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COMPARATIVE STUDY OF SOLUBILIZATION METHODS FOR ZINC AND MANGANESE RECOVERY FROM SPENT BATTERIES

MIHAELA ANTON[a], ADRIANA MANCIULEA[a], PETRU ILEA[a, *]

ABSTRACT. The solubilization of used batteries components is of great scientific and economic interest, on account of recycling requirement of these wastes and recovery of valuable materials. In this paper, the recovery of zinc and manganese from Zn-$ZnCl_2$-MnO_2 (Zn-carbon) spent batteries was studied through chemical and electrochemical acid leaching experiments. Experimental parameters, such as acid concentration, solid: liquid ratio (S: L), temperature, time and current intensity were studied related to the dissolution of the black powder of the Zn-MnO_2 batteries. Leaching tests were carried out using H_2SO_4, in order to maximize zinc extraction and minimize Mn and Fe extraction. The best conditions for acid leaching (98 % of Zn, 24 % of Mn and 18 % of Fe) were obtained with 2 M H_2SO_4, S: L= 1:5, room temperature and 1 hour leaching time. The results of electrochemical experiments showed selective leaching of Zn, together with a good recovery of metallic Zn (99.99% purity) at the cathode.

Keywords: *environmental protection, recycling, Zn–carbon batteries, chemical /electrochemical leaching.*

INTRODUCTION

The zinc–carbon and Zn–MnO_2 alkaline batteries are included as non-rechargeable batteries (primary cells), which are designed to be fully discharged only once, and then discarded [1].

Zn–$ZnCl_2$-MnO_2 (Zn-C) used batteries, that account for almost 90% of waste batteries, are mainly composed of Zn, MnO_2, Fe and discharge yields such as ZnO, Mn_2O_3 [2]. The presence of iron is due to the dismantling mode and the electrochemical manufacture of MnO_2.

Currently, these spent electrochemical power sources are treated as wastes and dumped in landfills or incinerated, representing a serious pollutant in terms of metals content when discarded in an inappropriate way. While

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[a] "Babes Bolyai" University, Faculty of Chemistry and Chemical Engineering, Kogălniceanu, No. 1, RO- 400084 Cluj- Napoca, Romania

[*] *pilea@chem.ubbcluj.ro*

the recycling and further reuse of metals from spent batteries are becoming essential due to environmental concerns, it is also important that these processes should be practical and cost-effective. The recycling of these wastes must be imperative and would offer economic benefits through the recovery of the valuable materials, as well as, the conservation of raw materials in the interest of the sustainable development. Recovered materials can be reused in battery production or other industries and would reduce the energy consumption and prevents pollution.

Several processes, as pyrometallurgical and hydrometallurgical, have been studied and developed to recover metals (Zn, Mn, Fe) and recycle batteries [3-8].

Depending on what follows in the recycling process, Zn and Mn recovery can be done in different ways, by means of acid and acid-reductive solubilization of black powder.

The use of different reducing agent in acidic leaching appears to be effective for solubilization of 80-90% Mn from spent batteries [4, 5]. Acid-reductive solubilization allows solubilization of large amounts of manganese, which will negatively influence the further recovery of zinc by electrodeposition [9-12].

To prevent electrode corrosion and to ensure high zinc purity, electrolytes must fulfil some minimum requirements related to metallic impurities concentrations. One of the most important metallic impurities is iron, because it is one of the major impurities. The maximum iron concentration tolerated in the electrolytic liquor is 10 mg/L [13]. As a result of this restriction, the liquor obtained in the leaching stage must be treated to remove most of this iron. Therefore it is necessary a separation of zinc, manganese and iron ions by precipitation from the leaching solution. The oxidative precipitation of manganese as insoluble manganese oxides, mainly MnO_2, has found a wide application for removal of manganese impurity from Zn, Co, and Ni electrowinning process. Various oxidants for Mn(II) have been studied and applied to the practical processes, including ozone, SO_2 /O_2 oxidizing mixture, Caro's acid, peroxydisulphuric acid, hypochlorite and chlorate [11, 14]. Additional manganese dioxide or potassium permanganate is usually introduced to the zinc sulphate electrolyte from the leaching process in order to oxidize iron impurities [15, 16].

