PRODUCTION OF ZINC OXIDE FROM HAZARDOUS WASTE – SAL AMMONIAC SKIMMING

J. Piroskova, J. Trpcevska, D. Orac*, M. Laubertova, H. Horvathova, B. Holkova

*Technical University of Kosice, Faculty of Materials, Metallurgy and Recycling, Institute of Recycling
Technologies, Kosice, Slovak Republic

(Received 21 June 2018; accepted 30 October 2018)

Abstract

This article deals with hydrometallurgical treatment with the subsequent precipitation of zinc from hazardous waste Sal-Ammoniac Skimming produced in wet hot-dip galvanizing process. Chemical analysis showed that skimming contained 46.64% Zn. X-ray diffraction analysis identified the Zn(OH)Cl phase (96.36%) and NH₄Cl (3.64%) in Sal-Ammoniac Skimming. The skimming was first subjected to leaching in order to extract zinc into the solution containing HCl, followed by precipitation of the zinc. The experiments were performed in a medium of HCl at concentrations of 0.25, 0.5, 1 and 2M. Complete dissolution of zinc was achieved in 0.5M HCl solution, at 40°C, L:S=20, max. 30 min. The apparent activation energy of leaching reaction by hydrochloric acid solution was Ea=5.543 kJ mol-1. Zn precipitation was carried out using Na₂CO₃ and NaOH. Zinc oxide with a purity of about 99% was obtained directly from the solution of 6M NaOH at a temperature of 60°C – 80°Cat pH 8.8.

Keywords: Sal Ammoniac Skimming; Zinc; Leaching; Precipitation; Zinc Oxide

1. Introduction

To extend the life of steel when is used, some treatment of its surface has to be applied. Very often, surface engineering applies hot-dip galvanizing for treating surfaces with metals such as zinc, chrome, etc. Decorative issues are also important. From this reason manganese is added into the bath [1]. Currently, plating steel parts consume about 60% of the worldwide zinc production. In practice, the two methods of hot-dip galvanizing for the formation of the zinc coating are the continuous technology and batch technology. Both of these technologies use the immersion of steel parts in molten zinc. The continuous galvanizing method is suitable for surface finishing of especially sheet metal, wires, and strips. The batch technology is suitable for galvanizing various steel structures and parts of smaller dimensions. The two types of conventional practices are the dry process and the wet hot-dip galvanizing process [2, 3].

In the wet hot-dip galvanizing process, the galvanizing bath is divided into two parts by a barrier. The flux is located on the surface of the molten zinc in the separated part of the bath.

The hot-dip galvanizing process is accompanied by the formation of by-products – waste. The individual process operations generate metal-bearing

waste (top and bottom dross, sal ammoniac skimming, zinc dust) and non-metallic waste (spent degreasing solutions, pickling, and flux solutions and rinse water). Of particular interest are solid wastes, characterized by the high content of Zn, and can, therefore, be considered a valuable secondary raw material. Specific waste resulting only from wet processes is Sal Ammoniac Skimming (SAS). SAS or (flux skimming, spent flux) is created by the interaction between molten Zn and flux (NH₄Cl) in the bath

Since zinc is among the deficient metals, recycling of zinc secondary raw materials is one of the possible ways to obtain the metal. The European Commission reacted to the shortage of primary raw materials issuing, in 2011, a list of critical metals necessary for energy policy. And then in 2014 and 2017, the Commission released a new updated list of critical raw materials, where 20 raw materials were identified as critical from the list of 54 materials assessed. The list reads that zinc has "a high economic importance" because of the broad application in industry [4]. According to The European Waste Catalogue & Hazardous Waste List, SAS is placed in the group of "hazardous waste" with catalog number 11 05 04 – spent flux [5].

According to the authors [6, 7], SAS consists mainly of ammonium chloride, oxides, and sulphides.



 $[*]Corresponding\ author: dusan. or ac@tuke.sk$

In addition to the original salts (NH₄Cl, ZnCl₂·2NH₄Cl), it also contains: 5.6 – 22% Zn, 27.4 - 61.43% ZnO, 48.1% ZnCl₂, 0.75% Fe₂O₃, 6.59% Cl⁻, 3.1% of aluminum chlorides, 6.26% moisture and other impurities, e.g. oxides of aluminum, iron, and cadmium.

