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# The pyrometallurgical recovery of zinc from the coarse-grained fraction of zinc ash by centrifugal force



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# ABSTRACT

Zinc ash generated during the hot dip galvanizing process is an important source of secondary zinc. The result of zinc ash processing technologies is the formation of zinc in the metallic form or in the form of zinc compounds. The present paper is aimed at possibilities of metallic zinc recovery from the coarse-grained fraction of zinc ash (d > 1.25 mm) from hot dip galvanizing by the pyrometallurgical process on designed laboratory equipment. Designed equipment for laboratory experiments used centrifugal force and protective atmosphere of a nitrogen flow during the process of melting and separation of zinc. The aim of the pyrometallurgical processing study on the designed equipment was to investigate the effect of time (30, 60, 90 min) and temperature (480, 500, 550, 600, 650, 700 °C) on recovery of smelted zinc. The most favourable conditions in terms of recovery of smelted zinc (88%) were obtained at the temperature of 500 °C and the melting time of 30 min. The influence of the melting time on zinc recovery was obvious only at the temperature of 480 °C, where extension of time led to an increase of zinc recovery.

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# 1. Introduction

Various surface treatment processes are used for increasing the corrosion or wear resistance, as well as for aesthetic reasons. The usage of zinc coatings for the corrosion protection of ferrous substrates is very widespread. In fact, 50% of annual zinc production is used for galvanizing to protect steel from corrosion (Gordon et al., 2003). There are various procedures on how to galvanize steel to prevent corrosion, but hot dip galvanizing is the oldest and the most used method among them. There are two different processes for applying a zinc coating to steel by the hot-dip method – "continuous" and "batch" process. Both of them involve immersing the steel in a bath of molten zinc (Chivers and Porter, 1994; Marder, 2000; Thomas, 2000). Galvanizing plants as major consumers of zinc generate a number of secondary products and wastes. Mainly solid waste generated by these plants is worth mentioning because this waste - due to its high content of zinc - is a valuable secondary raw material. In the batch hot dip galvanizing process, the following solid wastes arise: bottom dross, zinc ash, spent flux skimmings, and flue dust (Jha et al., 2001). Since the earth's natural resources of zinc are not unlimited, it is necessary to look for new methods on how to preserve them. Recycling of secondary sources of zinc is one of the possible ways.

During the batch hot dip galvanizing process, zinc ash is formed on the galvanizing bath surface as a thin layer. This waste is the result of

\* Corresponding author. *E-mail address:* jarmila.trpcevska@tuke.sk (J. Trpčevská). oxidation of molten zinc with the surrounding atmosphere and the result of reaction of flux components with molten zinc. A galvanizing plant produces typically approximately 80 tonnes of zinc ash annually. Its presence on the zinc bath surface is undesirable because it worsens the quality of the formed zinc coating, and therefore zinc ash is regularly removed from the zinc bath surface before each immersing, as well as after removal of a steel part. The amount and the composition of formed zinc ash vary as a result of differently influencing factors (bath temperature, chemical composition of the bath, etc.) (Maass and Peissker, 2011). From the chemical composition point of view, zinc ash contains: Zn (51–88%), Cl<sup>-</sup> (0.5–20%), Pb (0.02–2.45%), Al (0.17–3.3%) and other elements, such as Cu, Cd, Cr, Ni, Si, Mg, and Bi below 0.5%. Zinc is the most abundant element in the ash and occurs there in the form of pure (metallic) zinc, in the form of oxides (ZnO) and complex chlorides. Chlorides in the zinc ash are present in the form of phases, such as ZnCl<sub>2</sub> and  $Zn_5(OH)_8Cl_2 \cdot H_2O$  (simonkolleite) (Jha et al., 2001; Cinar et al., 2001; Vourlias et al., 2007).

