

PRELIMINARY INVESTIGATION ON LEACHING BEHAVIOR OF ZINC ASH

Oxide fraction of industrial zinc ash from hot dip galvanizing was characterized in terms of composition and leaching behaviour in 10% sulfuric acid solution. Waste product contained about 68% Zn, 6% Cl, 3% Al, 1% Fe, 0.7% Si, 0.5% Pb and minor percentages of other metals (Mn, Cu, Ti etc.). It consisted mainly of zinc oxide contaminated with metallic zinc, zinc hydroxide chloride and silica. Dissolution of the metals from the material was determined as a function of solid to liquid ratio (50-150 kg/m³), temperature (20°C and 35°C) and agitation rate (300 and 900 rpm). The best results (50 g/dm³ Zn(II) at 78% zinc recovery) were obtained for 100 kg/m³ and the temperature of 20°C. Increase in the agitation rate had weak effect on the zinc yield. The final solutions were contaminated mainly by Fe(II, III) ions. Leaching of the material was an exothermic process with the reaction heat of about 800 kJ/kg.

Keywords: zinc ash; hydrometallurgy; leaching; recovery

1. Introduction

Zinc provides usually 50 to 75 years of corrosion protection of iron and steel in many environments [1]. Empirical data collected about hot-dip galvanized steel performance in environments ranging from industrial via marine to suburban and rural indicate that zinc can prevent corrosion of the underlying steel more than other surface treatments as it corrodes at a rate about 1/30 of that for iron. It was estimated that the application of 30-70 kg of zinc (requiring 125-300 kWh of energy to make) can prolong the life of one tonne of steel products (requiring 2,500 kWh to make) by a factor of three to five times [2]. Zinc coated steel is commonly used in indoor and outdoor atmospheres, fresh or sea water, soils, concrete, and/or in contact with other metals, treated wood, at extreme temperatures as well as for the storage of hundreds of different chemicals [1,3,4].

Every year about 50% of total refined zinc is consumed for steel galvanizing [3,4]. The substrate can be coated using various processes, e.g.: hot dip galvanizing, electroplating, spray metalizing, sherardizing [4]. Hot dip galvanizing (HDG) is known for more than 250 years. Basically, it is the process of immersing of fabricated steel or iron into a kettle with a bath of molten zinc (or zinc alloy). The bath chemistry is specified by standards (e.g. PN-EN ISO 1461:2011, ASTM B6), and requires at least 98% pure zinc maintained at the temperature of 445-455°C [5]. Other bath constituents are: lead (to reduce surface tension of the bath, 0.6-0.8%), nickel (to improve molten zinc fluidity, 0.05-0.06%) and aluminum (for coating shine, 20-50 ppm) [6].

While immersed in the kettle, zinc reacts with iron in the steel to form a series of zinc-iron intermetallic alloy layers [7]. Once the fabricated items' coating growth is complete, they are withdrawn slowly from the galvanizing bath, the excess zinc is removed and the final product can be further subjected to a finishing treatment.

The HDG process is accompanied by a generation of some wastes [5,6]. The main of these are bottom dross and top ash. Both are classified as not dangerous, unless they contain hazardous metals (lead, cadmium etc.) [8]. Zinc dross (95-98% Zn) represents about 7-11% of zinc consumption [6]. It forms due to chemical reaction between molten zinc and iron creating fine particles of Fe-Zn intermetallic compounds [7]. Dross particles are slightly denser than molten zinc and settle to the bottom of the galvanizing bath. The residue is sellable and can be recycled (e.g. to zinc oxide) due to high zinc content. Zinc ash (60-85% Zn) is produced on the bath surface as a result of natural oxidation of molten zinc in the contact with air oxygen. It consists of crude zinc oxide, but contains also 10-25% of zinc lumps, iron and aluminum oxides and chloride/oxy-chloride residues originating from the steel pre-treatment stage (fluxing in a ZnCl₂-NH₄Cl mixture). Ash formation is normally 15-20% of total zinc consumption [6] and it is valuable material for zinc recovery.