Currently, zinc-rich waste is not processed but is deposited in a landfill for hazardous waste. The specialized literature provides very few publications on this matter. The processing operations of SAS in practice are also unknown.

Annual production of SAS in Slovakia and the Czech Republic is about 40 tones, and this amount is not sufficient to be treated by pyrometallurgical processing. For this purpose, processing SAS with other waste, characterized by similar chemical composition (e.g. waste from galvanic plating, dust, sludge, etc.) in a pyrometallurgical way is taken into account. The Waelz kiln process is often used for waste re-melting. Waste with a content of zinc is mixed with coke and pelletized.

Batch material with the content of some moist is first dried in a rotary kiln and preheated by rotary gas, flowing in a counter-current pattern. In the reaction zone, reduction of the metal oxides occurs around 1200°C as the zinc is vaporized as metal vapor into the gas cleaning system. The kiln atmosphere is operated with excess air (process air is injected from the kiln end), and volatilized zinc is then re-oxidized. Chlorine and alkalis volatilize along with the heavy metals, and the dust-laden off-gas is treated in a downstream off-gas system. The main product of the process is Waelz Zinc Oxide obtained by separation of cooled hot dust-laden off-gas in a high-efficiency collector, which is then delivered to zinc smelters for zinc production [8, 9].

The available specialized literature [10-13] reveals that Zn in metallic form or more components of the flux (NH₄Cl, ZnCl₂) were obtained in hydrometallurgical process of SAS, which are reused in the process of pre-treatment as a fluxing agent in the dry method.

To recover zinc products by hydrometallurgical treatment, leaching SAS in a solution of ammonium hydroxide is possible and it results in two products: metallic zinc (without ammonia compounds) and solution of ZnCl₂ and NH₄Cl in form ZnCl₂·2NH₄Cl. This double salt could be later reused as a flux in dry hot-dip galvanizing [10].

Eddelman [11] applied extraction in hydrochloric acid for recycling SAS and zinc scrap, and in the second step used electrolysis during which he acquired cathode zinc and acidic gaseous chlorine (HCl). Sagara [12] was focused in his study on recovery of metallic zinc from SAS by electrolysis from molten salts consisting of NaCl and NH₄Cl. Resulted product was cathodic zinc with 94% purity.

In another study, Cudahy et al. [13] used both hydrometallurgy and pyrometallurgical processes for waste treatment with the content of metallic zinc and zinc chlorides, such as electric arc furnace dust, hotdip galvanizing ash and dust. Waste was first leached in an aqueous solution of NH₄Cl followed by melting in a reduction atmosphere at 500°C. As resulting products, they recovered metallic zinc, zinc oxide, and ZnCl₂·NH₄Cl.

The purpose of this work was to set up the suitable conditions of SAS leaching to reach the highest extractions of zinc into the solutions with subsequent precipitation of zinc in the form of ZnO as a selling product. The experimental results were obtained in laboratory conditions.

The aim of the study was to determine:

- The chemical and phase composition of the SAS.
- The influence of temperature, time, hydrochloric acid concentration, and L:S ratio in the leaching process.
 - Value of apparent activation energy Ea.
- The influence of temperature and type of precipitate in the ZnO precipitation process.

2. Material and Method 2.1 Chemical and phase analysis of SAS

For the experimental study, a sample of SAS was obtained from a Slovak plant which applies the wet batch hot-dip galvanizing process. Since the delivered sample had hygroscopic properties, it had to be dried at 105°C for 24 hours before adjusting particle size. Loss on drying was about 1.5 wt. %. Adjusting particle size followed, and grinding was carried out on a vibration mill VM 4 for 30 seconds.

The obtained representative sample was subjected to chemical analysis. Elemental analysis was performed using the method of Atomic Absorbance Spectrophotometry (AAS). Chlorides were determined using titration method with a solution of 0.1M AgNO₃ with 5% K₂CrO₄ indicator.

