Zinc Enrichment in In-Plant Electrostatic Precipitator Dust Recycling by Air Classification in Converter Steelmaking

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1. Introduction

During steelmaking in a basic oxygen furnace (BOF, steel converter) a considerable amount of dust is produced. The reported values of dust generation are up to 24 kg t\(^{-1}\) liquid steel (LS) while average values are approximately 15 kg t\(^{-1}\) LS.[1] The annual total amount of residues from BOF off-gas de-dusting performed in this study show a certain dependence of the Zn concentration on the particle size. This size dependence is exploited by introducing an air classification step into the recycling process. The calculations for this novel process show that the required average number of times a Zn atom has to be volatilized and can be reduced by 35–72% depending on the underlying circumstances. Thus, the energy and reduction agent consumption required for dust recycling can be reduced substantially.

Steelmaking in a basic oxygen furnace generates a considerable amount of dust, which is separated in a growing number of plants by dry de-dusting systems. This dust is rich in Fe and therefore, suitable for recycling within the steel mill. Because of the elevated Zn content recycling via the sintering process is often not feasible. Therefore, several steel mills apply in-plant dust recycling where the dust is recycled back into the furnace. Thereby, the Zn content of the dust increases steadily until the desired concentration in the dust for discharge is reached. In this procedure, the Zn atoms in the dust are circulated several times consuming energy and reduction agent for the volatilization each time. Classification experiments with basic oxygen furnace dust performed in this study show a certain dependence of the Zn concentration on the particles size. This size dependence is exploited by introducing an air classification step into the recycling process. The calculations for this novel process show that the required average number of times a Zn atom has to be volatilized and can be reduced by 35–72% depending on the underlying circumstances. Thus, the energy and reduction agent consumption required for dust recycling can be reduced substantially.

Zn is such an element present in BOF dust because of its widespread use for corrosion protection of steel. The Zn enters the furnace with the cooling scrap which is added to the charge at approximately 30%. In the furnace, it is volatilized because of the high temperature and the reducing conditions. Zn leaves the process with the off-gas and is solidified during cooling of the off-gas. In the separated BOF dust Zn is present as Zn ferrite (ZnFe\(_2\)O\(_4\), franklinite), zinc oxide (ZnO, zincite), and zinc carbonate (ZnCO\(_3\)).[7] The Zn content of BOF dust or BOF sludge in case of a wet de-dusting system is in the range of 1.4–3.2%.[1,8] Depending on the Zn content of the scrap, Zn concentrations of > 10% are possible when in-plant dust recycling is applied.[1] As the BOF process is a batch process the Zn concentration of the dust is not constant. The concentration is usually highest shortly after the beginning of the blow and decreases with the blowing time.[9,10] However, in the dust discharged from the dust-separator, the dust is partly re-mixed.

In integrated steel mills, fine-grained residues are often recycled through the sinter plant because fine-grained Fe bearing material fits well into the sinter feed. However, the allowable amount of Zn in the sinter produced is limited for operational reasons at the blast furnace. In the sintering process, the volatilization of Zn is low under normal conditions.[11] Therefore, only BOF dust with a low Zn content can be recycled.
via the sinter plant. Recyling of dust with a higher Zn concentration is only possible back into the BOF (in-plant recycling). This case, usually agglomerates are produced from the dust by pelleting or briquetting.\textsuperscript{11,12} In a study performed in a steel mill including several hundreds of heats with recycling of dust briquettes, the authors concluded that a recycling rate of up to 2.5% of the capacity of the BOF can be recommended.\textsuperscript{13} When dry de-dusting is applied the BOF dust can be agglomerated also by hot briquetting. In this process the dust is heated up to 750 °C in a moving bed reactor by hot air and autothermic reactions and then briquettes are formed.

In-plant recycling increases the Zn concentration of the dust from heat to heat. Finally, when a Zn concentration in the dust of 20–24% is reached the dust is discharged to external processing for Zn recovery or sent to landfill.\textsuperscript{1,13,14}

Ma proposed a new concept for BOF off-gas de-dusting, where the efficiency of the first de-dusting stage is higher. In such a system, the amount of dust from the first de-dusting stage, which is quite low in Zn concentration would be higher. Thus, the fraction of BOF dust which can be recycled via the sinter plant would be increased.\textsuperscript{15} The drawback of such a system is the increased pressure drop of the first de-dusting stage. Additionally, more than 50% of the dust is very fine dust with an increased Zn concentration,\textsuperscript{15} which is not affected by this measure.