Recycling of the HDG by-products allows to recover zinc as metal or other compounds and return them to the production cycle, thus reducing the primary metal supply and improving the environmental protecting [2,9]. Zinc dross and ash can be treated by both pyrometallurgical [10,11] and hydrometallurgical [12,13] methods. The latter are effective, economical, relatively

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clean and can be adapted in small or medium scale industrial plants. The literature data on the hydrometallurgical processing of the secondaries is rather limited and considers predominantly sulfuric [14-16] or hydrochloric [17,18] acids as basic leaching agents for zinc recovery from the zinc ash [13]. Sulfuric acid solutions can be effective for the zinc dissolution from the top ash. However, it is accompanied by a transfer of chloride ions making the leachate not suitable as the electrolyte for subsequent zinc electrowinning stage due to corrosion problems of aluminum and lead electrodes [19]. This may be overcome by pre-treatment of the ash with sodium carbonate [20], leaching with liquid organic phase containing cation exchanger [21], precipitation of zinc carbonate from the aqueous leachate followed by re-dissolution in sulfuric acid [15], purification of the leachate using ion-exchange resins [18] or application of novel corrosion resistant electrode materials for the electrolysis [22,23]. Alternatively, the zinc ash can be leached with acid chloride solutions, but no detailed procedures for final zinc recovery have been recommended yet.

The present work reports results of preliminary studies on hydrometallurgical behavior of the zinc ash originating from an industrial source. Currently, such waste is treated by domestic zinc producers or sold to foreign recyclers. The aim of the research was to determine the influence of solid to liquid ratio, stirring rate and temperature on the efficiency of zinc leaching with sulfuric acid and the degree of the leachate contamination. Obtained results will be helpful to develop further treatment procedure to produce zinc alloy suitable for re-use in hot dip galvanizing.

2. Experimental

The industrial HDP zinc ash was crushed and screened to remove zinc lumps leaving oxide fraction used in this investigation. Morphology of the powdery oxide-type sample was observed with a scanning electron microscope (SEM, Hitachi). Specimen was prepared by submerging the powder in a conduc-

tive carbon resin. General and detailed analysis of the elemental composition of the waste was executed using energy dispersive X-ray spectroscopy (EDS), while phase composition was determined by X-ray diffractometry (Rigaku MiniFlex diffractometer, $\text{Cu}_{K\alpha}$ radiation). Granularity of the powder was estimated during microscopic observations (optical microscope, Nikon).

The material was leached in 10% sulfuric acid H_2SO_4 at two temperatures (20 and 35°C) for 5h or 1h. 200 cm^3 of the acid and 50-150 kg/m^3 of the solids were used. The solution was agitated using a magnetic stirrer (300 rpm or 900 rpm). During the process samples of the electrolyte were taken periodically to determine concentration of the metallic ions using atomic absorption spectrometry (Solaar M5, ThermoElemental). pH of the solutions was measured before and after the process.

Thermal effect of the leaching was determined using calorimetric method. Measurements were performed using isolated glass container equipped with a magnetic stirrer (500 rpm). 100 kg/m^3 of the ash was added to 100 cm^3 of 10% H_2SO_4 of known mass and initial temperature. The temperature ($\pm 0.1^\circ\text{C}$) of the leaching system was monitored every 15 s, while the temperature change required to evaluate the heat released in the reaction was determined graphically.

3. Results and discussion

3.1. Characterization of zinc ash oxide fraction

Oxide fraction of the zinc ash was heterogeneous powder with particle diameter in the range from below 10 μm to about 900 μm (Fig. 1). It was a mixture of various compounds. EDS analysis carried out on the areas (about 0.7 mm^2) of the sample surface identified about 68% Zn, 21% O, 6% Cl, 3% Al, 1% Fe, 0.5% Pb and less percentages of other elements like Mn, Cu, Ti, S, (Table 1). More detailed point microanalysis showed some particles of high and low zinc content (Fig. 1a). Phase analysis (Fig. 2) combined with the EDS results proved the presence of zinc oxide (P1, P2) mixed with low fractions of zinc oxy-chloride

