ZINC RECOVERY FROM INDUSTRIAL WASTE BY MEANS OF HYDRO- AND PYROMETALLURGICAL PROCESSES

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Abstract

The study reports the results of laboratory investigation to develop the method of the recovery of zinc in either a metallic or oxide form from production waste containing about 70% Zn and the compounds of Fe, Cd, Cu and Mn. Laboratory tests were conducted in two directions using, respectively, a pyrometallurgical method and a hydrometallurgical method. The scope of the investigation encompassed the obtaining of zinc oxide on the induction furnace extraction filters, while for the hydrometallurgical processes - leaching, electrolysis and solvent extraction. The most effective method has been considered to be leaching with a 1M HCl solution, because of the highest Zn concentration after the electrolysis process and a low level of process difficulty.

Keywords: Metallurgy, recovery, zinc, leaching, electrolysis

1. INTRODUCTION

Rapid depletion of natural resources which can be used for obtaining metals is observed in the recent years. Taking into account the occurrence of natural metal ores, their availability and possibilities of exploitation, one can distinguish the critical metals, i.e. metal which availability is necessary for advanced technologies, but is sensitive to political influences or economic fluctuations of supply. The group of critical metals includes e.g. indium, magnesium, rhenium, beryllium, antimony, gallium, cobalt, rare earth metals, or metals of platinum group.

However, the growing demand for metal products requires searching for other sources of metals, e.g. waste materials, even in the case of non-critical metals, and the quantity of industrial waste increases year by year, making its utilization necessary. Therefore the necessity of employing the metal recovery technologies forces the research studies on waste utilization in order to recover as large amounts of metals as possible.

The waste materials which can be a source of metals include scrap metal, used batteries and storage cells, cathode ray tube (CRT) glass, automotive catalytic converters, as well as production waste such as dust, slime, etc. [1, 2].

During the production of steel in arc furnaces, there arises the so-called electric arc furnace dust (EAF dust) in the amount of about 10 to 20 kg for each tonne of the produced steel. EAF dust contains mainly such metals (or their oxides) as zinc, cadmium, iron, lead, chromium, manganese. The dust can be subjected to pyro- and hydrometallurgical processes in order to recover mainly the metallic zinc. The choice between the pyrometallurgical and the hydrometallurgical zinc processing is imposed by the dust properties, including e.g. particle size, the quantity of valuable elements or mineral phases, which can indicate the number of components.

The process of pyrometallurgical zinc recovery consists in accumulation of zinc oxide and its reduction to the metallic form with the carbonaceous material [3, 4]. The following pyrometallurgical processes are in use: the process in the shaft furnace, in the arc furnace, and in horizontal or vertical retort. The negative side of these processes is the huge energy consumption and the disadvantageous influence to the environment.

The basic problem in hydrometallurgical processes is the selection of the leaching agent, which depends on the form of the processed waste. The leaching agent is chosen in such a way that it would elute either the required metal or the remaining material. The typical hydrometallurgical process consists of three stages. During the first stage (leaching) metals pass into water solution - in the possibly selective way - due to reactions with the leaching agent, e.g. inorganic or organic acid [5-8], strong base [9], or other compound. The processes using acids elute metals very effectively, but unfortunately their action is not selective, therefore also the undesirable metals as e.g. iron pass into the solution. Moreover, acid solutions harmfully affect the metallurgical equipment.

The following stage is separation of dissolved metals. It can be done by the liquid-liquid extraction [10-14], ion exchange, cementation, or the processes of transport of metal ions across liquid membranes. This stage allows for obtaining either pure metals (e.g. by means of the electrolytic process) or their compounds. The electrolytic deposition of zinc on the industrial scale is held with use of aluminium cathode and lead-silver anode (or reversely in the Tainton process). The zinc sulphate solution is used. As the electrolysis proceeds, zinc content in the solution decreases, and the sulphuric acid content grows. Zinc is deposited on the cathode.

The work presents the results of investigation on the attempt of zinc recovery from steelmaking dust containing also other metals, namely Fe, Cd, Cu, Pb, Mn, and Cr. The undertaken attempt employed both pyro- and hydrometallurgical methods.

2. ANALYSIS OF THE RESEARCH MATERIAL

According to the information provided by its supplier, the test material contains a considerable quantity of metallic zinc. The laboratory-scale tests were aimed to determine the possible methods of zinc or zinc oxide separation from the production dust. Hence, two testing directions were planned: the first of them, pyrometallurgical, was aimed at obtaining zinc oxide, and the second one, hydrometallurgical, including leaching, electrolysis and solvent extraction, was to obtain metallic zinc. The research material in the form of dust was subjected to grain analysis by means of Infrared Particle Sizer L (IPS-L) analyser, and the obtained results are presented in **Figure 1**.