## 2. Literature review of zinc ash recovery

Because of high heterogeneity of zinc ash it is very difficult to define precisely its chemical, phase and granulometric composition. For this reason it is very difficult to determine the optimum conditions for processing the waste. Current zinc ash recycling technologies are aimed at recovering primarily metallic zinc or its compounds, but not all technologies have achieved a satisfactory waste recycling rate of this waste. Possible industrial zinc ash processing technologies could be divided into: physico-metallurgical, pyrometallurgical, hydrometallurgical and combined technologies. Industrial physico-metallurgical processing methods are applied by galvanizing plants in-house. The efficiency of individual physico-metallurgical technologies is various and ranges from 50 to 70% (Jaye, 2004).

Pyrometallurgical processing technologies are the most used. Some pyrometallurgical technologies process zinc ash in-house and some of them outside the place of origin. The final product of the pyrometallurgical processing can be metallic zinc or zinc compounds. Pyrometallurgical processes can also be classified according to the processing temperature as processes operated at temperatures below 600 °C (MZR system) and above 1000 °C (Wealz process) (Chapter 6 Pyrometallurgical Processing, 2006). Pyrometallurgical technologies process zinc ash in the as-supplied state (non-sorted) or after ash sorting. Metalullix Zincoff Recovery (MZR) system is the only pyrometallurgical process used for in-house recovery of zinc, i.e. in galvanizing plants. The efficiency of zinc recovery by this process varies (50–85%), seeing that the procedure is modified in every galvanizing plant according to their conditions (Fryat, 2010).

Hydrometallurgical methods of zinc ash processing analogous to pyrometallurgical methods are used for recovery of metallic zinc (modified Zincex process) (Díaz et al., 2001) or zinc compounds (ZnSO<sub>4</sub> production). These procedures are used for processing of residuals from zinc ash melting or residuals after separating the metallic fraction from the non-metallic one. It is a fine grained material with a higher content of oxide and chloride compounds. For this reason hydrometallurgical procedures appear to be more effective than pyrometallurgical ones. These procedures are not applied in-house.

There are also combined procedures used for processing several zinc waste types, including zinc ash. These are based on pyro-hydrometallurgical procedures. These procedures are the most efficient in terms of completeness of processing of zinc waste and are not applied in galvanizing plants.

The aim of the physico-metallurgical processes is to minimize the amount of zinc accumulated in the zinc ash. These methods are the subject of laboratory study (Abd El-Rahman et al., 2005).

Research in the area of pyrometallurgical methods of zinc ash processing is oriented on the study of parameters influencing the efficiency of smelted zinc recovery, such as the temperature, the time period and the usage of fluxes. Muffle furnaces were most frequently used by researchers for recovering the metallic zinc from the coarse-grained fraction after sorting at the temperatures of 600–700 °C and time period of 15 min with and without using fluxes. The efficiency of laboratory pyrometallurgical procedures was 70–89% (Koros et al., 1996; Barakat, 1999; Dakhili et al., 2011).

At present, research in the area of hydrometallurgical procedures of zinc ash processing follows two routes. One course of research is specialized in recovery of metallic zinc by electrolyses from refined acid solutions (Nirdosh et al., 1988; Ramachandran et al., 2004; Dvořák and Jandová, 2005). The second route of research deals with possibilities of zinc compound recovery from acid or alkaline solutions. The effect of leaching media concentration, temperature, and liquid to solid ratio (L:S) on the zinc extraction into the solution was studied in both routes of research (Thorsen et al., 1981; Huajun et al., 2008; Vlad et al., 2011).

There are few published papers devoted to research of combined procedures of zinc ash processing under laboratory conditions. Laboratory research of combined procedures was aimed at processing of two main zinc ash fractions, where the coarse-grained fraction was processed by the pyrometallurgical method and the fine fraction by the hydrometallurgical method (Rabah and El-Sayed, 1995).

Zinc ash as a very important secondary source of zinc replaces its primary sources by means of recycling technologies. On the one hand, zinc ash is characterized by a higher portion of zinc comparing with primary sources; on the other hand, it is a composite material with high heterogeneity.

#### Table 1

Chemical composition of unsorted and sorted zinc ash fractions.