In this paper, the optimization of in-plant dust recycling in dry de-dusted BOF steelmaking as described in the “Best Available Techniques (BAT) Reference Document for Iron and Steel Production”\textsuperscript{4} is discussed with a focus on minimizing the number of cycles of Zn in the system. To achieve this optimization air classification of the BOF dust is applied. Thereby, the dust is split into two size fractions, a Zn-enriched fine fraction and a Zn-depleted coarse fraction. Air classification for Zn separation has been proposed for the dusts from blast furnace (BF) de-dusting.\textsuperscript{16–18} However, the process conditions in the BOF processes differ significantly from those in the BF process. First, the BOF process is a batch process while the BF process is a continuous process. Therefore, the concentration of Zn of the BOF dust is not constant but varies over time. Second, the particle size of BOF dust is much finer compared to BF dust.\textsuperscript{18}

The application of air classification in in-plant dust recycling has also been suggested for electric arc furnace (EAF) steelmaking.\textsuperscript{20} However, the Zn content of EAF dust is typically one order of magnitude higher compared to BOF dust. Therefore, the proposed recycling process in EAF dust steelmaking consists of a single loop. In contrast, multiple recycling of the Zn is required in the case of BOF dust in order to reach the desired Zn concentration in the discharged dust. In this study, air classification tests with a BOF dust from a dry de-dusting system were performed to determine the size dependence of the Zn concentration. Based on these results the benefit of air classification was calculated and the applicability of the proposed new process is discussed.

2. Experimental Section

2.1. Materials

The BOF dust sample investigated was obtained from the dry BOF off-gas de-dusting system of a steel mill. In this plant, in-plant recycling of agglomerated BOF dust is applied. Thereby, briquetted BOF dust is recycled to the converter. When a certain Zn concentration in the BOF dust is reached the dust is sent to external processing. A 2 dm\textsuperscript{3} BOF dust sample was collected from the dust discharge of the dry electrostatic precipitator, which is installed downstream of a spray cooler. The sample volume was reduced using sample dividers (Haver 12.5, Quantachrome Micro Riffer) to an amount suitable for the various laboratory tests. Figure 1 shows the cumulative size distribution of the collected BOF dust. The mass median diameter was 1.7 μm, which is slightly less than measured for the BOF dust used in a study by Vereš et al.\textsuperscript{21}

2.2. Methods

The BOF dust sample was air classified using a 100 MZR laboratory classifier from Hosokawa Alpine. Since BOF dust from dry off-gas de-dusting contains some metallic Fe, a nitrogen supply was connected to the air inlet of the classifier for safety reasons. A sequential classification procedure was applied where in several classification steps always the finest size fraction is separated from the bulk while the coarse fraction is used as feed in the subsequent classification step.\textsuperscript{16} Because of the limited collection efficiency of the outlet-cyclone of the classifier for very fine material in the first classification step some of the finest dust material (size fraction 0) passed through the cyclone and was collected in the subsequent fabric filter. The amount of this loss was obtained from a mass balance for this classification step. The speed of the classifier in the two classification steps was 21,000 rpm and 10,500 rpm and the nitrogen flow through the classifier was always 50 m\textsuperscript{3} h\textsuperscript{−1}.

The particle size distribution was measured using a laser diffraction instrument (Sympatec HELOS/RODOS) with dry sample dispersion. For the verification of the calibration a Sympatec SiC-P600’06 standard was used. Microscopic images of particles were taken with a scanning electron microscope TESCAN, type MIRA3.

The dust sample and the various size fractions were digested in concentrated boiling hydrochloric acid prior to chemical
analysis. The digestion procedure was performed according to Leclerc et al.\cite{22} The concentration of Zn was measured by flame atomic absorption spectrometry and Fe concentration was determined according to Zimmermann-Reinhardt. Details of the analytical procedure have been published previously.\cite{17} The concentration of Zn and Fe in the finest particle size fraction lost in the first classification step was also calculated by means of mass balances.