The phase composition was analyzed using X-Ray Diffraction method (XRD). The diffraction pattern was obtained using SEIFERT X-ray diffractometer 3003/PTS. The diffraction patterns were analyzed by DIFFRAC.EVA with PDF2 database, and TOPAS program by Rietveld method. Measuring parameters: generator 35kV, 40mA, Co lamp radiation, step 0.02 theta and measuring range 10-130° 2 theta.

2.2 Thermodynamic study

The thermodynamic analysis of leaching was performed by HSC Chemistry 6.1 software [14]. To predict whether the process of leaching in HCl will take place under chosen conditions, values of ΔG^0 were calculated for supposed chemical reactions.



2.3 Leaching of SAS

The leaching of SAS was carried out in a glass reactor which was placed in a water bath in a mechanical stirring apparatus at 20°C, 40°C, 60°C and 80°C. The aqueous solutions of 0.01, 0.25, 0.5, 1 and 2M hydrochloric acid with a volume of 400 ml were used as leaching reagents. Time of leaching was 90 minutes. The different L:S ratio (liquid: solid) 20, 40 and 80 were chosen in this experimental program. During the experiment, samples of 10 ml for zinc analysis were taken at the time 1, 5, 10, 15, 20, 30, 60 and 90 min. Optimal experimental conditions for the following Zn precipitation study were selected in order to achieve 100% extraction efficiency.

2.4 Precipitation of zinc oxide

The precipitation experiments were conducted after the leaching process, wherein the optimal conditions were determined when the maximum quantity of Zn passed into the solution. The precipitation was carried out using two agents separately: $\rm Na_2CO_3$ and NaOH. The experiments were conducted at $20-80^{\circ}\rm C$. Each solution volume used for precipitation was 200 ml with constant stirring of 200 rpm for 10 minutes.

Precipitation behavior of zinc from the hydrochloric acid system was first investigated theoretically by setup chemical reactions followed by calculation of their Gibbs energies by using Outotec's HSC 6.1. Chemistry Software. Phase distributions of possibly existing zinc forms in the hydrochloric acid environment during precipitation by chosen agents were depicted by creating fraction diagrams by using software Hydra/Medusa.

In the first sets of laboratory experiments sodium carbonate at one dose in a solid state was added into the solution in a stoichiometric amount (based on the zinc content in the solution). In the second sets sodium hydroxide in a liquid state with molarity 6M

was used and it was continuously added under stirring conditions until a white precipitate occurred. During experiments, pH changes in the solutions were continuously controlled by adding hydrochloric acid or NaOH/Na₂CO₃. After precipitation, precipitates were washed with water (60°C) and dried at 105°C for 24 hours and subjected to X-Ray diffraction phase analysis. To determine the morphology of precipitates, they were surveyed by a scanning electron microscope (SEM) MIRA3 FE-SEM.

3. Results and discussion

3.1 Chemical and phase analysis of SAS

The obtained representative sample of SAS with grain size ($d \le 1.25$ mm) was subjected to chemical analysis (Table 1).

Table 1. Chemical composition of SAS

Elements [wt.%]						
	Zn	Cl-	Fe	Al	Pb	
Average content	46.64	25.76	0.03	0.14	0.005	

The analysis of the chemical composition of the inlet sample (SAS) shows that zinc is a major element with an average content of zinc 46.64%. The second largest representations are chlorides with an average of 25.76% Cl⁻. The content of Fe and Al is below 1%. The average value of Pb is about 0.005%, however, its content, in most analyses, was below the AAS detection limit.

The evaluation of the results of the qualitative phase analysis identified two phases in the SAS input: Zn(OH)Cl and NH₄Cl (Fig. 1). The proportion of individual phases was determined using quantitative X-Ray analysis. The predominant phase is Zn(OH)Cl (96.36%) and NH₄Cl (3.64%).

