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Zinc Speciation in Dust from a Secondary Dedusting System of the Basic Oxygen Furnace

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Key words: Secondary BOF dust; zinc speciation; sequential extraction

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1. Introduction

In integrated steel mills, steel is produced from iron ore in two main process steps. In the blast furnace, coke serves as the reducing agent for converting iron ore into metallic iron, referred to as hot metal. This hot metal typically contains 4–5 wt.% carbon and various dissolved impurities such as silicon, phosphorus, and manganese. These impurities are removed in the subsequent steelmaking stage, which is carried out in the basic oxygen furnace (BOF) or steel converter [1]. In this process, high-purity oxygen is blown onto the surface of the molten iron. Due to the predominantly exothermic nature of the oxidation reactions, cooling scrap is added to absorb excess thermal energy, thereby enabling melting of additional metallic iron and increasing steel yield by up to 20% [2].

During oxygen blowing, the BOF vessel is positioned vertically, and the dust-laden off-gas arising from the process is extracted via the primary dedusting system. For charging hot metal and scrap, as well as for tapping of the liquid steel, the converter must be tilted. In this tilted position, emissions are not sufficiently captured by the primary off-gas system. Consequently, most steel plants are equipped with a secondary dedusting system, which collects these emissions using hoods mounted above the converter mouth and separates particulate matter by means of fabric filters [2]. The upward flow of ambient air is induced by the thermal energy released from the converter and the hot metal. Dust formation occurs particularly during charging of scrap and hot metal. Iron oxides are generated when hot metal comes into contact with atmospheric oxygen, while zinc originates mainly from galvanized scrap charged into the converter [3]. A portion of the zinc is volatilized already during charging when zinc coatings come into contact with the hot metal.

As the hot converter off-gas ascends toward the extraction hood, it mixes with cooler ambient air in the shop, resulting in rapid cooling and subsequent condensation of zinc species onto entrained dust particles. Further cooling occurs during gas transport through the ductwork to the secondary dedusting filter. For European BOF plants, an average specific dust generation from secondary dedusting of 0.1–1.2 kg per ton of liquid steel has been reported [1]. This dust consists predominantly of iron oxides (32–63 wt.%) [1]. Zinc concentrations strongly depend on scrap composition and range from 0.3 to 14.4 wt.% [1, 4], typically exceeding zinc contents observed in dusts from primary BOF dedusting systems (0.1–8.5 wt.%) [1, 5].

For primary BOF dusts, zinc compound speciation has been investigated [6]. In contrast, information on the chemical form of zinc in dusts from secondary BOF dedusting systems is currently lacking. This knowledge gap is of particular relevance, as increasing recycling of fine-grained iron-bearing residues is a key objective for integrated steel producers aiming to reduce landfill disposal [1, 7, 8].

Zinc poses a major challenge for internal recycling, as it accumulates in recycled material streams and can negatively affect furnace operation and refractory lifetime [1]. Effective reuse of iron-bearing residues containing zinc at elevated concentrations therefore requires prior reduction of their zinc content. Zinc removal can be achieved using pyrometallurgical or hydrometallurgical treatment routes. In pyrometallurgical processes, zinc is volatilized at high temperatures and

recovered from the off-gas, rendering these routes relatively insensitive to the specific zinc-bearing phases present in the material [9, 10]. In contrast, hydrometallurgical processes are strongly dependent on zinc speciation, as solubility, leaching kinetics, and selectivity vary significantly between zinc oxides, carbonates, sulphides and ferrites [11].

While hydrometallurgical treatment routes for primary BOF dusts have been extensively discussed in the literature [6, 12-15], comparable studies for secondary BOF dusts are absent. The objective of the present work was therefore to investigate dust from secondary BOF dedusting systems with respect to zinc distribution among different chemical fractions. Sequential extraction procedures, commonly applied for zinc speciation in metallurgical residues, were employed for this purpose [16-18].

2. Materials and Methods

2.1. Sample Preparation

The investigated dust originated from the secondary dedusting system of a BOF steelmaking shop and was collected at the dust discharge of the associated fabric filter. Approximately 2 dm^3 of dust were sampled. The bulk sample was homogenized and split to obtain representative subsamples for the different analytical methods using riffle splitters (Haver & Boecker HAVER RT and Quantachrome Micro Riffler).

