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DISSOLUTION OF ALKALINE BATTERIES IN REDUCTIVE ACIDIC MEDIA

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Abstract: In this paper, recovery of manganese and zinc from alkaline battery paste by leaching under atmospheric condition using elemental sulfur as a reductive agent and sulfuric acid was investigated. Different dissolution parameters, acid concentrations, liquid-to-solid ratios, reaction temperatures, leaching times and amounts of elemental sulfur were studied in detail. According to results, the Mn dissolution in reductive acidic media was an intermediate-controlled process with activation energy of 10.21±2.60 kJ/mol. After the leaching step, Mn and Zn were selectively precipitated from the leaching solution using sodium hydroxide. After solid/liquid separation, manganese(II,III) oxide (Mn_3O_4) was obtained by drying at 105 °C in air. Next, Mn_3O_4 was converted to manganese(IV) oxide (MnO_2) by heating at 800 °C in air. After that the solution containing $Zn(OH)_4^{2-}$ was treated with sulfuric acid to form zinc hydroxide, separated and next converted to zinc oxide by heating at 600 °C in air. The final products were characterized by XRD. The results showed that the proposed process can be effectively used for recovery of Mn and Zn from alkaline batteries.

Keywords: *alkaline battery, manganese, zinc, reductive leaching, sulfur*

Introduction

The growth of the world population in the last decades and the economic explosion of countries have caused an increase in consumption and in the amount of the wastes of end-of-life (EOL) products (e.g. zinc–carbon and alkaline batteries) (Crompton, 2000; Levenspiel, 1972; Pistoia et al., 2001). Owing to increasing environmental concerns and raw material consumptions, worldwide stringent regulations are being demanded for waste materials. In a long term, land filling of spent batteries is not an effective disposal method mainly due to limited storage capacities, hazardous waste issues, increasing landfill costs, and the increasing need for metal recoveries (Bernardes et al., 2004; Pistoia et al., 2001).

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The alkaline batteries basically are made from metallic zinc and manganese oxide (Bernardes et al., 2004; Crompton, 2000; Sayilgan et al., 2009). While battery is in use, the metallic zinc is oxidized to zinc oxide and the manganese(IV) oxide is converted to manganese(III) oxide. It is known that the reaction of these elements with sulfuric acid occurs when they are divalent. The trivalent or tetravalent manganese does not react with sulfuric acid. This situation was observed using an E-pH diagram in a study by Gega and Walkowiak (2011).

The chemical reaction in the battery is given by Eqs 1-3 (Lide, 2004; Sayilgan et al., 2009):

$$Zn^{o} + 2OH^{-} \rightarrow ZnO + H_2O + 2e^{-} \quad E^{\circ} = 1.28\ V \tag{1}$$

$$2MnO_2 + H_2O + 2e^{-} \rightarrow Mn_2O_3 + 2OH^{-} \quad E^{\circ} = 0.15\ V \tag{2}$$

with the overall reaction

$$2MnO_2 + Zn^{o} \rightarrow Mn_2O_3 + ZnO \quad E^{o} = 1.43\ V. \tag{3}$$

Until recently, numerous studies have been conducted on the recycling of spent alkaline and zinc–carbon batteries. Various technologies have been devised for the treatment of the spent batteries wastes including pyrometallurgical (reductive melting) and hydrometallurgical (leaching and electrolysis). The pyrometallurgical processes are widely used for the recovery of metals from the spent batteries (Bernardes et al., 2004; Sayilgan et al., 2009). However, hydrometallurgical processes have some inherent advantages including relatively simpler operation, less energy demand, and no gas emissions (Sayilgan et al., 2009).

