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DISSOLUTION AND PRECIPITATION OF ZINC AND MANGANESE OBTAINED FROM SPENT ZINC-CARBON AND ALKALINE BATTERY POWDER

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Abstract: The aim of this study was to investigate manganese and zinc recoveries from spent zinc-carbon and alkaline battery powder. The effect of sulfuric acid concentration, ascorbic acid dosage, reaction temperature and leaching time on zinc and manganese dissolutions was investigated. The optimum reductive acid leaching conditions were determined as: 3 hours, 70 °C, 0.5 M of sulfuric acid concentration, 13 g/dm³ of ascorbic acid dosage, 1/20 g/cm³ of solid/liquid ratio and 200 rpm of stirring speed. Under these conditions, dissolution efficiencies were 99.99% for Zn and 99.25% for Mn. In addition, dissolution kinetics of manganese was undertaken, and the activation energy was found to be 7.04 kJ/mol. Using 3 M NaOH as precipitating agent at room temperature, 95.35% of Zn (at pH 8) and 93.66% of Mn (at pH 10) were precipitated from the leaching solution. Under the same conditions, using 3 M KOH, precipitations of Zn and Mn were 91.63% and 96.39%, respectively. Based on the experimental results, a flowsheet of zinc and manganese recovery was proposed.

Keywords: *leaching, ascorbic acid, manganese, zinc, precipitation*

Introduction

Manganese is a key element in the development of different industrial fields such as zinc-carbon and alkaline batteries, steel production, preparation of dietary additives, fertilizers, fine chemicals, non-ferro alloys as well as some medicines (Sahoo et al., 2001; Ghafarizadeh et al., 2011). The world annual production of the total manganese alloys passed 10 Tg and it will increase (Lasheen et al., 2009).

A consumption of relatively rich manganese ores has focused attention on the possible exploitation of its low grade ores and wastes. Besides, the low grade manganese ores and wastes have also generated a lot of interest as a potential source of associated metal value such as zinc, nickel, copper, vanadium, chromium and molybdenum (Ghafarizadeh et al., 2011). Therefore, several hydrometallurgical

processes have been developed for these ores and wastes such as, dissolving manganese as a soluble sulphite or nitrate, purifying a obtained liquor each by different techniques such as precipitation (as sodium or potassium hydroxide), solvent extraction and electro-winning (Salgado et al., 2003; Mantuano et al., 2004; De Souza and Tenorio, 2004; Veleso et al., 2005; De Michelis et al., 2007; Sayilgan et al., 2010).

Recently, numerous reduction methods in acid media has been investigated such as lactose reduction leaching (Veglio et al., 2000), sucrose reduction leaching (Veglio et al., 1994), corncob reduction leaching (Tian et al., 2010), oxalic acid reduction leaching (Sahoo et al., 2001; Sayilgan et al., 2009), waste newspaper reduction leaching (Biswal et al., 2011), hydrogen peroxide reduction leaching (El Hazek et al., 2006; Zhang and Cheng, 2007), ascorbic/oxalic acid reduction leaching (Sayilgan et al., 2010; Kaya and Kursunoglu, 2012) and activated carbon powder reduction leaching (Kursunoglu and Kaya, 2013).

In the present work, the zinc-carbon and alkaline battery powder is reduced to zinc sulfate and manganese sulfate by employing ascorbic acid in sulfuric acid solution. The following reactions can be considered for the dissolution of zinc oxide and manganese dioxide from zinc-carbon and alkaline battery powder. According to Eq. (1), zinc oxide fully dissolves in sulfuric acid solution. On the other hand, Eq. (2) indicates that ascorbic acid can be used to dissolve manganese dioxide in sulfuric acid solution:



The aim of this study is to investigate manganese and zinc recovery from spent battery powder by sulfuric acid leaching in the presence of ascorbic acid as a reducing agent. The effects of dissolution time, sulfuric acid concentration, ascorbic acid dosage and temperature were investigated to determine dissolution kinetics of manganese in this system. In addition, precipitation studies were conducted to reveal structure of manganese hydroxide.

Experimental

Spent AA and AAA sized zinc-carbon and alkaline batteries were collected from Eskisehir Osmangazi University battery collection bins in Turkey. The batteries were first dismantled by a laboratory hammer crusher and then dry screened by a 2 mm sieve to remove manually steel cases, plastics and papers. Spent battery cells contain 55.3% battery powder, 28.94% steel cases, 6.12% papers and 2.25% plastics. The obtained black battery powder was put into oven at $105 \pm 5^\circ\text{C}$ for 24 h. The moisture content of the battery powder was found to be 7.4%. The dried battery powder was mixed carefully to ensure the homogeneity and then ground to the required particle

size of $-88 \mu\text{m}$ for 30 min in a laboratory Bond ball mill. All leaching tests were performed with the battery powder.

