INVESTIGATION OF DISSOLUTION KINETICS OF Zn AND Mn FROM SPENT ZINC-CARBON BATTERIES IN SULPHURIC ACID SOLUTION

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ABSTRACT
The aim of this study is to examine the dissolution kinetics of zinc and manganese from spent zinc-carbon battery in sulphuric acid solution. The leaching experiments were carried under the following conditions: leaching temperatures of 30°C, 40°C and 50°C; sulphuric acid concentration of 0.5 M; stirring speed of 400 rpm; solid/liquid ratio of 5/500 g/mL and particle size of -53 µm. In these conditions, while all of the zinc was dissolved, about 69% of manganese was dissolved. To determine the kinetics of dissolution of the zinc and manganese in sulphuric acid medium, different shrinking core models were applied to the dissolution recoveries obtained at variable temperatures. Kinetics analysis showed that the zinc and manganese dissolution from spent zinc-carbon battery could be described by diffusion from product layer. The activation energies (Ea) and Arrhenius constants for the dissolution reactions were calculated. Activation energies (Ea) were determined for Zn and Mn as 94.53 kJ/mol and 1.41 kJ/mol, respectively.

Keywords: Leaching, Dissolution kinetics, Zn–C battery, Zn, Mn, Activation energy, Sulphuric acid
1. INTRODUCTION

Zinc-carbon type dry cell batteries are being commonly used during last 150 years in the world. There are two types of zinc carbon batteries mainly as leclanche battery and zinc chloride battery. A battery is an apparatus which converts the chemical energy into electric energy by an oxidation–reduction (redox) reaction. They are widely used in small household apparatus like flash light, toys, radios, watches, etc. In these batteries, anode material is zinc and the cathode is a mixture of manganese dioxide and carbon. Because of the spent zinc–carbon batteries contain zinc, manganese dioxide and also zinc oxide and manganese (III) oxide produced from discharging reaction (Bernardes, et al., 2004; Park, et al., 2006; Shin, et al., 2009), they are important secondary source of Mn and Zn. During discharging, a chemical change occurs in the battery which can be expressed by the following reaction:

\[ \text{Zn} + 2\text{MnO}_2 \rightarrow \text{ZnO} + \text{Mn}_2\text{O}_3 \]  (1)

A lot of studies were found related with hydrometallurgical processes for recovery of manganese and zinc from spent zinc–carbon batteries in the literature (Shin, et al., 2009; Ferella, et al., 2008; Baba, et al., 2009; sayilgan, et al., 2010; Gęga and Walkowiak, 2011; Kursunoglu and Kaya, 2014; Buzatu, et al., 2014; Taner, et al., 2016; Abedin, et al., 2017; Chen, et al., 2017). Generally, these studies were carried out using only basic solution, acidic solution (hydrochloric acid, sulphuric acid) or reductive agents with these acid solutions. However, dissolution kinetics of manganese and zinc from spent zinc–carbon batteries were studied (Baba, et al., 2009; Gęga and Walkowiak, 2011; Taner, et al., 2016). Because, it is harmful to the environment discard of spent batteries is prohibited by stringent environmental regulations in most countries. In the event of the disposal or incineration of waste batteries, heavy metals may contaminate the environment. Therefore, it must be given to importance to collecting and recycling of spent batteries. Prevention of environmental pollution and research for the recycling of precious metals have become an important issue. For this reason, the application of hydrometallurgical processes has been carried out considering the economic and environmental suitability.

In this work, it is aimed to dissolution of manganese and zinc in sulphuric acid solution from spent zinc carbon batteries. In addition, the dissolution kinetics were studied and the activation energies required for dissolution were calculated.

2. MATERIAL AND METHOD

In this study, spent zinc–carbon batteries were used which collected from Selçuk University spent battery boxes. The plastic, paper and metal parts were removed from the zinc-carbon batteries that were passed through processes such as separation, dismantling. The separated pieces of the spent zinc-carbon battery were weighed and the weight percentages were determined as 56.42% black paste, 13.84% steel can, 11.58% zinc can, 7.65% carbon rod, 4.65% paper, 3.33% plastic and 2.53% metal cover and bottom. The obtained black paste was dried at 105°C for 24 hours. Moisture of black paste was calculated as 12.51%. The battery powder was ground using a ball mill and sieved to obtain particle size less than 106 μm. The original powder was washed to remove electrolyte with distilled water in a glass vessel at 60°C and dried to remove external impurities at 105°C for 24 hours. Then the powder was burned for one hour at 600°C in the furnace, to remove paper, plastic and carbon residues. Sieving was carried out and -106+75, -75+53, -53 μm particle size fractions were obtained. Approximately, 2 grams of sample was weighed and dissolved in the king water (HNO₃ + 3HCl) in a Teflon vessel. The solutions were diluted with distilled water to 100 ml in a volumetric flask. The amount of Mn and Zn was measured using a GBC brand SensAA model flame atomic absorption spectrometer (AAS). The manganese-zinc contents of waste battery powder of the original (-106 μm), washed (-106 μm) and -53 μm particle size were given in Table 1.