According to Eq. 4, zinc oxide completely dissolves in sulfuric acid aqueous solution but manganese(IV) and manganese(III) oxide do not (Sayilgan et al., 2010; Veloso et al., 2005). The reactions are:

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O \tag{4}$$

$$Mn_2O_3 + H_2SO_4 \rightarrow MnO_2 + MnSO_4 + H_2O \tag{5}$$

$$Mn_3O_4 + 2H_2SO_4 \rightarrow MnO_2 + 2MnSO_4 + 2H_2O. \tag{6}$$

Therefore, to improve the dissolution efficiency of manganese oxides to soluble Mn ions, a reducing agent is required. Recently, numerous reductants in acid media have been investigated for waste batteries and manganese ores. The organic reductant, such as lactose (Veglio et al., 2000), sucrose (Tian et al., 2010; Veglio and Toro, 1994; Veglio et al., 2000), corncob (Tian et al., 2010), oxalic acid (Ghafarizadeh et al., 2011; Sahoo et al., 2001; Sayilgan et al., 2010), ascorbic acid (Kursunoglu and Kaya, 2014; Sayilgan et al., 2010) cellulose (Sanigok and Bayramoglu, 1988), alcohols (Trifoni et al., 2001) were used. The inorganic reductant, for example, are hydrogen peroxide (Allen and Corwin, 1989; Ghafarizadeh et al., 2011; Jiang et al., 2004; Veloso et al., 2005) and activated carbon powder (Kursunoglu and Kaya, 2013), SO_2 (Avraamides et al., 2006; Ferella et al., 2008; Zhang and Cheng, 2007a).

After leaching, several separation methods can be used such as liquid–liquid extraction (Bernardes et al., 2004; Sayilgan et al., 2009; Zhang and Cheng, 2007c), precipitation (Kursunoglu and Kaya, 2014; Lasheen et al., 2009; Sayilgan et al., 2010; Veglio et al., 2000; Veloso et al., 2005; Zhang and Cheng, 2007c), and electro-winning (Sayilgan et al., 2010; Zhang and Cheng, 2007b).

In the present work, the recovery of zinc and manganese from alkaline paste by sulfuric acid leaching in the presence of elemental sulfur as the reducing agent, which has not been reported in the literature, was investigated. According to Eq. 7, 8 and 9, manganese dioxide completely dissolves in acid aqueous solution via elemental sulfur:

$$2MnO_2 + 8H^+ + 4e^- \rightarrow 2Mn^{2+} + 4H_2O \quad E° = 1.229\ V \tag{7}$$

$$S + 3H_2O \rightarrow H_2SO_3 + 4H^+ + 4e^- \quad E° = -0.449\ V \tag{8}$$

with the overall reaction

$$2MnO_2 + 4H^+ + S \rightarrow 2Mn^{2+} + H_2SO_3 + H_2O \quad E^o = 0.780\ V. \tag{9}$$

The following parameters were studied to determine dissolution kinetics of manganese and zinc in this system: amount of reducing agent, concentration of sulfuric acid, liquid/solid ratio, time and temperature. In addition, precipitation studies were conducted to reveal structure of manganese and zinc hydroxide. These products were characterized by XRD.

Materials and methods

Various alkaline batteries (Varta, Duracell, Maxwell, Sony, and Panasonic) were used in the study. Their composition is given in Table 1. Plastic and metallic cases were removed according to the manual procedure depicted by Bernardes et al. (2004). All the chemicals used were of analytical reagent grade (AR) and were obtained from Merck.

Table 1. Composition of alkaline batteries paste used in investigations

Component	Weight, %
Metallic Case	30.78
Battery Paste	55.32
Membrane and Plastics	5.25
Others	8.65

In order to determine the composition of the battery paste, three samples were analyzed for Mn, Zn and other elements by AAS (Perkin Elmer Analyst 800) using a standard protocol. The batteries were crushed, leached with water, dried, ground, sieved and homogenized using a three-dimensional shaker.