A semi-quantitative analysis of the battery powder was carried out using a Philips PW-2404 X-Ray Fluorescence spectrometer (XRF) for Mn, Zn, Cl, Fe, Si, Ni, Al, S, Mg and K after neutral leaching. The mineralogical composition of the washed battery powder was determined by a Bruker AXS-D8 Advance X-Ray Diffractometer (XRD), using Cu $K\alpha$ radiation generated at 30 mA and 40 kV.

The chemical composition of the washed battery powder was 32.80% Mn, 32.92% Zn, 1.29% Cl, 0.84% Fe, 0.62% Si, 0.54% Ni, 0.30% Al, 0.28% S, 0.27% Mg, and 0.24% K. The presence of Cl is due to ammonium chloride that is the electrolytes of zinc-carbon batteries (De Souza et al., 2001; Ferella et al., 2008). Based on the XRD analysis (Fig. 1) the major phases in the washed battery powder were manganese oxides (MnO_2 and Mn_3O_4), simonkolleite ($\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$), graphite (C) and zinc oxide (ZnO).

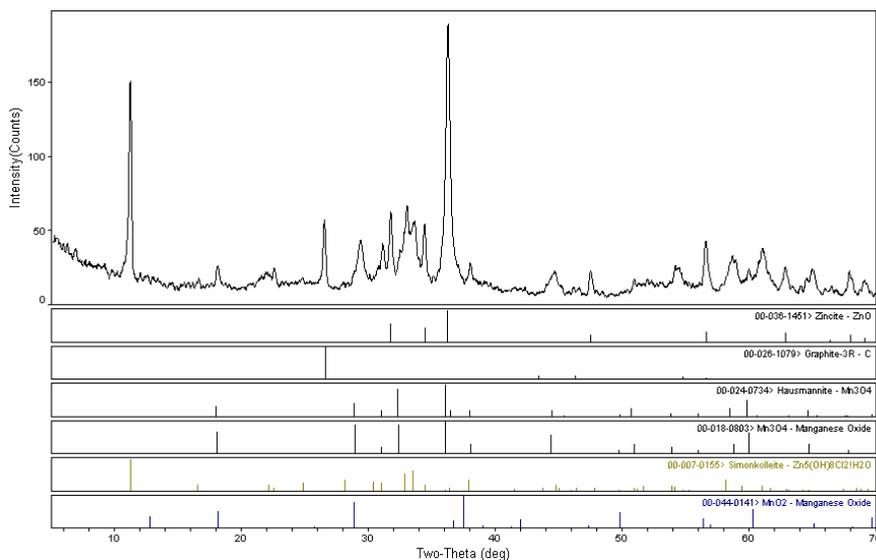


Fig. 1. XRD pattern of washed battery powder

Before reductive acid leaching tests, neutral leaching tests were performed in a 250 cm^3 Erlenmeyer flasks at a constant stirring speed of 200 rpm. The temperature was maintained at $60 \text{ }^\circ\text{C}$. The neutral leaching was carried out at solid/liquid ratio of $1/20 \text{ g/cm}^3$ and leaching time was 3 hours. After neutral leaching, the final solution pH was measured between 8.7 and 9.0 using a digital pH-meter (Hach, 40d).

In reductive acid leaching tests the battery powder was leached using ascorbic acid as a reducing agent in sulfuric acid solution. The 250 cm^3 Erlenmeyer flasks were dipped in a temperature-controlled water-bath. The slurry was agitated using a magnetic stirrer (Advantec, TBS 541 PA) at 200 rpm. Glass condensers were fitted

on the Erlenmeyer flasks in order to prevent liquid evaporation. The experimental set up used in experiments is shown in Fig. 2.

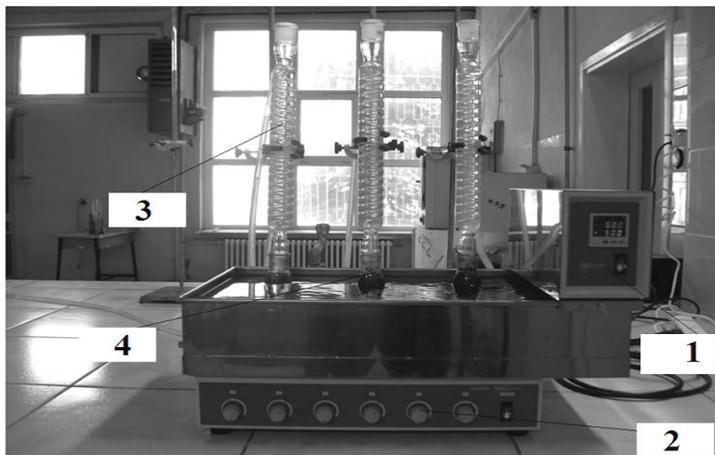


Fig. 2. Experimental set-up. 1 – temperature controlled water bath, 2 – stirring speed controller, 3 – glass condenser, 4 – 250 cm³ Erlenmeyer flask