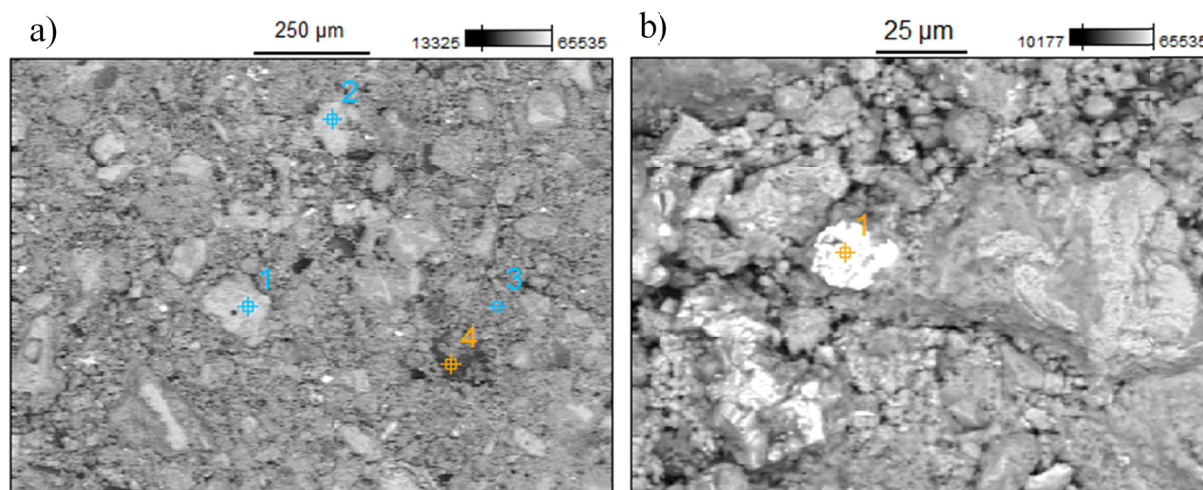


Fig. 1. Morphology of zinc ash oxide fraction

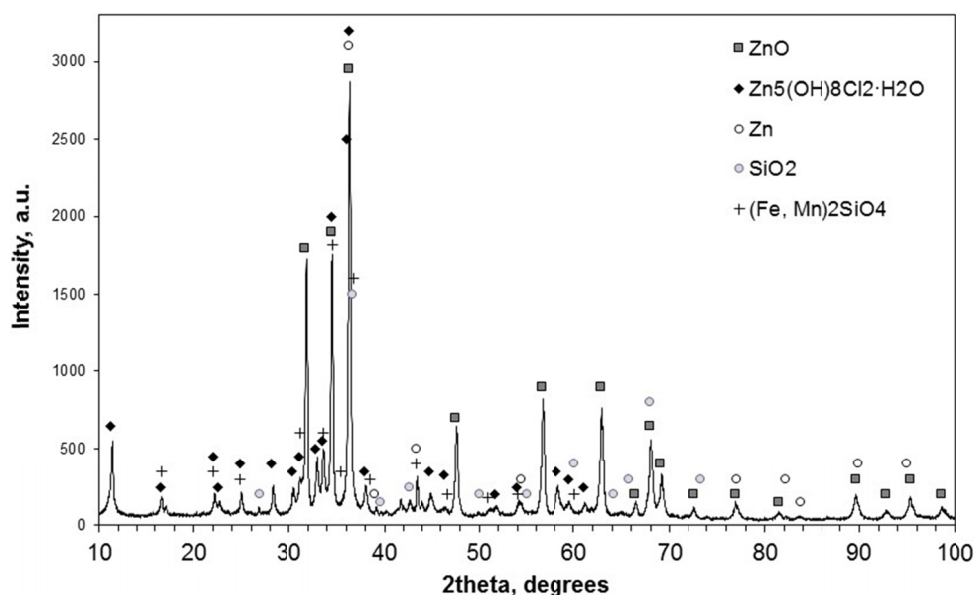


Fig. 2. Diffraction patterns of zinc ash

TABLE 1
General and detailed composition of the zinc ash (Fig. 1a)

