STUDIA UBB CHEMIA, LVII, 2, 2012 (p. 95 - 102)

HYDROMETALLURGICAL FLOW FOR ZINC RECOVERY FROM Zn-MnO_2 WASTE BATTERIES.
I. ZINC SOLUBILIZATION FROM ANODIC REMNANTS

M.S. ANTON[a], A. L. MANCIULEA[a], U. SCHMIDT[b],
A. BUND[b], P. ILEA[a]

ABSTRACT. The present study is focused on the electrochemical recovery of zinc anodic remnants from Zn-MnO_2 waste batteries and the development of a combined flow scheme that allows the recovery of zinc by electrodeposition with satisfactory energy consumption related to the amount of Zn deposited. Batch laboratory experiments were performed to evaluate the electrochemical dissolution/winning parameters (electrolyte composition, pH, current density) in acidic medium. The proposed flow scheme aims at the electrodissolution of anodic remnants from waste batteries. Using the electrochemical method were achieved a high cathodic current efficiencies, approximately 98 % for Zn electrodeposition and also an improvement of the solubilization degree in comparison with the chemical solubilization using as anode Zn remnants in 0.5 M H_2SO_4.

Keywords: *Zn-MnO_2 batteries, electrochemical dissolution, energy consumption*

INTRODUCTION

The solubilization of spent battery components is of great scientific and economic interest, on account of recycling requirement of wastes and ~~of~~ valuable materials recovery. After the solubilization of electrodic inactive material from Zn-MnO_2 batteries, solutions with a zinc content between 5 and 30 g/L were obtained, depending on the H_2SO_4 concentration [1]. Subsequent to a previous solubilisation of the anodic remnants, the solution can be further processed for electroextraction of high purity zinc. Electrowinning of zinc from relatively concentrated solutions with 160 g/L of Zn^{2+}, could be achieved, successively, with acceptable current efficiencies down to a concentration of 40 g/L [2].

Generally, during the solubilization process of the metal anode, several different phenomena, such as active dissolution, passivation, pitting and trans-passivation, etc., can occur with the change of potential and-concentration

---

[a] Babes Bolyai University, Faculty of Chemistry and Chemical Engineering, 11 Arany Janos Str., Cluj-Napoca, Romania

[b] Fachgebiet Elektrochemie und Galvanotechnik II, Technische Universität Ilmenau, Germany

of the anion [3]. Metal dissolution takes place essentially at the base of pores of a conductive layer of oxidation products which is progressively degraded by the anodic current [4]. However, concerning the anodic polarization processes of some metals, there is no passivation but only active dissolution, and the anodic reaction current increases with the positive shift of potential until ultimately reaches a diffusion limited current. Hence, the electrochemical solubilization rate of metal is controlled by the diffusion rate of the salt layer formed on the surface of the metal [5, 6].

One of the most important aspects for the electrowinning process is the selection of the electrolyte system [7]. The zinc solubilization process was studied in different electrolyte solutions: NH_3-NH_4Cl [7], NaOH [8, 9], NaCl [8], H_2SO_4 [10]. In alkaline electrolytes, the polarization is more significant than in acidic solutions, probably due to $Zn(OH)_2$ precipitation in the pores of the anode [8]. According to Z. Huajun et al. [7], the anodic dissolution in NH_3-NH_4Cl medium can go along quite well as long as the Zn concentration of the electrolyte is well controlled, under 60 g/L Zn^{2+}. At higher concentrations of Zn^{2+}, a white film, mainly composed of Zn(OH)Cl, appeared on the surface of the zinc anode, preventing further dissolution. In NaCl electrolyte, and the formation of ZnO on the zinc surface suggests the passivation of zinc [8].

