

*Original Research*

# Leaching of Zinc Ash with Hydrochloric Acid Solutions

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## Abstract

Fine-grained fraction (<1.25 mm) of industrial zinc ash was characterized in terms of chemical and phase compositions as well as leaching behaviour in hydrochloric acid solutions. Waste product contained about 55% Zn, 14% Cl, and less than 0.4% of other metals (Fe, Pb, Al, etc.). It was a mixture of metallic zinc, simonkolleite, zinc oxide, and zinc hydroxide chloride. Dissolution of metals from the zinc ash was determined depending on the solid-to-liquid ratio (1:80-1:20), acid concentration (0.23-2.0 M), and temperature (20-60°C). The best results (almost 100% zinc recovery) were obtained for 2M HCl at 20°C, S:L ratio 1:20, and leaching time 30 min. The final solutions were contaminated mainly by iron and lead ions (both below 0.15 g/L). Further treatment of the solution to obtain metallic zinc or zinc chloride was also proposed.

**Keywords:** hydrochloric acid, leaching, recovery, zinc ash

## Introduction

Waste zinc materials are critical and beneficial supplements to primary metal production [1]. Every year, more than 13 Mt of refined zinc is produced worldwide and it is estimated that recycled content in the product represents about 15% [2]. Zinc is recovered from various scraps and residues at all stages of production and use. The main secondary sources of the metal are [3-5]: sludges and tailings from the processing of some non-ferrous metals (e.g., lead, iron, copper), remelted zinc ingots or pigs, dust from electric arc furnace EAF and brass smelting, waste from hot dip galvanizing, spent batteries, and metallic scraps, etc. Zinc concentration in such materials ranges from 20-30 wt% in EAF dusts via 60-75 wt% in galvanizing

ashes, up to 92-95 wt% in zinc dust/overspray, and galvanization dross [6].

In recent years there has been a growing interest in the recovery of zinc from the waste produced during hot-dip galvanizing of steel [3]. Ashes with high content of the metal are formed by zinc oxidation at the molten metal surface and combustion of applied flux [7]. Zinc ash is collected under EWC catalogue number 11 05 02 [8] and is commonly sold as a secondary raw material for further processing by melting in a rotary furnace [3, 7]. Alternatively to the pyrometallurgical treatment, hydrometallurgical methods for zinc recovery were also proposed [3]. It was reported that sulfuric acid [9-13] can be useful for leaching of the zinc ash, while sodium hydroxide is selective for zinc dissolution from crude zinc oxide [3]. In turn, hydrochloric acid has not yet found any application, despite the fact that it is suitable for treatment of materials with high chlorine content [14]. Average chlorine concentration in the zinc ash from hot-

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dip galvanizing (HDG) ranges (in wt%) from 0.4-1.5% [10, 11, 14, 15] to about 7-12% [12, 14], but as high as 20% also has been reported [9]. The element originates from the use of chloride fluxes ( $\text{ZnCl}_2\text{-NH}_4\text{Cl}$ ) in the galvanizing process [7]. Thus, chemical composition of the zinc ash involves a mixture of simonkolleite  $\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot\text{H}_2\text{O}$ , zincite  $\text{ZnO}$ , and  $\text{Zn}$  [9, 11, 12, 15]. More detailed studies also have identified the presence of oxidized Zn-Fe phases, aluminium silicate, and iron-manganese oxide [11-12, 16]. Dakhili et al. [17] investigated coarse particles separated from the zinc slag skimmed from the zinc bath, indicating metallic zinc,  $\text{ZnO}$ ,  $\text{ZnCl}_2$ , and  $4\text{ZnO}\cdot\text{ZnCl}_2\cdot\text{H}_2\text{O}$  as main constituents.

The presence of chlorine in the raw material and, further, in typical acidic sulfate leachate leads to some problems during subsequent zinc electrowinning [18]. To overcome this complication, washing of the ash with distilled water and sodium carbonate [19-20] or pyrometallurgical pre-treatment [20] were proposed. No total elimination of chloride ions from the raw material was obtained, but results indicated that a combination of the roasting followed by alkali wash treatment could be useful in the removal of chlorides [20].