By applying electrochemical processes to the black powder of spent batteries Mn^{2+} ions in the electrolyte is oxidized to MnO^{4-} which react immediately with Mn^{2+} to form Mn^{3+} and finally MnO_2 [17]. Therefore generation of MnO^{4-} ions determines the precipitation of MnO_2 and $Fe(OH)_3$, lowering Mn^{2+} and Fe^{2+} concentration in the leaching solution.

In this study, selective acid leaching of Zn from spent Zn–C batteries was investigated by chemical and combined chemical/electrochemical methods. Under these circumstances, the black powder (BP) was used as obtained from the batteries. The effect of various conditions of solubilization was investigated such as sulphuric acid concentration, time, temperature, solid: liquid ratio and current intensity. Electrochemical experiments using low concentration of H_2SO_4 were performed in order to evaluate the improvement of Zn extraction compared to chemical solubilization.

RESULTS AND DISCUSSION

Metallic components of black powder from spent batteries

Black powder was divided in 5 granulometric classes and then solubilized using *aqua regia*. Metallic components concentrations measured by AAS method are presented in Table 1. Concerning the metals content, no relevant differences between different granulometric classes were observed. Therefore the experiments were carried out in the homogeneous mass of the material, without dividing it in granulometric classes. Metals content in black powder is in the range of those reported in the literature depending on the degree of discharge of the battery [7, 18].

Table 1. Metal content in the black powder (*)

Granulation (mm)	Zn %	Mn %	Fe %
3.15	16.7	25.0	0.42
2	22.4	30.6	0.80
1	22.7	30.0	0.78
0.5	20.5	31.0	0.97
<0.5	18.3	32.6	0.82

(*) percentages calculated in relation to the mass of solid taken for analysis; others miscellaneous parts (graphite and oxygen) represent the difference up to 100%.

Chemical solubilization

Acid concentration and solid-liquid ratio effects

The extraction degrees of Zn, Mn and Fe as a function of solid : liquid ratios (g/mL) at different concentrations of H_2SO_4 are shown in Figure 1.

At higher concentrations of H_2SO_4, for example 97% H_2SO_4 (data not shown), the extraction yield for Zn (6.84%) and Mn (7.13 %) were very low. Under these conditions, the leaching experiments were conducted with 0.5 M, 1 M and 2 M H_2SO_4.

As seen in Figure 1, in all cases, the leaching degree of Zn is much higher than for Mn and Fe.

Lower acid concentrations, 0.05 M H_2SO_4, provide a poor extraction degree, even with large S:L (Zn 51%, Mn 14%, 0.05 M H_2SO_4, S:L= 1:60, 1h, 25° C), while with increasing H_2SO_4 concentration, the extraction of metals increases.