We have studied previously [1, 11] the experimental conditions for Zn solubilization from the inactive electrodic material of the battery in H_2SO_4. The 2 M H_2SO_4 concentration ensures 98 % of zinc solubilization, together with 30 % manganese and 20 % iron. The resulting aqueous solution contains about 20 g/L Zn^{2+}, 6 g/L Mn^{2+} and 0.1 g/L Fe^{2+}. Experiments on the electrodeposition of zinc from these solutions showed low cathodic current efficiencies [12,13]. This is mainly due to the low concentration of zinc in the solution. As an alternative for increasing the Zn concentration in the electrolyte, the solubilization of Zn anodic remnants from the battery is proposed.

In this study, the solubilization process of zinc from the anodic remnants of Zn-MnO_2 waste batteries was studied in H_2SO_4 medium, through chemical and electrochemical methods. To determine the best conditions for the solubilization process, chemical (acid concentration, solid liquid mixing ratio) and electrochemical parameters (electrolyte composition, applied anodic current density) were assessed.

RESULTS AND DISCUSSIONS

1. Chemical dissolution of anodic remnants

The preliminary chemical leaching studies were carried out without agitation, using different concentrations of H_2SO_4 and mixing ratios (S: L) between 1:10 and 1:50 as shown in Table 1.

Table 1. Influence of the solid: liquid ratio and H_2SO_4 concentration on the solubilization degree of Zn anodic remnants

H_2SO_4 concentration (M)	**Solid: liquid ratio (g/mL)**	**Solubilization degree (%)**	
		24 hours	**48 hours**
1.5	1:10	53	86
	1:20	73	96
	1:50	91	96
2	1:10	98*	-
	1:20	99*	-
	1:50	99*	-
4	1:10	64	72
	1:20	71	75
	1:50	76	76

* Completely dissolved after 20 hours.

In 20 hours, chemical dissolution ensures 99 % dissolution of Zn anodic remnants in 2 M H_2SO_4, regardless of the mixing ratios. In 1.5 M H_2SO_4 a total dissolution was achieved only in 48 hours at mixing ratios higher than 1:10. The increase in H_2SO_4 concentration leads to a decrease in zinc dissolution, due to the passivation process.

2. Combined electrodissolution and electrodeposition of zinc

Given the relatively long duration of the waste's dissolution, an electrochemical process was developed, allowing anodic dissolution of waste and the zinc cathodic recovery.

Electrochemical dissolution of zinc remnants was focused on obtaining high solubilization degrees and low specific energy consumption. The effects of electrolyte composition and current densities on zinc dissolution in acidic sulphate electrolyte have been investigated.

The electrochemical dissolution of zinc remnants using an aqueous solution (H_2SO_4 and low concentration of Zn^{2+} ions) is determined by the following possible reactions:

(i) Direct anodic solubilization:

$Zn - 2e^- \rightarrow Zn^{2+}$ and

(ii) Electroless solubilization:

$Zn_{(s)} + H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)}$.

The electroless solubilization triggers an alkalinization of the solution near the anode surface, causing the formation of a white precipitate of Zn $(OH)_2$:

$Zn^{2+} + 2OH^- \rightarrow Zn\,(OH)_2$.

This hydroxide re-dissolves in acidic medium:

$Zn(OH)_2 + 2H_2SO_4 \rightarrow ZnSO_4 + H_2O$

Under these conditions, the following reactions take place at the cathode:

$Zn^{2+} + 2e^- \rightarrow Zn$

In acidic solutions, the hydrogen evolution reaction, HER also occurs:

$2\,H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$

To determine the best conditions for the solubilization tests the optimal current density has to be established, as well as the optimal composition of the leaching solution.

2.1. The influence of the anodic current density

The influence of the anodic current density on the current efficiencies and power consumptions was investigated under the following conditions: 0.5 M H_2SO_4, electrical charge fixed at 1485 C (which ensures the solubilization of approximately 50 % of Zn remnants). The anodic current density was between 217 and 1087 A/m^2. In order to diminish the acid consumption due to hydrogen evolution reaction, in the initial electrolyte solution were dissolved approximately 2 g/L Zn^{2+}. At the end of electrochemical solubilization the composition of the solutions was determined.

The evolution of parameters in electrochemical (chemical) solubilization for different anodic current densities, in 0.5 M H_2SO_4 solutions is summarized in Table 2.

