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Investigation of the Dissolution Behaviors in Different Solvents of the Zinc and Manganese Powders Obtained from the Spent Alkaline Batteries

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Abstract: In this study, after the zinc and manganese powders were individually obtained from the spent alkaline batteries, their dissolution behaviors in different solvents were examined to determine the appropriate leaching reagent for each species. The aqueous solutions of the sodium hydroxide, ammonia, ammonium chloride, ammonium acetate, acetic acid, sulfuric acid, and hydrochloric acid were used as the leaching reagents with the aim of dissolving the zinc and manganese powders. In the dissolution experiments, the values of the concentration of relevant reagent, reaction temperature, solid to liquid ratio, stirring speed, and particle size were fixed at 1 mol/L, 40 °C, 0,5/500 g/mL, 500 rpm, and -40+50 mesh, respectively. It was determined that the hydrochloric acid was more effective reagent for both powder samples. The dissolution extent of manganese powder in the hydrochloric acid solutions was found to be 41,5% after 120 minutes of reaction time. It was observed that the zinc powder was completely dissolved in the hydrochloric acid solutions in 20 minutes of reaction time.

Keywords: Dissolution; Spent Battery; Zinc; Manganese.

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INTRODUCTION

The recycling of various industrial and domestic solid wastes has been a popular research area from both environmental and economical perspectives in recent years. Among the solid wastes, the spent batteries are considered as hazardous wastes due to the heavy metal content of their. Zinc-carbon and alkaline zinc-manganese dioxide batteries are widely used because of the versatility, low maintenance, favorable electrical properties/price ratio and its requirements by the electronic industry. These batteries are consumed in very large quantities due to its wide range of uses, and consequently, much waste containing metal are generated. The storage of these wastes in private areas can be a way out to reduce the environmental pollution. However, number of this kind of special storage spaces are limited, and the disposal costs can be very high. Therefore, the recovery of the major metal values of waste batteries can appear to be a more beneficial way to prevent the environmental pollution and decrease the consumption of raw material used in battery production. Thereby, the spent batteries may be evaluated as secondary sources of zinc and manganese because they contain a high amount of metal (1-3).

Pyrometallurgical and hydrometallurgical methods are usually applied for recovering metals from the waste batteries. The hydrometallurgical treatment of the spent batteries is more environmentally suitable and economical when compared with pyrometallurgical technique. The hydrometallurgical processing consists of mainly three steps, including leaching, solution purification, and metal recovery. The most important step in this processing technique is probably the leaching stage, which is a mass transfer operation, because the recovery efficiency depends on effective implementation of this stage. In the leaching step, the metal values in the waste battery powder are transferred from solid powder to solution medium by means of an aqueous solution. The yield of leaching process is affected by various factors, such as the type of solvent, reaction temperature, solid-to-liquid ratio, stirring speed, and particle size. In the treatment of the spent battery powders by applying hydrometallurgical process, aqueous solutions of acidic and alkaline chemicals are generally utilized as leaching agent. For this aim, the aqueous solutions of sulfuric acid (4,5), hydrochloric acid (6), sodium hydroxide (7,8), ammonia (9) and ammonium acetate (10) have been used to dissolve the zinc and manganese in the waste battery powder.

In the alkaline zinc-manganese dioxide batteries, the zinc and manganese dioxide are used the anode and cathode materials, respectively. A simple schematic representation of an alkaline battery is shown in Figure 1. Finely powdered zinc metal is in the form of paste together with potassium hydroxide serving as electrolyte. The anode and cathode materials are separated by a separator, and they do not mix with each other. Thus, these components in the spent alkaline battery powder can be individually obtained. Taking advantage of this feature of alkaline batteries, the zinc and manganese in the waste battery powder can be separately dissolved in an aqueous solution and recovered. Accordingly, the determination of individual dissolution behavior of these species in the waste powder is an important subject in terms of the leaching yield, design of leaching reactor, and separation and recovery steps of hydrometallurgical process.

In this study, after the zinc and manganese powders were individually obtained from the spent alkaline batteries, their dissolution behaviors in different solvents were examined to determine the appropriate leaching reagent for each species.