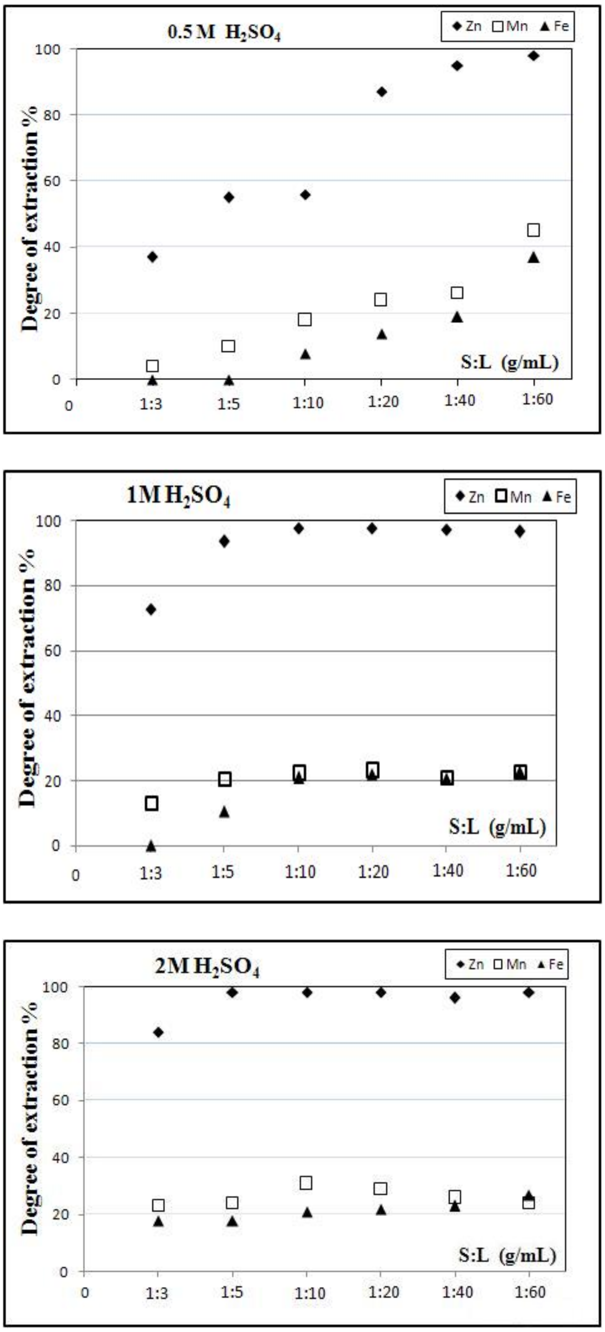

Figure 1. Influence of S:L ratio on the leaching degree of Zn, Mn and Fe after 1 hour, for different concentration of H_2SO_4, 25° C

Our aim was to have high extraction degree of zinc and minimum extraction degree for iron and manganese. For this reason, 2 M H_2SO_4 was considered sufficient, with a good leaching efficiency for S:L ratio of only 1:5. Figure 1 also shows that lower mixing ratios lead to an increase in the metals extraction degree. There are no relevant differences regarding the extraction yields between S:L of 1:5 and 1:40 or 1:60. Considering also that handling large volumes is difficult, the following experiments were carried out at S:L ratio of 1:5.

Effect of the solubilization time

Figure 2 shows the influence of time on the leaching of Zn, Mn and Fe in 1 M and 2 M H_2SO_4.

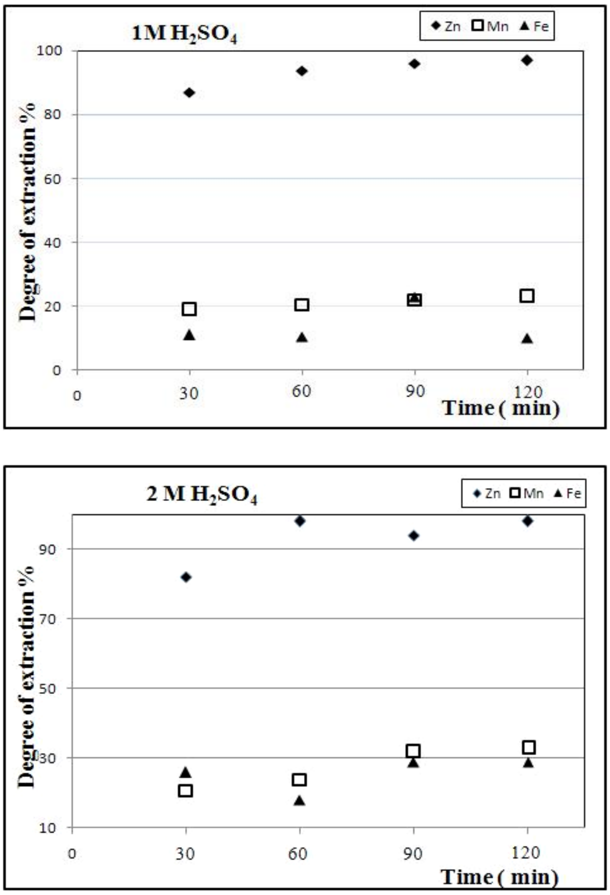

Figure 2. Influence of time on the extraction degree of Zn, Mn and Fe in 1 M and 2 M H_2SO_4 at 25ºC