After the reductive acid leaching step, selective precipitation tests were carried out at room temperature in a 1 dm³ beaker under constant stirring by a magnetic stirrer. A solution of 3 M NaOH or KOH was added slowly to the leach solution to increase the pH up to 11. The pH of the solution was controlled during precipitation test. A 5 cm³ sample was withdrawn at determined pH values, and then the samples were diluted with distilled water by 1:100. Zinc and manganese concentrations in the diluted solutions were determined by an Atomic Absorption Spectrometer (AAS). At the end of the precipitation, the solution in the beaker was filtered and the solid residue remained in the filter paper was dried in an oven at 105 °C for 24 hours. The dried solid residue was analyzed by the SEM-EDX to display its structure.

Results and discussion

Preliminary leaching tests

In order to determine the effect of sulfuric acid concentration on the zinc and manganese dissolution, the preliminary leaching tests were carried out at different sulfuric acid concentrations (0.05-3 M), a solid/liquid ratio of 1/20 g/cm³, stirring speed of 200 rpm and leaching temperature of 70°C for 3 hours leaching time in the absence of a reducer. The results obtained are given in Fig. 3. It shows that zinc dissolution increased significantly with increasing sulfuric acid concentration up to 0.15 M, and then gradually increased after that point. It can be seen that 98.25% of

zinc was dissolved in 0.5 M sulfuric acid concentration and thereafter remained constant.

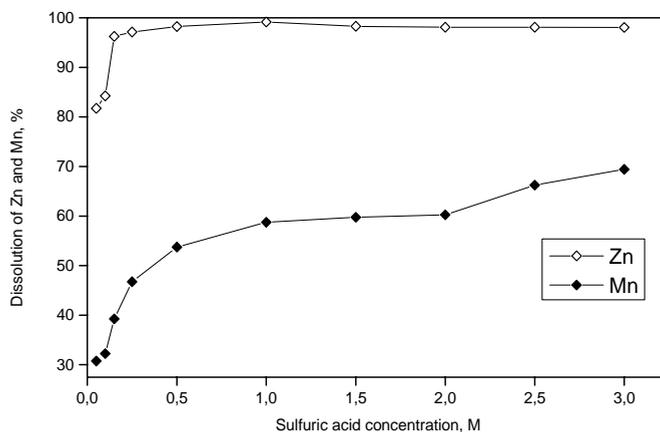


Fig. 3. Effect of acid concentration on dissolution of zinc and manganese (70 °C, 1/20 g/cm³, 200 rpm and 3 hours)

Manganese dissolution gradually increased with increasing sulfuric acid concentration. The maximum manganese dissolution at 3 M sulfuric acid concentration was found to be 69.42%. These results showed that sulfuric acid concentration was very effective on dissolution of zinc and manganese from zinc-carbon and alkaline battery powder, which is consistent with the results of previous studies (El-Nadi et al., 2007; Sayilgan et al., 2009; Gega et al., 2011). In order to dissolve zinc and manganese, ascorbic acid was used as a reducing agent to improve manganese dissolution. For this reason and environmental considerations, low sulfuric acid concentrations were chosen for the subsequent reductive acid leaching tests.

Reductive acid leaching tests

The effect of ascorbic acid dosage on the dissolution of manganese from zinc-carbon and alkaline battery powder was carried out at different ascorbic acid dosages (10-15 g/dm³) using 0.5M sulfuric acid concentration, at 70 °C, stirring speed of 200 rpm, solid/liquid ratio of 1/20 g/cm³ for 3 hours of leaching time. Figure 4 shows that the manganese dissolution increased with increasing ascorbic acid dosage. A 13 g/dm³ of ascorbic acid dosage was sufficient to leach almost all manganese from zinc-carbon and alkaline battery powder. After 13 g/dm³ of ascorbic acid dosage, manganese dissolution increased slightly remaining almost constant. There were small increases in the manganese dissolution values when the leaching tests were performed up to 15 g/dm³ ascorbic acid dosage.