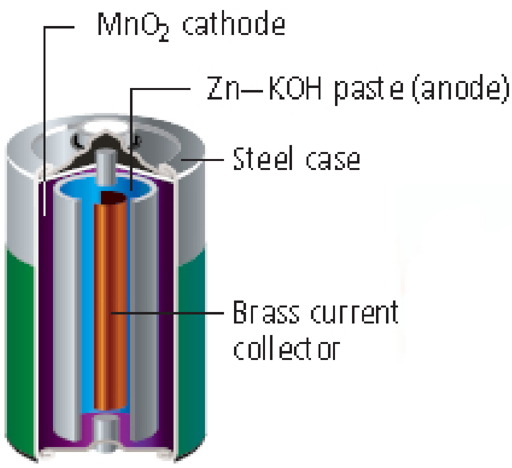

Figure 1. Schematic representation of an alkaline battery.

EXPERIMENTAL

The waste alkaline batteries used in this experimental study were collected in Malatya Province, Turkey. The collected waste batteries were shredded manually and the parts containing the zinc and manganese was separated from each other and other components of battery. After this procedure, the zinc and manganese powders were individually obtained. The battery powders prepared were dried at room temperature. The dried powders were sieved using standard sieves to prepare different particle size fractions. The mineralogical analysis of the battery powder samples were performed by using a Rigaku RadB-DMAX II model X-ray diffractometer. The results of the X-ray analyses are given in Figure 2 for the zinc powder and Figure 3 for the manganese powder. The dissolution tests were carried out in a 1 L jacketed glass reactor equipped with a mechanical stirrer, a temperature control unit, and a back-cooler. The aqueous solutions of the sodium hydroxide, ammonia, ammonium chloride, ammonium acetate, acetic acid, sulfuric acid, and hydrochloric acid were applied as the leaching reagents with the aim of dissolving the zinc and manganese powders. After putting 500 mL of aqueous solution of relevant reagent into the glass reactor and bringing it to operating reaction temperature, a given amount of the zinc or manganese powder was added to the solution, and the stirring speed was set. The dissolution process was performed for various reaction times. Aliquots of 5 mL sample were taken at regular intervals during the dissolution process, and it was filtered. The filtered samples were analyzed complexometrically for the zinc or manganese ions content using Titriplex III solution as titrant and puffertabletten as indicator. In the dissolution experiments, the values of the concentration of relevant reagent, reaction temperature, solid-to-liquid ratio, stirring speed, and particle size were fixed at 1 mol/L, 40 °C, 0,5/500 g/mL, 500 rpm, and -40+50 mesh, respectively.

The zinc or manganese amount passing into the solution was calculated as follows:

x= mass of metal ion passing to the solution/mass of metal in the battery powder sample.

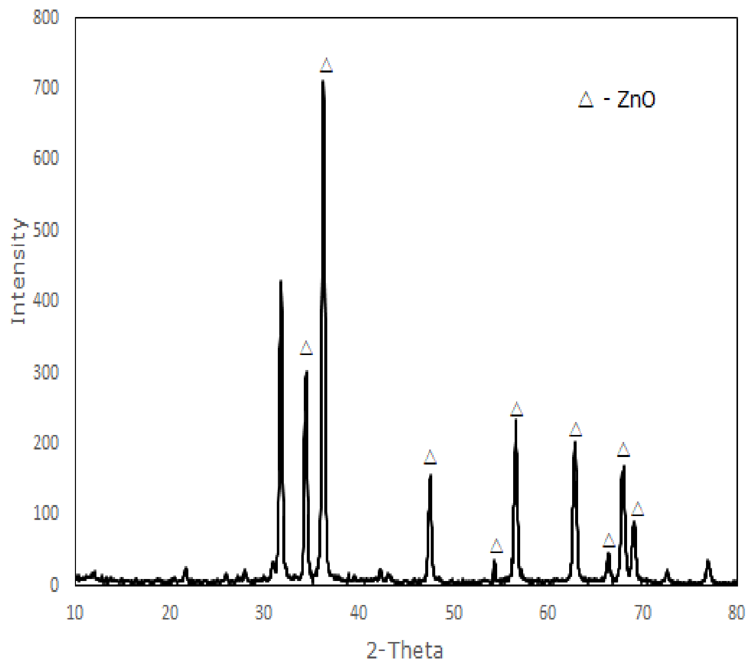

Figure 2. X-ray diffraction pattern of the zinc powder.