2.2. Analytical Methods

Particle size distribution was determined using a Sympatec HELOS/RODOS laser diffraction analyzer operated in dry dispersion mode. Instrument calibration was verified using a Sympatec SiC P600’06 reference material. Particle morphology was examined by scanning electron microscopy (SEM) using a TESCAN VEGA LM instrument. Elemental composition of individual particles and surface features was assessed by energy-dispersive X-ray spectroscopy (EDX).

The concentrations of zinc, iron and lead in the dust were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Thermo Scientific iCAP 7200 system after aqua regia digestion of the dust. Details of the analytical method can be found elsewhere [19].

Zinc speciation was investigated using a sequential extraction procedure comprising five consecutive leaching steps. In each step, the solid residue from the preceding extraction was used as input material for the subsequent one. The procedure differentiated zinc into five operationally defined fractions: exchangeable and readily water-soluble (F1), carbonate-bound (F2), oxide-bound (F3), reducible (F4), and residual (F5). Typical zinc species associated with these fractions include zinc chloride or zinc sulphate (F1), zinc carbonate (F2), zinc oxide (F3), zinc sulphide (F4), and zinc ferrite (F5).

The leaching protocol was adapted from previously published methods [6, 20] and is summarized in Table 1. During each extraction step, suspensions were stirred at 250 rpm using a magnetic stirrer. After leaching, solid and liquid phases were separated by vacuum filtration. Filtrates were

collected for chemical analysis, whereas the filter cakes were directly transferred to the next leaching step.

Zinc concentrations in the leachates were also determined by ICP-OES. Phase identification of the bulk dust was performed by X-ray diffraction (XRD) at the Technical University of Cluj-Napoca using a Shimadzu LabX XRD-6000 diffractometer under the measurement conditions: Cu anode, 40 kV accelerating voltage and 30 mA cathode current, divergence slit 1.00°, scatter slit 1.00°, receiving slit 0.30 mm: scan range 5–90.0, continuous scan, scan speed 2.5°/min, sampling pitch 0.02°, preset time 0.48 s and scan range 5–60.0, continuous scan, scan speed 2°/min, sampling pitch 0.02°, preset time 0.60 s.

Table 1. Leaching procedure

Step	Leachate	Temperature	Duration
F1	H_2O_{demi} (60 mL)	60°C	3h
F2	CH_3COONa (1 M, 54 mL) and CH_3COOH (1 M, 6 mL)	25°C	3h
F3	$Na_2S_2O_4$ (0.3 M, 20 mL), Na-citrate (1.175 M, 20 mL) and H-citrate (0.025 M, 20 mL)	25°C	4h
F4	H_2O_2 (35%, 24 mL), NH_4-acetate (3.2 M, 15 ml) and HNO_3 (20%, 21 ml)	25°C	3h
F5	Aqua Regia (HCl/HNO_3, 3:1, 60 mL)	refluxed at 108°C	5h

3. Results and Discussion

3.1. Particle Size Distribution

The particle size distribution of the secondary BOF dust is shown in Figure 1. The dust exhibits a very broad size distribution, with a span (d_{90}/d_{10}) of 186 [21]. The mass median diameter (d_{50}) was 22 μm, in good agreement with literature data for secondary BOF dedusting dusts [4, 22].