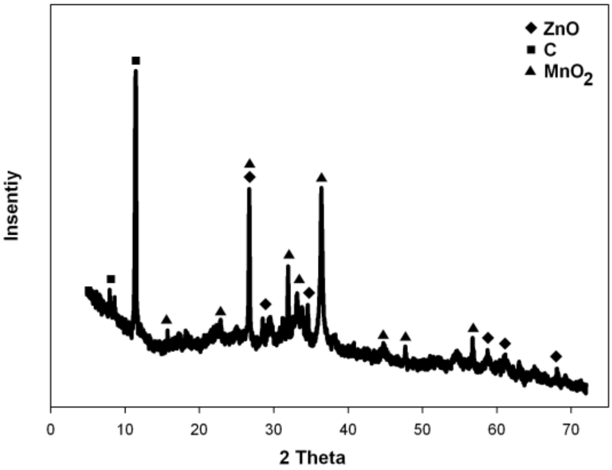

Fig. 1. XRD pattern of spent battery paste

The chemical composition and X-ray diffraction (XRD) pattern are given in Table 2 and Fig. 1, respectively. Figure 1 shows that MnO_2, ZnO and C were the major phases in the alkaline battery paste. Leaching experiments were performed in a 0.5 dm^3 capacity three-neck borosilicate tempered glass reactor fitted reflux condenser and continuously stirred. The system was refluxed to prevent evaporation losses. The reactor was heated in an oil bath with provision to control the bath temperature to maintaining the reactor temperature within ±1 °C (Fig. 2).

Table 2. Chemical composition of alkaline battery paste used in this study

Elements	Weight %
Mn	34.27
Zn	26.41
C	16.35
O	22.93
S	0.02
Fe	0.01
Pb	<0.01
Cd	N.D.*
Hg	N.D.*

*Not Detected

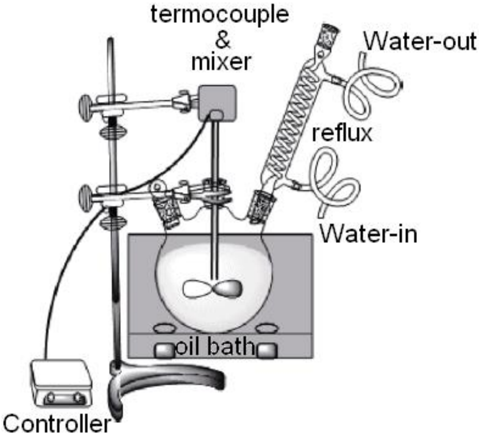

Fig. 2. Leaching reactor

At the end of each experiment, a solid/liquid separation was performed through a Whatman quantitative filter paper (ashless, grade 42, diameter 125 mm, 2.5 µm, slow filter paper).

The recovery was calculated using the following formula:

$$\text{Recovery, \%} = [M_t / (W \cdot M_i)] \cdot 100 \qquad (10)$$

where, W is the weight of the powder, M_i is the metal content of the powder and M_t is the metal amount in solution at the end of the experiment.

In order to understand the leaching behavior of the manganese from the battery paste, a kinetic study was performed. In the precipitation section, Mn and Zn were transformed into hydroxides using sodium hydroxide solution. At the end of the precipitation experiments, solid/liquid separation was performed. After dried process at 105 °C in air, the obtained the solid product Mn_3O_4 was converted to MnO_2 by heating at 800 °C in air. The $Zn(OH)_4^{2-}$ solution subsequently was treated with sulfuric acid to obtain $Zn(OH)_2$. Zinc hydroxide was converted to zinc oxide by heating at 600 °C in air.

For each experiment, 25 cm^3 of leaching solution with 4.0 M NaOH solution was employed using various solution pH. To determine chemical structure of the products, XRD analyses were performed.

Result and discussion

Effect of reducing agent

The recovery of Mn and Zn was assessed using a series of quantity of reducing agent (Fig. 3). The leaching experiments of alkaline battery paste was performed by varying the amount of elemental sulfur from 0 to 1.5 g with H_2SO_4 concentration of 2.0 M, L/S ratio of 6:1, leaching temperature of 80 °C, time of 90 min. As can be seen in Fig. 3, the manganese recovery increased with increasing amount of the reducing agent. The conversion of Mn^{4+}/Mn^{3+} to Mn^{2+} under reductive condition is thermodynamically more favorable when the reducing-to-manganese(IV) ion ratio is high (Eqs 5, 6, 7, 8 and 9). This result is in agreement with a study by Sayilgan et al. (2010), who recovered manganese using various reducing agent described herein.