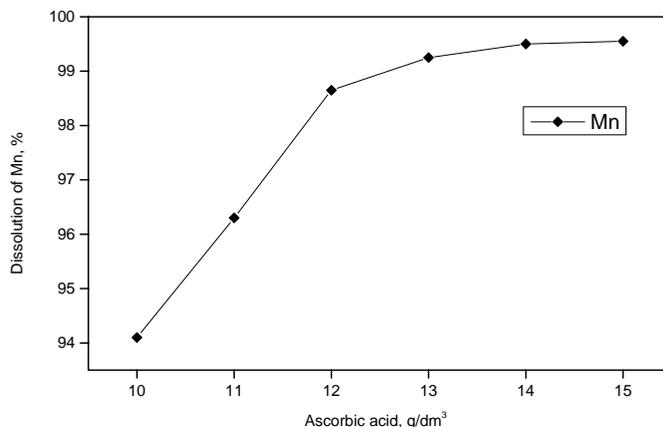


Fig. 4. Effect of ascorbic acid on dissolution of manganese (0.5 M sulfuric acid concentration, 70 °C, 200 rpm, 1/20 g/cm³ and 3 hours)

The effect of sulfuric acid on dissolution of zinc from zinc-carbon and alkaline battery powder was studied using 13 g/dm³ of ascorbic acid dosage, at 70 °C, stirring speed of 200 rpm, solid/liquid ratio of 1/20 g/cm³ for 3 hours of leaching time. Figure 5 shows that zinc dissolution increased with an increased sulfuric acid concentration up to 0.5 M and then remained constant. The maximum reached value of Zn dissolution was 99.99%.

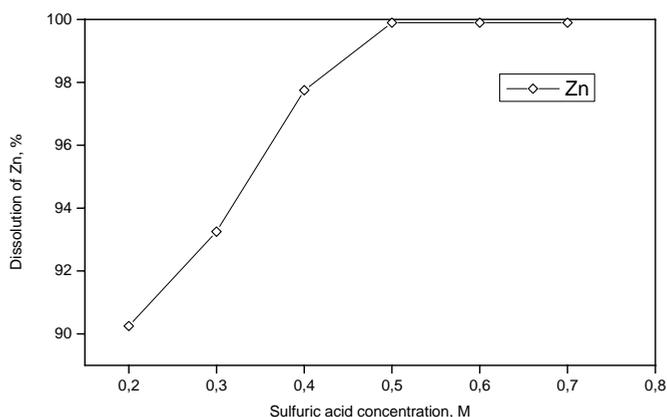


Fig. 5. Effect of sulfuric acid concentration on dissolution of zinc (13 g/dm³ of ascorbic acid dosage, 70 °C, 200 rpm, 1/20 g/cm³ and 3 hours)

Effect of solid/liquid ratio

Dissolution of zinc and manganese from zinc-carbon and alkaline battery powder by 0.5 M sulfuric acid concentration, 13 g/dm³ of ascorbic acid dosage, at 70 °C, stirring

speed of 200 rpm for 3 hours leaching time was tested by varying the solid/liquid ratios (1/20, 1/16, 1/10 and 1/5), as given in Fig. 6. Zinc and manganese dissolution significantly decreased with increasing solid/liquid ratio. When the solid/liquid ratio was lower than 0.10, leaching of zinc and manganese significantly increased, since most of zinc and manganese were leached into the solution to form ZnSO_4 and MnSO_4 . The highest dissolutions were found at solid/liquid ratio of 0.05 ($1/20 \text{ g/cm}^3$).

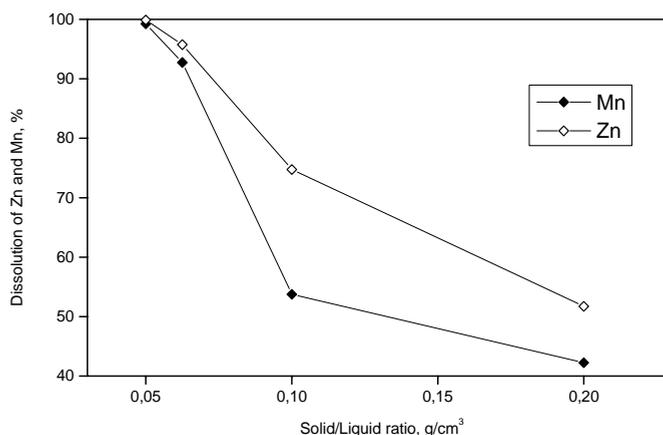


Fig. 6. Effect of solid/liquid ratio on dissolution of zinc and manganese (0.5 M sulfuric acid concentration, 13 g/dm^3 of ascorbic acid dosage, $70 \text{ }^\circ\text{C}$, 200 rpm and 3 hours)

Effects of leaching time and temperature

To determine the effects of time and temperature on dissolution of zinc and manganese from zinc-carbon and alkaline battery powder more accurately, leaching experiments were performed under constant conditions of 0.5 M sulfuric acid concentration, 13 g/dm^3 of ascorbic acid dosage, $1/20 \text{ g/cm}^3$ of solid/liquid ratio, 200 rpm stirring speed and $20\text{--}70 \text{ }^\circ\text{C}$ temperature range. The results obtained are shown in Fig. 7. Dissolution of manganese increased with increasing temperature. The maximum manganese dissolution values were 92.06% at $20 \text{ }^\circ\text{C}$, 98% at $50 \text{ }^\circ\text{C}$ and 99.75% at $70 \text{ }^\circ\text{C}$.

