

Short communication

Simultaneous recovery of zinc and manganese dioxide from household alkaline batteries through hydrometallurgical processing

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Received 14 April 2004; accepted 10 May 2004

Available online 2 July 2004

Abstract

This paper describes the leaching experiments and the electrowinning tests to recover Zn and Mn from spent household alkaline batteries. After the dismantling of the batteries, the black powder was analyzed and found to contain 21 wt.% Zn and 45% wt. Mn. Therefore, it was considered that recovery of these metals would be interesting due to their relatively large amounts in this kind of waste. Batch laboratory experiments were carried out to develop an acid leaching procedure and to determine appropriate leaching conditions to maximize zinc extraction and to study the leaching behavior of Mn. An experimental study was undertaken to evaluate the feasibility of simultaneous recovery of zinc and particulate manganese dioxide using a laboratory cell. The results from these electrowinning experiments are also presented in this paper.

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Keywords: Alkaline batteries; Recycling; Acid leaching; Zinc; Manganese dioxide; Electrowinning

1. Introduction

Nowadays, large amounts of materials have been discarded as waste, but some of them could be recovered instead. Recycling rates for metals are growing in many developed countries. In the 1980s, the lead, zinc and tin industries were in a crisis caused by stagnation of the market, and secondary raw materials from lead batteries, zinc plant leach operations and steel plant dusts were accumulated as observed by Engh [1], who predicted an increasing in metal recovery from scrap and wastes. Used household batteries could be one of the secondary sources of metals, and the recycling of these wastes would offer economic benefits through the recovery of the valuable materials, as well as the preservation of raw materials in the interest of the sustainable development.

During the last decade, the producers of batteries were engaged trying to find substitutes for toxic substances still used in batteries, to match environmental requirements; although, the basic systems of the batteries and its composition (steel, plastic, zinc, manganese dioxide, steel casings, paper, carbon, and brass) still remains the same.

Most of these materials can be technically recovered by means of mechanical and chemical treatment. The materials recovered show some advantages as they could be returned to the batteries production as raw material or can be used for other purposes. The steel scrap can be sold to steel mills; manganese could be sold to the steel industry, and zinc can be used in metallurgical industries.

Several processes for the recycling of batteries [2–9] have been proposed, mainly in Europe, and the pyrometallurgical processes are the most used.

Hydrometallurgical processes have also been proposed to recycle batteries. According to Bartolozzi [10] the recovery of Zn and MnO₂ was obtained after the acid leaching of batteries followed by electrolysis. The Batenus process that recycles mixed batteries uses sulfuric acid leaching and solvent extraction, electrolysis, ion exchange, precipitation and reverse osmosis to recover valuable products [11]. Rabah [12] studied the treatment of batteries by acid leaching and Zn precipitation by oxalic acid and Mn precipitation by Na₂CO₃.

2. Alkaline batteries

Most portable devices require AA, C or D batteries, which corresponds to the largest percentage of batteries used for

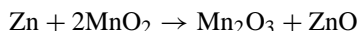
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general household purposes. Alkaline batteries are included in this group as non-rechargeable batteries (primary cells), which are designed to be fully discharged, and present the advantage of a life time longer than the zinc–carbon cells. The alkaline cell uses an electrochemical system where zinc and manganese dioxide are the anode and the cathode, respectively. Powdered zinc with a corrosion inhibitor and a compacted cathode of manganese dioxide is mixed with graphite, acetylene black, and an electrolyte made of concentrated KOH solution.

There is some disagreement in the literature about the products formed after complete discharging, although the reaction mechanism in an alkaline battery cell could be expressed as:



3. Experimental procedures

A consignment of used alkaline batteries was dismantled using a hammer mill, and the residual fine portion obtained (0.208 mm) containing the metals to be recovered was treated hydrometallurgically. After chemical analysis to determine the total composition of the samples, a leaching procedure was performed aiming to recover the metals from the aqueous solution using electrowinning of both metals, Zn and Mn.

All chemical analysis in this study were performed using an atomic absorption spectrometer.

3.1. Characterization of the powder

Particles below 0.208 mm originating from the first dismantling step were submitted to X-ray diffraction and atomic absorption spectrophotometer studies for qualitative and quantitative analysis.

3.2. Leaching

Dry powder was fed into a glass vessel, containing diluted sulfuric acid. A magnetic mixer with heating system was used to provide good contact between the sample and the leaching solution. The pH and temperature were monitored using respectively a pH meter and a simple mercury thermometer. After the leaching period, the material was filtered using a paper filter and a Büchner funnel. The filtered residue consisting of manganese dioxide, graphite and other metals was dried and the mass was measured. The liquor was stored for further tests.