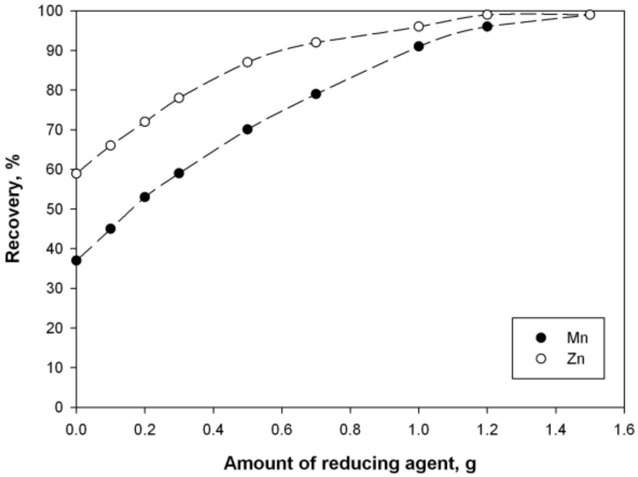

Fig. 3. Effect of reducing agent quantity on manganese and zinc recovery

It is known that zinc recovery is not dependent on the amount of reducing agent, because the reaction of zinc with sulfuric acid is thermodynamically more favorable (ΔG^o= -555 kJ/mol) (Lide, 2004). As can be seen in Fig. 3 for zinc, the recovery percentage increases when the amount of reductant quantity is increased because of more sulfate ions in media therefore, leaching power of sulfuric acid was increased. The Mn recovery also increased with increasing amount of quantity of the reducing agent. When the high quantities of reducing agent were used (such as 1.2 g S), the manganese recovery percentage was still below 100%. This result showed that acid concentration and reaction times were inadequate and the reaction should be done at higher temperatures. The amount of reducing agent of 0.5 g was selected for all subsequent experiments.

Effect of acid concentration

In this experimental series, the alkaline battery paste was treated by varying H_2SO_4 concentration from 1.0 to 4.0 M with quantity of S from 0.5 g, L/S ratio of 6:1, leaching temperature of 80 °C, and time of leaching 90 min. As can be seen from Fig. 4, the recovery of zinc increased with an increasing amount of H_2SO_4 up to 2.0 M.

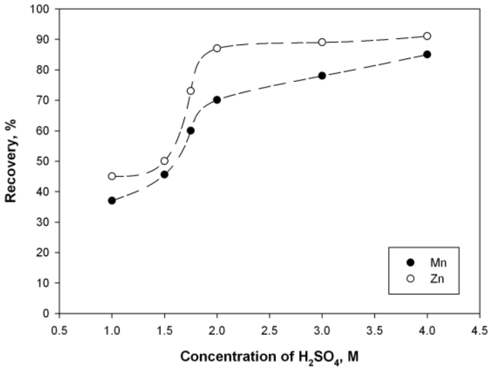

Fig. 4. Effect of sulfuric acid concentration on manganese and zinc recovery

The recovery of manganese continues to increase with increasing H_2SO_4 concentration because more acidic media and sulfate anion improved the dissolution of manganese. At a sulfuric acid concentration of 1.0 M, low zinc and manganese recoveries were obtained because acid concentration is not sufficient to dissolve zinc from the alkaline battery paste. A similar trend for the effect of acid concentration was observed in a study by Kursunoglu and Kaya (2014). It is understood that acid concentration considerably affects zinc and manganese recovery percentages.

Effect of liquid to solid ratio

The experiments were performed to understand the effects of liquid to solid ratio on the manganese and zinc recovery. The alkaline battery paste leaching was carried out by varying the liquid-to-solid ratio (L/S) from 4.0 to 10.0 with quantity of S equal to 0.5 g, H_2SO_4 concentration of 2.0 M, leaching temperature of 80 °C, and time of 90 min.