The Zn(OH)Cl phase, according to the source, may be produced by heating hydrated zinc chloride to form Zn(OH)Cl according to the following equation (1) [15, 16]:

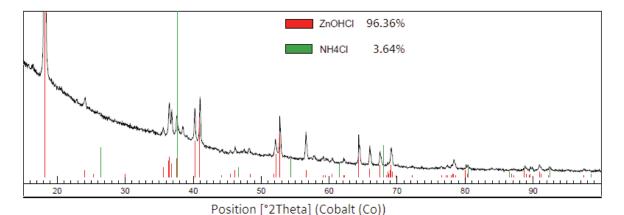


Figure 1. X-Ray diffraction pattern of input sample



$$ZnCl_2 \cdot 2H_2O = Zn(OH)Cl + HCl + H_2O$$
 (1)

3.2 Thermodynamic study

Leaching of Zn(OH)Cl in an aqueous solution of HCl may be carried out according to the following reaction (2) [15, 16]. The value of ΔG^0 of the mentioned equation was calculated at 20°C.

$$Zn(OH)Cl_{(s)} + HCl_{(aq)} = ZnCl_{2(aq)} + H_2O_{(l)}$$

 $\Delta G^0_{298} = -42.701 [kJ/mol]$ (2)

3.3 Leaching of SAS

The SAS leaching was performed in HCl with the aim to extract zinc into the solution. In the leaching process (Fig. 2 a-d), the effect of leaching medium, temperature and time of the extraction of zinc in the solution were studied. The results were already published by authors in literature [15, 16].

The leaching results (SAS) show that the process of zinc extraction in the aqueous HCl solution is very fast, wherein nearly 100% of Zn was passing into the solution during the first five minutes of leaching (Fig.

2b). Based on the experiments, the optimal conditions were determined: temperature 40°C, 0.5M HCl, ratio L:S 20 and the leaching time of maximum 30 minutes (Fig. 2b). Subsequently, a solution containing Zn²⁺ ions was applied in the process of precipitation of zinc from the solution [15, 16].

3.4 Leaching kinetics study of zinc

The kinetics of the leaching process was analyzed using the three most commonly applied kinetic models. For kinetic studies following models were applied [17-19]:

Liquid boundary layer diffusion control

$$X = kt \tag{3}$$

Chemical reaction control – Shrinking sphere model:

$$1 - (1 - X)^{1/3} = kt (4)$$

Diffusion of a reactive species/products through a porous solid layer control – Shrinking core model:

$$1 - \frac{2}{3}X - (1 - X)^{2/3} = kt \tag{5}$$

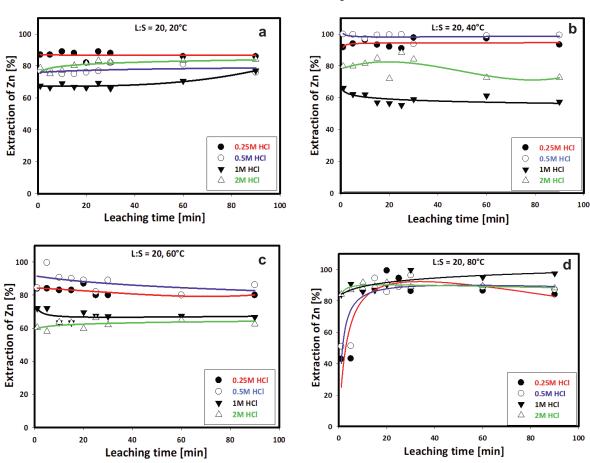


Figure 2. a-d Leaching curves of Zn extraction depending on the leaching agent concentration



$$X = \frac{\% \text{ Zn Extraction}}{100} \tag{6}$$

where X is conversion.

Within 90 minutes at individual time intervals, the linearity was determined according to the equations (3) - (5) of the studied temperature range. The highest determination coefficient (R²) was found in the first minute of the process (Table 2) for all three kinetic models. The apparent activation energy was calculated in the interval 0 - 1 minute, at the temperature range of $40 - 80^{\circ}$ C.

Table 2. Coefficients of determination determined from kinetic models

Interval [min]	R ²			
intervar [inini]	eq.(3)	eq.(4)	eq.(5)	
1	1	0.9946	0.9907	
5	0.969	0.9255	0.9116	
10	0.969	0.785	0.7805	
30	0.892	0.8138	0.8104	
60	0.8803	0.8329	0.8224	
90	0.9121	0.8444	0.8319	

In the temperature range, using the Arrhenius equation in the logarithmic form and the linear regression method, the apparent activation energies were calculated (Fig. 3). From the value R^2 follows that apparent activation energy is Ea = 5.543 kJ mol⁻¹ and the rate controlling step is liquid boundary layer diffusion.