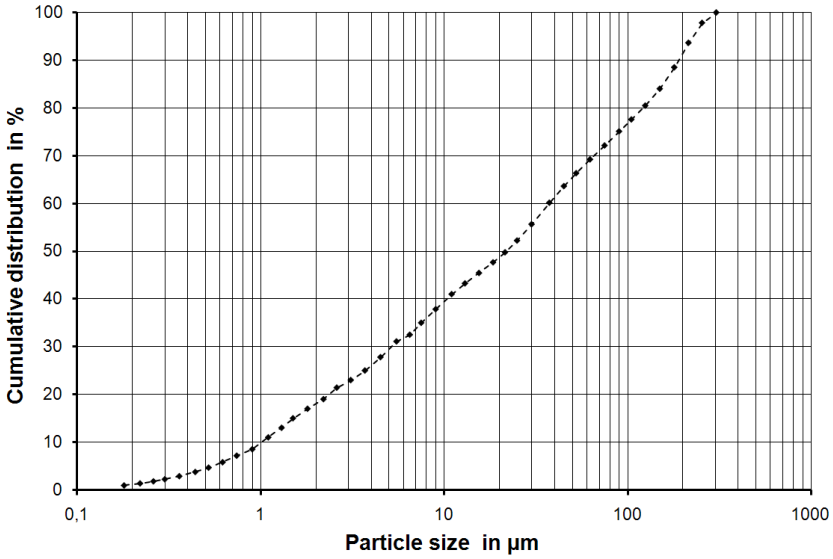


Figure 1. Particle size distribution of the secondary BOF dust

3.2. Chemical Composition and Morphology

The total zinc content of the dust was 133 g/kg. The concentrations of iron was 183 g/kg) and concentration of lead 5.96 g/kg. SEM images (Figure 2) reveal that many dust particles are coated with fine, crystal-like surface features. EDX analysis of these surface crystals showed zinc contents of approximately 50 wt.% along with iron and oxygen, markedly exceeding the average bulk zinc concentration. This observation is consistent with deposition of volatilized zinc species onto dust particles during cooling of the converter off-gas [23].