Given the low extraction degree of Zn during 1 h experiments, at S:L = 1:5 (55% Zn, 10% Mn), the time evaluation for 0.5 M H_2SO_4 was not considered necessary.

The extraction degree for Zn in 2 M H_2SO_4 had a 16% increase in time, from 30 to 60 minutes, whilst for Mn there is slight effect (3% increase). In 1 M H_2SO_4, the increase in metal extraction is not so great (7 % Zn, 2 % Mn from 30 to 60 minutes).

Increasing solubilization time from 30 to 120 minutes does not influence greatly the extraction degree of Zn and Mn.

Temperature effect

Figure 3 shows that the temperature has no major effect on the leaching of Zn in the range 25–80°C. At temperatures between 25 and 80 °C almost all the Zn is leached with 1 M and 2 M H_2SO_4. There is an increasing of Mn and Fe extraction degree with 2 M H_2SO_4 with the temperature increase. For Fe extraction with 1 M H_2SO_4 a decrease with temperature increase was observed.

Favorable impact of temperature increase will be analyzed in the following sections in conjunction with the others parameters.

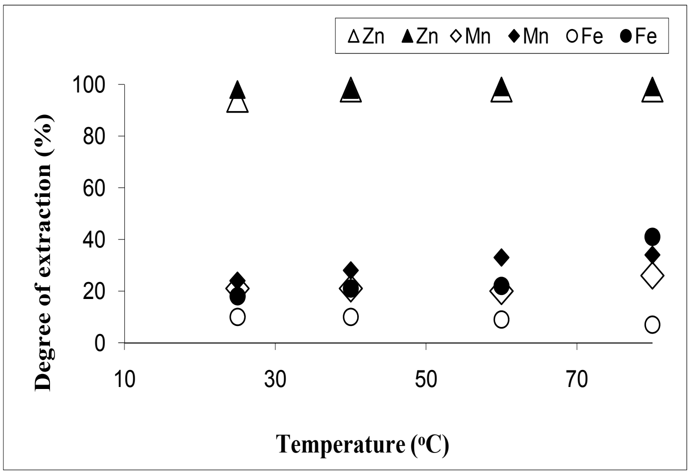

Figure 3. Influence of temperature on the leaching of Zn, Mn and Fe at different concentration of H_2SO_4, (Δ, ◊, o for 1 M and ▲, ♦, • for 2 M H_2SO_4)

Comparative analysis of experimental data for chemical solubilization

Regarding the performance of chemical solubilization process reported to previous studies presented in literature the following comparisons can be made. Based on the study of Senanayake and co-workers [19], the best leaching conditions for spent Zn–C batteries were: 1 M H_2SO_4, S: L= 1:10, 30-32 °C and 1 hour when the extraction efficiency obtained were 98% Zn and 35% Mn. Our experiments showed that the most favourable conditions for the extraction of zinc from BP are: 2 M H_2SO_4, S: L = 1:5, 25 °C and 1 hour. These conditions ensure the extraction of 98% Zn, 24% Mn and 18% Fe. In comparison with data reported by Senanayake and co-workers, the lower manganese leaching from our experiments is more convenient for the next step of Zn electroextraction process from leaching liquid. In other study carried out by El-Naidi *et al.* [18], the Zn and Mn efficiency extraction were lower (87% Zn and 7% Mn) than our results with the same H_2SO_4 concentration but higher temperature (50 °C) and longer time (2 hours).