Table 2. *The evolution of parameters during the electrochemical solubilization at different anodic current density, in 0.5 M H_2SO_4 solutions, electrical charge* 1485 C

Anodic current density	**Electrochemical solubilization**		**Zinc electrodeposition**	
	Solubilization degree	**Energy consumption**	**Current efficiency**	**Energy consumption**
A /m^2	**%**	**kWh/kg Zn**	**%**	**kWh/kg Zn**
1087	34	1.85	50	4.0
870	38	1.36	50	3.1
652	44	1.19	51	2.6
434	45	0.72	61	1.5
217	45	0.37	75	0.7

The solubilization process is slow and cannot be accelerated by increasing the current density. Low current densities give better process parameters (solubilization degree, current efficiency and specific energy consumption). The best results were obtained at a current density of 217 A/m^2, when the solubilization degree was 45 %, after approximately 4 hours of electrolysis. In case of chemical solubilization, under similar conditions, the solubilization degree was only 17 %. At the same time, the cathodic current efficiencies increase with decreasing current densities. During these experiments, the final Zn concentration in the electrolyte increased to approximately 8 g/L.

2.2. The influence of zinc concentration

As mentioned above (see section 2.1), the electrochemical solubilization was studied in the presence of a quantity of zinc in the initial solution in order to accelerate the electrodeposition process by decreasing the acidity of the solution. At the same time, the electrochemical solubilization increases the concentration of zinc in the solution, so it was considered necessary to study the influence of Zn^{2+} concentration on the process parameters.

The effect of zinc concentration (see Figures 1 and 2) on current efficiencies and power consumptions were investigated under the following conditions: current density of 217 A/m^2, different zinc concentrations (2, 10, 20 and 40 g/L) in 0.5 M H_2SO_4.

Figures 1 and 2 illustrate that high cathodic current efficiencies were obtained in the zinc concentration range of 10–40 g/L. The specific power consumptions, between 0.5 and 0.7 kWh/kg Zn, were much lower than in conventional zinc electrowinning (3 – 4.3 kWh/kg Zn) [14,15].

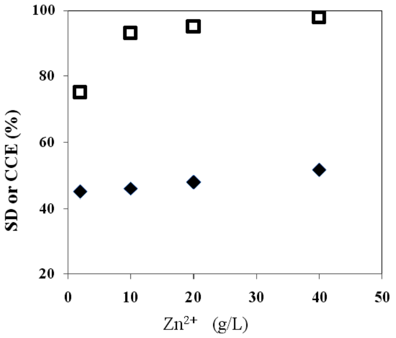

Figure 1. The effect of Zn^{2+} concentration on the solubilization degree (♦) and cathodic current efficiency (□)

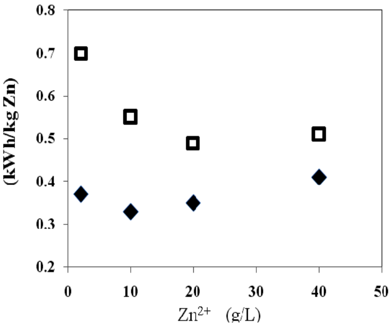

Figure 2. The effect of Zn^{2+} concentration on the specific energy consumption for the solubilization process (♦) and for Zn electrodeposition (□)

2.3. The influence of acid concentration

To study the effect of acid concentration on process parameters, the H_2SO_4 concentration was increased to 2 M. Figure 3 shows that the solubilization degree increases up to 75 %, while at the same time the cathodic current efficiency drastically drops. At high acid concentration a massive hydrogen evolution occurs, leading to low cathodic current efficiency and an excessive consumption of the zinc anode, thereby increasing the solubilization degree.

Furthermore, to assess the global parameters of the process, a complete solubilization test of the anodic Zn remnants was done using a solution containing 10 g/L Zn^{2+} in 0.5 M H_2SO_4 medium. For this test the amount of electrical charge was 1600 C. A solubilization degree of 100 % was achieved after 4.5 hours, demonstrating that the electrochemical process is more advantageous compared to the chemical one.

