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## LEACHING OF ZINC AND MANGANESE FROM USED UP ZINC-CARBON BATTERIES USING AQUEOUS SULFURIC ACID SOLUTIONS

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Zinc-carbon and alkaline zinc-manganese dioxide batteries are widely used for powering small appliances as they have favorable electrical properties/price ratio. Due to a large amount of these batteries sold every year they are a considerable secondary source of zinc and manganese. A hydrometallurgical method of recovering those metals seems to be attractive.

In this paper leaching tests have been presented to evaluate the leaching behavior of Zn and Mn and their compounds of interests under different conditions such as solid/liquid ratio (weight of sample/leaching solution volume), sulfuric acid concentrations, temperature and time of leaching. The acid concentration was investigated in the range of 0.2 to 5.0 M and the leaching time was from 30 minutes to 5 hours. The tests were carried out in temperature range of 20 – 80°C.

It was shown that the leaching recovery of zinc and manganese increases with increasing sulfuric acid concentration up to 2.0 M and zinc is dissolved under these conditions, whereas only around 50% of manganese is recovered. It was found that the rate of zinc leaching is higher than that of manganese and the rate of both reactions is increasing with temperature as well as with a decrease of the solid/liquid ratio.

*keywords: used up batteries, zinc, manganese, leaching, sulfuric acid*

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## 1. INTRODUCTION

Presently economical and environmental requirements impose a development of effective and inexpensive methods for recovering of valuable metals from secondary sources. Zinc-carbon and alkaline zinc-manganese dioxide batteries are widely used as they have good electrical properties/price ratio. Due to large amount of these batteries selling every year they can be thought over as a considerable secondary source of Zn and Mn. The comparison of price changes for zinc and manganese over last three years are shown in Fig. 1. A hydrometallurgical method of recovering those metals seems to be attractive. Recycling process of zinc-carbon and alkaline-manganese batteries should be developed to achieve environmental conservation as well as the effective utilization of metal resources.



Fig. 1. The comparison of price changes for zinc and manganese over last three years (www.infomine.com)

Several methods to recover metal values from used up batteries based on pyrometallurgical or hydrometallurgical technologies can be found in the literature. The pyrometallurgical method consists basically of selective volatilization of metals at elevated temperatures followed by condensation. The examples of such processes are BATREC, SNAM-SAVAN, SAB-NIFE and INMETCO (Bernardes et al., 2004; Espinosa et al., 2004; Kosarga et al., 2006; Salgado et al., 2003). Except of the BATREC process, the other methods are commonly used to recover cadmium from Ni-Cd batteries by volatilisation at temperatures around 900°C. On the other hand, the BATREC process recycles zinc and mercury from zinc-carbon and alkaline batteries at 1500°C. Highly pure zinc is obtained when no Ni-Cd batteries are present and treated because zinc and cadmium are not selectively volatilised in the furnace. Therefore, a classification step is necessary. Generally, pyrometallurgical routes do

not require batteries dismantling, however applied operations are very energy consuming and some emissions of dust and gases are expected.

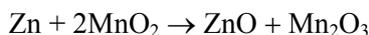
The hydrometallurgical routes are commonly found more economical and efficient than pyrometallurgical methods. The metal separation routes based on hydrometallurgical operations are characterised by lower energy consumption, higher metal selectivity and no air pollution, as there are no particles produced. However, some pre-treatment steps are necessary to improve metal dissolution rates in the aqueous phase, like batteries sorting, dismantling, magnetic separation and leaching. The examples of hydrometallurgical processes being in commercial use could be BATENUS (Fröhlich and Sewing, 1995), and MODIFIED ZINCEX (Martin et al., 2001). These processes differ basically in the metal separation method used to treat the obtained leach liquor. The BATENUS process can treat any type of batteries, except of button cells that contain high mercury levels. After leaching with sulfuric acid, zinc present in the liquor can be separated by solvent extraction (SX) while copper, nickel and cadmium can be selectively separated by an ion exchange (IX) technique and manganese is precipitated as  $MnCO_3$ . The MODIFIED ZINCEX process uses solvent extraction to produce a high quality zinc electrolyte solution suitable for producing zinc or zinc sulfate. Zinc extraction from the leaching liquor (PLS – pregnant leach solution) is performed with di-2-ethylhexyl phosphoric acid (D2EHPA) as extractant. Manganese is left in the raffinate and then is crystallized as  $MnSO_4$ .