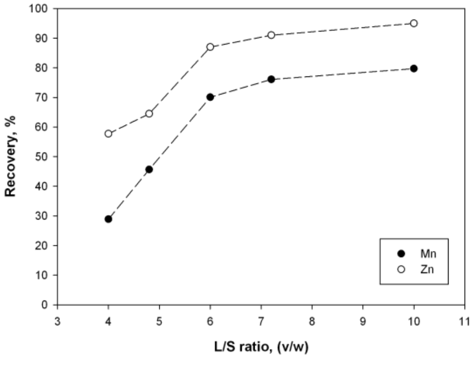

Fig. 5. Effect of liquid to solid ration on manganese and zinc recovery

According to experimental results presented in Fig. 5, it was found that the Mn and Zn recovery increased until the liquid-to-solid ratio was 6, where 71% of manganese and 87% of zinc was recovered. At the ratio higher than 6, there is no significant increase of recovery of these metals.

Effect of time and temperature

To determine the effect of time and temperature, the L/S ratio of 6.0, 0.5 g S, and H_2SO_4 concentration of 2.0 M was selected. Figures 6a and 6b display the variation in Zn and Mn recovery as a function of time at various temperatures, respectively. As can be seen from Fig. 6a, that when the temperature was increased from 70 to 100 °C at 30 min, the Mn recovery increased from 41% to 61%. Thus, the manganese recovery increased by 20%, indicating that the temperature plays a significant role in the recovery of Mn from alkaline batteries paste.

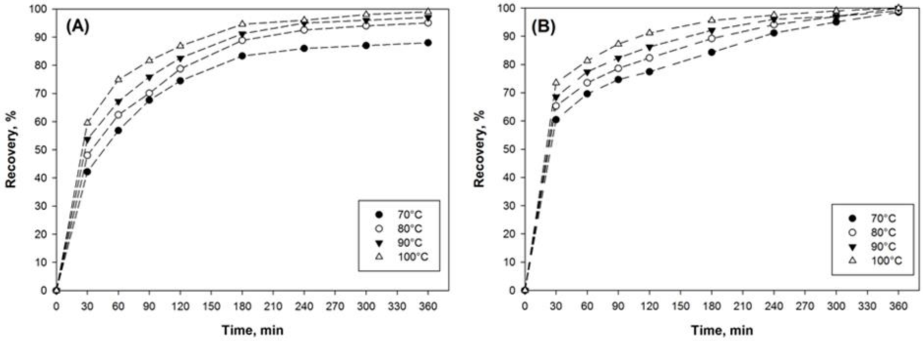

Fig. 6. Effect of temperature and time on recovery of manganese (a) and zinc (b)

The leaching time has a significant role in the recovery of manganese from the alkaline battery paste. For example, 42% recovery of Mn was obtained after 30 min at 70 °C. However, under the same conditions, 83% recovery of manganese was attained when the leaching time was prolonged to 180 min. The 83% recovery of manganese was found after 90 min at 100 °C. In addition to this, recovery of +95% was obtained for 180 min at 100 °C under the same conditions. With the exclusion of the results for 70 °C, after 240 min of reaction time no significant change was obtained. A similar result for the effect of time and temperature was found by Tang et al. (2014). As shown in Fig. 6b, +99% of zinc was dissolved at 80-100 °C. These results show that increasing temperature results in a higher recovery. After 300 minutes of leaching, the recovery of zinc was leveled off.

Leaching kinetics study of manganese

The leaching kinetic data provide reaction order based either on differential rate law or integrated rate. In our experiments, several mathematical models were studied for temperatures from 70 to 100 °C. The kinetic studies showed that a good fit was provided by the shrinking core model $[1-(2/3)X-(1-X)^{2/3}]$ (Fig.7a., Eq. 11).