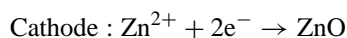
Leaching tests were conducted to evaluate the leaching behavior of the metals of interest under different conditions as to solid/liquid ratio (weight sample/leaching solution volume), temperature, sulfuric acid concentration, and period (time) of leaching test. Tests were carried out in a temperature range of 25–70 °C. Sulfuric acid concentrations were

used in the range of 0.3–0.7% (v/v). The total leaching time of the test was set in the range of 1–4 h.

3.3. Electrowinning tests

The objective of this step was to investigate the simultaneous recovery of zinc and manganese by electrowinning.

The literature reports similar simultaneous electrowinning of two metals from industrial effluents [13,14] and for treating zinc ores containing high amounts of manganese. In this case, Zn is collected on the cathode, while manganese is deposited in the form of manganese dioxide on the anode. The main reactions in the process are [14]:



According to Rodrigues [13], it is believed that firstly the anodic oxidation of Mn(II) to Mn(III) occurs and this undergoes disproportionation to Mn(II) and Mn(IV):



The manganic ions continue to react causing the precipitation of a dark MnO₂, which settles down in the bottom of the cell.

The experimental electrowinning cell for all experiments was composed of an anode and a cathode in each cell, which were mounted and fit into an acrylic rounded plate that was used to support and cover a 250 ml beaker. The distance between the electrodes was kept uniform and constant at 20 mm. A 50 mm × 50 mm × 2.5 mm aluminum cathode and a 50 mm × 50 mm × 2.0 mm lead anode were placed into the filtered solution. A magnetic stirrer provided stirring.

The mass of each cathode and anode was checked before the tests. After 1 h, the electrodes were removed, rinsed with water, dried, the mass gain was measured. Each material deposited during the tests was recovered by filtration and subsequently dried.

3.3.1. Current efficiency

Current efficiency is defined as follows:

Current efficiency = 100 × actual amount of metal deposit/amount of the same metal expected to be deposited according to Faraday's law.

Current densities in the range of 200–1200 A/m² were tested. In these experiments, the total reaction time was set in 1 h and the temperature was set at 25 °C.

4. Results and discussion

4.1. Characterization of dry powder

The X-ray diffraction spectrum is shown in Fig. 1 and the results of chemical analysis are listed in Table 1.

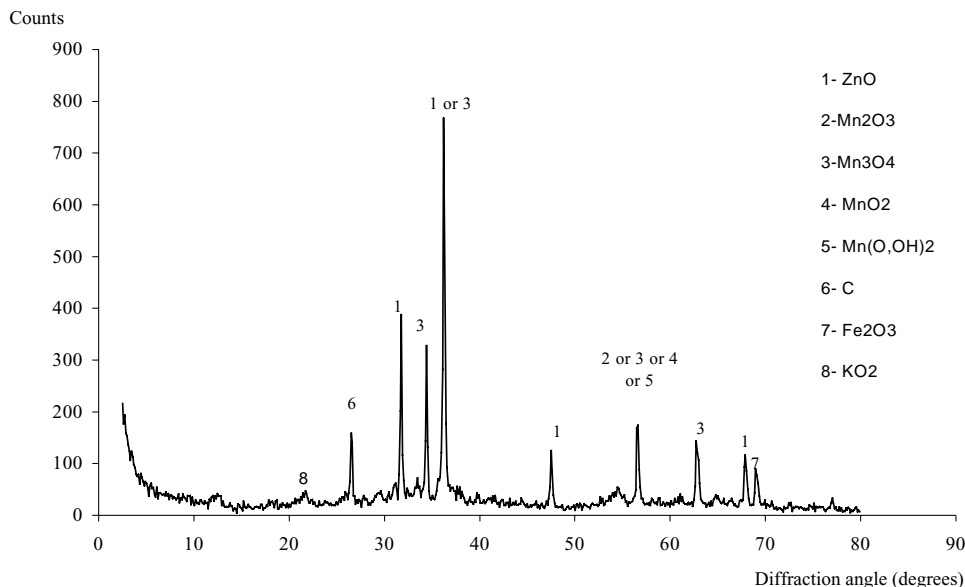


Fig. 1. X-ray spectra of alkaline battery powder showing peaks with the most probable compounds identified.

The results of chemical analysis show expressive amount of Zn and Mn, which represents 66% of the total mass of the sample. According to the X-ray spectrum, ZnO is the main zinc compound found in the dry powder. Mn of different valences was found in the X-ray spectrum, not only Mn₂O₃ as suggested by the literature. In fact, it can not be predicted that all batteries were submitted to the same discharging conditions, and for this reason, other manganese compounds were found, such as MnO₂, Mn(O,O)₂ and Mn₃O₇, consequently a collection of spent batteries is quite complex system.

K is derived from electrolyte, which is potassium hydroxide. The amount of iron detected is low in the dry powder, since its removal by the magnetic separation step was efficient during the prior mechanical treatment [15]. Pb, Hg and Cd were also detected in minor concentrations.

