

Chemical composition and zinc leaching test of dust from electric arc furnace emissions from the Steelwork of Ózd, Hungary

Az Ózdi Acélművek füstgázából leválasztott por kémiai összetételének és oldható cinktartalmának vizsgálata

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Abstract – The recycling of metallurgical by-products is vital for both economical or environmental reasons. Electric arc furnace dusts are considered as secondary raw materials for zinc production. In this paper we investigated the chemical composition of the EAF dusts of the Steelwork of Ózd, Hungary. The total zinc content of the EAF dust is 24-25 (m/m)%, and 16-17 (m/m)% is leachable with an ammonium carbonate solution. The EAF dust of Ózd Steelwork should be considered as a potential raw material for hydrometallurgical Zn production.

Összefoglalás – A fémipari hulladékok újrahasznosítása környezetvédelmi és gazdaságossági szempontból is lényeges. Az acélgártás során a füstgázokból leválasztott porok másodlagos nyersanyagokként elsősorban a cinktermelésben jöhetnek szóba. Jelen cikkünkben az Ózdi Acélművek ívkemencéjének füstgázából leválasztott por kémiai összetételét vizsgáltuk. A leválasztott por cinktartalma átlagosan 24-25 (m/m)%, melyből 16-17 (m/m)%-nyi mennyiség kioldható ammónium-karbonáttal. Véleményünk szerint a füstgázból leválasztott por hidrometallurgiai módszerekkel újrahasznosítható másodlagos nyersanyag.

Keywords – steel production, furnace dust, secondary raw material, Ózd

Tárgyszavak – acélgártás, füstgáz por, másodlagos nyersanyag, Ózd

Introduction

Electric arc furnace dust (EAF dust) is a by-product of the EAF-type steel-making technology. Since EAF dusts are characterized by high concentrations of leachable heavy metals (e.g. Zn, Pb, Cu, Cd, As), they are classified as hazardous wastes. Due to the large quantity of EAF dust (10-20kg per ton of steel) and its toxic nature, the safe disposal of the dust is a major challenge of the secondary steel industry. According to modern environmental protection and technological principles, the cost-effective recycling of by-products is desirable as well. To achieve these objectives, one must know the chemical and mineralogical composition of EAF dusts, and the variability of these properties.

The chemical composition of EAF dusts

The Ózd Steelwork Ltd uses large quantities of scrap steel as a source material. The scrap metal may contain a significant amount of volatile elements (e.g. Cd, Zn, Pb and Cl), which are enriched in the fumes and fly dusts.

The most important methods of EAF dust treatment are the following:

- Disposal as landfill. This is the least effective method, since the dust is not recycled, and the leachable toxic metals may pose an environmental threat (NYIRENDA & LUGTMEIJER 1993; PICHTEL & BRADWAY 2008).
- Glassification by thermal treatment to prevent the leaching of toxic metals (CHENG 2003).
- Treatment with alkaline solid materials, such as lime, portland cement or blast furnace slags (the latter is a by-product of iron smelting). The pH of the alkaline media should be adjusted to minimize the solubility of heavy metals (LAFORST & DUCHESNE 2007; SALIHOGKU & PINARLI 2008). EAF dusts are used by the construction industry as a component of portland cements. The high chloride and sulphate content of the dust limits the dust:cement ratio, since these

anions have an undesirable effect on the characteristics of the cement.

- Recycling by pyrometallurgical methods (DONALD & PICKLES 1996). The major objective of this method is the recovery of zinc. From an economical point of view, this method requires high zinc concentration of the EAF dust.
- Recycling by hydrometallurgical methods (NYIRENDA & LUGTMEIJER 1993; DUTRA et al. 2006; RUIZ et al. 2007). The objective of these treatments is the recovery of heavy metals, especially zinc. The two major zinc-bearing phases in EAF dusts are franklinite ($ZnFe_2O_4$) and zincite (ZnO) (DUTRA et al. 2006; LECLERC et al. 2003). Franklinite is a resistant mineral with spinel-type crystal structure and is soluble only in concentrated strong acids, while zincite is soluble under mild conditions, e.g. in dilute acidic or alkaline solutions or in the presence of complexing agents. For the same reason, franklinite is considered non-toxic. In several hydrometallurgical processes dilute acids are used as solvents to recover zinc (HLAVÍK et al. 2006; ASADI ZEYDABADI et al. 1997). A disadvantage of using acids is that other metallic elements dissolve as well, and their separation may significantly increase the cost of such methods. A more practical method is the leaching of Zn by using alkaline media, such as NaOH or ammonium carbonate solutions. A major advantage of alkaline leaching is that the iron oxides remain in the solid phase, therefore some degree of separation is achieved. Besides zinc, ammonium carbonate leaching will dissolve the cadmium, copper and lead compounds as well, and the remaining solid (mostly composed by iron oxides and franklinite) is non-toxic (NYIRENDA & LUGTMEIJER 1993; RUIZ et al. 1997). The latter three metals may be separated by reduction with metallic Zn. Thus, high-grade ZnO can be prepared, and the toxic heavy metals are concentrated in metallic form.