Zinc dissolution slightly increased with increasing leaching time. Zinc was almost fully dissolved at $70 \text{ }^\circ\text{C}$ for 3 hours leaching time. Dissolution behavior of zinc and manganese showed a similar trend for all temperatures and leaching times. Figure 7 shows that temperature and leaching time are important factors that affect the leaching process. After one hour of leaching at $20 \text{ }^\circ\text{C}$ in 0.5 M sulfuric acid solution using 13 g/dm^3 of ascorbic acid, dissolutions of manganese and zinc were 91.2% and 90.76%, respectively. However, when leaching temperature and time were $70 \text{ }^\circ\text{C}$ and 3 hours, dissolution of zinc and manganese increased to 99.99% and 99.25%, respectively.

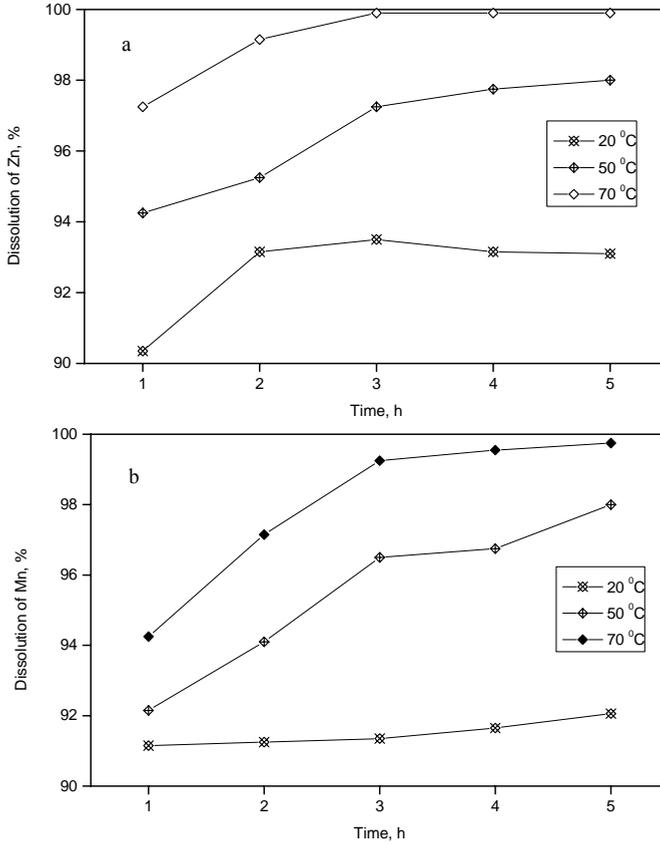


Fig. 7. Effect of leaching time on Zn and Mn dissolution at different leaching temperature (0.5 M sulfuric acid concentration, 13 g/dm³ of ascorbic acid dosage, 200 rpm, 1/20 g/cm³)

Kinetics of manganese from zinc-carbon and alkaline battery powder

Kinetics data collected at different temperatures for 0.5 M sulfuric acid, 13 g/dm³ of ascorbic acid dosage, 200 rpm of stirring speed, 1/20 of solid/liquid ratio for 3 hours leaching time were evaluated according to shrinking core model (Sohn and Wadsworth, 1979; Levenspiel, 1999). To determine chemical rate constant (k_p) of manganese dissolution in the temperature range of 20–70 °C (Fig. 8), the best linear relationship for manganese was obtained from equation:

$$1 - \frac{2}{3}x - (1-x)^{\frac{2}{3}} = k_p t, \quad (3)$$

where k_p is chemical rate constant (cm·min⁻¹), t time (min), x fraction reacted of manganese.