Size fraction [mm]	Chemical element [%]								
	Zn	Fe	Pb	Al	Cu	Cd	Mg	$Cl^{-}$	Rest
Unsorted	80.9	0.38	0.05	0.25	0.07	< 0.01	0.01	12.79	2.6
d ≥ 9.0	83.9	0.28	0.38	0.19	0.07	< 0.01	0.02	14.18	3.98
9.0 > d ≥ 4.0	80.8	0.11	0.37	0.2	0.08	< 0.01	0.03	17.73	0.68
4.0 > d ≥ 1.25	81.2	0.19	0.35	0.33	0.07	< 0.01	0.03	11.35	6.48
1.25 > d ≥ 0.63	73.4	0.32	0.32	0.43	0.07	< 0.01	0.02	21.23	4.21
0.63 > d ≥ 0.25	69.8	0.23	0.33	0.46	0.08	< 0.01	0.03	24.82	4.25
0.25 > d ≥ 0.125	69.8	0.5	0.29	0.98	0.07	< 0.01	0.02	21.23	7.11
d < 0.125	60.9	0.56	0.24	1.63	0.07	< 0.01	0.02	24.82	11.76

# 3. Material and methods

#### 3.1. Analysis of material

A zinc ash sample for the experiments was provided by a Slovak galvanizing plant which applies the hot dip galvanizing process. The prepared representative sample was subjected to chemical analysis. Atomic absorption spectroscopy (AAS) Varian AA-20<sup>++</sup> was used for elemental analysis of the sample. The results of chemical composition of the unsorted sample are shown in Table 1. Subsequently the zinc ash sample was subjected to sieve analysis on a dry mechanical sieve analysis apparatus using sieves with the mesh sizes: 9; 4; 1.25; 0.63; 0.25; and 0.125 mm (shaking time -10 min). It was found that the largest proportion by weight was represented by the fraction  $1.25 > d \ge 4 \text{ mm}$  (30.96%) and the smallest proportion by weight was represented by the fractions d < 0.125 mm, see Fig. 1. The samples of individual fractions were taken and then subjected to AAS analysis to determine the chemical composition of particular fractions, see Table 1. It is obvious from the table that Zn content slightly decreases with a decreasing fraction size. The opposite tendency was observed for the chloride content. The chloride content increases with a decreasing fraction size, while the content of other elements (Fe, Al) slightly increases. The content of other elements (Pb, Cu and Cd) was independent of the size fraction

Based on executed sieve analysis and chemical analysis of individual fractions two basic fractions were created from zinc ash: coarse-grained ( $d \ge 1.25$  mm) and fine-grained (d < 1.25 mm). The coarse-grained fraction contained 60% of the overall ash sample weight and the fine-grained fraction contained the residue (40%). The fractions were observed by microscope (Dino — Lite Pro AM 413 T), Fig. 2. The coarse-grained fraction showed irregular particles of various sizes with light grey up to dark grey and brownish shade. Light grey areas represent metallic zinc and brownish ones represent zinc parts with the ash surface. It is assumed that screening the zinc ash at 1.25 mm could be feasible in industrial application.

It was obvious from the chemical analysis that in the coarse-grained fraction the Zn content was about 80%, the content of chlorides about



Fig. 1. Distribution of zinc ash fractions.



Fig. 2. The coarse-grained fraction (HF) and the fine-grained fraction (JF) at  $60 \times$ .

14%, the Al content 0.2%, the Pb content 0.35% and the Fe content 0.2%. The fine-grained faction contained: 60–73% Zn, 23% Cl<sup>-</sup>, 0.32–0.56% Fe, 0.43–1.63% Al, and 0.24–0.33% Pb. The content of Cu was about 0.07%, the content of the Mg about 0.02% and content of the Cd was less than 0.1% in both fractions. The remaining elements in the samples could be: Ni, C, O, Bi, etc. It results from comparing the chemical composition of the coarse-grained and fine-grained fractions that the Zn content in the coarse-grained fraction was on average more than 10% higher than in the fine-grained fraction and the content of the chlorides is considerably higher in fine-grained fractions. The coarse-grained fraction vas chosen for pyrometallurgical processing because of higher portion of zinc in the metallic form. Processing of the fine-grained fraction could be cause passing, resp. clogging the openings of the glass-ceramic sieve. For the fine-grained fraction the hydrometallurgical process of processing was chosen, which was subject of further studies.