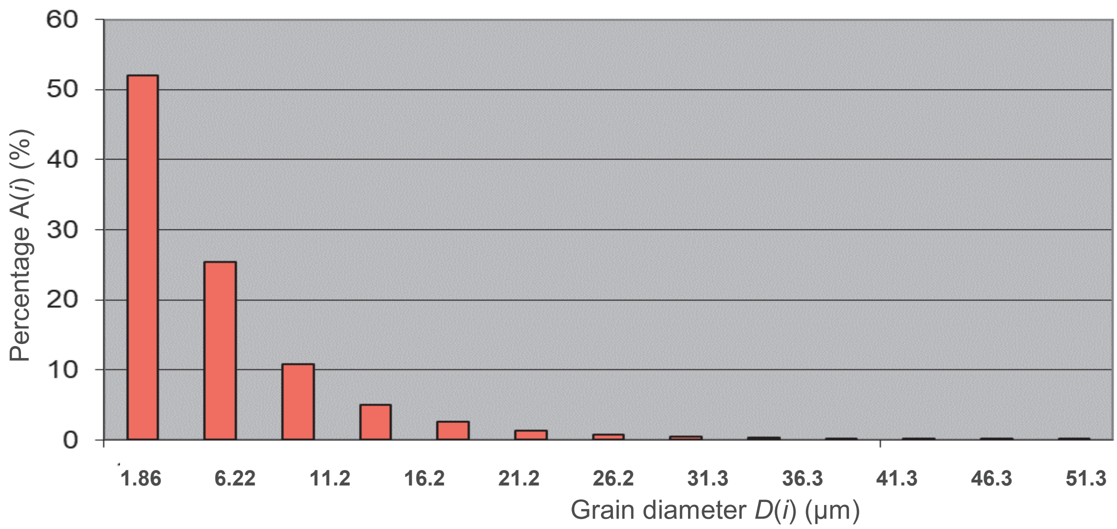

Figure 1 Percentage distribution of particles in the research material

It was found that about 90 % of the research material exhibits the grain diameter less than 20 μm, and about 50 % is characterised by the grain diameter less than 2 μm.

The research material in the form of dust with an addition of reducing agent was melted in the induction furnace, in the graphite crucible. The weighted dust sample was mixed with fly ash using 0.5 weight part of fly ash for 1 weight part of dust, and the whole mixture was put into the graphite crucible of the induction furnace. The melting was continued until evaporation of zinc. The evaporated zinc in the form of zinc oxide was collected on the extraction filter of an induction furnace during melting in an oxidizing atmosphere. The zinc oxide was indicated by the white colour, as well as the evaporation temperature, i.e. approx. 907 °C. As a result of the melting, after evaporating the zinc, an alloy sample was obtained, which was made up of approx. 25 weight parts of the charge and 5 weight parts of the slag. The obtained alloy sample was analysed by means of the scanning electron microscope Joel JSM 6610LV (SEM). The results of examination are presented in **Table 1** and **Figure 2**.

Table 1 Chemical composition of the analysed sample

Element	(wt.%)	(at.%)
C	10.24	34.55
Si	0.38	0.55
Cr	0.19	0.15
Mn	0.61	0.45
Fe	88.59	64.30

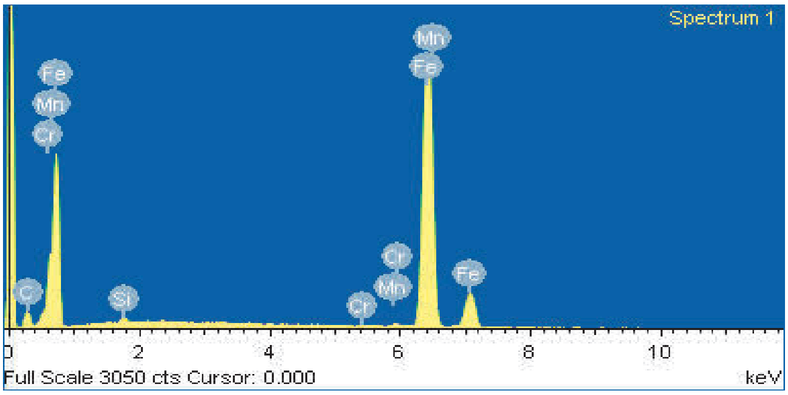

Figure 2 Characteristic X-radiation of precipitate in alloy

3. LEACHING PROCESS

Dust samples, each of mass equal to 10 g, were put into vessels and poured with 100 ml of the leaching solution, i.e. either HCl, or H_2SO_4, or HNO_3, or NaOH solution of concentration equal to 1 mol/dm^3. Time of the process duration was 180 minutes, and the temperature was 60 °C. The proportion of the solid phase (s) (mass of the treated material) to liquid phase (l) (volume of the reacting liquid) was equal 1:10 (kg/dm^3).