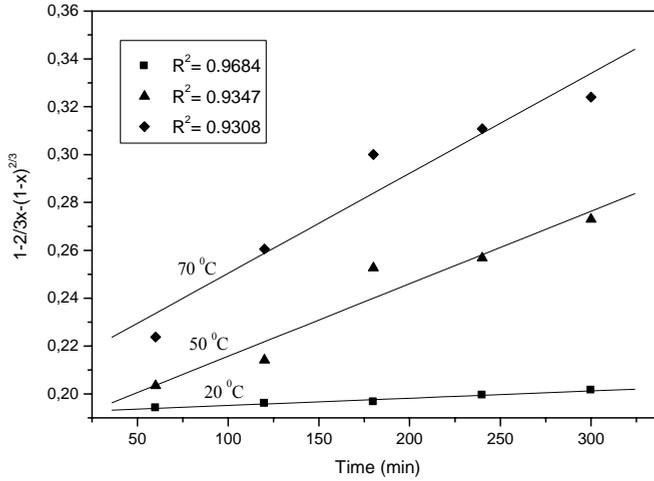


Fig. 8. Plot of $1 - \frac{2}{3}x - (1-x)^{\frac{2}{3}}$ versus time. R^2 is determination coefficient

The Arrhenius plot (Fig. 9) was constructed using the experimentally determined $\ln k_p$ values as a function of the reciprocal of leaching temperature ($1000/T$) as shown in Fig. 9. The activation energy for manganese dissolution was calculated to be 7.04 kJ/mol, which is consistent with the values of activation energy reported for diffusion-controlled leaching process (Habashi, 1969).

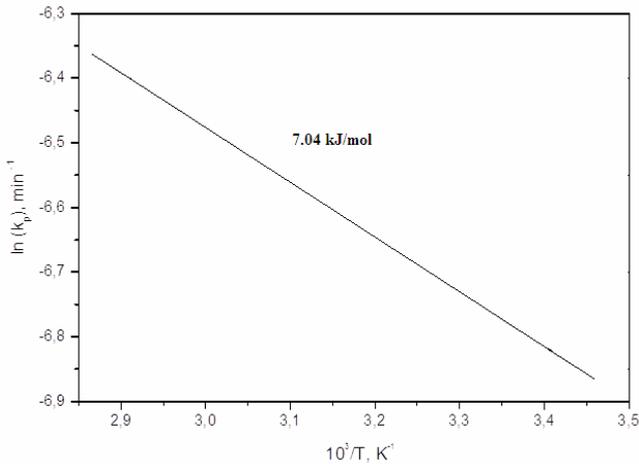


Fig. 9. The Arrhenius plot for manganese dissolution

Comparison of previous studies with present study

Table 1 compares the data between this paper and previous studies reported on the reductive acid leaching of zinc and manganese from zinc-carbon and alkaline battery powders or manganese dioxide ores. It is clear that present work has some advantages over other studies. For instance, the sulfuric acid and reductants concentrations and leaching temperature are lower and manganese dissolution is relatively higher than in previous studies.

Table 1. Comparison of the conditions and dissolutions of recent and present studies

	Battery/Ore Type	Leaching agents	Temperature (°C)	Leaching time (min)	S/L ratio	Dissolution of Zn (%)	Dissolution of Mn (%)
Sahoo et al. (2001)	Manganese dioxide ore	0.543 M H ₂ SO ₄ + 30.6 g/dm ³ oxalic acid	85	105	1/20	-	98.4%
Ferella et al. (2006)	Zn-C and Alkaline	1.8 M H ₂ SO ₄ + 59.4 g/dm ³ oxalic acid	80	300	1/20	100%	70%
Sayilgan et al. (2009)	Zn-C and Alkaline	+30 stoichiometric ratio H ₂ SO ₄ + -30 stoichiometric ratio oxalic acid	45	180	1/10	Full	91.2%
Sayilgan et al. (2010)	Zn-C and Alkaline	stoichiometric ratio H ₂ SO ₄ + (1.7 M) stoichiometric ratio ascorbic acid	45	180	1/15	Full	97%
Tian et al. (2010)	Manganese dioxide ore	1.9 M H ₂ SO ₄ + 3 g corncob	85	60	1/10	-	92.8%
Present Study	Mixed AA-AAA sized	0.5 M H ₂ SO ₄ + 13g/dm ³ ascorbic acid	70	180	1/20	99.99%	99.25%

Precipitation tests

Selective precipitation was previously reported by Veleso et al. (2005), De Michelis et al. (2007) and Poravazi et al. (2011) to separate metals present in spent batteries. In the current study, the precipitation tests were conducted using aqueous liquor obtained under the optimum test conditions found in the study of the reductive acid leaching tests (Table 2).

Table 2. Optimum reductive acid leaching test conditions

Sulfuric acid concentration (M)	Ascorbic acid dosage (g/dm ³)	Temperature (°C)	Time (hour)
0.5	13	70	3

Precipitations of zinc and manganese at different pH values adjusted with NaOH or KOH are given in Fig. 10. It shows that precipitation ratio of zinc and manganese increased with increasing pH value. The zinc precipitation increased from about 20-30% to near-complete precipitation with increasing solution pH from 6 to 8. The manganese precipitation gradually increased with increasing pH value up to pH 8. Nearly all manganese precipitation was achieved around pH 10 for both NaOH and KOH, which is consistent with previous study (Veleso et al., 2005). These results indicate that zinc and manganese can be selectively separated by adjusting solution of pH using NaOH or KOH (Zhang and Cheng, 2007).