| Particle size, μm | Zn, % | Mn, % |
|------------------|------|-------|
| Original (-106)  | 21.52| 34.34 |
| Washed (-106)    | 22.87| 35.87 |
| -53              | 20.11| 36.46 |

The washed powders were analyzed by X-ray diffraction (XRD) to determine the mineralogical composition of powders and shown in Fig. 1. XRD analyses showed the presence of ZnO, MnO₂ and Mn₃O₄.
RESULTS AND DISCUSSION

3.1. Experimental Results

Leaching experiments were carried out using 500 mL solution of 0.5 mol/L sulphuric acid concentration. Battery powder in -53 µm fraction was used. 5 g of battery powder was used. Leaching solution was stirred at 400 rpm at 60 min of leaching time. Under these conditions, leaching experiments were performed at different temperatures (30°C, 40°C and 50°C). The results of these experiments, Zn and Mn extraction recoveries were given in Table 2. It can be seen from the Table 2 that Zn and Mn extraction recoveries increased with increasing temperature and leaching time. In these conditions, while all of the zinc was dissolved, about 69% of manganese was dissolved. The reason of this, since the leaching rate of manganese was increasing slightly in sulfuric acid leaching experiment, due to the insoluble of Mn⁴⁺. The reduction potential needs to be modified to turn Mn⁴⁺ into Mn²⁺ (Takeno, 2005).

| Leaching Time (min) | 30°C | 40°C | 50°C |
|---------------------|------|------|------|
|                     | Zn   | Mn   | Zn   | Mn   | Zn   | Mn   |
| 5                   | 65.01| 29.79| 78.91| 49.21| 96.84| 58.03|
| 10                  | 65.79| 32.94| 80.32| 53.11| 97.43| 61.02|
| 15                  | 67.06| 33.80| 82.36| 55.06| 98.49| 62.11|
| 30                  | 68.02| 39.01| 90.94| 58.16| 100  | 64.02|
| 45                  | 69.03| 45.02| 92.66| 59.03| 100  | 66.03|
| 60                  | 71.35| 50.67| 95.66| 62.72| 100  | 68.46|

3.2. Kinetic Models

Generally, the leaching process for heterogeneous reactions uses the shrinking core models controlling by chemical reaction, diffusion, and the diffusion through the product layer these kinetic models (Habashi, 1969; Levenspiel, 1999; Sohn and Wadsworth, 1986). This model was chosen because it is the most suitable model for dissolution reactions. The dissolution of Zn and Mn from spent zinc-carbon battery can be explained by a shrinking core model which can be expressed as follows:
\( aA_{\text{mol}} + bB_{\text{particle}} \rightarrow \text{Product} \)  \( (2) \)

To describe the dissolution of Zn and Mn from battery powder, a kinetic investigation was applied to results in Table 2. In shrinking core model, if the reaction is controlled by surface reaction,

\[ 1 - (1 - x)^{1/3} = k_s t \]  \( (3) \)

if the reaction is controlled by film diffusion,

\[ 1 - (1 - x)^{2/3} = k_f t \]  \( (4) \)

if the reaction is controlled by diffusion from product layer

\[ 1 - 2/3x - (1 - x)^{2/3} = k_d t \]  \( (5) \)

Equations were used, where \( x \) is the fraction reacted, \( t \) is the reaction time (min), \( k_s, k_f \) and \( k_d \) are the rate constants (Levenspiel, 1999; Habashi, 1969). Eqs. (3, 5) were applied to the experimental results. The correlation coefficients and apparent rate constants for each temperature were given in Table 3.