Although a few of hydrometallurgical methods of processing of spent batteries are already in use there is still a need for new methods providing higher efficiency and lower operational costs. This paper presents results of leaching tests of spent zinc-carbon and alkaline zinc-manganese dioxide batteries with sulfuric acid solutions.

## 2. EXPERIMENTAL PROCEDURE

### 2.1. BATTERIES

Zinc-carbon and alkaline zinc-manganese dioxide batteries are popular and widely used. Detailed description of their construction can be found elsewhere (Linden and Reddy, 2001). The zinc-carbon battery consists of a zinc can (serves as the battery container and anode), a manganese dioxide cathode and an electrolyte of ammonium chloride and/or zinc chloride dissolved in water. Carbon (acetylene black) is mixed with manganese dioxide to improve conductivity and retain moisture and compressed under pressure to form a bobbin. The bobbin is the positive electrode and is also called black mix, depolarizer or cathode. A carbon rod, serving as the current collector for the positive electrode is inserted into the bobbin. The battery is inserted into a steel can with plastic separator. As the battery is discharged, the zinc is oxidized and the manganese dioxide is reduced. A simplified overall battery reaction can be written as:



Although the alkaline zinc-manganese dioxide battery uses the same anode and cathode material, its construction is quite different. The active materials in these batteries are manganese dioxide, an aqueous alkaline electrolyte, and powdered zinc metal. The electrolyte is a concentrated solution of KOH (usually 35 to 52%). Powdered zinc is used for the anode to provide a large surface area for reduced current density and to distribute solid and liquid phases more homogeneously. The components are inserted into a steel can. A simplified overall battery reaction can be written as:



In our research AA (R6) of different manufacturers were used. All batteries were dismantled. After separation of iron scrap, plastic and paper, the remaining part of battery was cut and crushed into small parts below 5 mm in size and then dried for 24 hours and ground. All the tests were carried out using homogeneous samples of this material. The average content of the main components of the mixture were determined by atomic absorption spectrometry after dissolution of the sample in aqua regia and are presented in Table 1. The obtained values correspond to those which can be found in literature (Bartolozzi et al., 1995; Salgado et al., 2003)

Table 1. Metal components content of investigated batteries

Battery type	Component contents (%)					
	Zn	Mn	K	Fe	Co	Ni
Zn-C	5.20	23.10	-	0.50	0.01	0.01
Alkaline	18.0	29.85	7.55	1.42	0.01	0.01

## 2.2. LEACHING TESTS

The two major components of the used up batteries are metallic zinc and manganese dioxide. An analysis of E-pH diagrams for the Zn-H<sub>2</sub>O and Mn-H<sub>2</sub>O systems (Fig. 2) allows to choose the leaching system. According to data presented in Fig. 2, in strongly acidic solutions, both zinc and manganese should be present in the form of divalent ions. In the case of manganese, it can also be in the form of solid MnO<sub>2</sub>. Therefore, acids seem to be suitable for leaching of used up Zn-MnO<sub>2</sub> batteries. Among them, sulfuric acid is attractive due to its accessibility and low price. For that reason leaching experiments were carried out using sulfuric acid solutions.

In each test a sample 2.0 g of the battery was leached in appropriate volume of H<sub>2</sub>SO<sub>4</sub> solutions of suitable concentrations in a thermostatic beaker under mechanical stirring at the rate of 600 rpm. Preliminary tests have shown that the rates above 500 rpm do not influence the rate of leaching. During and at the end of the experiments, samples of the leached pulp were taken and separated by filtration. The concentration

of metal ions in the leach aqueous solutions was determined by atomic absorption spectrometry (AAS).