Element	Composition, wt%				
	General	P1	P2	P3	P4
Zn	67.7	74.6	80.4	74.6	17.2
Pb	0.5	0	0	0	0
Fe	1.0	0.3	0.4	0.6	1.8
Al	2.7	2.6	—	1.0	9.6
Cd	0	0	0	0.1	0.2
Cu	0.1	0	0	0.1	0
Mn	0.3	0.5	0.1	0.4	1.8
Mg	—	—	—	—	0.4
Ca	0.3	0.2	0.2	—	—
Ti	0.2	—	—	—	—
Si	0.7	0.1	0.1	0.2	27.6
O	21.1	19.7	17.0	13.4	29.9
Cl	6.3	1.9	1.7	9.5	2.4
S	0.1	0	0.1	0	0.6
K	—	—	—	—	10.1

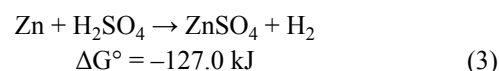
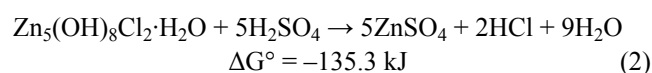
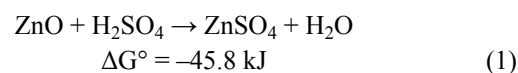
(P3) and metallic zinc. The point analysis confirmed also the presence of silicon oxide (P4). It resulted from the reaction of steel component with the molten zinc as silicon is the most reactive alloying element in structural steels [5]. It was also supposed that aluminum oxide and mixed iron-manganese oxide or silicate (P4) also occur in the material, but these were not evidenced in the diffraction pattern due to low phase contents and overlapping of the diffraction peaks (e.g. $(\text{Fe, Mn})_2\text{SiO}_3$ and $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$). Lead occurred as randomly dispersed oxidized particles (e.g. 50%Zn-30%Pb-10%Sn-5%Fe-5%O; point 1 in Fig. 1b) in the bulk of the material, since it forms a bottom layer in a galvanizing bath due to its low solubility in molten zinc. Contamination of the material with cadmium was low (below limit detection), but it was detected in some small particles of the powder.

Composition of the waste was very similar to the data reported in the literature (60-85% Zn, 2-12% Cl, 0.3-2.0% Pb, 0.2-1.5% Fe, up to 0.3% Al) [13]. Similarly, identification of

main zincous phases is confirmed by other authors [15,16]. Dvořák and Jandová [15] determined quantitatively percentages of the main compounds in the zinc ash of high chloride content (20% Cl). They reported 63% $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ (simonkolleite), 31% ZnO (zincite) and 6% Zn (metal). Takáčová et al. [17] investigated the phase composition of various particle fractions of the zinc ash (approx. 0.125-0.6 mm). It was found that coarse-grained fraction contained somewhat higher percentage of metallic zinc and zinc oxide and less amount of simonkolleite, than the fine-grained particles, where $\text{Zn}(\text{OH})\text{Cl}$ was also detected. Dakhili et al. [11] reported 52% Zn, 13% Cl, 4% Si, 3% Al, 2% Pb and 1.7% Fe in the form of Zn, ZnO, ZnCl_2 and $4\text{ZnO} \cdot \text{ZnCl}_2 \cdot \text{H}_2\text{O}$ as main phases in the coarse fraction of the slag skimmed from the zinc bath.

3.2. Leaching

The zinc ash was leached in H_2SO_4 . The acid attack on main phases can be described by the following reactions:



Thermodynamic calculations based on standard free energies of the individual compounds [24,25] show that all zinc forms can dissolve spontaneously in sulfuric acid.

Fig. 3 shows the changes of the concentration of metal ions in the solutions for different ratios of solid to liquid. It was found that the Zn(II) concentration in the lixiviate reached almost

constant levels after about 30 min of the process, while longer time stimulated only dissolution of the contaminations. At the bath loading of 50 kg/m³ final concentrations of zinc ions were the same (about 25 g/dm³), independently on the temperature used (20 and 35°C). Increase in the ash amount to 100 kg/m³ and 150 kg/m³ was accompanied by raising concentration of the

zinc ions to 50 g/dm³ and 73 g/dm³, respectively. In all cases the efficiency of the zinc dissolution was maintained practically on the same level (78.1% for 50-100 kg/m³ and 76.0% for 150 kg/m³).

