



Steelmaking Dust: Speciation of Zinc by Sequential Leaching

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Abstract

In electric arc furnace (EAF) steelmaking significant amounts of dust are generated. The main component in the dust is usually iron. Additionally, increased concentrations of metals which are volatile in the steelmaking process like zinc are found in the dusts. During cooling of the off-gas in the off-gas system the volatile metals are deposited on the dust particles. In electric arc furnace dust the zinc can be present in different compounds, for example as zinc oxide and zinc ferrite. Although recycling of EAF dust and utilization for zinc recovery are practiced in several countries approximately 50% of the EAF dust produced worldwide is still goes to landfill. In this study the EAF dust from a mini mill was investigated by chemical fractionation. The experiment was carried out in a sequence of five leaching steps, where the residue from a leaching step was treated in the next step. The total zinc content of the EAF dust was approximately 6.4%. In the water-soluble fraction no zinc was found, while the carbonated fraction and the oxide fraction each contained approximately 25% of the zinc. The reduced fraction contained approximately 8% of the zinc and the majority of the zinc was in the residual fraction.

Keywords: steelmaking dust, sequential leaching, zinc

Introduction

In electric arc furnace (EAF) steelmaking in mini mills significant amounts of dust in the range of 10-30 kg per ton of liquid steel (kg/t LS) are produced (Remus et al., 2013). Fe is usually the main component in EAF dust. For metals which are volatile under steelmaking conditions like Zn increased concentrations are often found in EAF dusts. These metals enter the furnace with the scrap and are subsequently volatilized because of the high temperature in the furnace and the reducing conditions. These metals leave the furnace with the off-gas and are deposited on the dust particles during off-gas cooling. Reported Zn concentrations of EAF dust are in the range of 2–43% (Remus et al., 2013). According to the literature, Zn is mainly present as Zn oxide (ZnO, zincite) and Zn ferrite (ZnFe₂O₄, franklinite) (Machado et al., 2006; Grillo et al., 2014). Although recycling of EAF dust and utilization for Zn recovery are practiced in several countries (Doronin and Svyazhin, 2011; Lin et al., 2017) approximately 50% of the EAF dust produced worldwide (4.5 million tons per year) is still landfilled (Antrekowitsch et al., 2015).

In this study the EAF dust from a mini mill was investigated for the distribution of Zn in various compounds.

Materials and methods

Two dust samples were collected at the dust discharge of the off-gas dedusting filter of an industrial EAF plant. In the laboratory the samples were dried and subsequently the sample volume was reduced to a volume suitable for the various laboratory tests using sample dividers (Haver&Boecker HAVER RT and Quantachrome Micro Riffler). If required, the sample dividers were applied repeatedly.

The particle size distribution of the dusts was measured using a laser diffraction instrument with dry sample dispersion from Sympatec, type HELOS/RODOS.

The leaching experiment was carried out in a sequence of five leaching steps, where the residue from a leaching step was used for the treatment in the next leaching step. Thereby, the amount of Zn can be separately determined in different fractions: the exchangeable, easily water-soluble fraction (L1), the carbonated fraction (L2), the oxides (L3), the reduced fraction (L4) and the residual fraction (L5).

Zn would be present in these fractions, for example, mostly as ZnCl₂ or ZnSO₄ (L1), as ZnCO₃ (L2), as ZnO (L3), as ZnS (L4) or as ZnFe₂O₄ (L5).

The leaching procedure, which was adapted from published leaching procedures (Sammur et al., 2008), is described in detail in Table 1.

During the leaching procedure the vessel was stirred at 250 rpm with a magnetic stirrer. After the leaching the undissolved residue was separated from the liquid by vacuum filtration. The filtrate was saved for chemical analysis, while the filter cake was transferred to the next leaching step.

The concentrations of Zn in the solutions were measured by Inductive Coupled Plasma Optical Emission Spectroscopy (iCAP 7000 Plus Series).

Results and discussion

The average particle size distribution is shown in Figure 1. Generally, the particle size of the dusts was very small. The average values of the d₁₀, d₅₀ and d₉₀ were 0.38 μm, 1.27 μm and 24 μm respectively. This is within the range of reported data for EAF dust (da Silva et al. 2008; Lanzerstorfer, 2018).