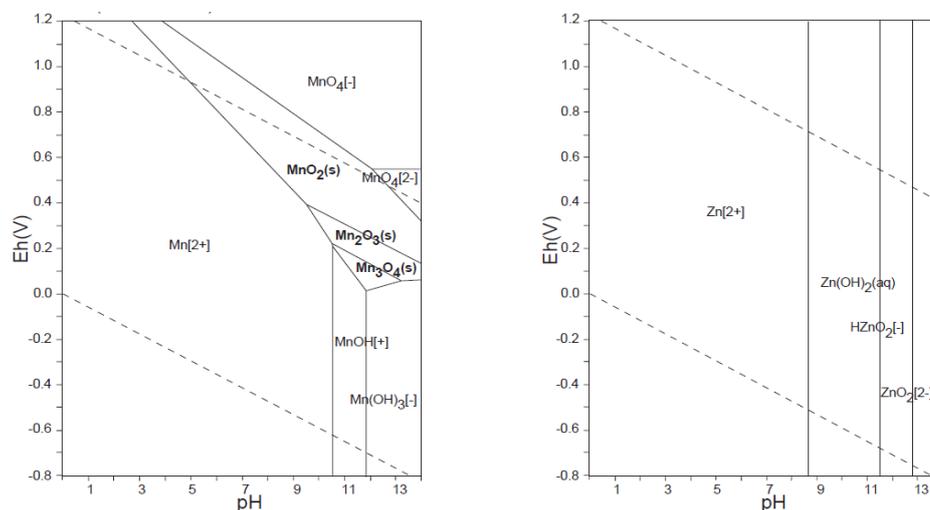


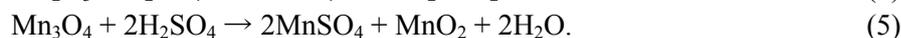
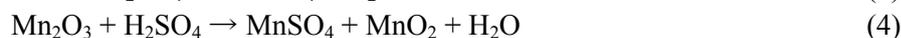
Fig. 2. E-pH diagrams for the Zn-H<sub>2</sub>O and Mn-H<sub>2</sub>O systems (Atlas of Eh-pH diagrams, 2005)

### 3. RESULTS AND DISCUSSION

The effect of four factors, i.e. H<sub>2</sub>SO<sub>4</sub> concentration, reaction time, temperature as well as solid to liquid ratio on metal leaching from the used up zinc carbon and zinc-manganese alkaline batteries was studied. Leaching of zinc and manganese as a function of time for two selected concentrations of sulfuric acid are shown in Figs 3a (2.0 mol dm<sup>-3</sup>) and 3b (0.2 mol dm<sup>-3</sup>). Taking into consideration that zinc occurs in batteries as a metal or metal oxide the following reactions can be written:



Manganese can be detected as MnO<sub>2</sub> and Mn<sub>2</sub>O<sub>3</sub> depending on a discharge level of the battery. The following leaching reaction are expected:



A relationship between metals leaching and sulfuric acid concentration at 20°C and after 1 hour of leaching is shown in Fig. 4. Leaching of zinc depended highly on the H<sub>2</sub>SO<sub>4</sub> concentration up to about 2.0 mol dm<sup>-3</sup>, but the leaching of manganese does not

depend so strongly on  $\text{H}_2\text{SO}_4$ . A further increase of acid concentration does not cause of leaching efficiency increase of metals. However, after 1 hour of leaching the percentage of leached zinc was slightly above 60% for alkaline and about 55% for zinc-carbon batteries. Leaching efficiency of manganese was always smaller than that for zinc. It is undoubtedly caused by the presence of  $\text{MnO}_2$  produced in reactions (4) and (5) which is insoluble in sulfuric acid solutions. The percentage of leached manganese does not exceed 20%.