The phase composition of the unsorted fraction, as well as of the coarse-grained and fine-grained fractions, was analysed by means of X-ray diffraction method (XRD). Diffractometer D8 Advance, Bruker with CuK $\alpha$  radiation, generated at 40 kV and 40 mA equipped with secondary beam graphite monochromator was used. Measuring took placed at an angle interval 10 < 2 $\Theta$  < 50° with step 0.030°. The measured

spectra were processed using Diffrac<sup>plus</sup> Basic programme. The analysis proved the presence of phases of metallic zinc (Zn), zincite (ZnO) and simonkolleite (Zn<sub>5</sub>(OH)<sub>8</sub>Cl<sub>2</sub> · nH<sub>2</sub>O) in each sample (unsorted, coarse-grained and fine-grained), see. Fig. 3.

Quantitative phase XRD analyses of coarse-grained and fine-grained fractions were made using the XRD diffractomer system from Seifert X-ray diffraction System XRD 3003 PTS with 3D goniometer and PSD detector, Co X-ray tube (wavelength =  $1.78 \times 10^{-10}$  Å), goniometer movements  $10^{\circ} < 20 < 120^{\circ}$ . The results of quantitative phase XRD analysis are shown in Fig. 4a–b with phase proportion statement. The coarse-grained fraction contained a slightly higher portion of metallic zinc (Zn) and zincite (ZnO) and a lower portion of simonkolleite (Zn<sub>5</sub>(OH)<sub>8</sub>Cl<sub>2</sub>·nH<sub>2</sub>O) than the fine-grained fraction. In the fine-grained fraction, the presence of the (Zn(OH)Cl) phase in amount of 2% was proved.

Thermal analysis (DTA) of the coarse-grained sample was made with the aim of investigating the thermal behaviour. The DTA analysis was made using NETZSCH STA 449F3-0861-M in an  $Al_2O_3$  crucible, at a heating rate of 10 °C/min, from the ambient temperature to 1400 °C, in the argon atmosphere. The sample weight was 96.897 mg. The DTA/TG pattern of the coarse-grained sample is shown in Fig. 5.



Fig. 3. X-ray pattern of unsorted, coarse-grained and fine-grained zinc ash fractions.



Fig. 4. X-ray pattern of coarse-grained fraction (a) and fine-grained fraction (b).

There was no change observed on the DTA/TG pattern of the coarsegrained fraction up to 100 °C. The first weight loss (1.8 wt.%) on the TG pattern was evident between 110 and 215 °C and may be due to release of H<sub>2</sub>O from the simonkolleite phase. The second endothermic peak on the DTA curve was observed at around 400-410 °C. No weight loss was observed on the TG curve in this temperature range. This suggested possible transformation metallic zinc from the solidus to liquidus state. Another weight loss (0.73 wt.%) on the TG curve is visible in the temperature range of 550–640 °C, which may be due to decomposition of one of the phases. It could not be identified from the DTA curve whether this reaction is exothermic or endothermic from such a negligible weight loss. This weight loss could be associated to volatilization of ZnCl<sub>2</sub> formed by simonkolleite decomposition. The largest weight loss was observed at 650-890 °C (51.96 wt.%). This weight loss is associated with the heat consumption which is proved by an endothermic peak on the DTA curve. This phenomenon could be associated with zinc evaporation. Above 860 °C, a slight weight loss (0.94%) was observed on the TG curve. The DTA curve showed a broad multi-stage drop, which could not be definitely interpreted. The residue after analysis amounted to 44.38%. It can be deduced that the residue mainly consisted of ZnO.