The leachate was gradually enriched in other ash components during the dissolution. The main impurity of the

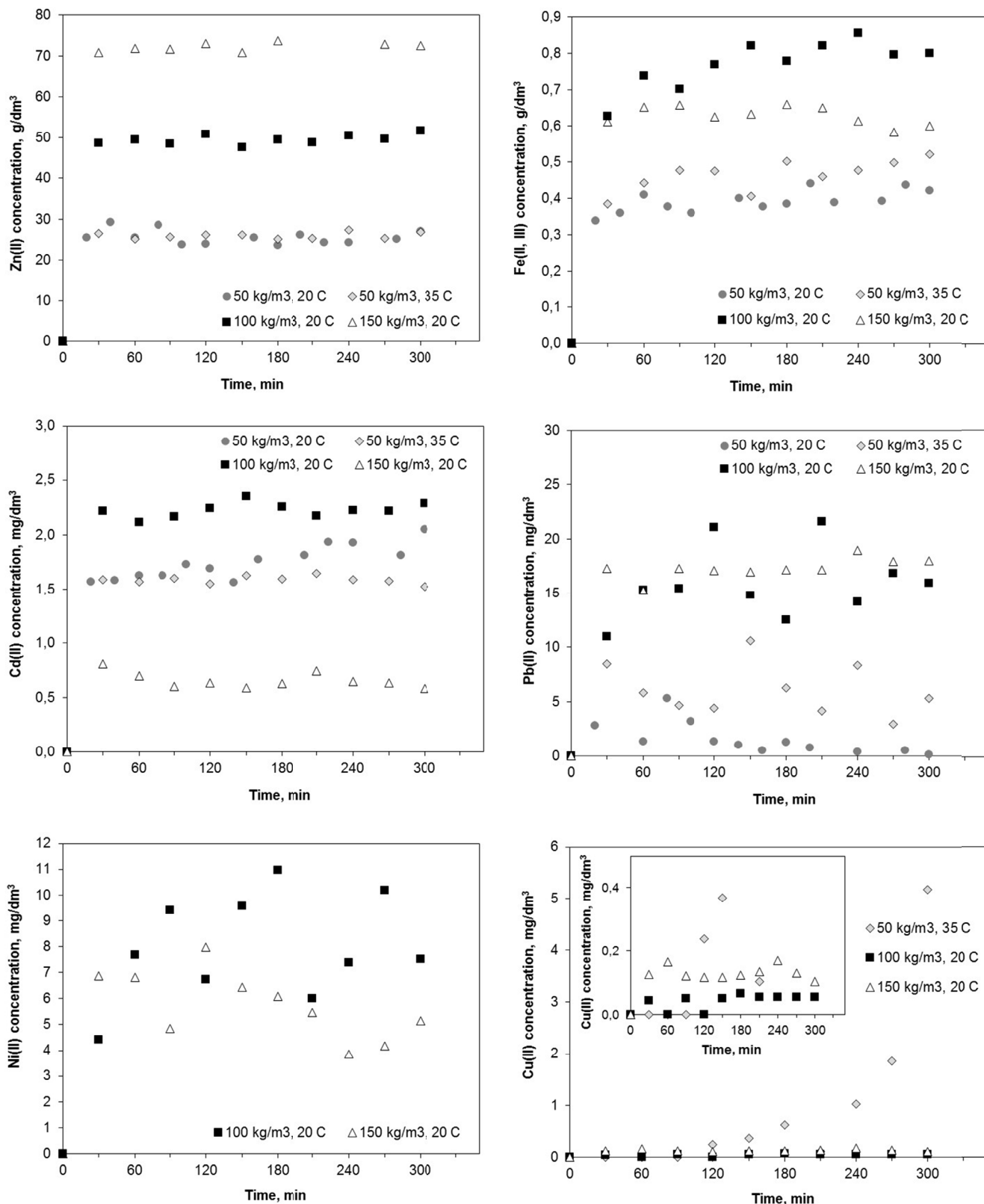


Fig. 3. Influence of bath loading and temperature on changes of metal ion concentrations with the leaching time

solution was iron (0.4-0.8 g/dm³). Less amounts of cadmium (up to 2.2 mg/dm³), lead (up to 20 mg/dm³), copper (typically 0.2 mg/dm³) were found, while at higher bath loading nickel ions (up to 10 mg/dm³) were also detected despite that nickel was not identified in the raw material (below detection limit). It seems that nickel can be present in magnetic fraction of the ash (some amounts of the solid were attached to the magnetic bar of the stirrer after completed leaching) and accidental sampling of nickel containing particles could be realized. Wide scatter of the Pb(II) concentration was observed due to secondary precipitation of lead sulfate PbSO₄ and accidental sampling with the solution.