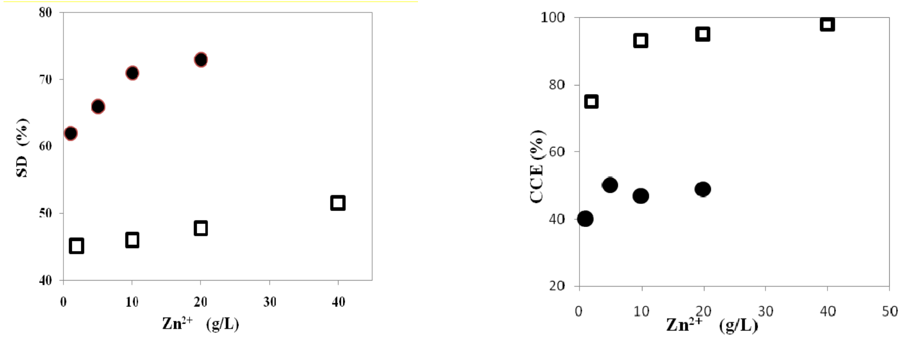

Figure 3. The evolution of the electrochemical parameters, CCE and SD, in 0.5 M (□) and 2 M H_2SO_4 (●) for different concentrations of Zn^{2+}, i =217 A/m^2

CONCLUSIONS

The electrochemical recycling of zinc reduces the amount of exhausted Zn–MnO_2 batteries in urban waste and protects the environment from contamination with toxic metals.

High current efficiencies, approximately 98 % for Zn electrodeposition process and an increase of the solubilization degree with 20 % in comparison with the chemical process were achieved using Zn remnants as anodes in 0.5 M H_2SO_4. Increasing the concentration of acid to 2 M decreased the current efficiency for electrodeposition (~50 %) and increased the solubilization degree to 69 % in comparison with the chemical process.

The results for the electrolyte's composition of Zn electrodeposition show that cathodic current efficiency decreased dramatically when the zinc content in the electrolyte decreases below 10 g/L in 0.5 M H_2SO_4. Electrowinning of Zn from such diluted solutions becomes uneconomical due to the poor quality of the recovered zinc, affected by the massive hydrogen production.

Electrochemical recovery of zinc anodic remnants allows shortening the dissolution time of the wastes and increases the solubilization degree with low specific energy consumption. This allows the recovery of pure metallic zinc, with high current efficiency and lower energy consumption than in conventional electrowinning cases.

EXPERIMENTAL SECTION

The electrochemical measurements were performed at room temperature (25 °C) in a conventional four electrode cell. The counter electrode (CE) was an aluminium plate, the working electrode (WE) were Zn anodic remnants recovered after dismantling the waste batteries and as reference electrodes (RE) we used $Ag/AgCl/KCl_{sat}$.

Aluminium is used as cathode because it forms no alloys with zinc, thus facilitating zinc separation at the end of the electrolysis [16]. For the cleaning of aluminium surfaces, electrodes were soaked in 6 M NaOH bath for 2 minutes. Prior to immersion in the electrolytic bath, the electrodes were rinsed with distilled water, dried and weighted, to determine the mass of deposited metal. In all experiments, the current efficiency was assessed by the difference in mass of the electrode before and after the experiment.

The electrolyte used was a synthetic solution containing different concentrations of Zn in different H_2SO_4 concentrations. All chemicals used ($ZnSO_4 \cdot 7H_2O$, H_2SO_4) were of analytical grade (Merck) and all solutions were prepared with Milli-Q water.

A Voltcraft current supply and multimeters were used to control and monitor the electrochemical processes. The solubilization degree (SD) and cathodic current efficiencies (CCE), as well as the specific current consumption (Ws) were evaluated.

