

METALS RECOVERY FROM SPENT Zn-MnO₂ BATTERIES BY HYDROMETALLURGY

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Abstract

A hydrometallurgical process for recycling spent Zn-MnO₂ batteries was developed, involving leaching with sulfuric acid, purification by precipitation and metals separation for further recovery. Leaching of zinc oxide was easily attained while for manganese oxide was rather difficult depending on temperature and acid concentration. At 90°C and with the liquid/solid ratio of 20 L/kg, more than 95% of zinc is recovered in 30 minutes with 0.5M H₂SO₄. To attain similar recovery for manganese, higher levels of acid concentration and time are needed (e.g 0.7 M and 2 hours). After leaching a purification step is necessary to remove iron co-dissolved through Fe(III) precipitation. Separation of zinc from manganese by solvent extraction with 1M DEHPA follows in the process route. The countercurrent multistage separation diagram developed allows the production of a zinc electrolyte with 120 g/L Zn and 0.005 g/L Mn, and a raffinate with 16 g/L Mn and 0.013 g/L Zn.

Introduction

The recycling of spent Zn-MnO₂ batteries is carried out by dedicated recyclers using several process alternatives [1]. Most of the running processes use pyrometallurgical technologies [2] based on zinc distillation. Alternative treatments by hydrometallurgy have been reported [3-5] but its application is scarce.

In order to contribute to the development of alternative solutions, a process for recycling batteries based on Zn-MnO₂ systems has been studied. The process is based on the hydrometallurgical treatment of spent batteries in sulfuric acid media (Figure 1). The process starts with the physical processing by shredding using cutting grinders, where the batteries are opened and size reduced, allowing the liberation of the interior electrode particles or pastes. The fines can be then separated and the coarse material containing the steel scrap can be treated to remove the remaining aggregate electrode. The final scrap also contains some plastics and other non-metal materials and can be further valorized.

The chemical treatment is carried out by leaching of the zinc and manganese oxides with sulfuric acid with formation of soluble metal sulfates. Some iron also dissolves and a purification step is thus necessary to remove iron from solution by oxidation/precipitation. The resulting leach liquor rich in Zn and Mn is processed by solvent extraction with di(2-ethylhexyl) phosphoric acid - DEHPA, where zinc is selectively extracted against manganese, leading to a pure manganese raffinate for recovery as a salt or precipitate (e.g. manganese sulfate or oxide/hydroxide). The organic extract containing zinc is stripped with an acidic electrolyte and

integrated in an electrowinning circuit to recover zinc as cathodes. The diagram presented is simply indicative, since other unit operations can be integrated, namely purification steps due to the presence of some minor elements (eg. nickel and copper).

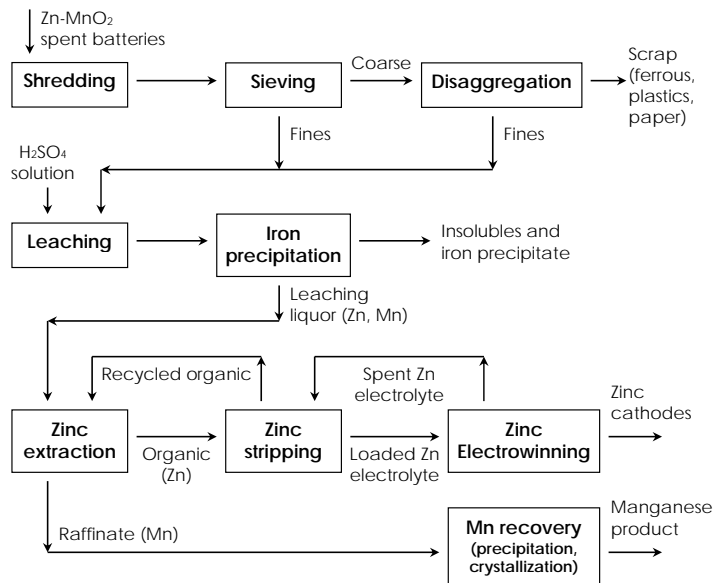


Figure 1. Simplified diagram of the process for recycling spent Zn-Mn batteries by hydrometallurgy.

In this paper some results concerning the development of this hydrometallurgical process for recycling spent Zn-MnO₂ batteries are presented and discussed, namely regarding batteries characterization, acid leaching, iron precipitation and zinc solvent extraction.

