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Selective Leaching of Zinc from Spent Zinc-Carbon Battery with Ammoniacal Ammonium Carbonate

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This paper describes the ammoniacal ammonium carbonate leaching behavior of zinc and manganese from spent zinc-carbon batteries. For selective extraction of Zn from the spent zinc-carbon battery, leaching tests were carried out as a function of process parameters such as concentration of $(NH_4)_2CO_3$, ammonia, temperature, time and pulp density. Physical methods of separation such as crushing was applied to reduce the material to 10–20 mm size followed by magnetic separation to separate iron with a recovery about 10 mass% leaving most of Zn and Mn in the non-magnetic fraction. Non-magnetic fraction was further subjected to sieving to separate 2.46 mm over and under size fractions. The oversize material was processed by eddy current separation to recover zinc sheet and carbon rods and plastics. The under size material with chemical composition of Zn 15.5 mass%, Mn 17.5 mass%, and Fe 1.4 mass% was used for leaching studies. Under the optimum leaching conditions (2.0 kmol/m^3 $(NH_4)_2CO_3$ and 4.0 kmol/m^3 ammonia, 40°C, 100 g/L pulp density, 30 min and 250 rpm), the leaching efficiency of zinc and manganese was 80.2% and less than 0.1%, respectively, indicating the selective recovery of zinc from the spent zinc-carbon battery. An overall zinc recovery is about 88%. [doi:10.2320/matertrans.MRA2008164]

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1. Introduction

Used zinc-carbon batteries can be regarded as one of the secondary sources for the recovery of valuable metals. Recycling of these wastes would offer economic benefits through the recovery of the valuable materials, as well as the preservation of raw metals in the interest of the sustainable development.

The spent zinc-carbon batteries are composed of approximately 20% of Mn, 20% of Zn, magnetic materials, carbon rod and small amounts of carbon powder, plastics and electrolyte. Some of the zinc metal in the spent battery oxidized to zinc oxides and some of the MnO_2 reduced into MnOOH during discharging reaction.[1,2)]

Hydrometallurgical methods of treatment have helped considerably in developing processes to extract and recover valuable metals from complex ores and metallurgical wastes. The hydrometallurgical processes are more environmentally suitable and economical to treat even low zinc containing materials on a small scale. It can process secondary resources containing different impurities.[3,4)] In particular, ammoniacal leaching is used for the selective dissolution of zinc from the secondary resources as ammonia forms a zinc amine complex leaving iron and manganese in the residue. The ammoniacal ammonium carbonate solution has been extensively employed for the recovery of zinc from different secondary resources.[5–7)]

In the present work, to study the leaching behavior of Zn and Mn in the zinc-carbon battery scrap, the selective leaching experiments were carried out under various experimental conditions such as reaction time, reaction temperature, concentration of ammonium carbonate/ammonia and pulp density on the dissolution behavior of metals.

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2. Experimental Procedure

2.1 Sample preparation

The crushed powder of zinc-carbon batteries collected from Seoul City was used in this study. A series of mechanical processing steps are conducted in the following sequence to yield enriched Zn and Mn particles: crushing, magnetic separation, sieving and classification. After spent zinc-carbon batteries were crushed and separated by magnetic separation, the non-magnetic material was subjected to screening with a 2.46 mm (8 mesh) sieve as shown in Fig. 1. Thus, the physical treatment applied herein yielded 3 kinds of fraction, namely, magnetic material, non-magnetic 8 mesh oversize and undersize.

The 2.46 mm undersize was used as a feedstock for the leaching experiment. The composition of the 2.46 mm undersize was determined to be 15.49 mass% Zn, 17.48 mass% Mn, and 1.42 mass% Fe.

2.2 Apparatus and reagents

A Varian make Atomic absorption spectrophotometer (AAS) of model Spectra AA-400 was used for chemical analysis and preferred crystal orientation of the zinc in the batteries was determined by X-ray diffractometer (XRD) of Rigaku Japan, make with Cu Kα as a target material. Reagent grade ammonium carbonate (Kanto chemical Co., Japan) and ammonia (Junsei chemical Co., Japan) chemicals were used for leaching experiments.