### 2.3. Improved Process Concept

The improved process concept for in-plant dust recycling in dry de-dusted BOFs applies air classification before recycling of the dust. Thereby, the dust is separated into two size fractions: a coarse fraction depleted in Zn which would be recycled into the BOF and a Zn enriched fine fraction which is discharged. Compared to the current procedure as shown in Figure 2 as “STATE OF THE ART”, where all the dust is recycled until a certain Zn concentration is reached in the BOF dust, the mass of recycled Zn would be less. This reduction will save energy because Zn is volatilized via the reduction to metallic Zn which is accompanied by considerable energy and reduction agent consumption. When the Zn vapor is oxidized and re-condensed in the off-gas system the reaction enthalpy of 115 kcal mol\(^{-1}\) is released thus increasing the off-gas cooling requirements.\cite{23}

In the case of air classification for enrichment and depletion of Zn in the two size fractions of BF dust,\cite{16,17,24} the Zn concentration is quite constant. In contrast, the Zn concentration of BOF dust is not constant over the time. This problem can be solved by measuring the real-time Zn concentration of dust real-time by laser-induced breakdown spectroscopy (LIBS) or by X-ray fluorescence spectrometry.\cite{1,25} In contrast to in-plant dust recycling in EAF steelmaking, the Zn content of BOF dust is typically one order of magnitude lower,\cite{20} which makes multiple recycling of the dust necessary. Figure 2 shows a schematic flow diagram of the improved process. When the Zn content of the dust is above a certain limit concentration the dust is directed to air classification. Otherwise, it is sent directly to agglomeration for recycling. In the air classifier, the fine fraction is separated for external utilization. Varying dust composition can be handled by adaption of the operation parameters of the air classifier. For control of the classifier the Zn concentration of the fine size fraction produced is used. The coarse fraction is stored in a silo to be agglomerated separately. These agglomerates are recycled only when the Zn content in the dust from this cycle is already high enough to reach the Zn limit concentration for classification in the next cycle.

### 3. Results and Discussion

#### 3.1. Air Classification

The mass fractions of the particle size fractions and the results of the chemical analysis are summarized in Table 1. The Zn and Fe content of the finest dust material (size fraction 0) which passed the cyclone separator of the classifier was calculated by a mass balance. The particle size distribution of the BOF dust investigated was somewhat finer with a mass median diameter

![Figure 2. Schematic flow diagram of the improved dust recycling concept.](image-url)
The Zn content of the BOF dust was comparatively high. This is because of the in-plant dust recycling which is applied in the plant where the dust sample was taken. The Zn concentration in the finest particles was nearly twice as high as in the original dust, while the Zn concentration in the coarse fraction was only half. In contrast, the concentration of Fe varied only little with the particle size.

When the size dependence of the Zn concentration \( c_{Zn} \) is expressed by an approximation function of the type \( c_{Zn} \approx 1/d_{50}^N \)

the exponent \( N \) is 0.32. For other steelmaking dusts somewhat higher values for this exponent were reported: 0.55 for electric arc furnace (EAF) dust\(^{[20]}\) and 0.41 for BOF secondary de-dusting\(^{[26]}\). The comparatively low value of the exponent in the case of BOF dust might be explained by the increased specific surface area of the coarser particles caused by their structure (Figure 3). Many of these particles are aggregates of very fine individual particles attached to each other by some material solidified when the dust particles cooled in the off-gas system. Similar observations of the particle structure have been published previously.\(^{[27,28]}\)

### 3.2. Zn Enrichment and Depletion

A Zn partition diagram can be produced based on the data given in Table 1. This diagram shows the Zn concentration of the both size fractions as a function of the mass fraction of the coarse material (Figure 4a). The required calculations are described elsewhere.\(^{[29]}\) In this calculation, a similar sharpness of the separation as in the classification experiment is assumed.

The enrichment and the depletion of the Zn concentration in relation to the Zn concentration of the original BOF dust is shown in Figure 4b. The approximation equations for the Zn-enrichment factor in the fine fraction \( F_f \) and in the coarse fraction \( F_c \) were derived by linear regression from the data. The approximation equations are assumed to be valid independent of the Zn concentration of the dust (Equation (1, 2)):

\[
F_f = 0.94 \cdot x_c + 0.96
\]

\[
F_c = 0.76 \cdot x_c + 0.24
\]

In the equations \( x_c \) is the mass fraction of coarse material obtained in the classification process.