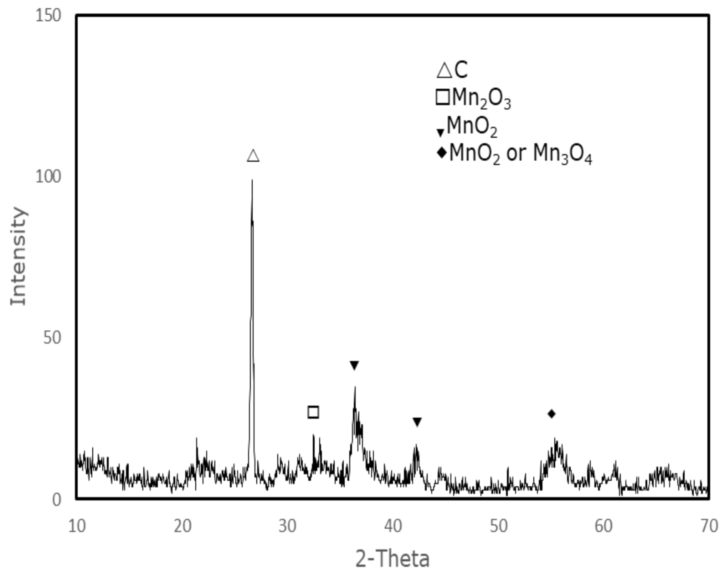

Figure 3. X-ray diffraction pattern of the manganese powder

RESULTS AND DISCUSSIONS

As mentioned above, in an alkaline zinc-manganese dioxide battery, the anode and cathode materials are the powdered zinc metal and manganese dioxide powder, respectively. A concentrated solution of KOH is used as electrolyte solution. During the discharge of battery, the metallic zinc powder is oxidized according to Eq. 1 while the manganese dioxide is reduced in accordance with reaction shown in Eq. 2.

$$Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^- \quad (1)$$
$$2MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + 2OH^- \quad (2)$$

A simplified overall battery reaction can be written as follows considering the anode and cathode reactions given above.

$$Zn + 2MnO_2 \rightleftharpoons ZnO + Mn_2O_3 \quad (3)$$

Thus, the spent alkaline zinc-manganese dioxide batteries contain mainly Zn, ZnO, MnO_2, and Mn_2O_3. If it is thought that the batteries are extremely consumed, it can be understood how much metal is found in the generated waste. Therefore, the recovery of metallic values from the spent batteries is a highly important issue especially in terms of economy. The solubility of a solid material in aqueous solutions varies from solvent to solvent. A solid material may generally easily dissolve in the strong and less acidic solutions while it may not readily dissolve in basic solutions. Some solid materials may sufficiently dissolve in basic solutions while some of them may dissolve in sufficient amount in both acidic and basic solutions. Therefore, the determination of an appropriate solvent for the dissolution process is a significant matter to reach the adequate yield.

The zinc oxide containing part of the waste battery powder dissolves in both acidic and basic solvents because of the amphoteric characteristic of zinc. The leaching reagents used in this study are the strong acid (sulfuric acid and hydrochloric acid), strong base (sodium hydroxide), weak acid (acetic acid and ammonium chloride), weak base (ammonia), and neutral salt (ammonium acetate). In aqueous solution of these reagents, the dissolution reactions of solid zinc oxide can be simply written as follow.

$$ZnO + 2OH^- \rightarrow ZnO_2^{2-} + H_2O \quad (4)$$

(in NaOH solution)

$$ZnO + 2H_3O+ + 4NH_3 \longrightarrow Zn(NH_3)_4^{2+} + 3H_2O \quad (5)$$

(in ammonium acetate, ammonia and ammonium chloride)

$$ZnO + 2H_3O^+ \rightarrow Zn^{2+} + 3H_2O \quad (6)$$

(in sulfuric acid, hydrochloric acid and acetic acid)

The dissolution results of zinc powder in the solution mentioned above are given in Figure 4. As can be seen from Figure 4, the zinc powder was dissolved more or less in all solution utilized as reagent. The highest dissolution was observed in hydrochloric acid solution.

The manganese oxides containing part of the waste battery powder was also dissolved in both acidic and basic solvents. For the dissolution of manganese oxides, the following reactions equations can be simply written.

$$2MnO_2 + 3NaOH \leftrightarrows Na_3MnO_4 + MnOOH + H_2O \quad (7)$$

$$Mn_2O_3 + H_2SO_4 \rightarrow MnO_2 + MnSO_4 + H_2O \quad (8)$$

The dissolution results of manganese powder are given in Figure 5. As can be seen from Figure 5, the dissolution of manganese powder is at very low levels in the solutions of sodium hydroxide, ammonia, ammonium chloride, and ammonium acetate and can be practically ignored. The value of the highest dissolution was reached in the hydrochloric acid solution.