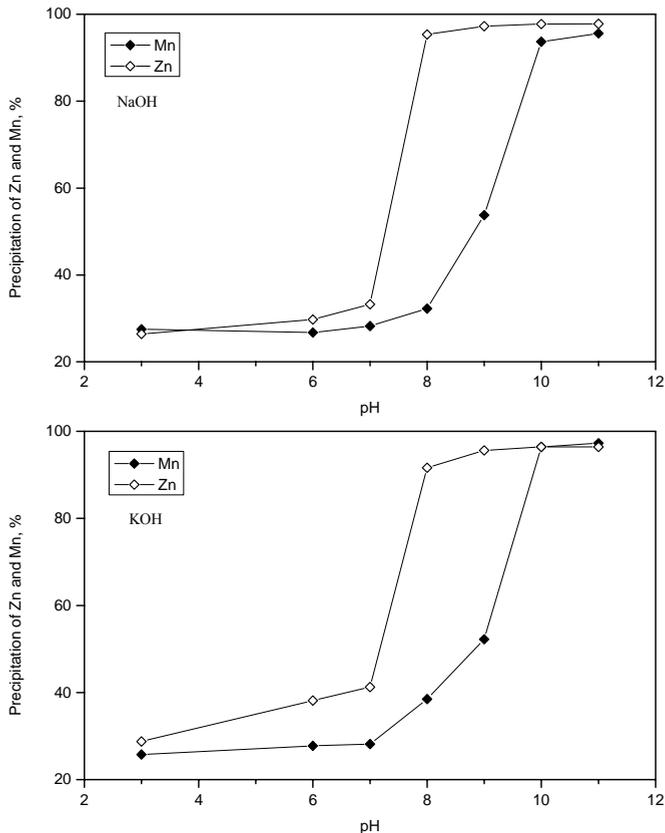


Fig. 10. Precipitation of Mn and Zn in the presence of NaOH and KOH at different pH's

The SEM-EDX images of the precipitated manganese hydroxide are given in Fig. 11. The manganese hydroxide particles precipitated by NaOH were heterogeneous in size and had a fractured structure. This may be resulted from hydrogen embrittlement.

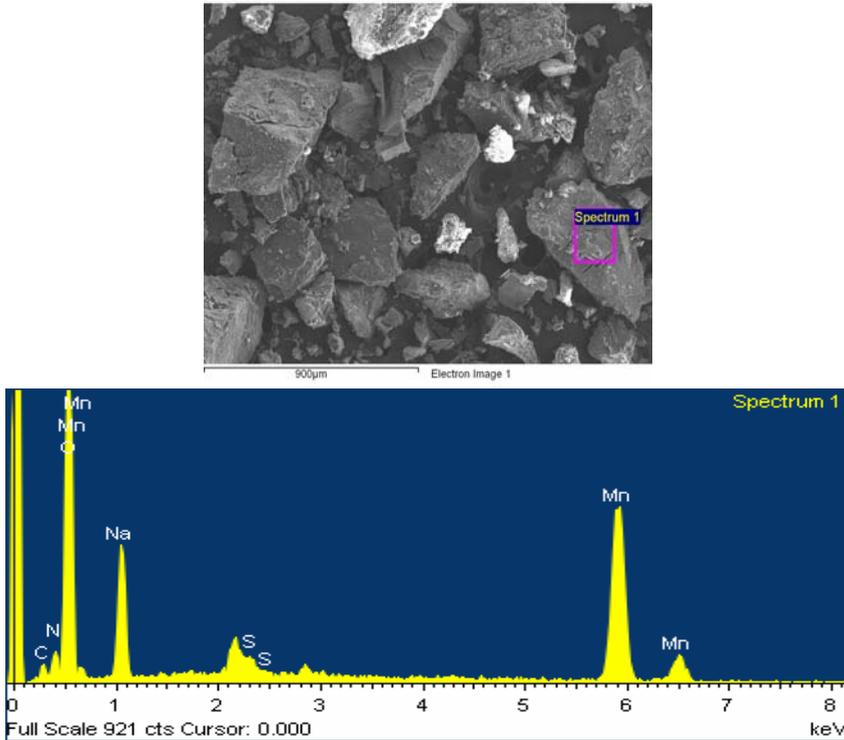


Fig. 11. SEM-EDX images of precipitated manganese hydroxide

Table 3. EDX analysis

Element	Weight (%)	Atomic (%)
C	4.57	8.13
N	7.53	11.49
O	40.45	54.09
Na	14.23	13.24
S	0.40	0.27
Mn	32.83	12.78
Totals	100	

For the spot indicated as spectrum 1, EDX analysis was performed and the results are given in Table 3. It shows that manganese and oxygen contents were detected in that point, indicating the presence of large amount of manganese hydroxide. The EDX

analysis also indicated a small amount of sulfur in the sample. This may originate from the elemental sulfur, which starts to form and produce a layer around particles during the reductive acid leaching process.