Experimental

Characterization and shredding of the spent batteries sample

The spent batteries used in this research work were obtained from a household collection point. The batteries were initially sorted by types (saline, alkaline and other) and then classified by sizes/shapes in order to characterize the sample. Since batteries from the Zn-Mn systems (saline and alkaline) represent more than 90%, only these types were considered for this work being the other (button-type, lithium and nickel-based batteries) rejected. After characterization, the batteries were again mixed and shredded using a laboratory Cutting Mill (Retsch SM 2000) with a 6 mm bottom sieve. The shredded materials were physically characterized by sieving. Elemental analysis of the main metals (Zn, Mn and Fe) was carried out by Atomic Absorption Spectrometry (AAS, GBC 906AA) after sample dissolution by acid digestion in microwave furnace (CEM MDS-2000).

Leaching tests

The solid samples used in the leaching experiments were prepared by sampling of the shredded batteries, using initially a Jones sampler and afterwards a rotating divider. Typically 5-10 g of solids was utilized in each trial, depending on the liquid/solid (L/S) ratio used. The sulfuric acid

solutions were prepared from p.a. grade H_2SO_4 (95-97%, Merck). The leaching tests were carried out in orbitally shaken 250 mL closed round flasks, in a temperature controlled oven. The leach solution was previously heated to the preset temperature and then the solids were added and the reaction time was initiated. At the end the remaining solids were filtered, dried, weighted and analyzed. Leaching efficiencies for each metal were determined from leach liquor composition and the final solids analysis provided comparative values for accuracy evaluation.

Solvent extraction tests

The extractant used in this investigation was DEHPA, kindly supplied by Albright and Wilson Americas, used as received and diluted in the aliphatic diluent n-dodecane. The aqueous feed solutions were obtained from the leaching tests of spent batteries and were purified by precipitation of the contained iron. The solvent extraction experiments were carried out in blade-stirred open cylindrical vessels (when pH control was necessary) or in shaken separatory flasks (in tests without pH control). For acidity or pH adjustment, sulfuric acid p.a. and sodium hydroxide r.g. were used. After each contact, the solutions (organic and aqueous) were settled, filtered and processed for elemental analysis by AAS. Before analysis organic samples were previously stripped twice with 1 M H_2SO_4 and the acid aliquots were therefore analyzed.

Results and Discussion

Characterization and shredding of spent batteries

After collection and sorting, a representative sample of batteries was shredded and the resulting material was characterized in what concerns size distribution and elemental chemical composition (Table I). Concerning size characterization, about 90% of the material weight was below 4 mm. Most of the electrode materials containing zinc and manganese were liberated as powder or small particles while iron from the steel cases was essentially present in coarse fragments which also contained some stuck electrode. The results showed that sieving at 2 mm allowed removing about 95% of iron above the sieve but with a corresponding loss of 30% of zinc and 20% of manganese. To recover these amounts a disaggregation step using a stirred washing device or an impact grinder is proposed. Alternatively, the chemical processing of all the shredded material, without a physical separation step, was evaluated in order to maximize the recovery of zinc and manganese. This approach was tested as the most unfavorable way in what concerns iron contamination of the solutions in the aqueous processing steps. The results here reported are concerned to this option.

Leaching of spent batteries

The leaching operation was developed in order to minimize acid consumption together with attaining high metal recovery yields. The effects of several processing parameters on the leaching efficiencies were evaluated, being temperature and acid concentration found very significative. The influence of temperature is observed in Figure 2: manganese and iron dissolution is very dependent from this parameter while zinc leaching is easily attained. The reaction time is also important: for 2 hours of reaction, zinc leaching is practically total even at room temperature whereas manganese recovery up to 90% is only achieved at 90°C. Iron contamination of leach solutions is much related with manganese yields.

Table I. Characterization of battery sample.

| Distribution by cell types | | Characteristic diameters of shredded material | |
|----------------------------|-----|---|---------------------|
| % w/w | | | |
| Alcaline | | d_{10} (mm) | 0.097 |
| MIGNON (AA) | 38 | d_{50} (mm) | 1.26 |
| MONO (D) | 17 | d_{90} (mm) | 3.97 |
| BABY (C) | 16 | | |
| E-BLOCK (9V) | 7 | Elemental composition of sample | |
| MICRO (AAA) | 8 | | |
| Saline | | Element | Composition (% w/w) |
| MIGNON (AA) | 10 | Zn | 19 |
| MONO (D) | 2 | Mn | 25 |
| BABY (C) | 1 | Fe | 27 |
| MICRO (AAA) | 1 | | |
| Total | 100 | | |