2.3 Leaching procedure

Leaching solution containing specified amounts of liquor ammonia (2–6 kmol/m^3) and ammonium carbonate (1–3 kmol/m^3) was prepared. Experimental equipment as shown in Fig. 2 was used for all leaching tests. 500 ml of leaching solution was introduced into the five-neck glass

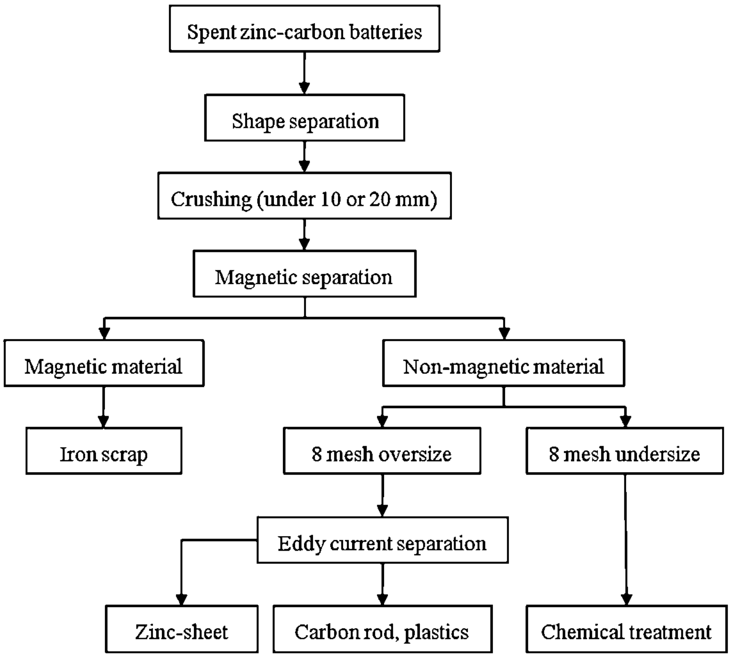

Fig. 1 Process diagram for physical treatment of spent zinc-carbon batteries.

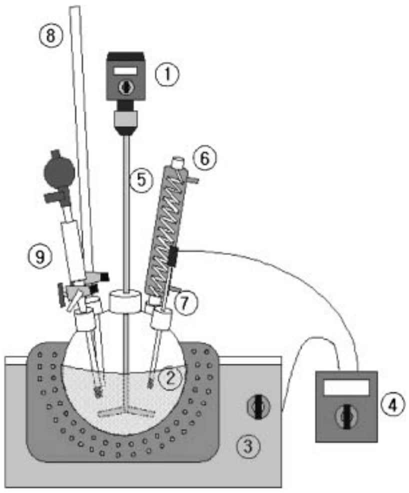

Fig. 2 Schematic diagram of leaching apparatus. ① stirrer ② reactor ③ heating mantle ④ controller ⑤ impeller ⑥ condenser ⑦ thermometer ⑧ burette ⑨ sampler

flask kept in a heating mantle. After stabilization of the solution to a suitable temperature, the spent battery powder was added and the solution was agitated with a PTFE paddle maintained at constant agitation speed of 250 rpm for different time periods (10 min to 60 min). For analysis, 5 ml of liquors were withdrawn at different time intervals during the leaching experiments. The sample was filtered and analyzed for Mn and Zn by AAS after suitable dilutions.

3. Results and Discussion

3.1 Weight fraction different materials in spent zinc-carbon batteries

The weight percentage of 10 and 20 mm size fractions present in different types of spent zinc-carbon batteries after magnetic separation is presented in Table 1. The average

Table 1 The weight-percentage of magnetic and non-magnetic materials on various types of spent zinc-carbon batteries.

Battery type	sieve size (mm)	Magnetic Material (mass%)	Non-magnetic material (mass%)			Loss (mass%)
			Total	+2.46 mm	−2.46 mm	
AA	10	12.8	85.3	31.3	54.0	1.9
C	20	15.0	83.5	25.3	58.2	1.5
D	20	12.8	87.1	26.2	60.9	0.2
4R25A	20	0.8	97.5	40.4	57.1	1.8
Average sample	20	10.3	88.4	30.8	57.6	1.3

weight fraction of spent zinc-carbon batteries were separated into three samples; 10.3 mass% magnetic material and 88.4 mass% non-magnetic material consisting of 30.8 mass% 2.46 mm oversize and 57.6 mass% 2.46 mm undersize, being a loss of 1.3 mass%.