A simpler method applies direct leaching of the zinc ash with hydrochloric acid solutions, having high ability to dissolve zinc compounds. Therefore, the aim of the present work was to find optimal conditions for zinc recovery from the HDG zinc ash. The influence of HCl acid concentration, solid-to-liquid ratios, and temperature on the efficiency of zinc leaching was determined. The leaching stage can be followed by solvent extraction at the purification stage [21-22], and final zinc electrowinning from the chloride bath [23-24].

## Materials and Methods

Zinc ash used in this study originated from an industrial dry batch hot-dip galvanizing process. It was fine-grained oxide fraction with grain diameters

below 1.25 mm. Elemental composition of the material was determined using classical wet analysis by means of atomic absorption spectrometry (AAS, Varian AA-20 ++). Quantitative phase analysis was performed using a Segert x-ray diffraction analyzer (XRD 3003 PTS XG) with a 3D goniometer with a PSD detector (Co lamp providing x-rays with a wavelength of 1.78 Å). Zinc ash was subjected to microscopic study using a SEM TESLA BS 340 scanning electron microscope linked to an Oxford Instrument LINK ISIS 300 EDX microanalysis system.

Leaching of the zinc ash was carried out in a glass beaker immersed in a water bath at temperatures of 20-60°C. Hydrochloric acid solutions (400 cm<sup>3</sup>) of various concentration (0.25-2.0 M) were used as a leaching medium. Different solid-to-liquid ratios (1:80, 1:40, 1:20; S:L in g/cm<sup>3</sup>) were chosen in this experimental study. The suspension was agitated with a mechanical stirrer at constant rate (300 rpm). Leaching time was 90 min. During the process, samples of the electrolyte were taken periodically to determine concentrations of metal ions (AAS method).

## Results and Discussion

### Characterization of Zinc Ash

Zinc ash from an industrial source was a powdery mixture of various compounds. The fine-grained fraction contained about 55% Zn, 14% Cl, 0.3% Fe, 0.4% Al, 0.3% Pb, and less than 0.05% of other elements (Cd, Cu, Si, Mg). Other elements such as Ni, C, O, and Bi, etc., can also be found in the zinc ash samples. Detailed analysis of a few samples of the fine-grained fraction (Table 1) showed some inhomogeneity of the waste, which consisted of particles of high and low zinc (50-80%) and chlorine (6-25%) contents, while percentages of other elements were practically at the same levels. Chemical analysis was made from eight

Table 1. Chemical analysis of fine-grained fraction of zinc ash.

Fine-grained fraction (d < 1.25 mm)										
Measurement	Chemical element (wt%)									
	Zn	Fe	Pb	Al	Cd	Si	Cu	Mg	Cl	Residue
1	50.1	0.42	0.32	0.43	<0.01	0.03	0.02	0.02	21.23	27.43
2	53.8	0.29	0.32	0.43	<0.01	0.05	0.01	0.01	17.73	27.36
3	67.7	0.31	0.32	0.44	<0.01	0.03	0.02	0.02	14.18	16.98
4	50.8	0.41	0.27	0.47	<0.01	0.03	0.02	0.01	24.82	23.17
5	62.8	0.48	0.33	0.46	<0.01	0.02	0.01	0.01	17.73	18.16
7	88.0	0.29	0.33	0.36	<0.01	0	0.01	0.01	5.67	5.33
8	67.9	0.48	0.26	0.26	<0.01	0.02	0.03	0.02	13.23	17.79
Average	55.14	0.34	0.29	0.36	<0.01	0.02	0.02	0.01	14.32	17.02