# 3.2. Method of pyrometallurgical processing

A laboratory thermo-mechanical unit was constructed for pyrometallurgical processing of the coarse-grained ash fraction. An electric resistivity furnace controlled by a thermoregulation unit was used for melting the charge. Centrifugal force was evolved using a laboratory mixer after melting the charge. The process ran in a nitrogen protective atmosphere. The main parts of the equipment are shown in Fig. 6. The following procedure was used in experiments:

- The weighed amount of the sample was placed into a perforated (rotating) cylinder, lined with a glass-ceramic sieve, which was then closed with a lid. The part served as a collecting point for the residue after melting and centrifuging.
- The perforated (rotating) cylinder was placed into a stainless steel cylinder, which was closed with a lid.
- The basic unit of the equipment, prepared in this way, was placed into a furnace space, where the perforated cylinder was connected to the electric mixer that served as a source of centrifugal force. The furnace space was closed with a lid.
- A hose through which nitrogen flowed was connected to the tube leading from the stationary cylinder. Nitrogen flowed into the furnace space throughout the melting period of the sample as well as cooling of already smelted zinc.
- Relevant melting conditions (temperature, pre-heating time and melting) were set on the thermoregulation unit of the furnace device. The whole melting process of the sample was initiated by a switch on the thermoregulation unit.
- After the melting process was finished, the electric mixer was turned on for 30 s to centrifuge smelted zinc. Smelted zinc was collected in the stationary cylinder.
- After cooling (approx. 30 min) the basic part (stationary cylinder + perforated cylinder) was removed out of the furnace space. The basic parts (perforated cylinder and stationary cylinder) were disassembled to obtain products of melting (smelted zinc and remaining ash).
- The obtained products were weighed for evaluation of the process efficiency under the chosen conditions and subsequently their qualities were investigated.



Fig. 5. DTA/TG pattern of coarse-grained fraction.



- 1 Perforated stainless rotating cylinder
- 2 Glass ceramic sieve
- 3 Stainless cylinder, (stationary part)
- 4 Lid for stainless cylinder
- 5 Electric blender (source of centrifugal force)
- 6 Furnace with connected thermocouple
- 7 Thermoregulation unit
- 8 Nitrogen supply

Fig. 6. The main parts of equipment.

There are numerous technical solutions and devices which use centrifugal force for separation in many fields (Balatović, 2011; Jiang and Han, 1992).

The aim of the experiments was to find out the most suitable conditions of processing based on the quantitative results (material balance), as well as on the qualitative results (chemical analysis, microstructural analysis) of smelted zinc. The conditions of pyrometallurgical processing of the coarse-grained fraction of Zn ash were as shown in Table 2.

# Table 2

Conditions of pyrometallurgical processing of the coarse-grained fraction.

Fiz	xed conditions	
Sa	mple weight	50 g
Pr	e-heating time	45 min
Pr	otective atmosphere	$N_2$ (99.9%), flow rate $N_2$ 0.18 dm <sup>3</sup> /melting (during melting) and 0.35 dm <sup>3</sup> /melting (centrifuging and cooling)
Μ	esh size of sieve	$0.5 \times 0.5 \text{ mm}$
Ce	entrifuging time	30 s
0	perating speed	29.1 rpm/s
Ce	entrifugal force	29.85 N
Сс	ooling time	30 min
VC	iriable conditions	
Μ	elting temperature	480, 500, 550, 600, 650, 700 °C
Μ	elting time	30, 60, 90 min



Fig. 7. Procedure of pyrometallurgical processing.

The principle of pyrometallurgical processing in the constructed equipment is shown in Fig. 7. In the first processing phase "a" there were no important changes in consequence of an insufficient temperature and time period. In a detailed picture of the structure, metallic zinc particles are visible as light-grey regions, covered by ash particles (dark-grey and brown regions). In the second phase "b", partial melting of the coarse-grained fraction occurred. Ash particles were disrupted enabling zinc melting. Smelted zinc was concentrated at the direction of inclination of the perforated cylinder. Ash particles were concentrated on the smelted zinc surface. In the third phase "c", smelted zinc was separated by centrifugal force. In this phase, smelted zinc was separated from the perforated cylinder to the stationary cylinder, where it was collected at the direction of inclination of the equipment. The residual ash stayed in the perforated cylinder.