The elemental analysis of the average sample of spent zinc-carbon batteries is shown in Table 2. The magnetic material contains 10.2 mass% Fe whereas the non-magnetic material for the 2.46 mm oversize and 2.46 mm undersize contain only 0.12 mass% and 1.42 mass% Fe, respectively. Therefore, most of Fe in the batteries can be readily recovered by magnetic separation. It is interesting to note that the non-magnetic 2.46 mm undersize contains most of the Mn (91.8 mass%) and a large portion of Zn (63.6 mass%) available in the feed. 37.4 mass% zinc was still remained in 2.46 mm oversize because the shape of zinc in the spent zinc carbon battery is like a sheet type which is similar a beverage can, so there were powder type of zinc as well as thin platy type of zinc in the crushed battery sample. This zinc sheets in non-magnetic 2.46 mm oversize also could be recovered by eddy current separation from plastics and vinyl.[2)]

Table 2 Contents of valuable metals in the average sample of spent zinc-carbon battery.

%		Fe	Mn	Zn
magnetic material		10.2	0.05	0.02
non-magnetic material	+8 mesh	0.1	2.3	8.9
	−8 mesh	1.4	17.5	15.5
Total		11.8	19.8	24.4

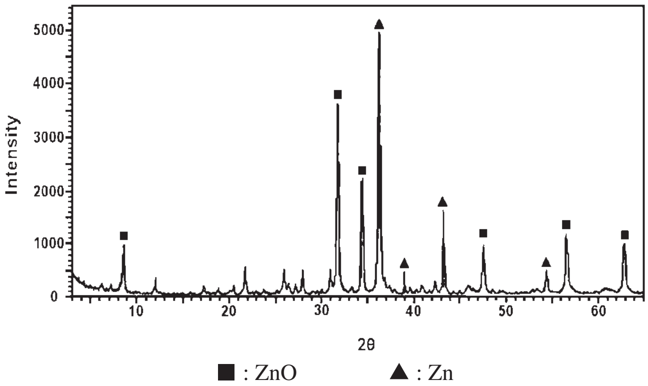

Fig. 3 XRD diffraction patterns of zinc sheet obtained from spent zinc-carbon battery.

3.2 Characterization of sample

In order to confirm the chemical crystallization of zinc which is target for ammonium carbonate leaching, only zinc was separated from raw battery and this zinc sample was analyzed by XRD. As the result of XRD shown in Fig. 3, we found the peak of Zn metal in the sample.

3.3 Leaching chemistry of Zn and Mn using ammoniacal ammonium carbonate

The feed of spent zinc-carbon battery used for the present leaching test contains 15.5 mass% Zn, 17.5 mass% Mn, and 1.4 mass% Fe. Ammoniacal ammonium carbonate leaching method is applied for the selective dissolution of zinc as ammonia forms a zinc amine complex leaving most of the manganese in the residue.[4,8)]

In the Zn-NH_3-H_2O system, there are two stable regions for zinc hydroxide. Zinc tetraammine, $Zn(NH_3)_4{}^{2+}$, which is stable only in the pH range of 8 to 11. The stability region of the solid phase decreases or even disappears as the activity of the soluble species or ammonia concentration increases. This is one of the reasons why ammonia is often used to precipitate zinc from acidic solutions despite a certain stability of zinc-ammine in ammoniacal solutions as indicated in the Eh-pH diagram.[9)]

In the case of manganese and manganous oxides, dissolution of these phases results in the formation of manganese ammonium carbamate complex in the first instance, then precipitate as manganese carbonate or manganese dioxide. The reactions are:[7)]

$$Mn + (NH_4)_2CO_3 \rightarrow MnCO_3\text{-}NH_2\text{-}NH_4 + H_2. \quad (1)$$

The ammonium carbonate also forms a ammonium carbamate compound:

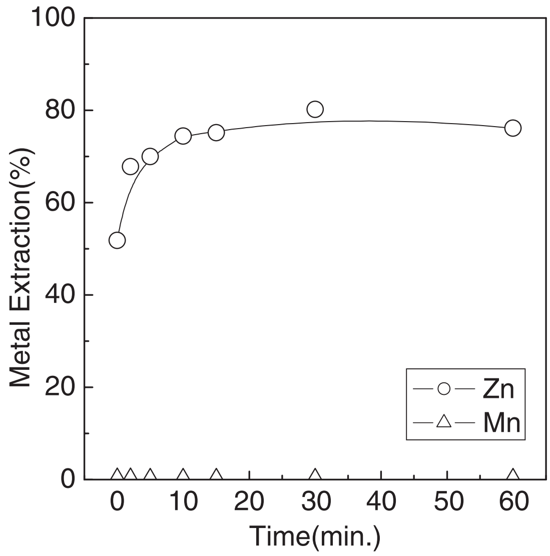

Fig. 4 The effect of reacting time on the leaching of Zn and Mn. (2.0 kmol/m^3 $(NH_4)_2CO_3$, 4.0 kmol/m^3 NH_4OH, 60°C, 100 g/L pulp density, 250 rpm)