### 3.3. In-Plant Recycling Dust with and without Air Classification

The Zn content in BOF dust without recycling is in the low percent range.\(^{[1,8]}\) Thus, Zn has to be recycled several times to reach the aimed Zn concentration in the dust discharge. In the following calculations, the assumptions were made that, firstly, the Zn contained in recycled dust is volatized and can be found in the emitted dust,\(^{[13,30]}\) and secondly, that no additional emission of non-volatile components is caused by the recycling of the briquetted dust. The mass of Zn which is volatilized is therefore increasing linearly with the number of heats with dust recycling until finally the target concentration of Zn in the dust for discharge \( x_{Zn,d} \) is reached and the whole amount of dust is discharged. The concentration of Zn in the dust \( x_{Zn,i} \) does not increase linearly but according to Equation (3)

\[
x_{Zn,i} = \frac{x_{Zn,0} \cdot i}{1 + (i - 1) \cdot x_{Zn,0}}
\]

### Table 1. BOF dust mass fractions, mass median diameter, and composition.

| BOF dust | Size fraction 0 | Size fraction 1 | Size fraction 2 | Size fraction 3 |
|----------|----------------|----------------|----------------|----------------|
| Mass fraction in % | 100 | 10.0 | 22.2 | 34.1 | 33.7 |
| \( d_{50} \) in \( \mu m \) | 1.67 | — | 0.99 | 1.5 | 20 |
| Zn\(^{[a]}\) | 165 | 300 | 208 | 165 | 77 |
| Fe\(^{[a]}\) | 435 | 450 | 447 | 408 | 453 |

\(^{[a]}\) concentration in g kg\(^{-1}\) d·w.

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\[
x_{Zn,i} = \frac{x_{Zn,0} \cdot i}{1 + (i - 1) \cdot x_{Zn,0}}
\]
where \( i \) is the number of the heat in the recycling series starting with 1 for the first heat without any recycled dust and \( x_{Zn,0} \) is the Zn content of the dust produced when no dust recycling is applied. The minimum number of recycling cycles \( n_d \) to reach the target Zn concentration in the dust can be obtained by Equation (4):

\[
n_d = \frac{x_{Zn,d}}{x_{Zn,0}} \frac{1 - x_{Zn,0}}{1 - x_{Zn,d}}
\]  

(4)

The average number of times a Zn atom has to be volatilized in the furnace results from \( V_{Zn} = \frac{n_t - 1}{2} + n_t \).

When air classification of the dust is applied the required Zn content in the dust \( x_{Zn,s} \) is lower as the target Zn concentration in the dust for discharge \( x_{Zn,d} \) is achieved in the fine fraction produced by classification (Equation (5)):

\[
x_{Zn,d} = x_{Zn,s} \cdot F_f
\]  

(5)

With the enrichment in fine fraction \( F_f \) (Equation (1)) the required number of heats \( n_i \) can be calculated for various values of the mass fraction of coarse material \( x_c \) using Equation (6):

\[
n_i = \frac{x_{Zn,i}}{x_{Zn,0}} \frac{1 - x_{Zn,0}}{1 - x_{Zn,i} / F_f}
\]  

(6)

The coarse fraction from air classification has to be recycled. To minimize the amount of Zn volatilization required the coarse fraction is not recycled to the first heat but to the last possible heat \( n_i \) in which the Zn content of the dust \( x_{Zn,i} \) required before air classification is reached. Figure 5 shows the schedule of the heats in comparison to the schedule without air classification of the dust. The number of this heat is obtained by \( n_i = s \cdot (1 - F_f \cdot x_c) \). The average number of times a Zn atom had to be volatilized when air classification is applied can be calculated using Equation (7):

\[
V_{Zn,Class} = \frac{n_t - 1}{2} + n_t
\]  

(7)

The calculations can be performed using real numbers although in an actual plant \( n_d, n_i, \) and \( n_t \) have to be natural numbers.

Table 2 shows the calculated values of \( V_{Zn} \) for the typical range of the Zn content of BOF dust without recycling (1–3%) and Zn target concentrations in the discharged dust between 15% and 30%. The required number of recycling loops for Zn decreases with increasing Zn input and increases with increasing Zn target concentration.