Fig. 8. Effect of temperature on recovery of smelted zinc at 30 min.

The centrifugal force acting in the process of centrifuging of the smelted zinc from a perforated cylinder lined with a glass–ceramic sieve was calculated under the chosen melting conditions for the coarse grained fraction (30 min, 500 °C).

The centrifugal force was calculated according to the following equation:

$$\mathbf{F} = \mathbf{m} \cdot \boldsymbol{\omega}^2 \cdot \mathbf{r} \tag{1}$$

where: m is the mass (mass of coarse grained fraction), r is the radius (the radius of perforated cylinder), and  $\omega$  is the angular velocity.

The angular velocity was calculated according to the following equation:

$$\omega = 2 \cdot \pi \cdot f \tag{2}$$

The counter type C 571 was used for determination of the frequency. The measuring conditions were: temperature 500 °C, melting time 30 min and centrifuging time 30 s. The measured frequency was 29.4133 Hz. The calculated angular velocity was 184.7 rad s<sup>-1</sup>.

The calculated centrifugal force for m = 0.05 kg,  $\omega = 184.7$  rad s<sup>-1</sup> and r = 0.0175 m was: 29.85 N.

The gravitational force for comparison with the centrifugal force was calculated according to the following equation:

$$F_{g} = m \cdot g \tag{3}$$

where: m is the mass and g is the gravitational constant  $(9.81 \text{ m} \cdot \text{s}^{-2})$ . The calculated F<sub>g</sub> was 0.49 N.

It follows from comparing the centrifugal force with the gravitational force 29.85 N/0.49 N = 60.9 that the centrifugal force acting on the melting charge is 60.9 times higher than the gravitational force. The centrifugal force enabled the smelted zinc to pass through the glass-ceramic sieve.

Innovation of the designed equipment consists in a combination of all the technical conditions of the experiment — the centrifugal force, the glass–ceramic sieve in a perforated cylinder, the protective atmosphere, and the heating technique.

# 4. Results and discussion

# 4.1. Results of recovery products

Pyrometallurgical processing of the coarse-grained fraction of zinc ash was made in the constructed laboratory equipment at the temperatures of 480, 500, 550, 600, 650, and 700 °C and the melting time of 30 min. The specified temperatures and the melting time were chosen on the basis of pilot experiments. It was found out that below 480 °C and at the melting time shorter than 30 min (namely 15 min) the recovery of smelted zinc was low (<50%). For the melting times of 60 and



Fig. 9. Effect of temperature on recovery of smelted zinc at 60 min.



Fig. 10. Effect of temperature on recovery of smelted zinc at 90 min.

90 min, the temperatures of 480, 500, and 550 °C were chosen. Recovery of smelted zinc as well as residual ash and losses at particular temperatures of pyrometallurgical processing of the coarse-grained fraction at the melting time of 30 min are shown in Fig. 8.

The lowest recovery of smelted zinc (68%) was at the temperature of 480 °C. The reason is that the chosen shortest melting time of 30 min at the temperature of 480 °C was insufficient for disruption of ash particles covering the metallic zinc. This corresponded with the highest weight of residual ash at these processing conditions when compared to the weight of residual ash obtained under other conditions. The highest zinc recovery (87 and 88%) was observed at 500 and 550 °C (melting time 30 min). Further increase of temperature above 550 °C up to 700 °C has caused 6–10% decrease of zinc recovery. Further, higher losses were observed at higher temperatures, and the highest losses (7%) were determined at the highest temperature, 700 °C. The losses could be associated with evaporation of ZnCl<sub>2</sub>, formed by decomposition of the simonkolleite phase, see DTA/TG analysis. Generally, losses were associated with evaporation of surface moisture and water bound in the simonkolleite phase, as well as incomplete removal of smelted zinc from the stationary cylinder walls. Based on the obtained results of experiments carried out at the melting time of 30 min, further experiments were carried out at the temperatures of 480, 500, and 550 °C and the melting times of 60 and 90 min. Recovery of smelted zinc and residual ash and losses after pyrometallurgical processing of the coarse-grained zinc ash fraction at the temperatures of 480, 500, and 550 °C and the melting times of 60 min are shown in Fig. 9.