3.5 Precipitation of zinc oxide

After the leaching experiments, the process of Zn precipitation from the solution followed. The theoretical thermodynamic study of precipitation zinc from leachate by Na₂CO₃ and NaOH was conducted using the HSC Chemistry 6.1 [14]. The calculation of

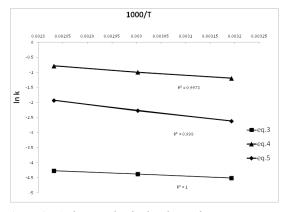


Figure 3. Arrhenius plot for leaching of zinc

Gibbs energy for mentioned chemical reactions 7-10 was carried out at a normal atmospheric pressure 0.1 MPa, and at temperature 20°C (293K) and 80°C (353K) [14]:

$$5ZnCl_{2} + 2Na_{2}CO_{3} + 6H_{2}O = Zn_{5}(OH)_{6}(CO_{3})_{2}$$

$$+ 4NaCl_{(aq)} + 6HCl_{(aq)}$$
 (7)
$$\Delta G^{0}_{293} = -113.451 \ kJ \ mol^{-1}$$

$$\Delta G^{0}_{353} = -98.200 \ kJ \ mol^{-1}$$

$$ZnCl_{2(aq)} + Na_{2}CO_{3} = ZnO + 2NaCl + CO_{2(g)}$$
 (8)
$$\Delta G^{0}_{293} = -22.855 \ kJ \ mol^{-1}$$

$$\Delta G^{0}_{353} = -31.516 \ kJ \ mol^{-1}$$

$$ZnCl_{2(aq)} + 2NaOH_{(l)} = Zn(OH)_{2} + 2Na^{+} + 2Cl^{-}$$
 (9)
$$\Delta G^{0}_{293} = -179.922 \ kJ \ mol^{-1}$$

$$\Delta G^{0}_{353} = -181.028 \ kJ \ mol^{-1}$$

$$ZnCl_{2(aq)} + 2NaOH_{(l)} = ZnO + 2NaCl_{(aq)} + H_{2}O$$
 (10)
$$\Delta G^{0}_{293} = -174.795 \ kJ \ mol^{-1}$$

$$\Delta G^{0}_{353} = -179.277 \ kJ \ mol^{-1}$$

It follows from the thermodynamic study that all the equations, at the selected temperatures, show negative $\Delta G^0_{~298}$ and $\Delta G^0_{~353}$ indicating that the reactions will proceed in the direction of products formation. The distribution species diagrams (Fig. 4), constructed by software Hydra/Medusa [20], describe the presence of molar fraction zinc species in the chloride medium during chosen precipitation agents (Na₂CO₃ and NaOH). The diagrams for describing chemical systems were depicted according to real results of the molar concentration of Zn and Na presented in the leachate and the molar concentration of precipitation agents in stoichiometric excess. Fig. 4a) shows that with using Na₂CO₃ as precipitation agent, phase Zn₅(OH)₆(CO₃), in pH range from 5.4 to 10 is mainly formed. Another possible existing phase is also $Zn_s(OH)_sCl_2$. From pH = 8 also ZnO is slowly formed and at higher pH than 10.5, only this phase is in the system. Fig. 4b) shows the behavior of zinc species in the presence of NaOH. The main phase created during precipitation is Zn_s(OH)_oCl₂ which exist in the system from pH 5.4 to 8.4. With increasing pH value over 8.4 is formed ZnO.

Fig. 5 illustrates diffraction patterns of the precipitate obtained by precipitation agent Na_2CO_3 at temperatures of 20, 40, 60 and 80°C, in the range of pH = 8.7 - 9.86, and constant precipitation time of 10 minutes. The $Zn_5(OH)_6(CO_3)_2$ (hydrozincite) and ZnO phases were identified in diffraction patterns. The precipitation experiments confirmed the theoretical assumption of the formation of $Zn_5(OH)_6(CO_3)_2$ phase according to the equation (7). The efficiency of the precipitation under the above conditions was over 99%.