Tab. 1. Leaching procedure (a special preparation procedure was applied)
 Tab. 1. Procedura wymywania (zastosowano specjalną procedurę przygotowawczą)

Step	Leachate	Temperature	Time
L1	H ₂ O _{demi} (60 mL)	60°C	3h
L2	CH ₃ COONa (1 M, 54 mL) and CH ₃ COOH (1 M, 6 mL)	Room temperature	3h
L3	Na ₂ S ₂ O ₄ (0.3 M, 20 mL), Na-citrate (1.175 M, 20 mL) and H-citrate (0.025 M, 20 mL)	Room temperature	4h
L4	H ₂ O ₂ (30%, 24 mL) in HNO ₃ ^a (60 mL)	refluxed at 95°C	3h
L5	Aqua Regia (HCl/HNO ₃ , 3:1, 60 mL)	refluxed at 90°C	3h

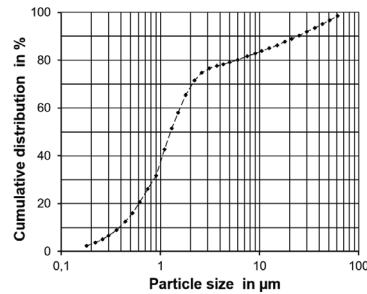


Fig. 1. Average size distribution of the EAF dusts
 Rys. 1. Średni rozkład wielkości pyłów EAF

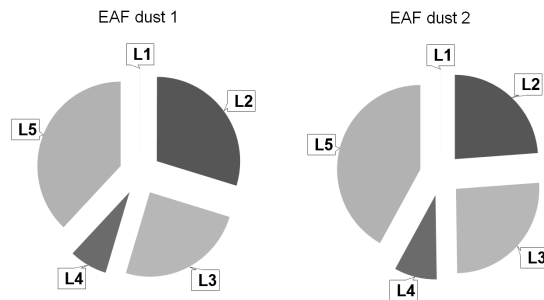


Fig. 2. Fraction of Zn in the various leaching fractions
 Rys. 2. Frakcja Zn w różnych frakcjach ługujących

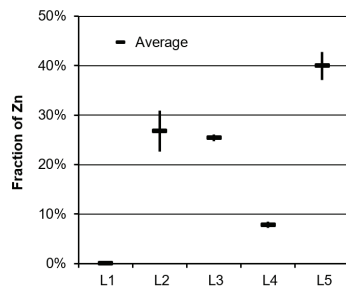


Fig. 3. Fraction of Zn in the various leaching fractions
 Rys. 3. Frakcja Zn w różnych frakcjach ługujących

The total Zn content was $6.5 \pm 0.4\%$ for the first EAF dust sample and $6.4 \pm 0.3\%$ for the second sample. The distribution of the Zn in the various leaching fractions L1 to L5 is shown in Figure 2. The differences between the two samples were quite small.

Figure 3 shows the variation of the Zn fraction (average fraction \pm standard deviation) found in the leachates. In the water-soluble fraction (L1) no Zn was found. In the carbonated fraction (L2) as well as in the oxide fraction (L3) approximately 25% of the Zn was found. However, the variation

was larger for the carbonated fraction. The reduced fraction (L4) contained approximately 8% of the Zn. The majority of the Zn, approximately 40%, was found in the residual fraction (L5).

The presence of Zn in the form of Zn oxide and Zn ferrite is in accordance with published data. (Machado et al., 2006; Grillo et al., 2014). However, the presence of approximately one third of the Zn in the carbonated and reduced fraction is somewhat surprising. Further investigations are required to confirm these findings.

Conclusion

The investigated EAF dust samples were within the typical values with respect to particle size and total Zn content.

The speciation of Zn by sequential leaching revealed that approximately two thirds of the total Zn can be found as Zn oxide and Zn ferrite. However, the remaining third of the total Zn content was found in the carbonated and reduced fractions. To confirm these findings further investigations are required.

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Pył stalowniczy: specjacja cynku metodą sekwencyjnego ługowania

W elektrycznym piecu łukowym (EAF) wytwarzającym stal wytwarzane są znaczne ilości pyłu. Głównym składnikiem pyłu jest zwykłe żelazo. Ponadto w pyłach znajdują się podwyższone stężenia metali lotnych w procesie hutnictwa, takich jak cynk. Podczas chłodzenia gazu odlotowego w układzie gazu odlotowego lotne metale osadzają się na cząstkach pyłu. W pyłach z elektrycznych pieców łukowych cynk może występować w różnych związkach, na przykład jako tlenek cynku i ferryt cynku. Chociaż recykling pyłu z EAF i wykorzystanie do odzysku cynku są praktykowane w kilku krajach, około 50% pyłu z EAF wytwarzanego na całym świecie nadal trafia na składowisko odpadów. W przedstawionych badaniach pył EAF z mini-młyna zbadano przez frakcjonowanie chemiczne. Eksperyment przeprowadzono w sekwencji pięciu etapów ługowania, przy czym pozostałość z etapu ługowania poddawano obróbce w następnym etapie. Całkowita zawartość cynku w pyłach EAF wyniosła około 6,4%. We frakcji rozpuszczalnej w wodzie nie znaleziono cynku, podczas gdy frakcja węglanowa i frakcja tlenkowa zawierały około 25% cynku. Zredukowana frakcja zawierała około 8% cynku, a większość cynku znajdowała się we frakcji resztkowej.

Słowa kluczowe: pył stalowy, ługowanie sekwencyjne, cynk