The results show that an important change occurred at the melting time of 60 min and the temperature of 480 °C, where recovery of melt zinc increased by 20% (from 68% to 88%) in comparison with the melting time of 30 min. It was confirmed that at the temperature of 480 °C the melting time of 30 min was insufficient.

At the melting time of 60 min the increase of the temperature to 500 and 550 °C did not cause any important increase of smelted zinc recovery.

Recovery of smelted zinc and residual ash and losses after pyrometallurgical processing of the coarse-grained zinc ash fraction at the temperatures of 480, 500 and 550 °C and the melting time of 90 min are shown in Fig. 10.

The increase of the melting time from 60 min to 90 min did not lead to any changes in recovery of smelted zinc at the chosen temperatures.

Table 3EDX chemical analysis of smelted zinc samples.

Element [%]	BH 500; 30 min		BH 600; 3	0 min.	BH 700; 30 min		
	Wt	At	Wt	At	Wt	At	
Zn	100	100	99.86	99.83	99.96	99.95	
Fe	0.0	0.0	0.14	0.17	0.04	0.05	
$\sum$	100	100	100	100	100	100	



Fig. 11. Microstructure (SEM) and EDX analysis of smelted zinc (500 °C, 30 min.)

Based on the obtained results it can be concluded that the most favourable conditions in terms of recovery of smelted zinc were the process temperature of 500 °C and the melting time of 30 min. Under these conditions the recovery of smelted zinc amounted to 87% ( $\pm$ 2%).

# 4.2. Characteristics of smelted products

Samples of smelted zinc obtained by processing at the temperatures of 500, 600, and 700 °C and the melting time of 30 min were subjected to analysis on Scanning electron microscope MIRA FE-SEM, from TESCAN Inc. The results of EDX analysis are shown in Table 3. The size of the analysed area was given by the size of the observed area at the chosen magnification (70×).

The highest purity was achieved in the sample of smelted zinc obtained by processing at the temperature of 500 °C and the melting time of 30 min. The microstructure of smelted zinc (500 °C, 30 min.) at a higher magnification is shown in Fig. 11. Results of EDX analyses from marked locations shown in Fig. 11 are given in Table 4.

The microstructural component (spectrum 25) corresponded to the intermetallic particle of  $Fe_mZn_n$  type. EDX analysis of the microstructural component (spectrum 24) showed the occurrence of Pb. Lead was added to the zinc bath intentionally.

Residual ash as a by-product after processing of the coarse-grained fraction was concentrated in the perforated part (glass-ceramic sieve lined) of the equipment. The samples of residual ash were subjected to chemical and phase analyses. The results of chemical analysis of residual ash obtained by AAS under individual conditions are shown in Table 5. Chemical analysis showed that zinc was the most abundant element (76–58%). The highest content of zinc was determined in residual ash obtained by processing at 480 °C and the melting time of 30 min. In terms of zinc recovery it was confirmed that the melting time of 30 min is insufficient at the given temperature. Precise determination of the chemical composition of residual ash was difficult because of high heterogeneity of the input material.

EDX analysis of the zinc ash sample (500 °C, 30 min.), 1000×.