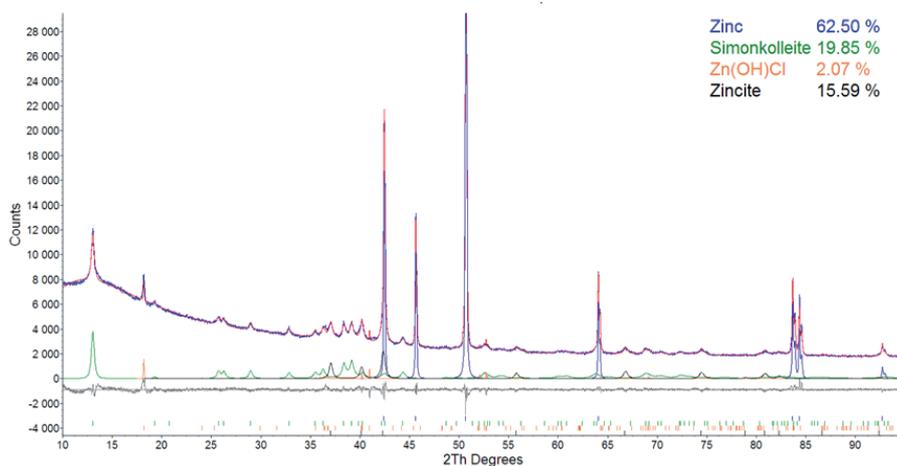


Fig. 1. XRD pattern of the fine-grained fraction of the zinc ash.

particular samples of fine-grained fraction of zinc ash (Table 1) with the aim to achieve average values of element contents.

Phase analysis of the ash (Fig. 1) indicated the presence of metallic zinc as a main component (62.5%), while comparable percentages of zincite ZnO (about 20%) and simonkolleite  $Zn_3(OH)_8Cl_2 \cdot H_2O$  (16%) were found. A low fraction of zinc hydroxide chloride Zn(OH)Cl (2%) was also identified. Obtained results are close to those reported by Bakarar [15], who showed that metallic zinc is the major constituent (76%) of the coarse fraction (+0.9 mm, with total 94% Zn) of the zinc ash, while the fine-grained portion of the material (-0.9 mm, with total 79% Zn) was depleted in zinc (64%). Chlorine content in both particle fractions was similar ( $0.40 \pm 0.05\%$ ). In turn, Dvořák and Jandová [9] found chemical compounds as main phases (63% simonkolleite and 31% zincite) in the ash, while the metallic fraction represented only 6% (zinc). However, it should be emphasized that the material contained about 75% Zn and 20% Cl, while the fraction of the ash particles with a diameter above 1 mm was 21 wt%. Takáčová et al. [14] determined chemical composition of unsorted

(78% Zn and 12% Cl) and several fractions of the zinc ash originated from dry batch HDG. It was found that the increase in the grain size from below 0.125 mm to above 0.6 mm was accompanied by a gradual enrichment in zinc from 63% to 86%, and a small decrease in the chlorine content (16% to 13%). Analysis of the data shows that despite similar general phase composition of the zinc ash originating from hot-dip galvanizing, the percentage of contents of particular phases are quite different, depending on the elemental composition of the material and its granulation.

The morphology of the ash particles is shown in Fig. 2. They were rather porous and characterized by an oval shape. Results of semi-quantitative EDS analysis from the marked points (JF 1-3) are presented in Table 2. Composition of the grains showed somewhat higher contents of zinc and aluminum than were found during wet chemical analysis, but confirmed chlorine and iron percentages. However, it is necessary to mention that determining the percentage of light elements (like oxygen) by EDS analysis from a non-flat surface is not quite reliable.

## Leaching

The zinc ash was leached in HCl solutions at different temperatures using various solid-to-liquid ratios. The sample for leaching experiments was withdrawn from homogenized fine-grained fraction of the zinc ash (without any relation to samples 1-8 shown in Table 1), and the acquired average values of chemical analyses (Table 1) were used for subsequent calculations.

Figs 3-5 show the changes of the recovery of metal ions from the raw material. It was found that the Zn dissolution reached almost constant levels after about 30 min of the process (Fig. 3), while extending the leaching promoted the transfer of the impurities (mainly Pb and Cu) to the bath (Fig. 5). The highest zinc extraction was achieved in 2M HCl independently on S:L ratios, reaching over 95-99%.