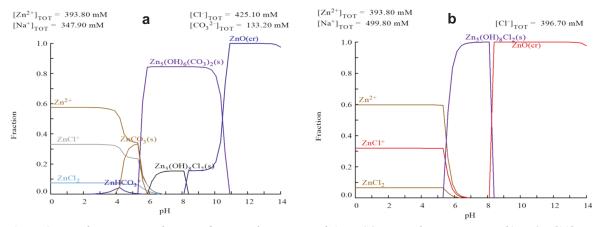


Figure 4. Distribution species diagrams for Zn in the presence of a) Na₂CO₃ in stoichiometric excess, b) NaOH [20]

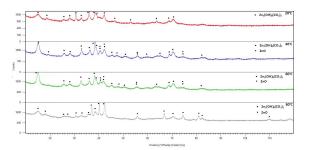


Figure 5. X-Ray diffraction pattern of white precipitate (Na,CO₂)

The precipitate was subjected to calcination at 600°C for one hour. The calcination process seems to occur according to the following reaction (11):

$$Zn_5(OH)_6(CO_3)_2 = 5ZnO + 3H_2O_{(g)} + 2CO_{2(g)}$$

 $\Delta G^{\circ}_T = -326.844 \, kJ$ (11)

During calcination at 600°C, Zn₅(OH)₆(CO₂)₂ phase is decomposed to ZnO, water vapor and carbon dioxide [22, 23]. The value of ΔG°_{T} of the equation (11) is negative which means that it probably occurs in the direction of product formation and also ZnO is formed. Fig. 6 shows the X-Ray diffraction pattern of the precipitate before calcination (Fig. 6a) and after calcination (Fig. 6b). In the diffraction pattern, a change in the phase composition can be observed, and the ZnO phase was identified in the precipitate after calcination (Fig. 6b). Zinc oxide with a purity of about 96% was obtained from the solution. Around 50 -60% of the world-production ZnO is consumed in a rubber product with a ZnO purity of about 93 -99.7%. The thermodynamic assumption of reaction was confirmed.

With the aim to obtain Zn oxide with higher purity, another precipitation agent was applied (6M NaOH). The precipitation conditions were similar as for the precipitation with solid sodium carbonate:

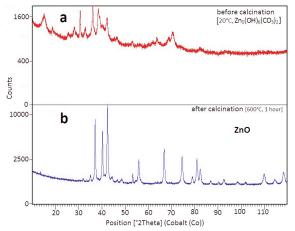


Figure 6. X-Ray diffraction pattern of samples: a) before calcination, b) after calcination

temperature $20 - 80^{\circ}$ C, pH in the range from 8.83 to 9, constant precipitation time of 10 minutes. The efficiency of the precipitation under the above conditions was 100%. After washing and drying, the precipitate was subjected to X-Ray diffraction phase analysis shown in Fig. 7.

In the diffraction pattern, the effect of temperature in the process of Zn precipitation from the solution can be observed. In the temperature interval, 20 to 40°C a white precipitate was formed, where three Zn phases were identified: $Zn_5(OH)_8Cl_2 \cdot H_2O$

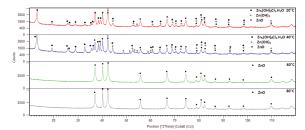


Figure 7. X-Ray diffraction pattern of white precipitate (NaOH)



(simonkolleite), $Zn(OH)_2$ and ZnO. Formation of $Zn_5(OH)_8Cl_2\cdot H_2O$ phase, according to the reaction (12), requires free Zn cations, chloride and hydroxyl anions [22].

$$5Zn^{2+} + 2Cl^{-} + 8OH^{-} + H_2O \iff Zn_5(OH)_8Cl_2 \cdot H_2O$$
 (12)

With increasing temperature from 60 to 80°C a precipitate was formed, in which ZnO phase was identified. The purity of recovered ZnO was 99%. The advantage of this process is that high purity ZnO can be obtained directly from the solution at 60°C without subsequent calcination of the product. Subsequently, the precipitates formed at lower temperatures (20°C and 40°C) were subjected to calcination at 600°C for one hour (Fig. 8). It is assumed that decomposition of the phases present occures and ZnO phase is formed (13). During calcination, the Zn(OH)₂ phase decomposes according to the following reaction:

$$Zn(OH)_2 = ZnO + H_2O_{(g)}$$
 (13)
 $\Delta G^{\circ}_T = -21.879 \text{ kJ mol}^{-1}$