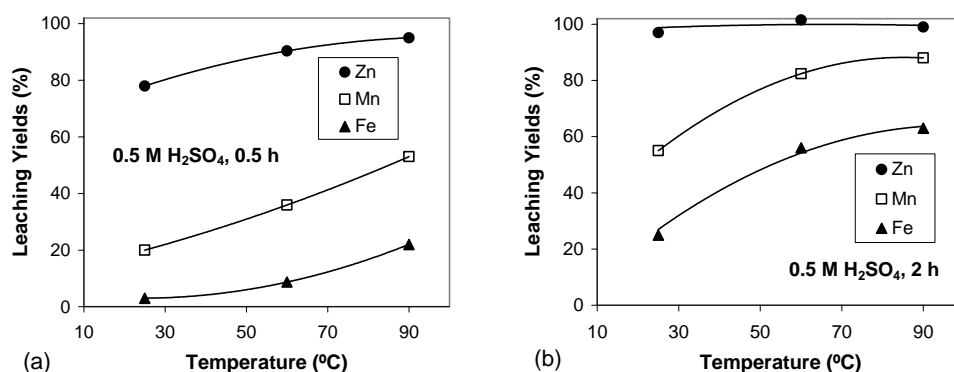


Figure 2. Effect of temperature on the metals leaching yields, with 0.5 M H₂SO₄ and L/S=20 L/kg, for (a) 0.5 h and (b) 2 h reaction time.

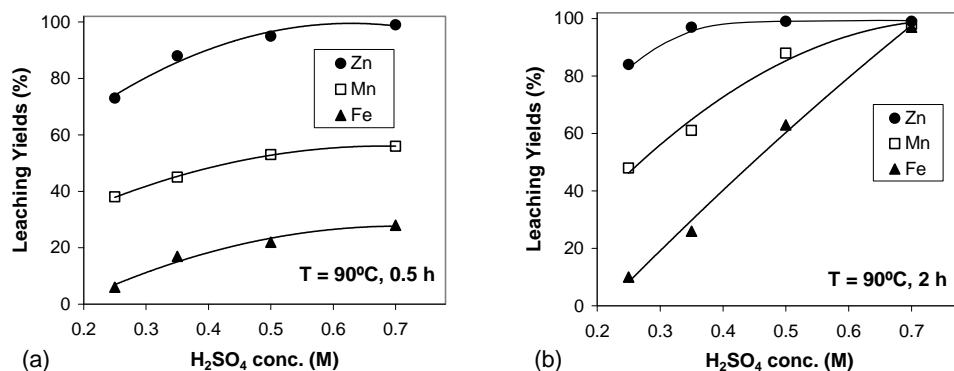


Figure 3. Effect of acid concentration on the metals leaching yields, at 90°C and using a ratio L/S=20 L/kg, for (a) 0.5 h and (b) 2 h reaction time.

The influence of H₂SO₄ concentration was also relevant (Figure 3). Considering the ratio L/S used and the composition of solids, the concentration of 0.5 M corresponds more or less to the stoichiometric quantity of acid for Zn and Mn, supposing these metal species in oxidation states II and III, respectively. For 2 hours of reaction, total zinc recovery can be attained above 0.3 M but the same result for manganese is only achieved with a large acid excess (0.7 M) together with

the dissolution of practically all the iron from the steel scrap. Using 0.5 M H_2SO_4 , the final pH of the leach liquor was about 2.5 which is adequate to proceed with solution purification by precipitation of iron and subsequent zinc/manganese separation by solvent extraction.

The influence of L/S ratio was also tested and it was not found a substantial effect on the leaching yields providing that the same acid availability was maintained. By changing the L/S ratio from 20 to 10 L/kg and simultaneously the acid concentration from 0.5 to 1.0 M, the leaching yields of zinc were close to 100% while manganese recoveries were in the range 83-88%. The solution compositions differ according with the L/S ratio, increasing from about 10 to 20 g/L of Zn and Mn when L/S decreased.