The only way to increase the leaching efficiency is to increase the temperature of leaching process. The effect of temperature on the leaching efficiency of zinc and manganese was studied using 2M  $\text{H}_2\text{SO}_4$  and solid/liquid ratio equal to 100 at leaching time equal to 1 hour. The results are shown in Fig. 5.

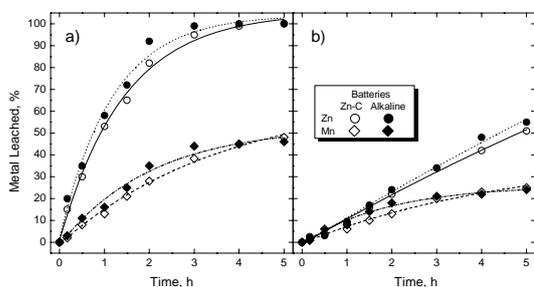


Fig. 3. Leaching efficiency of zinc and manganese in sulfuric acid solutions as a function of time.  $\text{H}_2\text{SO}_4$  concentration:  $2.0 \text{ mol dm}^{-3}$  (a) and  $0.2 \text{ mol dm}^{-3}$  (b), temperature:  $20^\circ\text{C}$ , solid/liquid ratio: 1:100

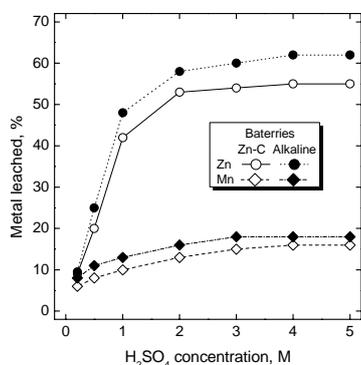


Fig. 4. Leaching efficiency of zinc and manganese as a function of sulfuric acid concentration. Temperature:  $20^\circ\text{C}$ , solid/liquid ratio: 1:100, process time: 1 hour

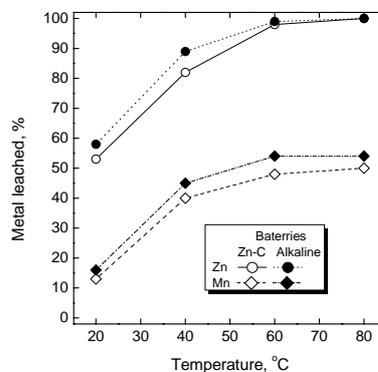


Fig. 5. Leaching efficiency of zinc and manganese as a function of process temperature.  $\text{H}_2\text{SO}_4$  concentration:  $2.0 \text{ mol dm}^{-3}$ , solid/liquid ratio: 1:100, process time: 1 hour

The results presented in Fig. 5 indicate that in the case of Zn-Mn batteries only about 55% of zinc and 16% of manganese can be leached at  $20^\circ\text{C}$ . In the same conditions the leaching efficiency for alkaline batteries were slightly higher and were

about 62% and 18% for zinc and manganese, respectively. The leaching efficiency of the both metals increased with increase in leaching temperature up to 60°C. Further increase in temperature did not show any significant increase in the recovery of zinc as well as manganese. At the temperature of 60°C all amount of zinc and zinc oxide was leached but only about 50% of manganese compounds were leached. This is because of the insoluble  $\text{MnO}_2$  presence of in sulfuric acid solutions.

The effect of solid/liquid ratio on the leaching efficiency of zinc (i.e. higher leached metal) was studied in the range of 1:20 to 1:200. The experimental conditions were 2.0 M  $\text{H}_2\text{SO}_4$ , and 60°C. The results of leaching are presented in Fig. 6 as the relationships between leaching efficiency and leaching time for fixed solid/liquid ratio. The results indicate that the leaching efficiency of zinc is similar for both type batteries and increases with increase of ratio of solid to liquid, i.e. from about 80% for 1:20 to 100% for 1:100 and 1:200.