Chemical/electrochemical solubilization of the black powder

To improve the performance of the solubilization process mixed solubilization tests (chemical and electrochemical) were carried out.

Table 2 shows the comparative results between the chemical extraction (C) and a mixed chemical/electrochemical (CE) extraction. Using these methods the degree of extraction in 0.5 and 2 M H_2SO_4, S:L = 1:10 and 1 hour of leaching time was evaluated. The CE method used an electrochemical reactor, operated galvanostatically at 0.2, 0.4 and 0.6 A, respectively. The Zn deposit was obtained on an Al cathode, with a purity of 99.99%, iron being the only impurity in the deposit.

As can be seen in Table 2, for 0.5 M H_2SO_4, by using electrochemical method the Zn solubilization was increased up to more then 80%, the Mn content decreased to 2-3% and the Fe solubilization decreased slightly.

Table 2. Degree of extraction for Zn, Mn and Fe by chemical and chemical/electrochemical solubilization in H_2SO_4 at 25°C

Extraction methods	**I(A)**	**H_2SO_4 concentration, M**					
		0.5			**2**		
		Zn	**Mn**	**Fe**	**Zn**	**Mn**	**Fe**
		Extraction degree, %					
C	-	56	18	8	98	24	18
CE	0.2	90	3	7	96	27	23
	0.4	83	2	4	98	25	28
	0.6	91	3	5	96	17	20

For 2 M H_2SO_4, an attempt was made in order to assess the content of metals in relation to the applied current intensity. The results for the experiments at four current intensities (0.1, 0.2, 0.4, 0.6 A), S:L= 1:10 are shown in Figure 4.

It can be seen a decrease of the extraction degree for Mn and Fe with increasing the current intensities. The concentration level for Zn decreases due to the process of electrodeposition.