Fig. 4 summarizes final concentrations of major metallic ions in the solutions after 5 h and 1 h leaching of various portions of the solid. Shortening of the leaching time resulted in actual decrease in the process efficiency, especially for the highest bath loading. Total zinc recoveries were 71% and 50% for 100 kg/m³ and 150 kg/m³, respectively. To improve acid action, the experiment at faster agitation for 150 kg/m³ was performed. However, the obtained results were not satisfactory enough (60% zinc yield).

Reaction of the zinc ash with the acid caused the increase in the solution pH from the initial value of -0.17 (10% H₂SO₄) even up to 4 for 150 kg/m³ (Fig. 5). In such case, the acid was completely consumed for partial dissolution of the zinc ash and

there was no reagent left for the dissolution of the rest material. Because of this reason, the large fraction of the ash remained as the solid residues. Moreover, higher pH (above 3.5) provided conditions for secondary reaction of hydrolytic precipitation of hydrated ferric oxide.

It was indicated that the efficiency of the leaching was not improved at higher temperature of the solution. However, measurements showed fast change of the temperature of the reacting system. It makes needless to use pre-heating of the lixiviate.

Thermal effect of the leaching Q was calculated according to the calorimetric measurements. During the leaching of 100 kg/m³ of the solid in 10% H₂SO₄, the temperature was registered and plotted in Fig. 6. It was observed that the reactions were fast and accompanied by sudden rise of the temperature to the constant level. The temperature increase ΔT was determined graphically and used for the calculations according to the following formula:

$$Q = -\frac{(m_G \cdot c_G + m_A \cdot c_A) \cdot \Delta T}{m} \quad (4)$$

where: m_G – mass of the isolated glass reactor, m_A – mass of the acid solution, m – mass of the leached material, c_G – specific heat of glass (0.75 kJ/kg K), c_A – specific heat of 10% acid solution (3.91 kJ/kgK) [24].