The technology of EAF dust separation in the Steelwork of Ózd

The fumes of the electric arc furnace are conducted into a post-combustion unit, where the larger particles (few millimetres in diameter) are removed. Then the fume is cooled below 120°C through a heat exchanger, and the fine dust is removed by bag filters. The EAF dust is deposited as specific landfill near the village of Sajókaza.

Aims

In this paper we investigated the recycling possibilities of the EAF dust of the Steelwork of Ózd. The investigation concerned the following:

- (i) determination of the chemical composition of the EAF dust;
- (ii) investigation of the compositional changes during a charge-time. Since zinc is more volatile than iron, one might expect that zinc is enriched in the fumes during the early stages of the steelmaking process. If so, the early-stage EAF dusts may be collected separately in order to obtain an economically more valuable raw material for zinc production.
- (iii) Determination of the ammonium-carbonate-soluble fraction of the total Zn content of the EAF dusts.

Materials and methods*Sampling*

The sampling of the EAF dust was carried out at 6th February, 2008. Samples were taken from the bag filter of the steelwork in 3-minute intervals during a charge. One charge of the steelmaking process lasts for cca. 80 minutes, thus we took 25 samples. The mass of each sample was about 200g. Due to the fine grain size, homogenization and grinding was not necessary.

Sample preparation

To determine the total concentrations of the investigated elements (Ca, Cd, Fe, K, Na, Pb, Zn), 0.1mg EAF dust samples were measured with a precision of 0.0001g, and the samples were boiled with 15ml of aqua regia. The solutions were evaporated to cca. 1ml, then diluted to 50ml in volumetric flasks with deionised water. A small amount of black solid residue was observed after the acid digestion. We identified this residue as carbon, since it was not present in those samples which were heat treated at 1000°C prior to aqua regia digestion.

In order to examine the possibility of re-using the EAF dust as a raw material for zinc production, we leached the dust samples with ammonium carbonate. 0.2g dust samples were leached with 9ml 10 (m/m)% ammonium carbonate solution. The pH of the leaching solution was adjusted to 10.5 with 25 (m/m)% ammonia solution. The leaching time was 2 hours, and the suspensions were thoroughly shaken every 30 minutes. The suspensions were left to settle for 12 hours. 0.5ml of the clear supernatant liquid was taken with a pipette and diluted to 250ml in a volumetric flask. The zinc concentrations of these solutions were determined.

Analysis

The concentrations of Cd, Fe, K, Pb and Zn were measured by using flame atomic absorption spectroscopy. Concentrations of Ca, K and Na were determined by flame atomic emission method. The calibrating solutions were made by using commercial single-element 1000mg/l stock solutions. The measurements were carried out on a Zeiss-Jena AAS-1 spectrometer. The sample solutions were diluted when it was necessary.

Results and discussion*Results of aqua regia digestion*

The results of the chemical analyses are shown in *Table 1*, and the plots are shown in *Figure 1*. According to the practice of the laboratory of the Steelwork of Ózd, concentrations of Ca, K and Na are given as oxides in (m/m)%, while the heavy metals are given as elements in (m/m)%. Data for Cd is given in mg/kg.

The pseudo-total concentrations of the observed elements did not show significant changes with charge-time. The concentrations of the observed elements were fairly constant with time. The outlying values may be associated with the possible inhomogeneities of the samples. The relative standard deviations (RSD) of the concentrations were between 3 and 12%. The lowest RSD value was found in the case of Fe, while the highest was in the case of Ca.

The results suggest that the bulk chemistry of the EAF dusts does not change significantly with the charge-time, and the dust can not be separated into fractions with different chemical compositions.

Results of ammonium carbonate leaching

The alkaline ammonium carbonate solution dissolved 15-18 (m/m)% Zn from the EAF dust samples. The average leachable Zn content was 16.6 (m/m)%. The total Zn varied between 22.5-27 (m/m)%, the average was 25.5 (m/m)%. The average dissolved fraction was 65% of the total Zn, which is equal to 16.6% Zn content. The fraction of ammonium carbonate soluble zinc slightly decreased with charge-time from cca. 70% soluble fraction (18% Zn) to 60% soluble (15% Zn).