Due to the fact that in the absence of polarization deposited zinc could dissolve in acid medium, at the end of the experiment the polarization was maintained until the deposit was washed with double distilled water. Dry electrodes were weighed before and after the experiment, to determine the mass of metal deposited, respectively dissolved. Based on these weights the cathodic current yields, respectively the solubilization degrees were calculated. The current efficiencies, CCE were evaluated using the expression:

$$CCE = \frac{m}{m_t} \cdot 100$$

where: m is the mass of substance deposited at the electrodes, and

m_t- theoretical mass calculated from Faraday's law:

$$m_t = \frac{I \cdot t \cdot M}{z \cdot F}$$

where: z is the number of electrons transferred in the reduction of zinc ions (z=2), F-Faraday's constant (F=96500 C/mol), M-molecular weight (65 g/mol), I- the total electric current (A) and t- electrolysis time (s).

The solubilization degree of zinc anodic remnants obtained in the electrochemical process was evaluated taking in consideration the amount of zinc chemically dissolved, under similar experimental conditions (average mass of 0.4626 g Zn chemically dissolved), as shown in the formula:

$$SD = \frac{m_{Zn,f} \cdot 100}{m_{Zn,i} - 0.4626}$$

where: $m_{Zn,i}$, respectively $m_{Zn,f}$ are the initial, respectively de final mass of zinc anodic remnants, weighed before and after the experiment.

The initial and final composition of the solutions was determined for each step of the process, using a Fischerscope X-ray System XDVM (Helmut Fischer GmbH, Sindelfingen, Germany).

ACKNOWLEDGEMENTS

The authors wish to thank for financial support the projects co-financed by the Sectorial Operational Program For Human Resources Development 2007 – 2013 - contract no.: **POSDRU/88/1.5/S/60185** – “Innovative doctoral studies in a Knowledge Based Society” and - contract no.: **POSDRU/89/1.5/S/60189** – “Postdoctoral Programs for Sustainable Development in a Knowledge Based Society”.

REFERENCES

1. M. Anton, A. Manciulea, P. Ilea, *Studia UBB Chemia*, **2011**, *LVI (4),* 223.
2. A.E. Saba, A.E. Elsherief, *Hydrometallurgy,* **2000**, *54*, 91.
3. M. Ojaghi Ilkhchi, H. Yoozbashizadeh, M. Sadegh Safarzadeh, *Chemical Engineering and Processing,* **2007**, *46,* 757.
4. A.B. Velinchenko, J. Portillo, M. Sarret and C. Muller, *Journal of Applied Electrochemistry,* **1999**, *29,* 1119.
5. M. Datta, *Electrochemical Science and Technology,* **1993**, *37,* 207.
6. C.H.A.O. Liyan, M. Ishikawa, M. Okido, *Transactions of Nonferrous Metals Society of China*, **2002**, *03*, 757.
7. Z. Huajun, G. Zhenghai, Z. Jinhuan, *Hydrometallurgy*, **2007**, *89*, 369.
8. M. Mouanga, P. Berçot, J.Y. Rauch, *Corrosion Science*, **2010**, *52*, 3984.
9. M. Mokaddem, P. Volovitch, K. Ogl, *Electrochimica Acta*, **2010**, *55*, 7867.
10. M.B.J.G. Freitas, M.K. de Pietre, *Journal of Power Sources*, **2004**, *128*, 343.
11. M. Anton, F. Imre-Lucaci, S.-A. Dorneanu, P. Ilea, National Conference with international participation: “*Corrosion and AntiCorrosive Protection”,* 16-18 September **2010**, Cluj-Napoca.
12. C.C.B. Martha de Souza, J. A.Soares Tenório, *Journal of Power Sources,* **2004**, *136,* 191.
13. Q.B Zhang, Y.Hua, *Hydrometallurgy,* **2009**, *99,* 249.
14. Francesco Ferella, Ida De Michelis, Francesco Veglio, *Journal of Power Sources,* **2008**, *183*, 805.
15. K.I. Popov, S.S. Djokic, B. N. Grgur, *Kluwer Academic Publishers, New York*, **2002**, 179.
16. A.Recéndiz, I. González, J. L. Nava, *Electrochimica Acta,* **2007**, *52*, 6880.