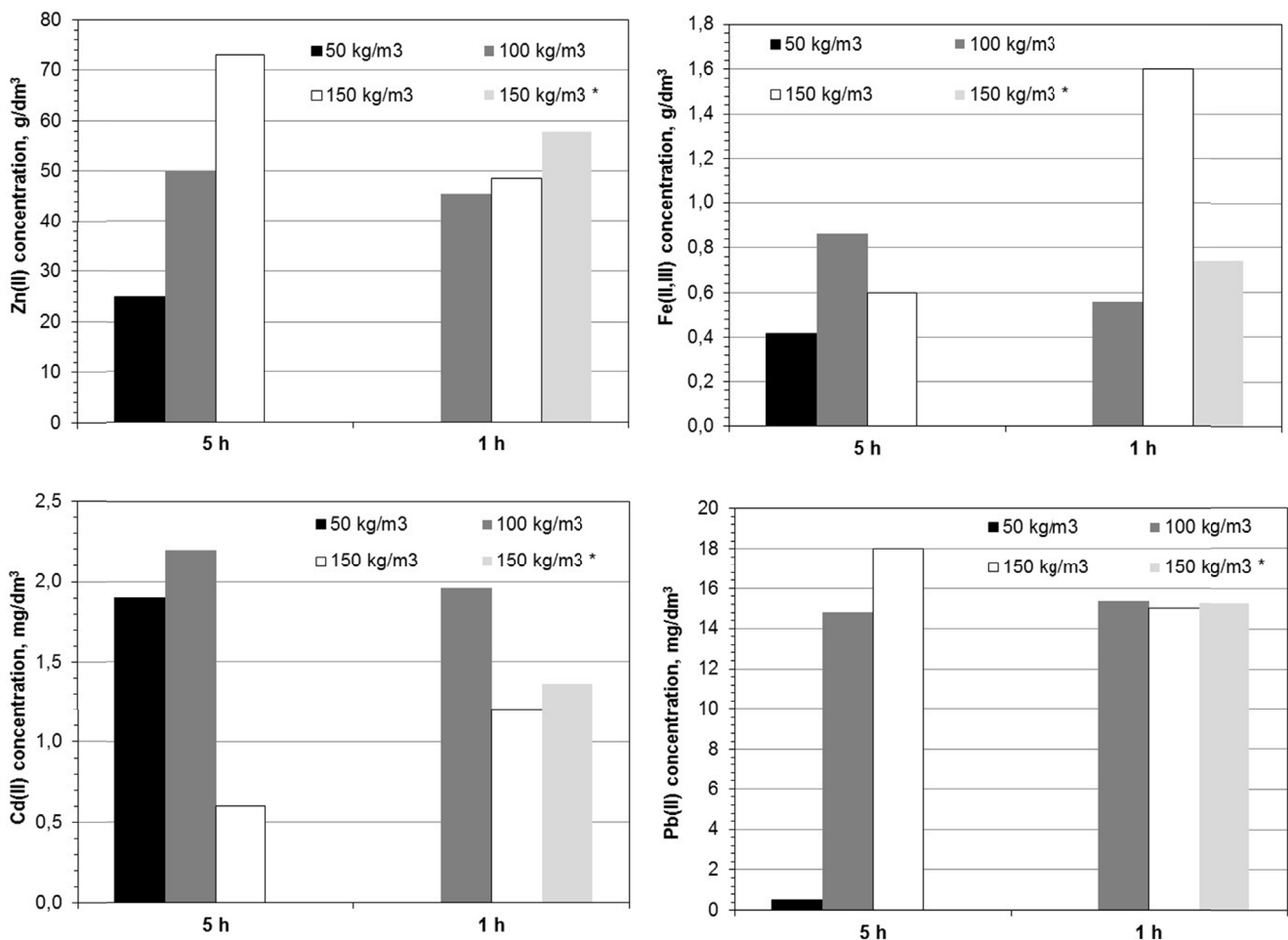


Fig. 4. Influence of the leaching time, bath loading and agitation rate (300 rpm and 900 rpm *) on the final concentrations of metal ions in the solutions (20°C)

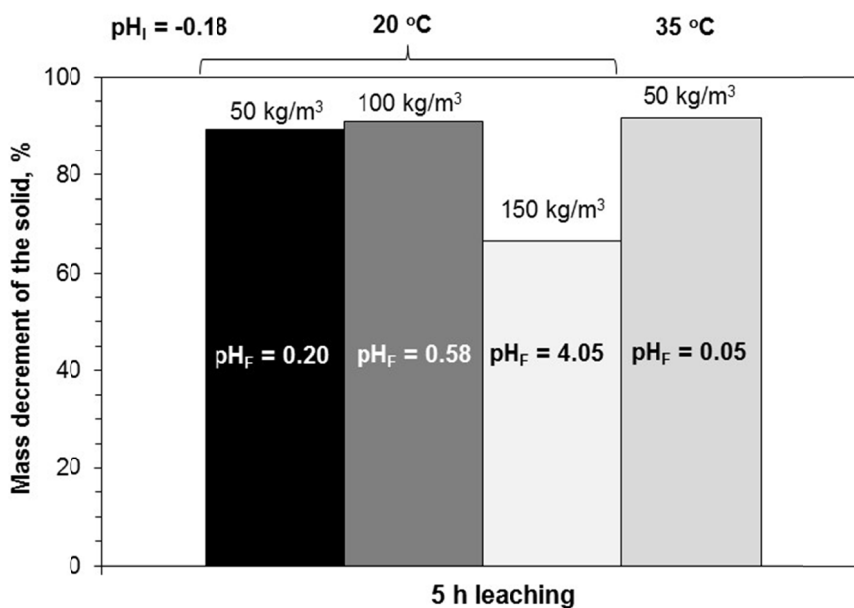


Fig. 5. Mass decrements of solid and changes pH of the leaching solutions after the process (5h, 300 rpm)