Figure 6 shows the calculated results for in-plant dust recycling applying air classification. The required average number of times a Zn atom has to be volatilized \( V_{Zn,Class} \) is shown as a function of the mass fraction of fine material for discharge \( x_f \) (where \( x_f = 1 - x_c \)) for various Zn concentrations of the dust under non-recycling conditions. The Zn target
concentration for the dust discharge in Figure 6a–d is 15% Zn, 20% Zn, 25% Zn, and 30% Zn, respectively. All curves are characterized by a minimum which means that there is an optimum fraction of coarse for recycling. For a given target Zn concentration, the position of the minimum is shifted to higher values of $x_f$ by an increased Zn input. At a fixed Zn input the minimum is shifted to lower values of $x_f$ when the Zn target concentration is increased.

In Table 3, the reduction of the required average number of times a Zn atom has to be volatilized which can be achieved by air classification is shown. The calculated reduction is in the range of 35–72% depending on the underlying conditions. The positive effect of air classification is highest when the Zn input into the BOF is low and the Zn target concentration for the dust discharge is high.

Another option which can be achieved by air classification in combination with in-plant dust recycling is to increase the Zn content of the discharged dust without increasing the maximum Zn content in the process. In the “Best Available Techniques (BAT) Reference Document for Iron and Steel Production”[1] dust recycling in dry de-dusted BOF steelmaking is considered as feasible technology. The reduction in the number of volatilization cycles Zn has to get through until the required Zn concentration is reached, which can be achieved by air classification of the dust shows large potential to further increase the feasibility of such BOF dust recycling.

Table 2. Average number of times Zn has to be volatilized.

| Target Zn concentration in the discharged dust | Zn concentration in the dust without dust recycling |
|-----------------------------------------------|---------------------------------------------------|
|                                               | 1.0% | 1.5% | 2%  | 3%  |
| 15%                                           | 9.2  | 6.3  | 4.8 | 3.4 |
| 20%                                           | 12.9 | 8.7  | 6.6 | 4.5 |
| 25%                                           | 17.0 | 11.4 | 8.7 | 5.9 |
| 30%                                           | 21.7 | 14.6 | 11.0| 7.4 |

Table 3. Reduction of the average number of times a Zn atom has to be volatilized by application of air classification.

| Target Zn concentration in the discharged dust | Zn concentration in the dust without dust recycling |
|-----------------------------------------------|---------------------------------------------------|
|                                               | 1.0% | 1.5% | 2.0% | 3.0% |
| 15%                                           | 57%  | 49%  | 42%  | 35%  |
| 20%                                           | 64%  | 56%  | 50%  | 42%  |
| 25%                                           | 69%  | 62%  | 57%  | 49%  |
| 30%                                           | 72%  | 66%  | 62%  | 54%  |

Figure 6. Required average number of times a Zn atom has to be volatilized for various values of the Zn target concentration in the discharge. a) 15% Zn; b) 20% Zn; c) 25% Zn; d) 30% Zn.
recycling. The cost of air classification of dusts strongly depend on the throughput of the classification system. Thus, the profitability of the application of air classification has to be investigated separately for individual steel mills.

4. Conclusion

The classification experiments with BOF dust from a dry de-dusting system showed a certain dependence of the Zn concentration on the particle size. This dependence was less pronounced than reported for BF and EAF dust, which might be explained by the structure of the coarser dust particles.

In in-plant dust recycling, this size dependence of the Zn content can be exploited by introducing an air classification step into the recycling process. The calculations for this novel process showed that the required average number of times a Zn atom has to be volatilized can be reduced by classification of the dust. Depending on the underlying circumstances the calculated reduction was 35–72%. Thereby, the energy and reduction agent consumption for Zn volatilization is reduced by the same amount. Additionally, the maximum Zn concentration in the furnace is reduced while the same Zn concentration is achieved in the discharged dust.

Another aim of utilizing air classification could be to increase the Zn concentration in the discharged dust while the amount of Zn volatilization is kept at the current value.

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Conflict of Interest

The author declares no conflict of interest.

Keywords

air classification, BOF dust, dust recycling, zinc

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