zinc was lost from the samples within the 30 min of experimentation, the iron was completely reduced to its metallic form. The product resembles DRI and as such can offer a material to the steel industry which can lower costs and allow for the recycling of valuable material, reducing coal consumption.

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