Element	Spectrum 23		Spectrum	24	Spectrum 25		
	wt.%	at.%	wt.%	at.%	wt.%	at.%	
Zn	100	100	4.48	12.94	94.72	93.88	
Fe	0.00	0.00	0.00	0.00	5.28	6.12	
Pb	0.00	0.00	95.52	87.06	0.00	0.00	
$\sum$	100.00	100.00	100.00	100.00	100.00	100.00	

In addition, the residual ash samples were subjected to X-ray diffraction analyses using diffractomer Philips PW 1710, X-Pert Pro (Co K $\alpha$  radiation, generated at 40 kV and 30 mA). Measuring was carried out at an angle interval  $10 < 2\Theta < 119^{\circ}$  with step 0.017°. The obtained spectra were processed by RIFRANE® programme. The coarse-grained sample contained metallic zinc (Zn), zincite (ZnO) and simonkolleite (Zn<sub>5</sub>(OH)<sub>8</sub>Cl<sub>2</sub>·H<sub>2</sub>O), see Fig. 12. The simonkolleite phase was not identified in the sample of residual ash (Fig. 13) obtained after processing at 700 °C and the melting time of 30 min; however, occurrence of new peaks corresponding to zincite was observed.

The occurrence of new peaks corresponding to the ZnO phase was observed in residual ash samples processed at the melting time of 30 min from the temperature of 500 °C, but also an increase of the intensity of these peaks was observed with the temperature increase (Fig. 14). The formation of ZnO is associated with decomposition of simonkolleite. In this XRD pattern no occurrence of simonolleite was observed, which confirmed its decomposition.

XRD patterns of residual ash samples after processing at the melting times of 60 and 90 min are shown in Figs. 15 and 16. The occurrence of new peaks corresponding to ZnO was observed already at the temperature of 480 °C when the melting time was extended to 60 and 90 min. No significant changes in the phase composition were observed at the given melting times and the temperatures of 500 and 550 °C in comparison with the melting time of 30 min.

## 5. Conclusion

Laboratory equipment for pyrometallurgical processing of the coarse-grained zinc ash fraction with the aim of metallic zinc recovery

able 5	
Chemical composition of residual ash samples after pyrometallurgical processing.	

Time [min]	Temperature [°C]	Zn	Fe	Rest
30	480	75.9	0.39	23.71
	500	68.6	0.52	30.88
	550	65.4	0.95	33.65
	600	68.2	0.83	31.20
	650	65.5	0.85	33.65
	700	67.7	0.8	31.50
60	480	63.0	1.1	36.71
	500	58.0	1.95	40.05
	550	58.9	1.06	40.04
90	480	72.6	0.65	26.7
	500	71.1	1.23	27.67
	550	63.0	0.82	36.18



Fig. 12. XRD pattern of coarse-grained fraction.



Fig. 13. XRD pattern of residual ash (700 °C, 30 min.)

was designed and subsequently constructed. The effect of the temperature (480, 500, 550, 600, 650, 700 °C) and the melting time (30, 60, 90 °C) on the metallic zinc recovery was studied. Based on obtained results it was found that increasing the temperature of processing up to 550 °C caused increased recovery of smelted zinc. Further temperature increase above 600 °C caused decrease of zinc recovery by 5–10% (in comparison to the temperatures 500 and 550 °C). The highest zinc recovery 87–88% was achieved at the melting time of 30 min at 500 and 550 °C. The influence of the melting time on zinc recovery was obvious only at the temperature of 480 °C, where extension of time from 30 min to 60 min led to an increase of zinc recovery by 20%. Extension of the melting time at 500 and 550 °C had no significant effect on zinc recovery. Based on executed analysis it can be concluded that the most favourable conditions in terms of recovery of smelted zinc (88%) were obtained at the temperature of 500 °C and the melting time of 30 min. The choice of lower temperature of processing, 500 °C is favourable from the saving of energy viewpoint. Microscopic analysis proved a high purity of the smelted zinc. Smelted zinc could be returned into the hot dip galvanizing process. Residual ash as a by-product of the process contained more than 60% of zinc. This residual ash in consequence of a relatively high zinc content (in metallic, oxide and oxochloride forms) could be subjected, along with the fine-grained



Fig. 14. XRD patterns of residual ashes (melting time 30 min.)



Fig. 15. XRD patterns of residual ashes (melting time, 60 min.)



Fig. 16. XRD patterns of residual ashes (melting time, 90 min.)

zinc ash fraction, to hydrometallurgical processing with the aim of zinc compound recovery.

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