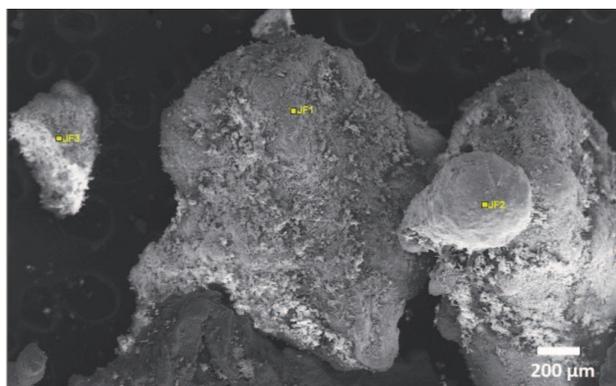


Fig. 2. Morphology of particles of fine-grained fraction of zinc ash.

Table 2. Results of EDS point analysis of zinc ash particles (Fig. 2).

Mark	Chemical element (wt%)							
	Zn	Al	Cl	Si	K	Mn	Fe	O
JF1	72.88	1.33	17.87	0	0.37	0.32	0.74	6.50
JF2	77.35	1.66	13.81	0	0	0	0.40	6.78
JF3	73.11	1.15	16.78	0	0	0.44	1.33	7.19

It was also found that increases in the temperature enhanced dissolution of the ash, but this effect was especially visible for HCl concentrations of below 1M (Fig. 4). For example, for 0.25 M HCl at the S:L ratio of 1:20 rising of the temperature from 20-60°C improved total recovery of zinc 20-53%, while at the S:L ratio of 1:80 it was 57-82%. In turn, for 1M and 2M acid solutions, final extraction of zinc was less affected by temperature, but it was governed rather by the S:L ratios. Therefore, values of about 92% for 1:80 and about 98% for 1:40 were obtained in 1M HCl (20-60°C), while for 1:20 ratio more evident changes of the zinc dissolution were observed (from 66% at 20°C to 97% at 60°C).

It is clear from the kinetic curves that 2M HCl and a temperature of 20°C are the most optimal conditions for zinc recovery, since high dissolution of the material is achieved without no additional heating of the system. Based on the above facts, the S:L ratio of 1:20 and leaching time of 30 min were selected as the best parameters.

Kinetics of the leaching of other metals present in the ash was studied under optimal conditions. Four metals were chosen: Fe, Al, Pb, and Cu based on the chemical composition of the solid and in terms of their possible influence on zinc dissolution. The kinetic curves for these impurities are shown in Fig. 5. We observed that