On the basis of the total and ammonium carbonate soluble zinc concentrations, the amount of major zinc-bearing minerals (franklinite and zincite) were calculated as follows:

$$\text{Zincite \%} = (\text{Zn}_{\text{soluble}}\%) \cdot (\text{A}_{\text{Zn}} + \text{A}_{\text{O}}) / \text{A}_{\text{Zn}}$$

$$\text{Franklinite \%} = (\text{Zn}_{\text{total}}\% - \text{Zn}_{\text{soluble}}\%) \cdot (\text{A}_{\text{Zn}} + 2\text{A}_{\text{Fe}} + 4\text{A}_{\text{O}}) / \text{A}_{\text{Zn}}$$

where $\text{Zn}_{\text{soluble}}\%$ is the ammonium carbonate soluble Zn content, given as (m/m)%; $\text{Zn}_{\text{total}}\%$ is the aqua regia soluble zinc content, (m/m)%; $\text{A}_{\text{Zn}} = 65.37\text{g/mol}$; $\text{A}_{\text{O}} = 16.0\text{g/mol}$; $\text{A}_{\text{Fe}} = 55.85\text{g/mol}$.

The most abundant Zn-bearing mineral phase was franklinite (ZnFe_2O_4) with an average concentration of 32.7 (m/m)%. The average concentration of zincite (ZnO) was 20.7 (m/m)%. However, only 30-40% of the total zinc

content is present in franklinite, the remaining 60-70 (m/m)% of the total zinc is in zincite form.

The fraction of zincite slightly decreased (from 72% to 64%), while the fraction of franklinite increased (from 28% to 36%) with charge-time. This may be due to the increasingly oxidative properties of the fume gases, which cause the oxidation of Fe(II) minerals to Fe(III) oxides. Ferric oxides can react with ZnO and form franklinite.

Summary

Our results suggest that the EAF dusts of the Ózd Steelwork contain a high fraction of leachable Zn, thus may be economically used as a raw material for hydrometallurgical Zn production. The leaching tests might be used as useful tool for the mineralogical investigations of EAD dusts and other metallurgical by-products.

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time min	CaO %	Na ₂ O %	K ₂ O %	Fe %	Pb %	Cd mg/kg	Zn _{total} %	Zn _{soluble} %	Zincite %	Franklinite %
3	2.59	2.20	2.51	24.8	3.49	728	25.5	17.8	22.1	28.6
6	2.83	2.36	2.49	25.7	3.49	669	28.0	18.0	22.4	36.9
9	2.66	2.29	2.50	25.4	3.81	699	25.4	17.5	21.7	29.4
12	2.39	2.47	2.50	24.7	3.39	763	24.2	16.8	21.0	27.1
15	2.47	2.29	2.46	25.7	3.17	713	22.5	16.5	20.5	22.4
18	2.64	2.01	2.66	24.9	3.32	685	25.4	18.4	22.9	26.0
21	2.41	2.38	2.58	25.2	3.36	667	23.9	16.3	20.3	28.0
24	2.50	2.45	2.43	25.0	3.39	667	25.5	17.0	21.1	31.4
27	2.63	2.26	2.46	25.3	3.33	705	25.5	17.0	21.1	31.5
30	2.56	2.27	2.47	24.4	3.36	692	25.7	18.4	22.9	26.9
33	2.48	2.37	2.22	25.4	3.47	681	26.5	15.0	18.7	42.2
36	2.73	2.26	2.49	25.6	3.38	723	24.1	15.0	18.6	33.7
39	3.06	2.26	2.42	23.9	3.53	863	24.7	15.6	19.5	33.3
42	2.57	2.21	2.41	24.9	3.34	732	25.7	16.6	20.7	33.5
45	3.73	2.14	2.48	25.9	3.28	694	24.0	15.9	19.8	29.8
48	2.67	2.18	2.36	26.6	3.43	650	24.5	16.2	20.1	30.8
51	2.73	2.61	2.50	25.4	3.48	725	25.4	16.7	20.8	32.2
54	2.50	2.19	2.60	25.7	3.55	698	27.9	15.5	19.3	46.0
57	2.97	2.27	2.29	25.5	3.40	702	26.3	16.6	20.7	35.6
60	2.37	2.04	2.48	26.7	3.62	782	25.2	16.7	20.8	31.4
63	2.69	2.08	2.49	27.1	3.47	634	25.4	17.9	22.3	27.5
66	2.20	2.39	2.49	24.9	3.45	698	26.7	16.8	20.9	36.6
69	2.44	2.10	2.50	24.7	3.57	688	26.8	16.7	20.7	37.3
72	2.56	2.18	2.30	24.3	3.59	673	25.7	15.3	19.1	38.3
75	2.30	2.32	2.41	24.2	3.59	705	26.9	16.0	19.9	40.4
Mean	2.63	2.26	2.46	25.3	3.45	705.32	25.5	16.6	20.7	32.7
RSD %	11.48	6.13	3.88	3.03	3.81	6.56	4.93	5.81	5.81	16.90

Table 1. Changes in the concentration of the measured elements and zinc-bearing minerals with time during one steelmaking charge.