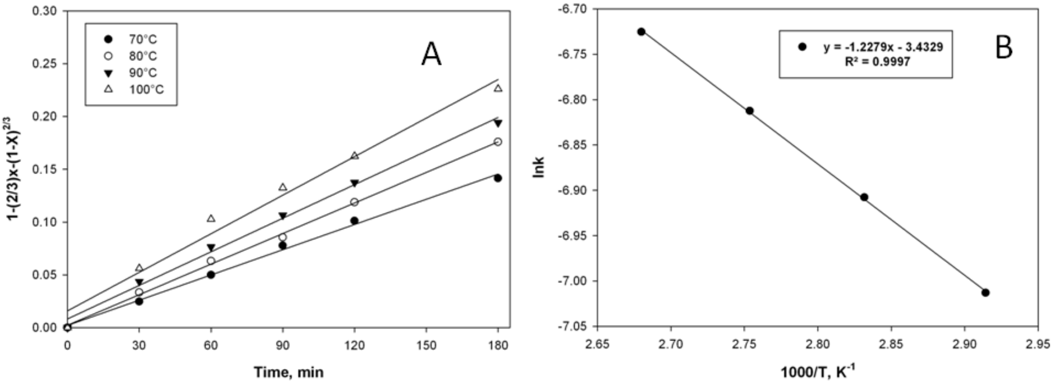

Fig. 7. a) Relationship between $[1-(2/3)X-(1-X)\ 2/3]$ and time as a function of temperature, b) activation energy of manganese leaching

$$kt = 1-(2/3)\,X-(1-X)^{2/3} \tag{11}$$

where k is rate constant, t time (min), X fraction of leached Mn.

The activation energy (E_a) was calculated using the Arrhenius equation, according to the following formula:

$$\ln k = \ln A - E_a/\mathrm{R}T \tag{12}$$

where R is the gas constant and T is the temperature (K).

Figure 7b shows the Arrhenius plot of ln$k$ versus 1000/T for Mn dissolution. The activation energy for manganese was calculated to be 10.21±2.60 kJ/mol, which indicates that this is an intermediate-controlled process (Jiang et al., 2004; Kursunoglu and Kaya, 2014; Tang et al., 2014).

Selective precipitation of manganese and zinc using sodium hydroxide

The optimum leaching results were obtained under the condition of 120 min reaction time, in the mixture of 25 g battery paste with 2.0 M H_2SO_4 at 100 °C. After that, two hundred alkaline battery pastes were leached under these optimum conditions. After Mn and Zn were dissolved in the acid solution, it was diluted to 2 dm^3 with distilled-deionized water. The solution contained 42.04 g/dm^3 Mn^{2+} and 32.94 g/dm^3 Zn^{2+}. The pH was 1.10. It was treated with sodium hydroxide to yield $Mn(OH)_2$ and $Zn(OH)_2$. For each experiment, 25 cm^3 of the leaching solution was employed with 4.0 M NaOH solution in a falcon tube for 90 min at 200 rpm.

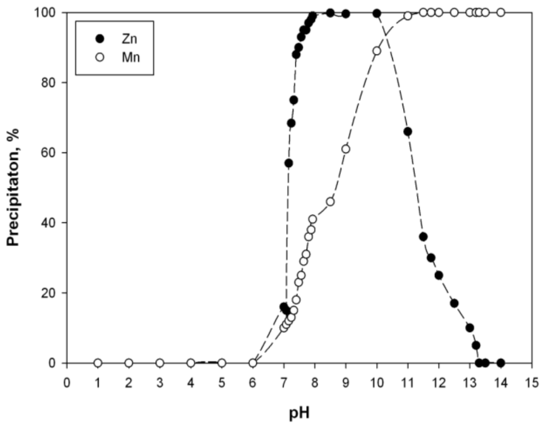

Fig. 9. Precipitation of manganese and zinc as a function of solution pH

According to Eqs. 13 and 14 (Lide, 2004), $Mn(OH)_2$ and $Zn(OH)_2$ have low solubility product. However, zinc shows an amphoteric character and re-dissolves in the sodium hydroxide solution to form a zinc hydroxide complex (Eq. 15) as a zincate ($Zn(OH)_4^{2-}$)

$$Mn(OH)_{2(s)} \rightarrow Mn^{2+}_{(aq)} + 2OH^{-}_{(aq)} \quad K_{sp}=1.8\times10^{-10} \tag{13}$$

$$Zn(OH)_{2(s)} \rightarrow Zn^{2+}_{(aq)} + 2OH^{-}_{(aq)} \quad K_{sp} = 3.0\times10^{-17} \tag{14}$$

$$Zn(OH)_{2(s)} + 2OH^{-}_{(aq)} \rightarrow Zn(OH)_4^{2-} \quad K_f = 2.8\times10^{15}. \tag{15}$$