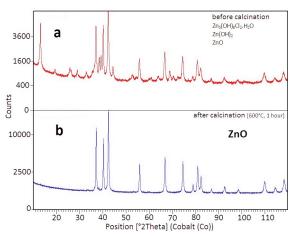


Figure 8. X-Ray diffraction pattern of samples: a) before calcination, b) after calcination

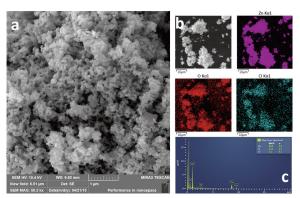


Figure 9. The SEM and EDX analysis of the product - observed by precipitation with Na₂CO₃ and calcination

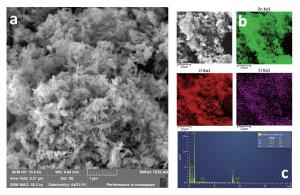


Figure 10. The SEM and EDX analysis of the product - observed by precipitation with NaOH

A change in the phase composition can be observed in the diffraction pattern of Fig. 9b, and the ZnO phase was identified in the product after calcination. The morphology of the product after calcination is shown in Fig. 9 where a spherical shape of particles can be observed. Fig. 9b shows the morphology of a white precipitate directly precipitated from a solution at 80°C using 6M NaOH. The white precipitate (without calcination), as can be seen in Fig. 10, has a needle-like morphology.

4. Conclusions

The aim of the experimental study was to obtain zinc oxide of high purity from SAS using hydrometallurgical method. SAS is a hazardous waste, which is produced in the wet batch hot-dip galvanizing process. The material is characterized by its heterogeneity with high Zn of approximately 46.64%. At present, this hazardous waste is not processed.

The study showed the following conclusions:

- The phase analysis identified two phases Zn(OH)Cl and NH₄Cl. The predominant phase is Zn(OH)Cl (96.36%) and NH₄Cl (3.64%).
- The optimal leaching conditionswere 0.5M HCl, at 40°C, L:S = 20, leaching time 30 minutes.
- The value of apparent activation energy of the leaching process was calculated $Ea = 5.543 \text{ kJ mol}^{-1}$ and the rate controlling step was determined as liquid boundary layer diffusion.
- The experiments of precipitation showed that production of ZnO of high purity is possible by using Na₂CO₃ and also NaOH.
- By using Na₂CO₃, zinc was precipitated in phase Zn₅(OH)₆(CO₃)₂ and subsequently by calcination ZnO was produced.
- By using NaOH, zinc was precipitated at lower temperatures ($<40^{\circ}$ C) in phase $Zn_{5}(OH)_{8}Cl_{2}\cdot H_{2}O_{2}$ and subsequently, ZnO was produced at higher temperatures ($>40^{\circ}$ C) directly by calcination and ZnO was precipitated.



Acknowledgement

This work was fully supported by Ministry of Education of the Slovak Republic under Grant VEGA No 1/0442/17 project and VEGA No 1/0724/17 project.

References

- [1] M. Godzsák, G. Lévai, K. Vad, A. Csik, J. Hakl, T. Kulcsár, G. Kaptay, J. Min. Metall. Sect. B-Metall. 53 (3) B (2017) 319 – 326.
- [2] A.R. Marder, Prog. Mater. Sci., 45 (2000) 191.
- [3] M.A. Barakat, JOM., 55 (8) (2003) 26-29.
- [4] European Academies' Science Advisory Council, Priorities for critical materials for a circular economy. DVZ-Daten-Service GmbH, Germany, (2016) 1-34. Available on website https://www.easac.eu/fileadmin/PDF_s/reports_state ments/Circular_Economy/EASAC_Critical_Materials _web_corrected_Jan_2017.pdf>
- [5] Europen Waste Catalogue and Hazardous Waste List, EPA, Valid from 1 January (2002) p.45. Available on w e b s i t e http://www.nwcpo.ie/forms/EWC_code_book.pdf>
- [6] M.K. Jha, V. Kumar, R.J. Sing, Resources, Conservation and Recycling, 33 (1) (2001) 1-22.
- [7] D. Krištofová, Recyklace neželezných kovů, VŠB-TU Ostrava, Ostrava, 2003, p.60 (In Czech).
- [8] T. Suetens, B. Klaasen, K.V. Acker, B. Blanpain, Journal of Cleaner Production, 65 (2014) 152-167.
- [9] X. Lin, Z. Peng, J. Yan, Z. Li, J.Y. Hwang, Y. Zhang, G.