1. Táblázat. A vizsgált elemek koncentrációjának változása, valamint a fő cinkásványok mennyisége a szállóporban az adagidő során.

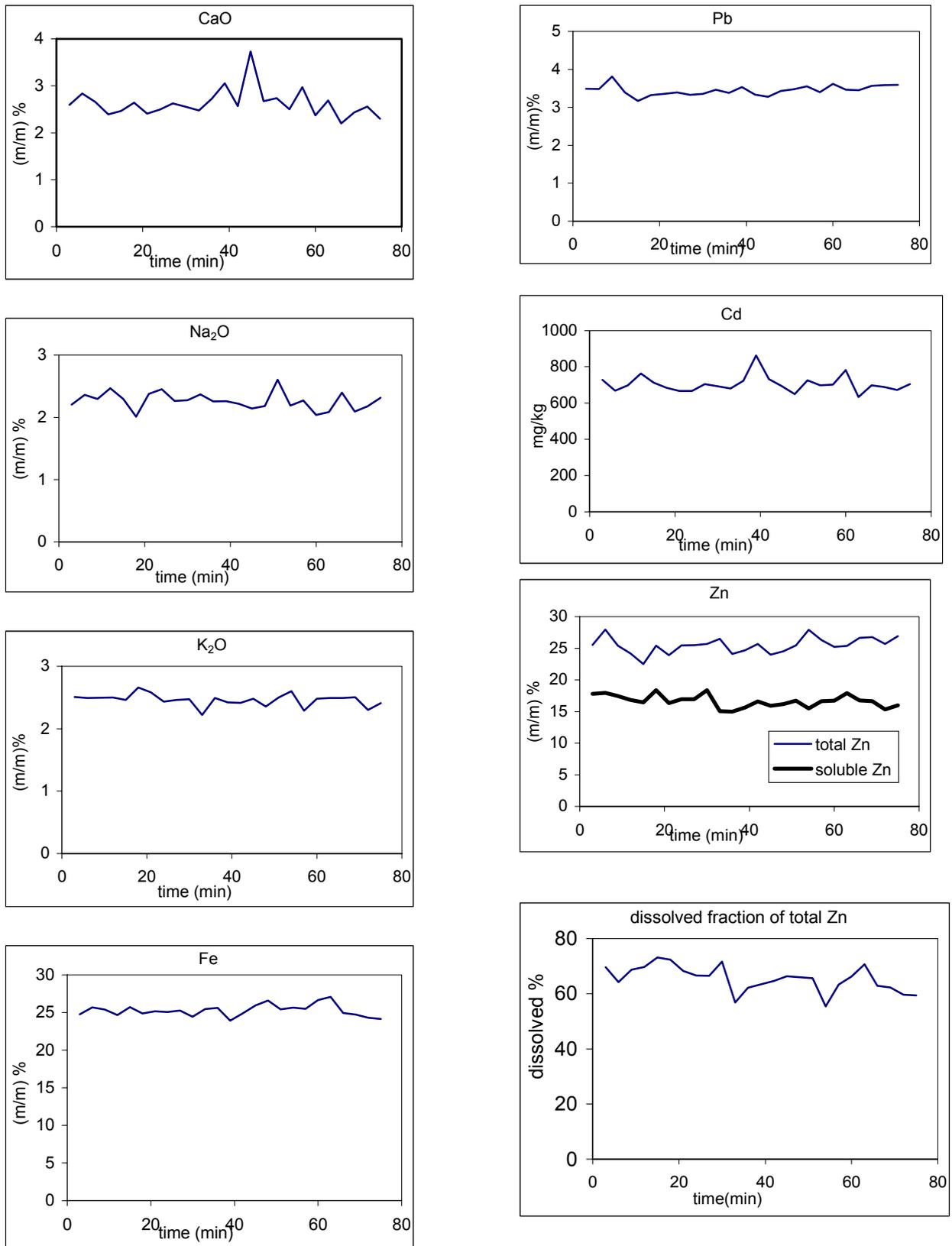


Figure 1: Changes of the concentration of the observed components and the soluble fraction of Zn during a charge-time
 1. ábra: A vizsgált komponensek koncentrációjának és a cink oldható bányadának változása az adagidő során