Considering the values given in Table 3, manganese and zinc dissolution from spent zinc–carbon battery could be described by the diffusion from product layer. Plots of 1-2/3x-(1-x)^{2/3} for various temperatures of Zn and Mn were given in Fig. 3 and Fig. 4.

| Temperature, °C | Surface Reaction 1-(1-x)^{1/3} | Film Diffusion 1-(1-x)^{2/3} | Diffusion from Product Layer 1-2/3x-(1-x)^{2/3} |
|-----------------|---------------------------------|-------------------------------|-----------------------------------------------|
|                 | Apparent rate constant \( (k_s) \times 10^3 \) for Zn | Correlation coefficient, \( (R^2) \) | Apparent rate constant \( (k_f) \times 10^3 \) for Zn | Correlation coefficient, \( (R^2) \) | Apparent rate constant \( (k_d) \times 10^3 \) for Zn | Correlation coefficient, \( (R^2) \) |
| 30              | 0.74921                         | 0.97                          | 0.97                                          | 0.97                                          | 0.97                                          | 0.97                                          |
| 40              | 4.58120                         | 0.97                          | 4.37922                                      | 0.96                                          | 6.74515                                      | 0.97                                          |
| 50              | 6.57444                         | 0.96                          | 4.09939                                      | 0.99                                          | 9.75871                                      | 0.99                                          |

| Temperature, °C | Surface Reaction 1-(1-x)^{1/3} | Film Diffusion 1-(1-x)^{2/3} | Diffusion from Product Layer 1-2/3x-(1-x)^{2/3} |
|-----------------|---------------------------------|-------------------------------|-----------------------------------------------|
|                 | Apparent rate constant \( (k_s) \times 10^3 \) for Mn | Correlation coefficient, \( (R^2) \) | Apparent rate constant \( (k_f) \times 10^3 \) for Mn | Correlation coefficient, \( (R^2) \) | Apparent rate constant \( (k_d) \times 10^3 \) for Mn | Correlation coefficient, \( (R^2) \) |
| 30              | 1.74282                         | 0.99                          | 2.92762                                      | 0.99                                          | 1.39855                                      | 0.99                                          |
| 40              | 1.22527                         | 0.96                          | 1.85357                                      | 0.96                                          | 1.35096                                      | 0.97                                          |
| 50              | 1.09626                         | 0.96                          | 1.56221                                      | 0.95                                          | 1.36704                                      | 0.97                                          |

**Fig. 3.** The variation in 1-2/3x-(1-x)^{2/3} with time at various temperatures for Zn.

**Fig. 4.** The variation in 1-2/3x-(1-x)^{2/3} with time at various temperatures for Mn.

Table 3. Values of \( k_s, k_f, k_d \) and correlation coefficients for variable temperatures.
3.3. Determination of Activation Energy

Apparent rate constants (k) at different temperatures were obtained from the slope of the linear plots in Fig. 3 and Fig. 4 for zinc and manganese respectively. Then the values of reaction rate constants (k) were plotted according to the Arrhenius type equation. The plot of ln k vs. 1000/T(K) was straight line for both zinc and manganese. The Arrhenius graphics were plotted using the apparent rate constants obtained by application of Eq. (5) (Figs. 5, 6). The activation energies required for dissolution of Zn and Mn were calculated as to be 94.53 kJ/mol and 1.41 kJ/mol, respectively. Similarly, in some kinetic studies using various acid media related with zinc and manganese dissolution from spent zinc–carbon batteries, shrinking core model was used. In these studies, activation energies were given as 22.78 kJ/mol, 23.03 kJ/mol for Zn (Baba, et al., 2009; Taner, et al., 2016) and 7.04 kJ/mol, 31.80 kJ/mol for Mn, respectively (Kursunoglu and Kaya, 2014; Taner, et al., 2016).

![Arrhenius plot of reaction rate against reciprocal temperature for dissolution of Zn.](image1)

![Arrhenius plot of reaction rate against reciprocal temperature for dissolution of Mn.](image2)

Fig. 5. Arrhenius plot of reaction rate against reciprocal temperature for dissolution of Zn.

Fig. 6. Arrhenius plot of reaction rate against reciprocal temperature for dissolution of Mn.

4. CONCLUSION

Dissolution kinetics of zinc and manganese from spent zinc-carbon batteries in sulphuric acid solution was investigated. Therefore, leaching experiments were performed using some constant parameters (sulphuric acid concentration of 0.5 M; stirring speed of 400 rpm; solid/liquid ratio of 5/500 g/mL and particle size of ~53 µm) at different temperatures (30°C, 40°C and 50°C). It was found that the dissolution rate increased with increase in the leaching temperature and leaching time. At 30°C, dissolution of Mn and Zn was reached at 60 min 50.67% and 71.35%, respectively. At 50°C, the best dissolutions of Mn and Zn were obtained as to be 68.46% and 100%.

In order to determine the dissolution kinetics of Zn and Mn, shrinking core model was applied to dissolution recoveries obtained at different temperatures. It was determined that zinc and manganese dissolved in sulphuric acid solution from spent zinc-carbon batteries by diffusion from product layer. Activation energies (Ea) were calculated for Zn and Mn as 94.53 kJ/mol and 1.41 kJ/mol, respectively.

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