- Li, T. Jiang, Journal of Cleaner Production., 149 (2017) 1079-1100.
- [10] R. J. Kepfer, Recovery of Zinc Values, US2288405 (1942) 1-4.
- [11] W.L. Eddelman, Method for recovery of metallic zinc from chlorine contaminated skimmings, US4169776 (1979) 1-6.
- [12] M. Sagara, Bulletin of the Kyushu Institute of Technology, 3 (1953) 32-39
- [13] M. W. Cudahy, A. S. Myerson, Method for the Production of Galvanizing Fluxes and Flux Feedstocks. US5810946 A (1998) 1-8.
- [14] A. Roine, HSC Chemistry, ver. 6.1 software Outotec Research Oy.
- [15] J. Piroskova, J. Trpcevska, M. Laubertova, B. Holkova, E. Smincakova, Metall., 7-8 (2014) 302-306.
- [16] J. Piroskova, J. Trpcevska, E. Smincakova, B. Holkova, M. Laubertova, H. Horvathova, Metall., 1-2 (2016) 28-32
- [17] I.M Ahmed, A.A. Nayl, J.A. Daound, Journal of Saudi Chemical Socienty., 20 (2016) 280-285.
- [18] F. Habashi, Principles of Extractive Metallurgy, General Principles, Gordon & Breach, New York – London – Paris, 1969, p. 413.
- [19] E. Sminčáková, J. Trpčevská, J. Pirošková, JOM, 69 (10) (2016) 1869-1875.
- [20] I. Puigdomenech: MEDUSA, 32 bit 16.12.2010 software Royal Institute of Technology, Sweden.
- [21] J. Cheng, K.M. Poduska, Nanomaterials., 3 (3) (2013) 317-324.
- [22] K.A. Radzimska, T. Jesinowski, Materials, 7 (4) (2014) 2833-2881.

DOBIJANJE CINK OKSIDA IZ OPASNOG OTPADA- PENE AMONIJUM HLORIDA

J. Piroskova, J. Trpcevska, D. Orac*, M. Laubertova, H. Horvathova, B. Holkova

* Tehnološki univerzitet u Košicama, Metalurški fakultet, Institut za reciklažne tehnologije, Košice, Slovačka

Apstrakt

Ovaj rad se bavi hidrometalurškim postupkom sa naknadnim taloženjem cinka iz opasnog otpada, odnosno pene amonijum hlorida nastale tokom postupka toplog cinkovanja u vlažnim uslovima. Hemijska analiza je pokazala da pena sadrži 46,64% cinka. Rentgenskom difrakcijom je ustanovljeno postojanje dve faze u peni amonijum hidroksida, faza Zn(OH)Cl (96.36%) kao i faza NH4Cl (3.64%). Pena je najpre lužena da bi se izdvojio cink u rastvoru HCl, da bi nakon toga došlo do taloženja cinka. Eksperimenti su izvedeni u prisustvu HCl, pri koncentracijama 0,25, 0,5, 1 i 2M. Potpuno razlaganje cinka je postignuto u rastvoru HCl koncentracije 0,5M, na 40°C, u odnosu T:Č=20, u periodu od maksimalno 30 min. Dobijena energija aktivacije reakcije luženja u prisustvu hlorovodonične kiseline iznosila je Ea=5.543 kJ mol-1. Taloženje cinka je postignuto u prisustvu Na2CO3 i NaOH. Cink oksid, čistoće 99%, dobijen je direktno iz rastvora 6M NaOH na temperaturi od 60°C – 80°C pri pH vrednosti 8,8.

Ključne reči: Pena amonijum hlorida; Cink; Luženje; Taloženje; Cink oksid