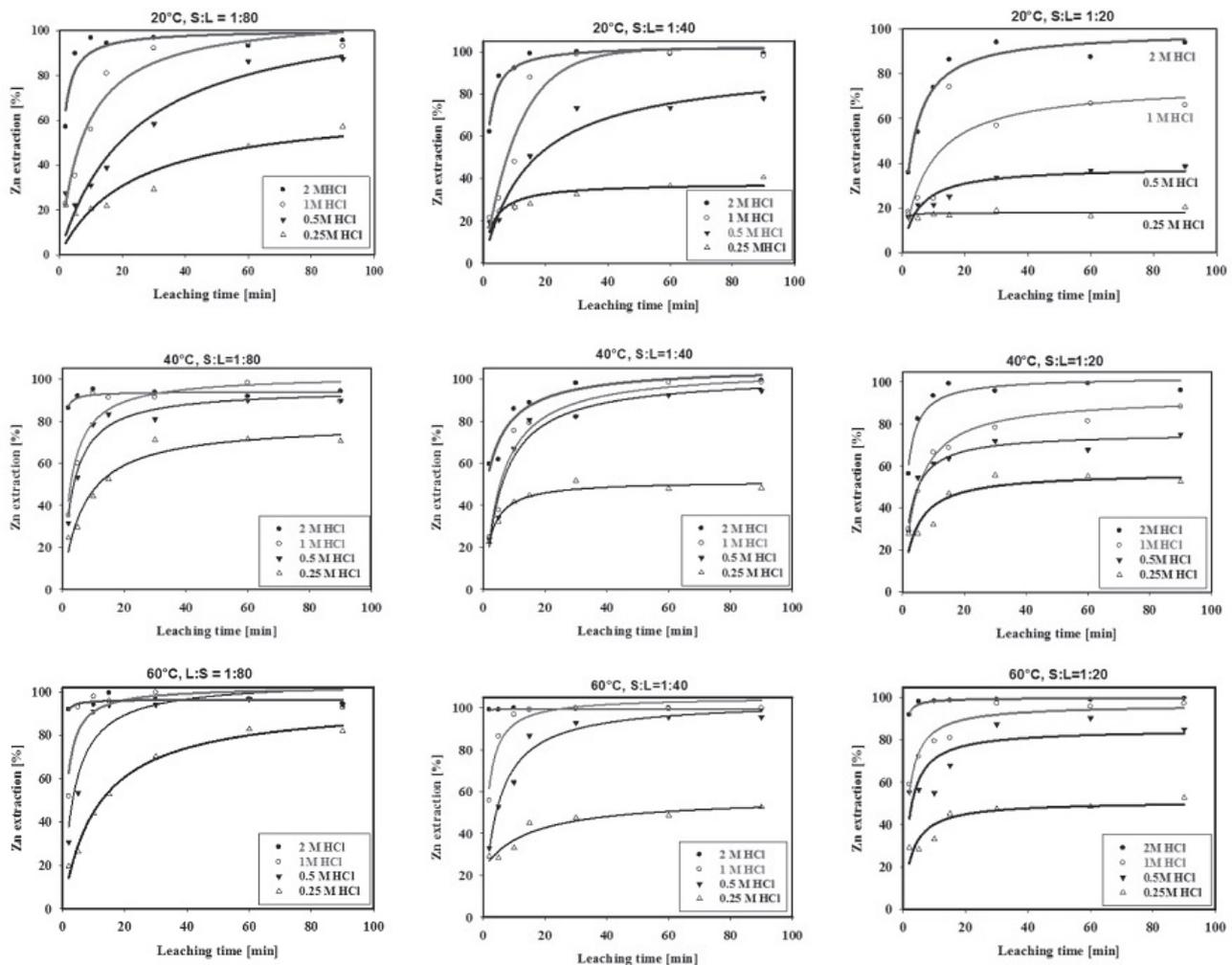


Fig. 3. Influence of HCl concentration, temperature, solid-to-liquid ratio, and time on efficiency of zinc leaching from ash.

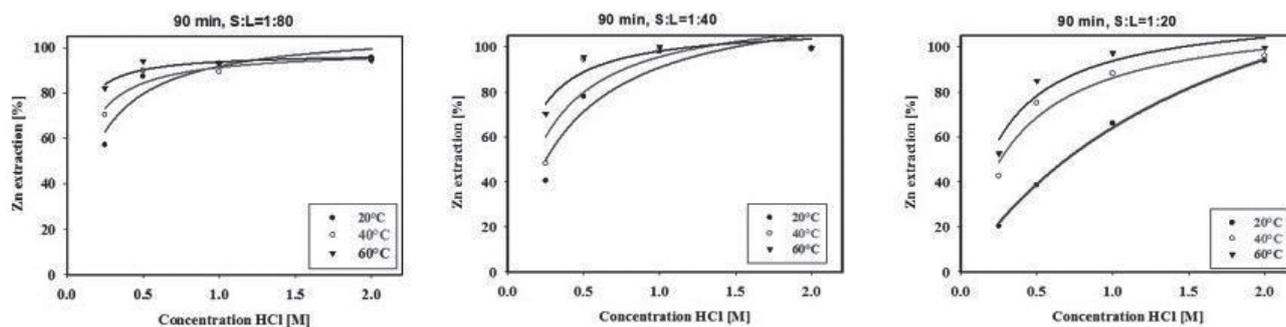


Fig. 4. Influence of HCl concentration, temperature, solid-to-liquid ratio, and time on final efficiency of zinc leaching from ash (after 90 min).