The effect of pH on precipitation of Mn and Zn were investigated and the results are illustrated in Fig. 9. Based on the results obtained, a flow sheet for separation of Mn and Zn was developed and tested. Evidently (Fig. 9) Zn and Mn were not separated at the neutral pH value. However, $Zn(OH)_2$ dissolves again at pH values greater than 10.5 because the Zn^{2+} ions dissolve under highly basic conditions, unlike Mn(II), which forms a complex stable even to pH 14 .

The precipitated manganese compounds were rinsed with cold water five times and then dried for 2 h at 105 °C in air. It was observed that dried $Mn(OH)_2$ compound was convert to Mn_3O_4 (Fig. 10a) (Reidies, 1990; Peng et al., 2010).

Normally, it is expected that manganese hydroxide occurs with the reaction of manganese sulfate and sodium hydroxide. However, interestingly, it was found that manganese hydroxide just occurred in liquid solution. After solid/liquid separation, the solid was converted to manganese(II,III) oxide by air immediately. Because precipitated manganese(II) hydroxide is oxidized at room temperature by air or oxygen to trivalent, tetravalent manganese oxides in the presence of traces of alkali, while conversion to manganates (i.e., the tetra, penta- and hexavalent states) requires much higher temperatures and high alkali concentrations (180°C for 60–70% NaOH or KOH) (Reidies, 1990; Peng et al., 2010). Furthermore, Eh-pH diagram is the evidence of this situation (Fig.10b).

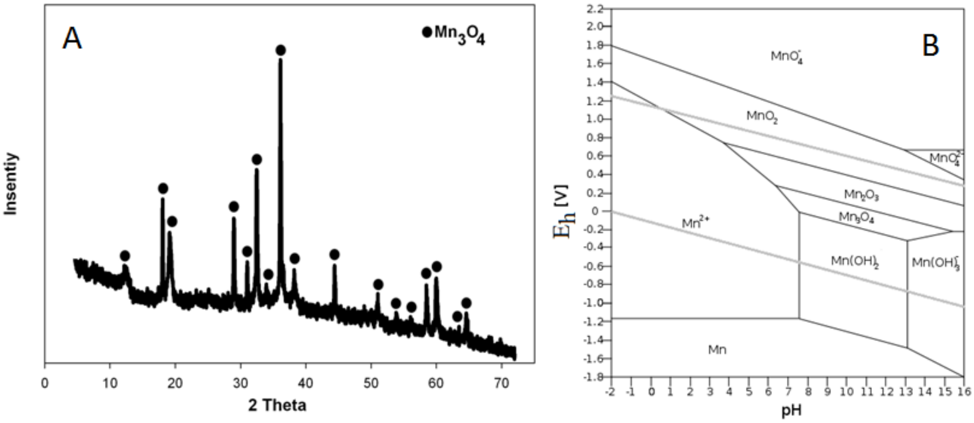

Fig. 10. XRD pattern of Mn_3O_4 (a) and manganese Eh-pH diagram (b)

As seen from Eh-pH diagram, the equilibrium between $Mn(OH)_2$ and the Mn_3O_4 is:

$$Mn_3O_4 + 2e^- + 2H^+ + 2H_2O = 3\,Mn(OH)_2. \tag{16}$$

The net standard free-energy charge in this equilibrium, ΔG^o is 89.745 kJ/mol, and standard electrode potential can be calculated from the relation

$$E^o = -\frac{\Delta G^\circ}{nF} = 0.466\,V. \tag{17}$$

The value for the oxidation potential of the system when the participating substances are not at unit activity can be compared form the Nernst equation

$$Eh = 0.466 + \frac{0.0592}{2}\log\frac{[\mathrm{Mn_3O_4}][\mathrm{H_2O}]^2[\mathrm{H^+}]^2}{[\mathrm{Mn(OH)_2}]^3}. \tag{18}$$