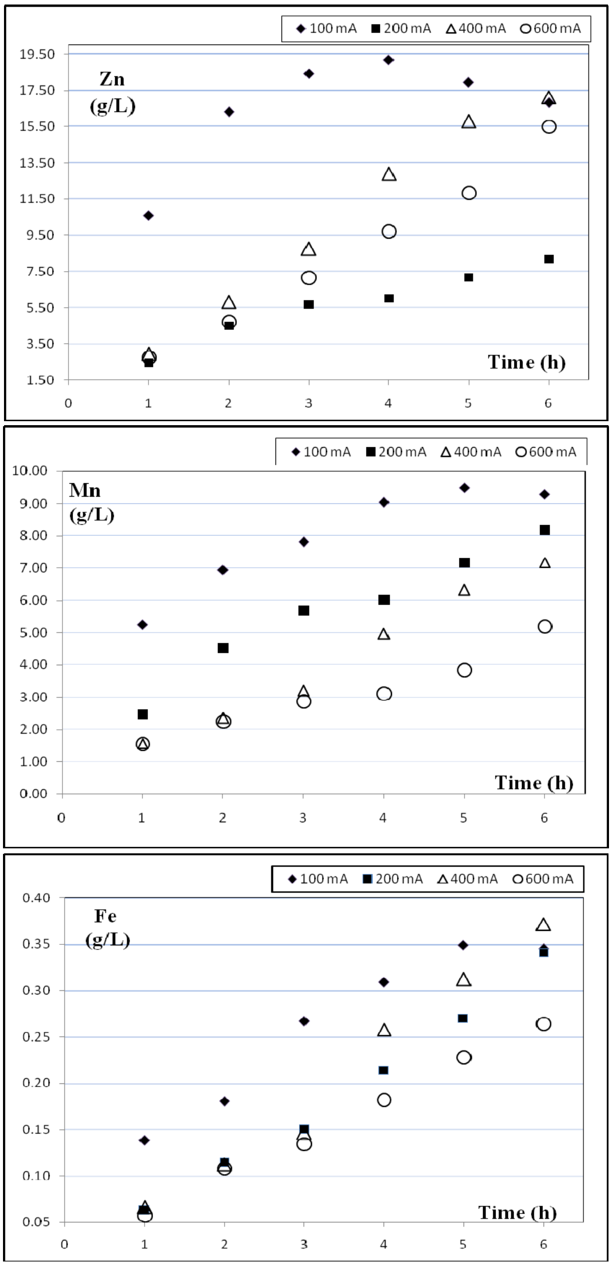

Figure 4. Variation of Zn, Mn and Fe concentration with time at different current intensities (0.1, 0.2, 0.4 and 0.6 A) with 2 M H_2SO_4, S: L= 1:10.

In the electrochemical experiments with 0.5 M H_2SO_4, the low degree of extraction for Mn and Fe can be explained by the oxidative precipitation of manganese and iron as insoluble compounds, mainly MnO_2 and $Fe(OH)_3$. During the anodic solubilization process, the electrolyte solution had pink coloration specific to MnO_4^- ions, which oxidized Mn(II) and Fe(II) to higher valence oxides.

CONCLUSIONS

The appropriate leaching conditions of BP Zn-C spent batteries, by using chemical and electrochemical methods, were investigated in order to obtain a high extraction of zinc and to minimize the iron and manganese solubilization. Chemical solubilization was evaluated taking into consideration the influence of different parameters such as acid concentration, solid-liquid mixing ratio, solubilization time and temperature. The results showed that the increasing of acid concentration leads to an increase in the degree of extraction. For a mixing ratio S: L = 1:5, provided a degree of extraction of 94-98% Zn, 21-24% Mn and 10-18% Fe in 1 M or 2 M H_2SO_4, in 1 hour.

The combined chemical and electrochemical solubilization using diluted H_2SO_4 allowed efficient manganese and iron removal at room temperature, by oxidative precipitation, avoiding high temperature alternative processes and addition of other reagents.

When the current intensity increases from 0.2 A to 0.6 A, the combined solubilization in 2 M H_2SO_4 showed a decrease in Mn and Fe concentrations with approximately 60%, respectively 70%, due to the oxidative precipitation without supplementary addition of reagents. Under these circumstances, the subsequent electroextraction of pure Zn is simpler and more efficient than in presence of higher concentrations of Mn and Fe.

EXPERIMENTAL SECTION

The reagents used were of analytical reagent (AR) grade. The leaching solutions consisted of aqua regia (3:1 HCl: HNO_3 ratio), H_2SO_4 solutions at specified concentrations.

Spent Zn-carbon batteries, collected from waste yard and used during this study were R20 size. These cells were manually cut into halves along with their longitudinal axes using a saw blade. The active paste inside the cell has been removed and its weight represented 71% of the total weight of the spent batteries. Black powder, a mixture of MnO_2, ZnO, $ZnCl_2$, FeO and coal, was crushed after being disassembled and divided into granulometric classes <0.5 mm, 0.5 mm, 1 mm, 2 mm, 3.15 mm. Metal content was determined by atomic absorption spectroscopy (AAS) for each grain size class in part by solubilization in aqua regia for 2 hours, 1:10 ratio (Table 1).

Chemical leaching was performed under constant stirring, using H_2SO_4 (concentration: 0.5 M, 1 M, 2 M), different solid: liquid ratios (1:3, 1:5, 1:10, 1:20, 1:40, 1:60), time (30, 60, 90, 120 minutes).

The electrochemical experiments were performed using a DXC240 computer controlled bipotentiostat. Anodic solubilization tests were carried out in 0.5 M and 2 M H_2SO_4, in a volume of 100 mL. The current intensity values were from 0.1 A to 0.6 A, in order to investigate the degree of extraction of metals from black powder. Working electrodes used were aluminium plate (4.8 cm^2) as a cathode and lead (16.8 cm^2) as current collector. Lead plate was inserted in a nylon bag, which contained the black powder of batteries and then immersed in electrolyte solution.

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