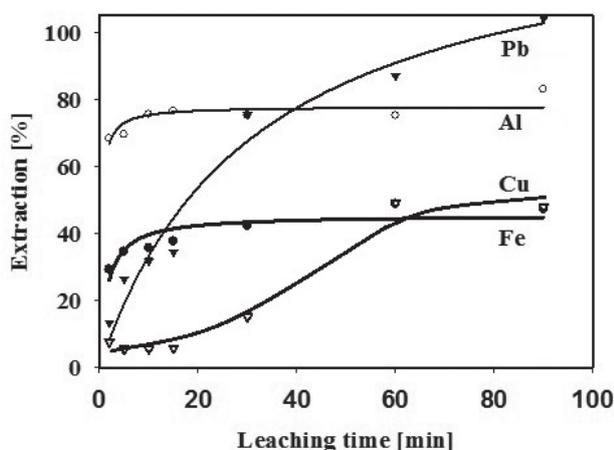


Fig. 5. Efficiency of Fe, Al, Pb, and Cu leaching from zinc ash (2M HCl, 20°C, S:L = 1:20).

dissolution of aluminum and iron compounds stabilized after about 20 min, corresponding to approximately 78% and 40% recovery, respectively. In turn, the continuous transfer of lead ions to the bath was observed and after 90 min practically all amount of lead was present in the solution. Other behaviour was observed for copper. In this case, the transfer of ions from ash was hindered at the initial period of the process, but it started after 20 min, reaching a constant final level of about 45%

after 60 min. The kinetic curves presented in Fig. 5 show that the ash contains some phases resistant to the action of HCl solution, and that some non-ferrous metals remained in the solid residue, despite the fact that they can form soluble chlorides or chloride complexes. It is useful for further treatment of the bath. Low content of the impurities in the raw material combined with low leaching efficiency results in their low concentrations in the leachate (below 0.15 g/L for Fe and Pb, below 0.1 g/L for Al and about 5 ppm Cu). Therefore, purification of the electrolyte before zinc electrowinning seems to be not problematic.

Fig. 6 shows correlation among leaching parameters and final concentrations of zinc ions in the solution. We observed that for the S:L ratio of 1:80 there was no significant change in the Zn content in the leachate with increased acid concentration and temperature, thus the final metal ion concentrations were 8-10 g/L. Twice higher content of the raw material in the lixiviant practically twice increased the Zn(II) concentration in the solution, but for HCl concentrations 1-2M the values were similar. The most clear changes were observed for the S:L ratio of 1:20, where a gradual increase in the zinc concentration in the solution was observed with both acid amount and temperature. The highest Zn(II) concentrations (40-50 g/L) were found for the leaching conducted with 2M HCl. This confirms that the most concentrated leachant used in this study gave the best leaching results.

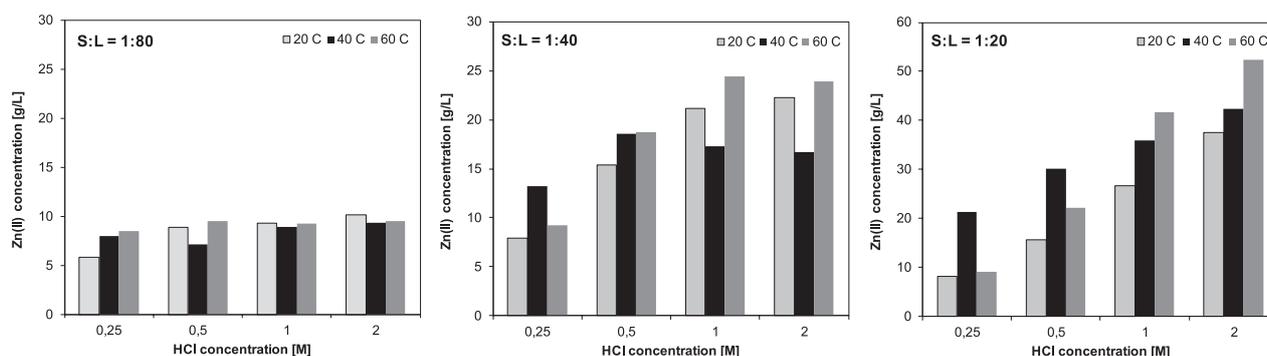


Fig. 6. Influence of HCl concentration, temperature, and solid-to-liquid ratio on final zinc ion concentrations in the solution (90 min).