Leaching and precipitation conditions and proposed process flowsheet

The optimum leaching and precipitation variables are given in Table 4. Figure 12 shows the proposed flowsheet by referring our laboratory experimental tests. The results show that it was possible to dissolve 99.99% of zinc and 99.25% of manganese from the battery powder. In the precipitation stage, zinc and manganese sulfates were precipitated in as zinc and manganese hydroxides. It was possible to precipitate more than 95% of zinc at pH value of 8 and 96% of manganese at pH value of 10.

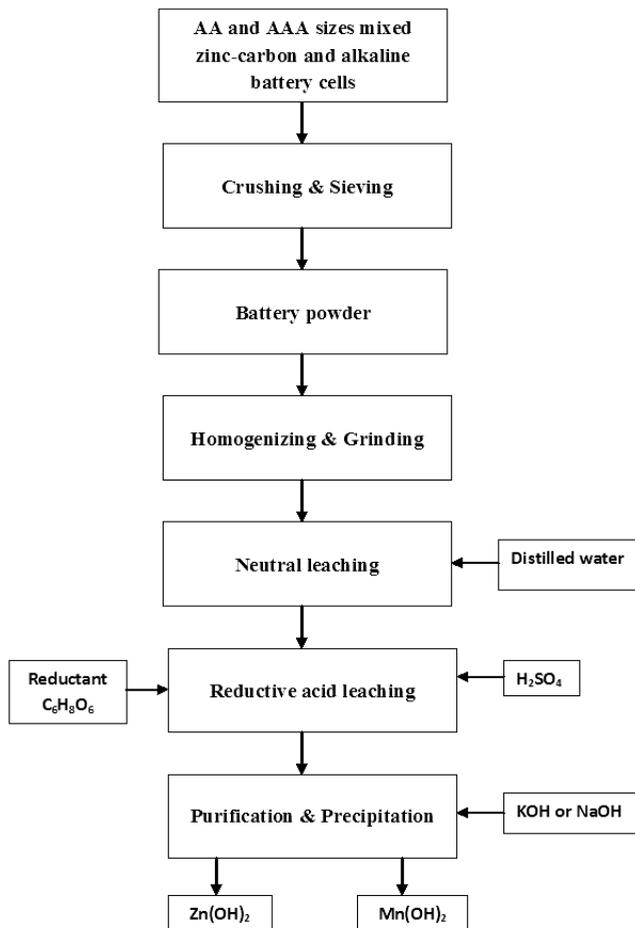


Fig. 12. Hydrometallurgical flowsheet proposed for zinc and manganese recovery zinc-carbon and alkaline battery cells

Table 4. The optimum leaching and precipitation experimental laboratory conditions

Sulfuric acid concentration (M)	Ascorbic acid dosage (g/dm ³)	Temperature (°C)	Time (hour)	Precipitation stage	pH	pH
				NaOH or KOH concentration (M)	Zn	Mn
0.5	13	70	3	3	8	10

Conclusions

In this study, simultaneous zinc and manganese recoveries from zinc-carbon and alkaline battery powder were studied. A hydrometallurgical flowsheet was developed for recovery of zinc and manganese from spent AA and AAA sized zinc-carbon and alkaline battery cells. The optimum reductive acid leaching conditions were determined as 3 hours of leaching time, 70 °C of leaching temperature, 0.5 M of sulfuric acid concentration, 13 g/dm³ of ascorbic acid dosage, 1/20 g/cm³ of solid/liquid ratio and 200 rpm of stirring speed. Under these conditions, the dissolution efficiencies were 99.99% for Zn and 99.25% for Mn. An activation energy of 7.04 kJ/mol was determined for manganese dissolution, which indicates that this is a diffusion-controlled leaching process. Using 3 M NaOH as precipitating agent at room temperature, a 95.35% of Zn (pH 8) and 93.66% of Mn (pH 10) were precipitated from the leaching solution. Under the same conditions, using 3 M KOH, precipitations of Zn and Mn were 91.63% and 96.39%, respectively.

Acknowledgements

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