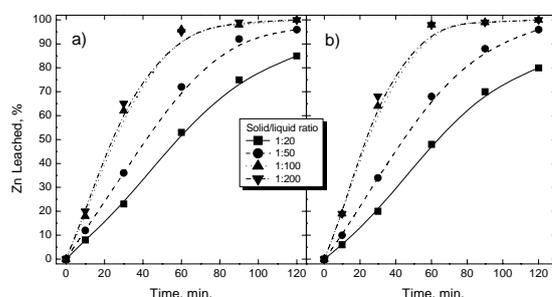


Fig. 6. Leaching efficiency of zinc in 2.0 M sulfuric acid solutions as a function of time and solid/liquid ratio for zinc-carbon (a) and zinc-manganese alkaline (b) spent batteries. Temperature of process: 60°C

Based on the above experimental results, the final optimum conditions for leaching process were determined to be 2.0 M sulfuric acid, a process temperature of 60°C and a solid to liquid ratio of 1:100. Under these conditions 100% of zinc and about 50% of manganese could be leached in the time of 1 hour.

#### 4. CONCLUSION

Due to a large amount of zinc-carbon and alkaline batteries selling every year they are a promising secondary source of zinc and manganese. This paper discusses and demonstrates the alternative use of leaching with sulfuric acid as Zn and Mn recovery process from batteries. The results of the examinations indicate that the method of leaching with sulfuric acid for an acid concentration of 2.0 M  $\text{H}_2\text{SO}_4$ , liquid/solid ratio of 1:100 and temperature of 60°C is suitable for recovering of almost 100% of Zn as the aqueous solution of  $\text{ZnSO}_4$ . However, in these conditions only about 50% of manganese could be transferred into solution, what is caused probably by the insoluble  $\text{MnO}_2$  formation during leaching process of manganese compounds. To solve this problem leaching with a moderate reductive agent (like glucose,  $\text{Cl}^-$  ions,  $\text{SO}_2$ , hydrogen peroxide etc.) can be used. This study will be a subject of next papers.

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**Gęga, J., Walkowiak, W.,** *Ługowanie cynku i manganu z zużytych baterii cynkowo-węglowych z użyciem roztworów kwasu siarkowego*, *Physicochem. Probl. Miner. Process.*, 46 (2011) 155-162, (w jęz. ang), <http://www.minproc.pwr.wroc.pl/journal>

Elektrochemiczne ogniwa cynkowo-węglowe oraz alkaliczne cynkowo-manganowe są obecnie najczęściej stosowanymi źródłami zasilania małowatowych urządzeń elektrycznych powszechnego użytku przede wszystkim z powodu korzystnego stosunku ceny do parametrów elektrycznych. Biorąc pod uwagę dużą ilość sprzedawanych corocznie ogniw tego rodzaju i stosunkowo krótki okres ich użytkowania mogą stanowić one znaczące wtórne źródło cynku i manganu oraz ich związków.

W prezentowanej pracy przedstawiono wyniki ługowania zużytych ogniw  $Zn-MnO_2$  za pomocą roztworów kwasu siarkowego(VI). Badano wpływ na efektywność ługowania takich parametrów, jak: stężenie kwasu, temperatura, czas prowadzenia procesu oraz stosunek fazy stałej do ciekłej (masa próbki poddawanej ługowaniu do objętości roztworu ługującego). Stężenie kwasu siarkowego(VI) zmieniano w zakresie od 0,2 do 5,0 M, a ługowanie prowadzono w czasie od 30 minut do 5 godzin. Temperatura procesu była zmieniana w zakresie od 20 do 80°C.

Stwierdzono, że stopień wyługowania cynku i manganu wzrasta ze wzrostem stężenia kwasu do wartości 2,0 M. W tych warunkach uzyskano całkowite wyługowanie cynku przy jednoczesnym ok. 50% wyługowaniu manganu. Szybkość ługowania cynku była większa od szybkości ługowania manganu a w obydwu przypadkach wzrost temperatury oraz zwiększanie stosunku fazy stałej do ciekłej powodowały zwiększenie szybkości ługowania.

*słowa kluczowe: zużyte baterie, cynk, mangan, ługowanie, kwas siarkowy(VI)*