Figure 4 shows the evolution of metals in solution in a one-step sequential leaching-precipitation operation carried out in a blade-stirred reactor. After half hour of leaching, zinc was practically all solubilized and manganese in solution continued to increase until 80% recovery after 3 hours. Concerning iron, a decrease in concentration was found after 1 hour of reaction due to partial precipitation of Fe(III) occurring as the pH increased. The characteristics of the reactor, a stirred vessel with air access, contributed to this behavior, in opposition with the previously reported results using closed flasks. Following the leaching, the addition of a neutralizer like soda or lime and an oxidant like hydrogen peroxide promoted the quantitative removal of iron from the solution until very low levels like less than 10 mg/L Fe.

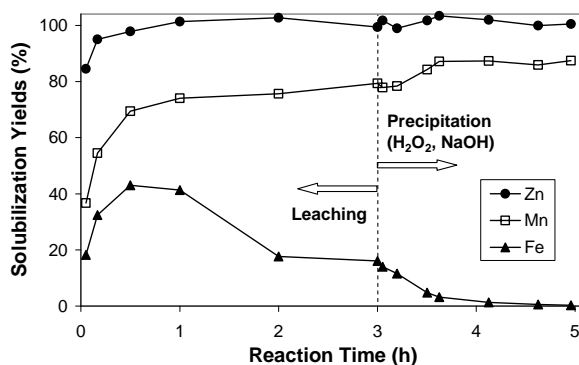


Figure 4. Evolution of metals in solution in leaching and precipitation operations. Conditions: process temperature: 90°C; initial H_2SO_4 concentration: 0.7 M; L/S = 14 L/kg.

Zinc separation by solvent extraction

The separation of zinc from manganese by solvent extraction was developed using 1 M DEHPA as extractant. The influence of pH and phase ratio was initially accessed and it was concluded that in the range of pH 1.8-2.2 it was possible to achieve high zinc loadings in organic phase with low manganese contamination, providing that the phase ratios organic/aqueous (O/A) were kept appropriate. The determination of the extraction and stripping isotherms allowed simulating countercurrent circuits for the separation of metals, like Figure 5 illustrates. In the 3 stages extraction operation, from a feed solution containing 15 g/L Zn and 15.3 g/L Mn, at O/A=0.72, an organic phase with 21 g/L Zn can be obtained, together with a raffinate with 15.6 g/L Mn and only 0.013 g/L Zn. After a purifying scrubbing operation, the organic can be stripped with an acidic solution (150 g/L H_2SO_4), in 2 stages at O/A=3.1, to remove 99% of zinc. The stripping operation was designed to be included in an electrowinning loop, at high zinc concentrations, were this metal is reduced from 120 to 55 g/L Zn.

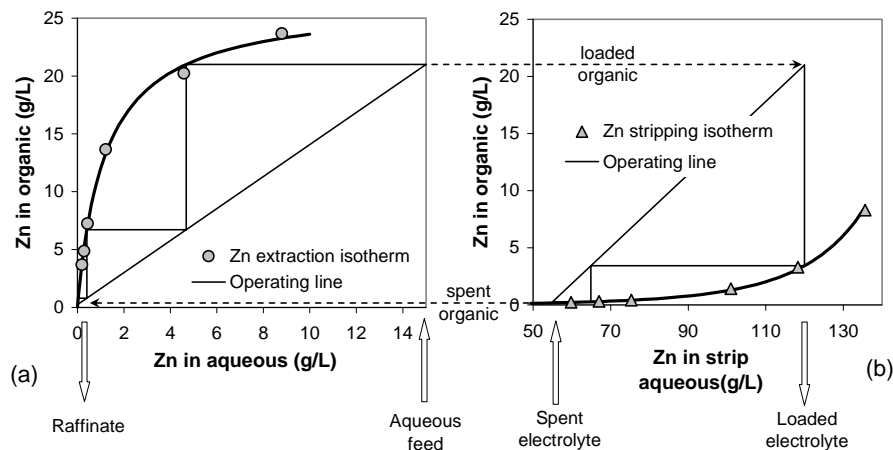


Figure 5. Simulation of countercurrent solvent extraction of zinc with 1M DEHPA including (a) extraction in 3 stages at pH=2, and (b) stripping in 2 stages with 150 g/L H₂SO₄.

Conclusions

The recovery of metals from spent Zn-MnO₂ batteries by hydrometallurgical processing in sulfate media was successfully achieved. The process involves physical processing, leaching with sulfuric acid with minimum acid consumption, iron precipitation and zinc-manganese separation by solvent extraction with DEHPA. Recoveries near 100% for zinc and close to 80% for manganese were attained.

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