### Further Treatment of the Solution

Analysis of the obtained results shows that leaching of the zinc ash in the HCl solutions results in the formation of acidic zinc chloride solutions (up to 40-50 g/L Zn(II)) contaminated mainly by iron and lead ions (both below 0.15 g/L). Simulation of the bath speciation (HySS 2009 software) using a stability constant of zinc complexes [25] shows that all metal ions are present as simple cations (not as chloride complexes) in the solutions of pH below 3.5. The presence of iron ions is usually disadvantageous for metal electrowinning stage due to possible reduction from Fe(III) to Fe(II) at the cathode and Fe(II) to Fe(III) oxidation at the anode. The cathodic reaction of Fe(III) results in a decrease in the current efficiency of the zinc electrodeposition. In turn, lead ions do not show a negative effect on the zinc electrowinning due to high hydrogen overpotential on metallic lead [26].

To prevent any problem during zinc electrodeposition [27], solvent extraction can be used to purify the bath [28]. Literature data [29] shows that Kelex 100 can remove Fe(III) ions from acidic chloride solutions (pH 0-1), remaining zinc ions in the aqueous phase (extraction of zinc occurs at pH above 5). More recent studies showed good applicability of novel hydrophobic extractants for removing iron [30] and lead [31] ions from zinc chloride solutions.

Electrowinning of zinc from acidic chloride solutions is often proposed as an alternative to the electrolysis carried out using traditional sulfate electrolytes. Higher solubility and higher electrical conductance of the zinc chloride bath as well as fast zinc deposition rate with cathodic current efficiencies over 90% are very advantageous from an economical point of view [23-24]. However, the evolution of chlorine gas at the anode is often mentioned as problematic [32-33]. This may be overcome by separation of anode and cathode compartments with membranes [24, 34].

Finally, as an alternative, zinc chloride can be produced from the acidic chloride solution [35] and can be obtained by crystallization method by heating under vacuum followed by further purification by recrystallization using some organic solvents (e.g., acetone) [36].

### Environmental Aspects

The zinc ash originating from the hot dip galvanizing process contains a high percentage of zinc and can be used as a source of secondary metal [10]. This is especially important in view of current zinc production and supply [2] showing increasing global demand for metals together with the decreasing production of metals from ores [37]. Thus the recovery and reuse of the metals from the wastes are important from both environmental protection and economic points of view [38]. In Europe, steady improvement in waste treatment and reduction of impact from waste disposal, growing rates of waste

recycling, and efficient recovery of energy from the remaining waste is observed [39]. The European Union and domestic regulations on collection, recycling, and transboundary transport [40] reviewed the status of the zinc ash and there was a recommendation with the United Nations Conference on Trade and Development that zinc ash should not be dangerous goods. Presently, zinc ash is considered not to be hazardous waste only if it has no unsafe characteristics and does not develop flammable gases in contact with water [41]. The hydrometallurgical treatment of zinc ash proposed in this paper is comparatively clean and can be adapted in small- and medium-scale industries. It can allow us to produce metallic zinc for reuse in hot dip galvanizing or zinc chloride as an excellent source of zinc in liquid fertilizer.

### Conclusions

Fine-grained fraction of zinc ash with particle diameter below 1.25 mm was used in this study. Industrial waste product originated from the hot-dip galvanizing process. The main elements in the material were Zn (55%) and Cl (14%) in the form of metallic zinc, simonkolleite, zinc oxide, and zinc hydroxide chloride. Dissolution of zinc was determined as a function of solid-to-liquid ratio (1:80-1:20), acid concentration (0.23-2.0 M), and temperature (20-60°C). The optimal leaching conditions (almost 100% zinc recovery corresponding to 40 g/L Zn(II) in the leachate) were obtained for 2M HCl, 20°C, S:L ratio 1:20. The final solutions were contaminated mainly by iron and lead ions, but their concentrations were below 0.15 g/L.

Further treatment of the final solution was also proposed. It includes removal of the impurities using solvent extraction and subsequent zinc electrowinning from acidic chloride electrolyte or the production of zinc chloride by crystallization.

Finally, it should be noted that recycling secondary raw materials represents a crucial part of industrial response in both developed and developing countries. The characteristic pollution caused by solid wastes and useful components that can be recovered from such resources come down in favor of production of metals or valuable compounds from secondary materials.

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