It can be observed from the experimental results that the manganese powder does not practically dissolve in basic medium while the zinc powder dissolves in basic solutions. This feature can provide an advantage for the leaching process of the waste battery powders. The manganese and zinc in the waste batteries can be selectively leached using a basic solution. Thus, the leach solution with low impurities can be obtained for the step of the metal recovery of the hydrometallurgical process.

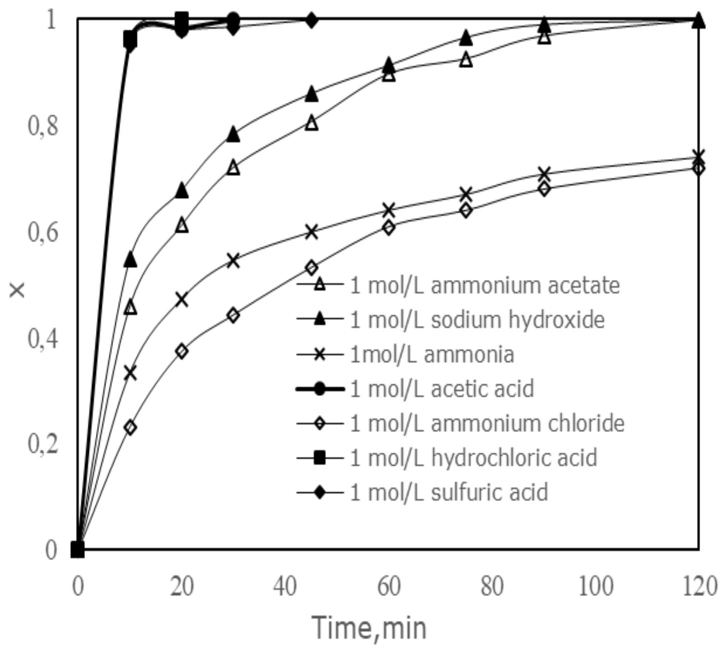

Figure 4. Effect of solvents on solvent dissolution for zinc powder.

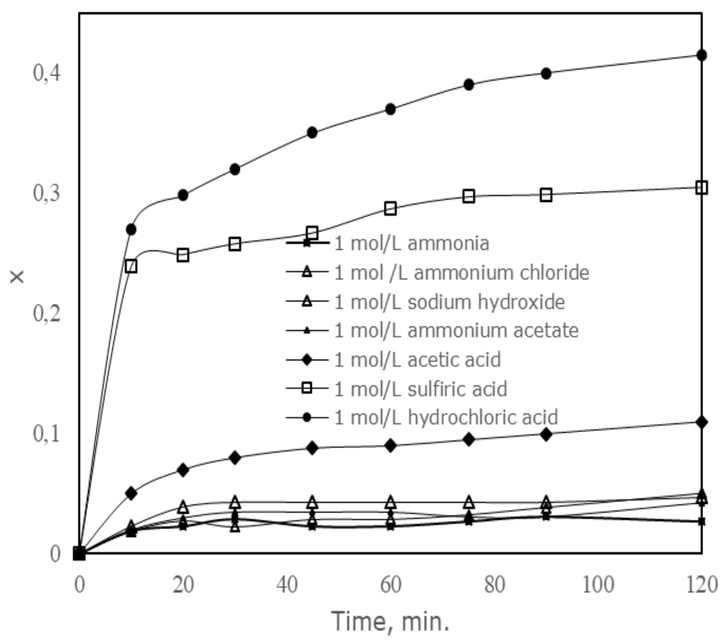

Figure 5. Effect of solvents on solvent dissolution for manganese powder.

CONCLUSIONS

In this study, the manganese and zinc powders in the spent alkaline batteries were separately obtained, and they were dissolved by using different leaching reagents. It was determined that the zinc powder dissolved at satisfactory amounts in all reagents while the manganese powder dissolved at remarkable amounts in the hydrochloric acid and sulfuric acid solutions. It was observed that the hydrochloric acid was more effective reagent for both powder samples. According to the results obtained, it can be said that the zinc and manganese in the waste alkaline batteries could be selectively dissolved and recovered by applying hydrometallurgical treatment.

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