$$(NH_4)_2CO_3 \leftrightarrow NH_2\text{-C-O-ONH}_4 + H_2O. \quad (2)$$

The ammonium carbamate compound reacts with MnO as follows:

$$MnO + NH_2\text{-C-O-ONH}_4 \rightarrow Mn\text{-}NH_2\text{-O-C-O-ONH}_4. \quad (3)$$

The extraction reaction of zinc oxide using ammoniacal ammonium carbonate follows:

$$ZnO + (NH_4)_2CO_3 + 2NH_4OH \rightarrow Zn(NH_3)_4{}^{2+} + CO_3{}^{2-} + 3H_2O. \quad (4)$$

3.4 Effect of leaching time

Figure 4 shows the effect of leaching time on leaching efficiency of Zn and Mn during leaching time from 1 min to 60 min maintained at 100 g/L pulp density, 2.0 kmol/m^3 $(NH_4)_2CO_3$ and 4 kmol/m^3 ammonia and 4.0 kmol/m^3 NH_4OH, 250 rpm and 60°C. The leaching efficiency of Zn increased from 51.8 to 80.2% as the leaching time increased from 0 min to 60 min and the reaction was almost completed in 10 min. On the other hand, less than 0.1% Mn was extracted over the entire range of the leaching time. The results demonstrated that about 15–30 min duration is sufficient to achieve maximum efficiency. The low leaching efficiency of Zn is due to the presence of not leachable Zn metallic phase with the ammonium carbonate leachant, which was confirmed by XRD of sample as shown in Fig. 3.

3.5 Effect of ammoniacal ammonium carbonate concentration

Figure 5 shows the leaching efficiency of Zn and Mn as a function of ammoniacal ammonium carbonate concentration in the range from 0.5 to 3 kmol/m^3 and ammonia in the range from 1 to 6 kmol/m^3 (ratio of ammonia/ammonium carbonate = 2) under the leaching conditions of 100 g/L pulp density, 60°C, 250 rpm and 60 min. The Zn

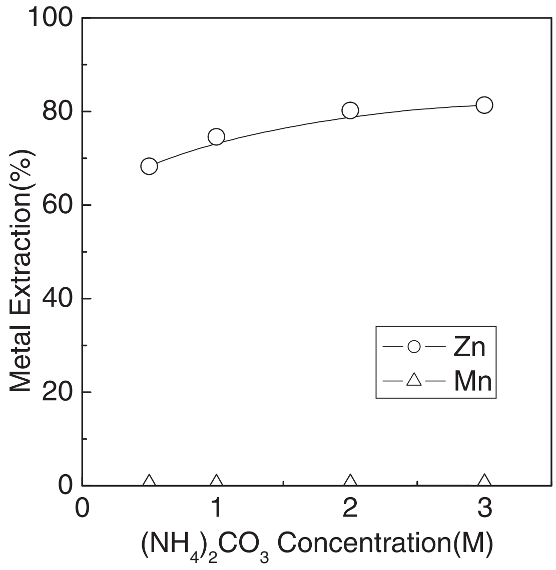

Fig. 5 The effect of $(NH_4)_2CO_3$ concentration on the leaching of Zn and Mn. (60°C, 100 g/L pulp density, 250 rpm, 30 min)