After the leaching process had been finished, samples of solutions were taken, diluted, and subjected to the analysis of metal concentration performed by means of Agilent MP-AES 4200 emission spectroscope, which uses microwave excited nitrogen plasma of the temperature equal to 5000 K for the purpose of exciting elements. The spectrometer is equipped with the Agilent 4107 nitrogen generator, taking nitrogen directly from the air supplied by a compressor. **Table 2** presents concentration of metals in the examined solutions after 3 hours of leaching, i.e. after completion of the process.

Table 2 Concentration of metals in solutions after the leaching process (mg/dm^3)

Leaching agent	Zn(II)	Cd(II)	Fe(II)	Cu(II)	Pb(II)	Mn(II)	Cr(II)
1M HNO_3	6500	6	521	35	722	145	9
1M H_2SO_4	22840	52	2967	59	17	421	33
1M HCl	29040	7	509	27	167	170	9
1M NaOH	134	0	0	0	533	0	0

It was observed that, beside zinc, also other metals occurring in the steelmaking dust are transferred to the solution. The analysis of the solution composition showed also the presence of iron, manganese, copper, cadmium, and chromium. The application of NaOH solution as a leaching agent resulted in large selectivity of the process, since only zinc and lead were dissolved under such conditions. Application of acids (HCl, HNO_3, H_2SO_4) caused the extraction of significantly greater amount of zinc, the relatively large amount of iron and manganese, and small quantities of other metals, i.e. lead, chromium, and cadmium.

4. ELECTROLYTIC PROCESS

The next stage of the study dealt with the electrolysis of solutions obtained by leaching processes without prior separation of various metal ions present in the solution. All the solutions obtained from leaching processes were subjected to electrolytic deposition. The aim of the process was to deposit metallic zinc on the cathode. Electrolysis was carried out at the temperature of 60°C for 180 minutes. Graphite electrodes were used. The current value was 0.2 A, the voltage was equal to 5 V. After completion of the process, the water solutions were again tested with respect to metal concentration. Results are given in **Table 3**.

Table 3 Concentration of metals in solutions after the electrolytic process (mg/dm^3)

Leaching agent	Zn(II)	Cd(II)	Fe(II)	Cu(II)	Pb(II)	Mn(II)	Cr(II)
1M HNO_3	6500	0	510	0	8	82	5
1M H_2SO_4	22790	2	2910	0	0	421	25
1M HCl	29100	0	486	0	5	165	3
1M NaOH	12	0	0	0	2.4	0	0

The results show that the selective leaching observed for the sodium hydroxide (NaOH) solution was followed by deposition of both dissolved metals on the cathode. They can be later separated by the pyrometallurgical processes.

For the first three solutions, based on nitric, sulphuric (VI), or hydrochloric acid, the analysis of composition of the solutions indicated that such metals as Cu, Pb and Cr were deposited on cathode, while ions of three other metals (Zn, Fe, and Mn) stayed in the solution. The next step was separation of these metals in the solvent extraction process.

5. SEPARATION OF Zn(II), Fe(II), AND Mn(II) IN THE SOLVENT EXTRACTION PROCESS

The analysis of the concentrations of metals in solutions after the electrolysis process (**Table 3**) showed the presence of the ions of Zn, Fe and Mn in acid solutions. For the process of separation, an HCl solution was selected because of the highest Zn ion concentration and a low level of process difficulty. The aqueous phase used for examination was the chloride solution obtained after the leaching process carried out with HCl solution and subsequent electrolytic removal of some metals (Cu, Pb, Cd, and Cr). The concentration of zinc, iron, and manganese in the examined solution was equal to 0.4, 0.01, and 0.002 mol/dm3, respectively. The organic phase was 2M solution of di-(2-ethylhexyl)phosphoric acid (D2EHPA) in kerosene, which is a selective extractant with respect to the dissolved metals. Both phases, 50 ml of each, were shaked for 15 minutes by means of the WU-4 laboratory shaker/vibrator (Premed, Warsaw) at the frequency of 200 vibrations per minute and the temperature of 20 °C and left for 24 hours. After that, both phases were separated and the water solution was again examined with respect to metal concentration.