The equation may then be simplified to

$$Eh = 0.466 - 0.0592\,\mathrm{pH}. \tag{19}$$

The vertical boundaries already drawn in Fig. 11 determine the lateral extent of the $Mn(OH)_2$ field. At a pH of 12.3, the *Eh* becomes -0.26 V, and at a pH of 11.4 the *Eh* value is -0.22 V.

A line connecting these points is then drawn to define the border between $Mn(OH)_2$ and Mn_3O_4 (Dhaouadi et al., 2012; Al Sagheer et al., 1999; Kirillov et al., 2009). The Mn_3O_4 oxide was heated to 800 °C to yield manganese(IV) oxide (MnO_2) under air atmosphere (Zhang and Cheng, 2007c). The XRD pattern of the MnO_2 is displayed in Fig. 12a.

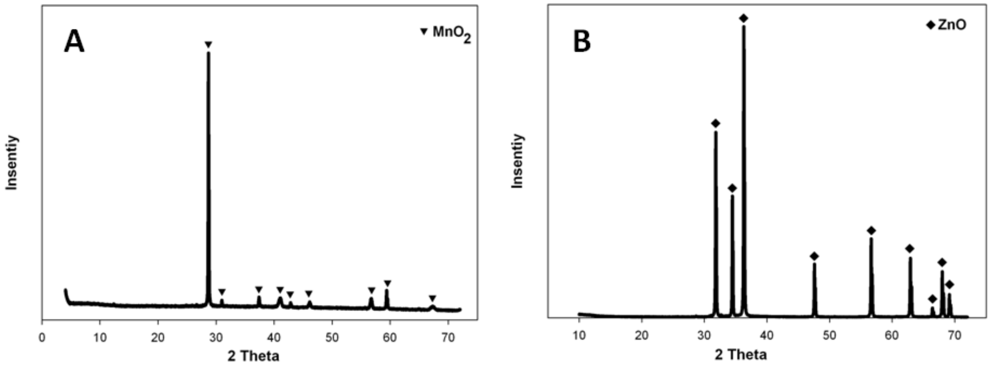

Fig. 12. XRD pattern of a) MnO_2 and b) ZnO

After the manganese was recovered, the author attempted to recover Zn as hydroxide. First, the $Zn(OH)_4^{2-}$ solution was treated with diluted H_2SO_4 to yield $Zn(OH)_2$. And then, the zinc hydroxide was rinsed with cold water five times and subsequently dried for 2 h at 105 °C. The resulted white-yellow powder precipitated in 99%. Then, zinc oxide was obtained by calcinations at 500 °C for 3 h (Aktas and Morcali, 2011). The XRD pattern of the product (ZnO) is shown in Fig.12b.

Conclusion

In this work a combined recovery process was proposed to separate zinc and manganese from spent alkaline batteries, which included reductive leaching of manganese in 2 M sulfuric acid medium in the presence of elemental sulfur. The results have shown that it is possible to leach Mn and Zn from the alkaline battery paste with a recovery of +98% using the mixture of 25 g battery paste, 150 cm^3 of 2 M H_2SO_4 at 100 °C and 120 min reaction time. The activation energy of Mn leaching was 10.21±2.60 kJ/mol. Moreover, selective separation of Mn and Zn were studied. Selective precipitation of manganese using NaOH solutions in a neutral leaching step as precipitant agent was studied to separate Zn and Mn from the liquors produced in the acidic leaching step. Subsequently, metal oxides (e.g. MnO_2, ZnO) were obtained with the help of sodium hydroxide after conversion to metal oxides, which was confirmed by XRD, by heating. From these products, it is possible to make other valuable products.

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