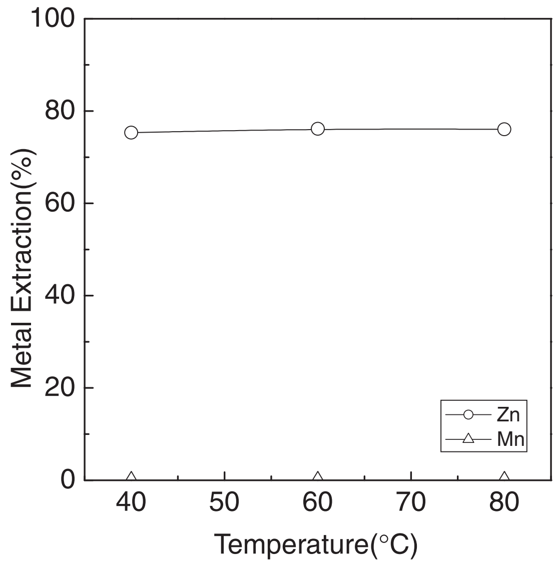

Fig. 6 The effect of temperature on the leaching of Zn and Mn. (2.0 kmol/m^3 $(NH_4)_2CO_3$, 4.0 kmol/m^3 NH_4OH, 100 g/L pulp density, 250 rpm, 30 min)

extraction gradually increased with increasing $(NH_4)_2CO_3$ concentration from 68.3 to 81.3%. The Mn extraction, however, was less than 0.1% over the entire range of the ammoniacal ammonium carbonate concentration. The leaching efficiency of zinc was almost same beyond 2.0 kmol/m^3 $(NH_4)_2CO_3$.

3.6 Effect of reaction temperature

Figure 6 shows the effect of leaching temperature in the range of 40 to 80°C on the leaching efficiency of zinc and manganese under the conditions of 2.0 kmol/m^3 $(NH_4)_2CO_3$, 4.0 kmol/m^3 NH_4OH, 100 g/L pulp density, 250 rpm and 30 min. Effect of temperature has negligible effect on the leaching efficiencies of metals.

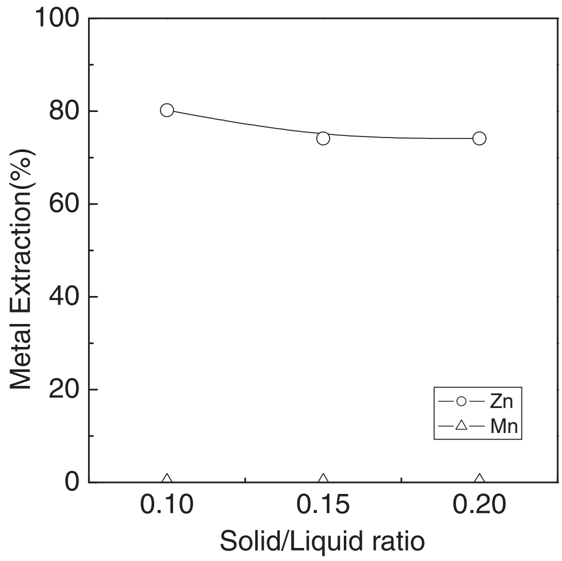

Fig. 7 The effect of Solid/Liquid ratio on the leaching of Zn and Mn. (2.0 kmol/m^3 $(NH_4)_2CO_3$, 4.0 kmol/m^3 NH_4OH, 40°C, 250 rpm, 30 min)

3.7 Effect of pulp density

The Zn and Mn extraction as a function of pulp density under the conditions of 2.0 kmol/m^3 $(NH_4)_2CO_3$, 4.0 kmol/m^3 NH_4OH, 40°C, 250 rpm and 30 min is shown in Fig. 7. As expected, the Zn extraction gradually decreased from 81.3% to 74.1% as the pulp density increased from 10 to 20%. Under optimum conditions of leaching (2.0 kmol/m^3 $(NH_4)_2CO_3$, 4.0 kmol/m^3 NH_4OH, 100 g/L pulp density, 40°C, 250 rpm, 30 min), the compositions of leaching liquor contain 18.9 g/L Zn and less than 5 ppm Mn corresponding to a leaching efficiency of 80.2% Zn and $<$0.1% Mn.

4. Conclusions

In this study, leaching behavior of the spent zinc-carbon battery powder was investigated for selective extraction of zinc value in the batteries. The following conclusions can be drawn:

(1) The chemical composition of 2.46 mm under size material gained by physical treatment was Zn 15.5 mass%, Mn 17.5 mass%, and Fe 1.4 mass% used for leaching studies.
(2) Zinc was selectively leached to about 81% leaving most of Mn in the residue.
(3) Temperature and pulp density have little effect on Zn recovery in the investigated conditions of leaching.
(4) About 88% zinc could be recovered by the present process from total the zinc content of the spent zinc carbon battery.

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