The measured metal concentration values allowed for calculation of the extraction efficiency (%E) according to the **Equation 1**:

$$\%E = \frac{C_{i,aq} - C_{f,aq}}{C_{i,aq}} \cdot 100\%, \quad (1)$$

where $C_{i,aq}$ denotes the initial concentration of metal in the aqueous phase, while $C_{f,aq}$ is the final concentration of metal in the aqueous phase. **Figure 3** presents the results of examination.

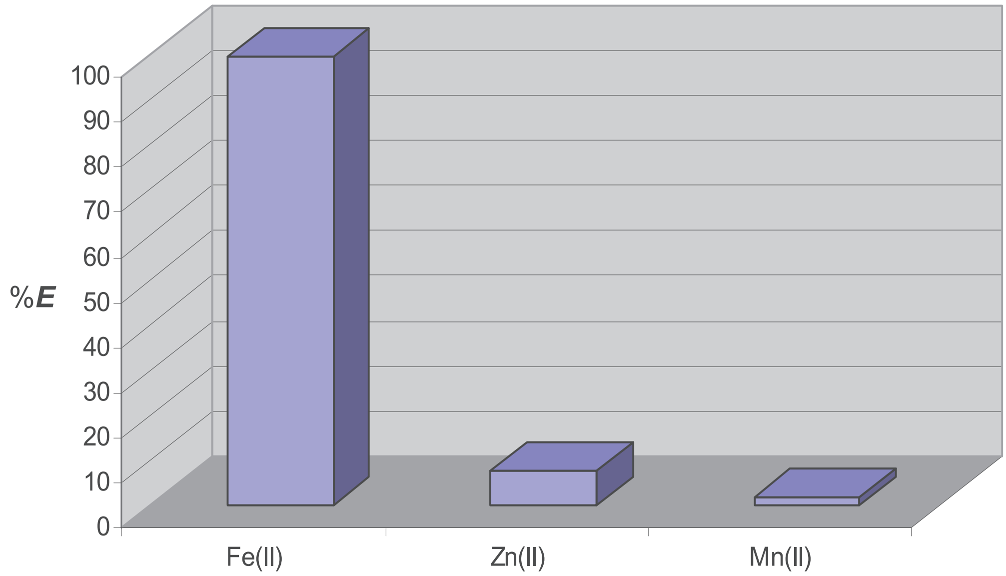

Figure 3 The efficiency of extraction of Zn(II), Fe(II), and Mn(II) ions from the chloride solution. The aqueous phase: chloride solution, pH -0.1. The organic phase: 0.5 M solution of D2EHPA in kerosene

It can be seen in **Figure 3** that the solution after extraction process contains zinc ions and trace amount of manganese. The iron ions were completely removed to the organic phase. Zinc can be then separated either by electrolysis or by precipitation of $ZnCO_3$ and its subsequent roasting leading to its chemical change into ZnO.

6. CONCLUSIONS

The carried out research work concerning the possibility of zinc recovery from the steelmaking dust allow to state that:

- The examined material was EAF dust of grain size less than 20 µm, containing as much as 70 % of zinc, the remaining part consisting of Fe, Cd, Cu, Pb, Mn, and Cr compounds, what was confirmed by the examination results.
- The solution containing NaOH exhibits selective leaching properties with respect to the analysed dust; only zinc and lead were dissolved under the experimental conditions. Application of acids (HCl, HNO_3, and H_2SO_4) resulted in the extraction of significantly increased amount of zinc, iron, and manganese, and also caused the dissolution of small amounts of other metals, i.e. Cu, Pb, Cr, and Cd in the aqueous solution.
- The selective action of NaOH solution made possible the deposition of Zn and Pb on the cathode during the electrolysis. Further separation can be done by the already known pyrometallurgical methods.
- Zinc can either be separated from the analysed solutions by electrolysis or precipitated in the form of $ZnCO_3$ by means of a selective extractant, which in turn can be roasted to obtain ZnO.

- Zinc recovery by the hydrometallurgical methods requires more stages, i.e. leaching, electrolysis, liquid-liquid extraction, repeated electrolysis or precipitation, but it allows also for recovery of metals other than zinc, which are present in the considered dust. The hydrometallurgical methods are less expensive and less detrimental to the environment.

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