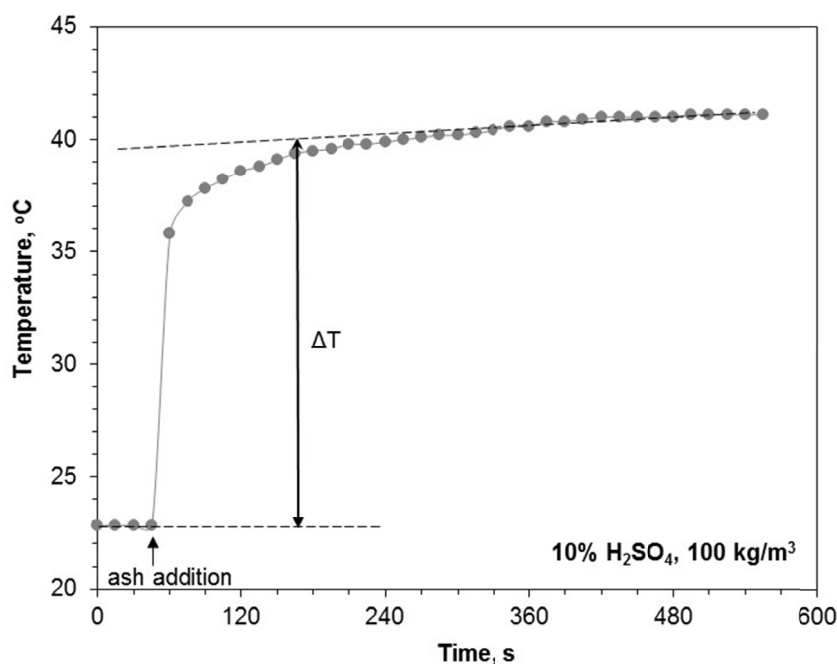
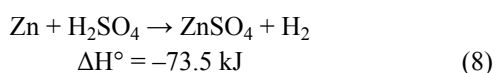
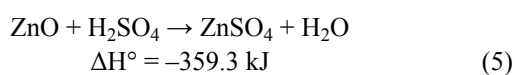


Fig. 6. Changes of solution temperature during initial stages of zinc ash leaching (calorimetric measurement)

The amount of the heat produced during the leaching was determined per 1 kg of the solid phase and the value of -800 kJ/kg was obtained. It shows that the dissolution of highly oxidized material is accompanied by the heat release, which is useful for the acceleration of the reaction rate itself.

The experimental results can be confirmed by thermodynamic calculations [24,25], assuming that changes of standard reaction enthalpy can correspond to heat effects:



Negative values of ΔH° represent exothermic character of the reactions, hence increased temperature cannot result in a positive way on the course of the processes. No similar calculations could be made for reaction of $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ with H_2SO_4 due to lack data of the standard enthalpy of simonkolleite formation (value of 0 kJ/mol is reported in the data bases, e.g. [26]).

Preliminary studies on the leaching showed that application of 10% H_2SO_4 resulted in partial recovery of zinc from the raw material. This indicates that further research should be focused on the application of two-stage leaching or more concentrated acid solution. However, it should be emphasized that first option can result in the leachate with rather low concentration of valuable

metal ions, while serious increase in the H_2SO_4 concentration can hinder zinc leachability [27] due to limited solubility of zinc salt [24]. Therefore, the application of medium concentrated acid (e.g. 20-25%) in one step leaching should be more advantageous from both technical and economical points of view.

4. Conclusions

The zinc ash from hot dip galvanizing contained about 68% Zn, 6% Cl, 3% Al, 1% Fe, 0.5% Pb and less percentages of other elements. It represented a mixture of zinc oxide with zinc hydroxide chloride, metallic zinc and silica. Leaching efficiency of zinc was dependent on the amount of added solid phase and the most efficient result (50 g/dm³ at 78% zinc recovery) was obtained for 100 kg/m³, 10% H_2SO_4 and initial lixiviate temperature of 20°C. The final solutions were contaminated mainly by Fe(II, III) ions.

Preliminary studies on the leaching showed that application of 10% H_2SO_4 resulted in incomplete dissolution of zinc from the raw material. Therefore, medium concentrated acid (20-25%) in one step leaching can be recommended for further research.

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