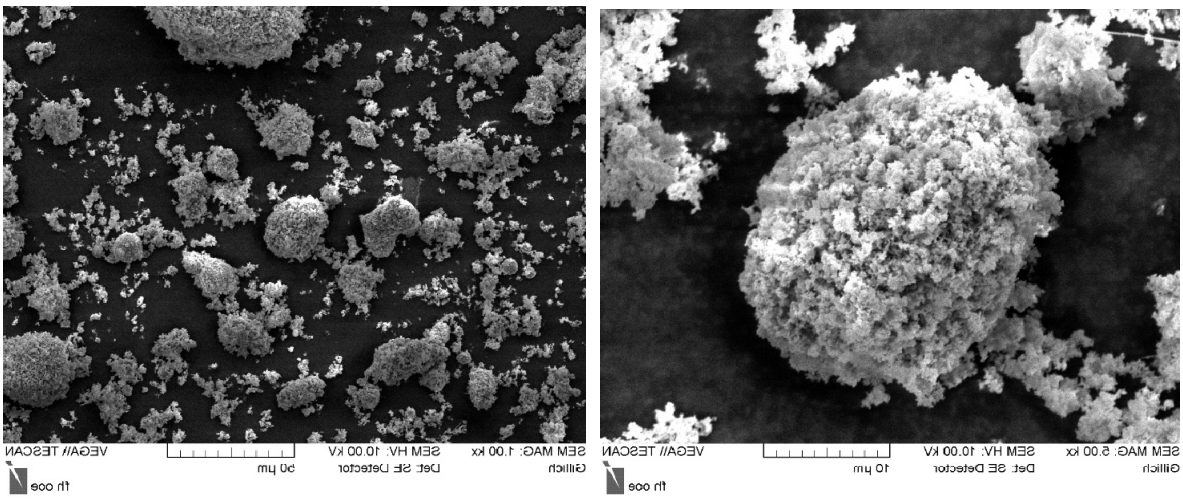


Figure 2 SEM images of dust particles

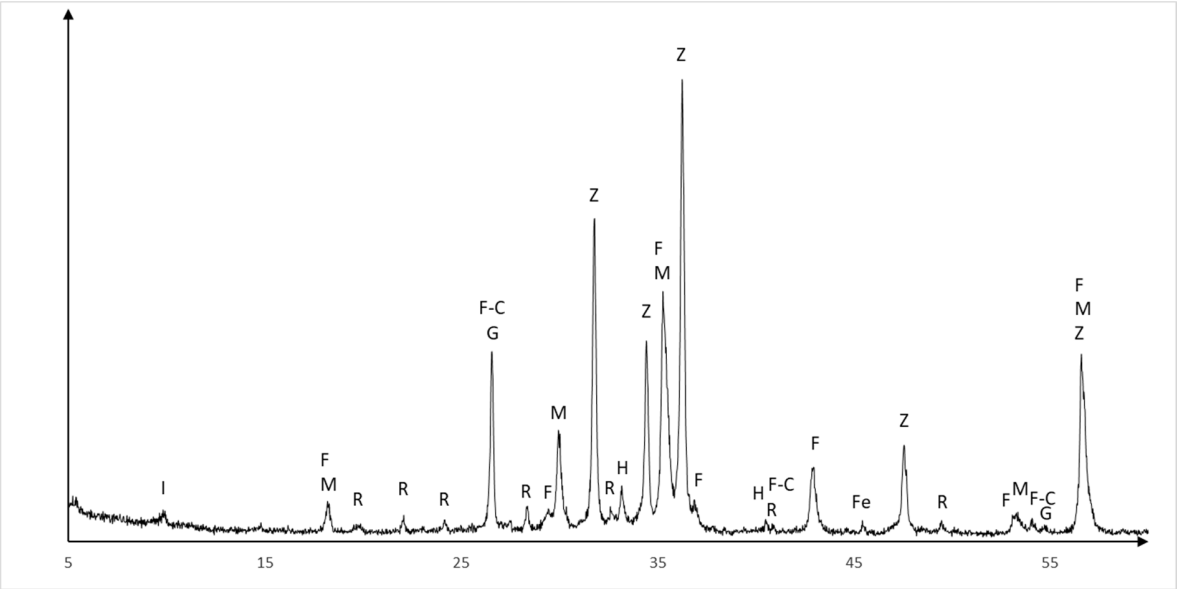
3.3. Zinc Speciation

Results of the sequential extraction procedure are summarized in Table 2. The dominant zinc fraction is the oxide-associated fraction (F3), accounting for approximately 54% of the total zinc content. Zinc was not detected in the exchangeable and readily water-soluble fraction (F1). The remaining zinc was distributed relatively evenly among the carbonate-bound fraction (F2), the reducible fraction (F4), and the residual fraction (F5).

XRD analysis confirmed the presence of zinc oxide (zincite) and zinc ferrite (franklinite), with an approximate zinc oxide to zinc ferrite ratio of 4:1 (Figure 3). Compared to dusts from primary BOF dedusting systems or electric arc furnace (EAF) dust, secondary dedusting dusts exhibit a significantly higher proportion of zinc present as zinc oxide and a correspondingly lower fraction of zinc incorporated into zinc ferrite [6, 23]. This can be explained by the high oxygen concentration in the secondary dedusting gas promoting the formation of solid zinc oxide. In primary dedusting the oxidation of zinc to zinc oxide is suppressed during the blow causing zinc to stay longer in its vapour phase and increasing the opportunity to react with iron to form zinc ferrite [24].

Table 2 Distribution of Zn in the various fractions of dusts from steelmaking

Typical Zn-compounds	Leaching fractions	BOF secondary dedusting (this study)	BOF primary dedusting [6]	EAF dedusting [20]
$ZnCl_2$, $ZnSO_4$	F1	0%	0%	0%
$ZnCO_3$	F2	12%	23%	27%
ZnO	F3	54%	16%	25%
ZnS	F4	18%	18%	8%
$ZnFe_2O_4$	F5	16%	43%	40%



Z- Zincite, F- Franklinite, M – Magnetite, F-C – Iron Carbide(Fe_3C), G- Graphite (Carbon), Fe – Metallic Iron, H – Hematite, R – Rankinite ($Ca_3Si_2O_7$), I – Fillosilicat.
Figure 3 XRD pattern of BOF secondary dust

This difference in zinc speciation has important implications for recycling. Zinc oxide is considerably more reactive and soluble under hydrometallurgical conditions than zinc ferrite, which is known for its high thermodynamic stability and low leachability in both acidic and alkaline media. Consequently, secondary BOF dusts are expected to be more amenable to selective zinc extraction using hydrometallurgical treatment routes.

4. Conclusions

The present study provides novel insights into the chemical form and distribution of zinc in dusts originating from secondary BOF dedusting systems. The investigated dust is characterized by a fine particle size, high zinc content, and pronounced surface enrichment of zinc phases resulting from deposition during off-gas cooling.

Sequential extraction and XRD analysis revealed that the majority of zinc in secondary BOF dust occurs in the oxide-associated fraction, predominantly as zinc oxide. In contrast, only a minor proportion of zinc is present as zinc ferrite which is typically the dominant zinc-bearing phase in primary BOF dusts. This distinct zinc speciation might be attributed to the presence of oxygen in the gas promoting the formation of solid zinc oxide. From a recycling perspective, the high zinc oxide content and low proportion of zinc ferrite are particularly advantageous. Zinc oxide exhibits significantly higher solubility and faster leaching kinetics than zinc ferrite, enabling selective zinc removal under comparatively mild hydrometallurgical conditions. As a result, secondary BOF dusts represent a more favourable feed material for hydrometallurgical zinc removal prior to internal recycling of the iron-rich residue.

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