4.2. Leaching tests

Since ZnO is the main Zn compound present in the sample, a dilute acid solution readily dissolves it. It is observed from the experiments that a dilute H₂SO₄ solution is strong

enough to extract Zn, as shown in Fig. 2. Mn was also leached; this fact confirms the occurrence of Mn(III) and Mn(II) in the dry powder as was detected in the X-ray spectrum.

Data from the leaching experiments is shown in Fig. 3. This figure shows that as the leaching time is increased Zn and Mn extraction increases.

Under temperatures between 25 and 40 °C about 60–70% of zinc is leached. An increase in Zn extraction is observed at temperatures above 50 °C using 0.7% H₂SO₄ solution (0.13 M) and a total leaching time of 2 h (Fig. 4).

From the obtained results, the optimum conditions of the leaching step were:

- Temperature, 70 °C;
- solid/liquid ratio, 1/60;
- total leaching time, 4 h; and
- initial H₂SO₄ concentration, 0.7%.

This condition assured that all Zn and 40% of Mn present in the sample are leached.

Table 1
Chemical analysis for dry alkaline battery powder

Element	Wt.%
Zn (%)	21
Mn (%)	45
K (%)	4.7
Fe (%)	0.36
Pb (%)	0.03
Hg (ppm)	1
Cd (ppm)	0.06
Others (%)	±30

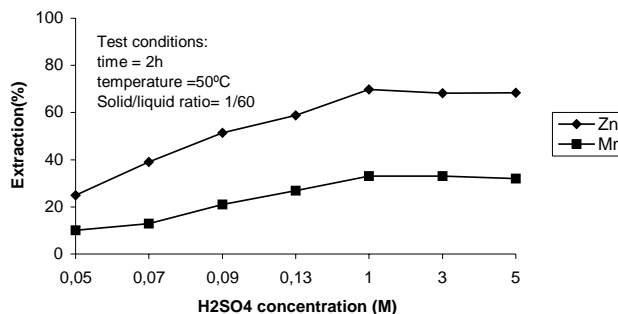


Fig. 2. Effect of H₂SO₄ concentration in Zn and Mn leaching.

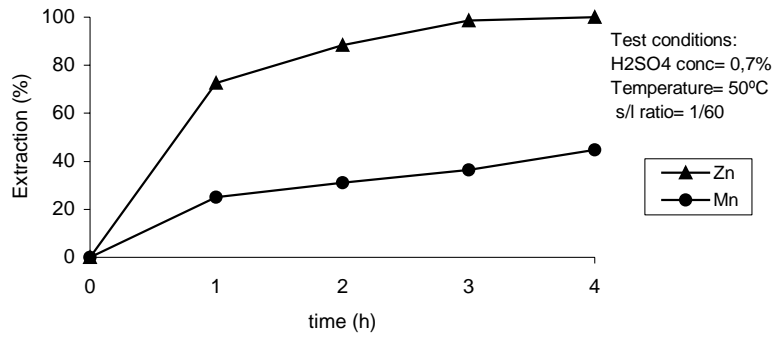


Fig. 3. Extraction of Zn and Mn as a function of leaching times.

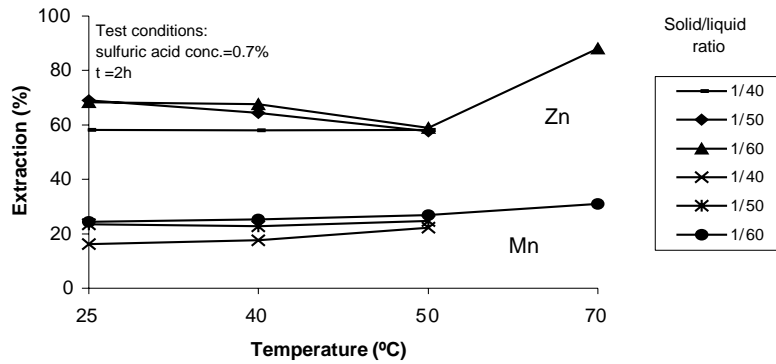


Fig. 4. Effect of temperature in the Zn and Mn leaching.

Table 2
Electrolyte composition for electrowinning experiments

ZnSO ₄ (g/l)	3.85–4.0
MnSO ₄ (g/l)	9.2–9.5
H ₂ SO ₄ (g/l)	12.9–13.5

4.3. Electrowinning of leached solutions

The initial electrolyte composition in electrowinning tests is shown in Table 2.

Zinc deposition was observed on the aluminum cathode, while manganese dioxide, MnO₂ settled down on the bottom of the cell. Zinc presented a homogeneous bright silver

surface. Zinc purity was 99.8 wt.%, and Fe and Pb were the main contaminants. Fe and Pb concentrations were both equal to 0.01 wt.%, other elements were not detected.

Small, thin, light, and easily removable flakes were observed on the anode surface. The deposit presented a dark brown color. In the beginning of the electrowinning process, it was observed that the leached solution changed its color from white to light pink. At the end of the experiment, a layer of fine dark brown precipitates were found in the bottom of the. The mechanical stirring seemed to keep the anode without any manganese dioxide moving the precipitate away from the anode surface. The X-ray diffraction spectrum from the precipitate presented diffractions peaks that correspond to MnO₂, as shown in Fig. 5.

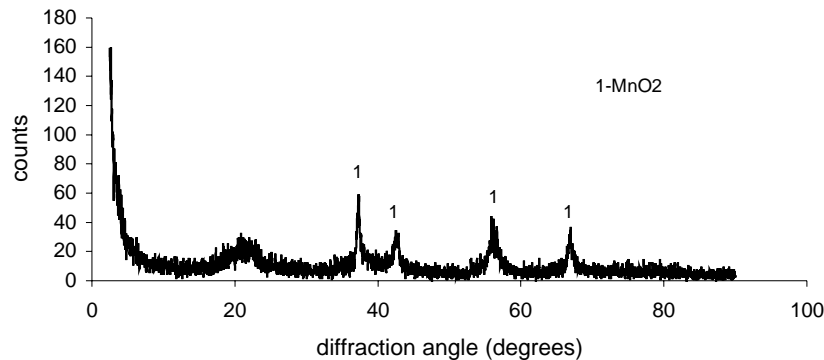


Fig. 5. X-ray diffraction spectrum for the material deposited in the cathode.

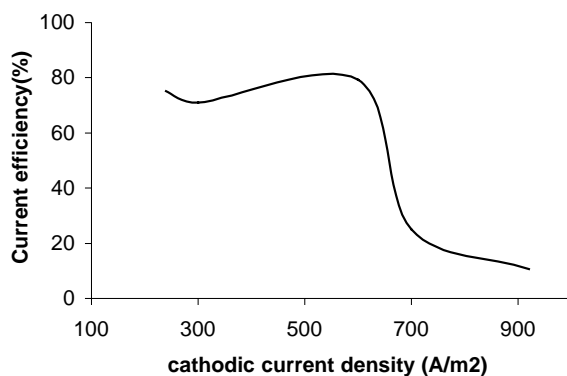


Fig. 6. Effect of current density in the cathodic current efficiency.

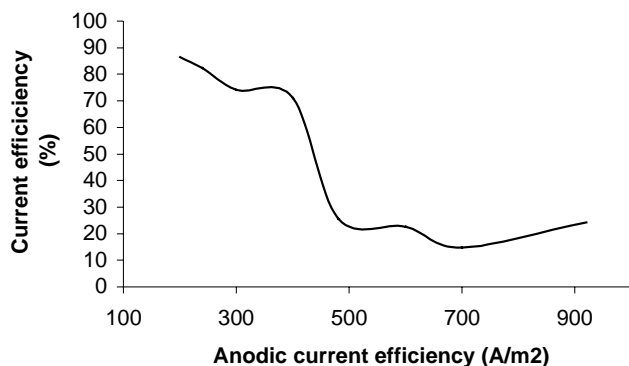


Fig. 7. Effect of current density in the anodic current efficiency.

The results of the tests on the effect of cathodic and anodic current density are shown in Figs. 6 and 7. At current densities above 120 A/m^2 the cathodic current efficiency dropped drastically. Under low current densities, e.g., near 40 A/m^2 , the quality of the surface of the zinc deposit was good and the stripping was easy.

According to Fig. 7, the increase in the anodic current density causes a decrease in current efficiency due to the increase in the amount of material deposited on the anode, because MnO_2 acts as an electrical insulator increasing the electrode resistance. The same behavior was observed by Binsfield [14].

Actually, the current efficiency is affected by many factors. Some reactions between oxygen and hydrogen or even sulfates could affect current efficiency. According to Hayes [6], the current efficiency is lowered by hydrogen evolution caused by impurities in the solution. On the other hand, Van Arsdale [16] reported that low zinc concentration in the solution cause hydrogen evolution. The low current efficiency encountered in this work is also thought to partly be a consequence of a too dilute solution.

5. Conclusions

1. The presence of 45% Mn and 21% Zn in pulverized alkaline battery powder makes this an attractive source for a simultaneous recovery.

2. Leaching at low acid concentration can dissolve all Zn and 40% of Mn contained in dry powder.
3. Zinc and manganese can be recovered by simultaneous electrowinning of its aqueous solutions with lead anode and aluminum.

Acknowledgements

The authors would like to thank to Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP), project 98/10882-9 and 98/01227-7, for the financial support for this project.

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