

Process for the treatment of alkaline spent batteries

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In recent years there has been a growing interest in processes for the treatment of spent portable batteries, due to problem of environmental impact connected with the presence of significant quantities of heavy metals. As a matter of fact, batteries are considered special waste by current legislation that establishes specific rules for the collection, treatment, recycling and disposal of spent batteries and accumulators.

In this work a process for the treatment of spent alkaline batteries is presented (Toro et al., 2006). The hydrometallurgic process comprises the following stages:

- Pre-treatment
- Acid-reducing leaching using carbohydrate as reducing agent
- Leach-liquor purification
- Separation and recovery of metallic Zn and MnO₂ (by electrowinning)

The aim of this work is the optimization of the operating conditions for the selective recovery of Zn. Leaching tests were performed both at room temperature and at 90°C. Experimental results denoted that at room temperature a quantitative zinc extraction was obtained with selectivity higher than at 90°C. Leach-liquor solution after purification (iron precipitation and cementation) was used in electrowinning process for recovery of zinc which was obtained with 98-99% purity.

1. Introduction

An alkaline battery contains zinc powder as negative electrode (anode), a mixture of MnO₂ and graphite as positive electrode (cathode) and KOH solution as electrolyte. In 2007 members of the European Battery Recycling Association (EBRA) recycled about 31.079 tonnes of portable batteries and accumulators. Compared to 2005, there was an increase of 0,7% (30.865 tonnes recycled in 2006) (EBRA, 2008). In detail, the quantities of batteries recycled by EBRA's members were 26.940 tonnes (~87%) of primary alkaline, and 4.138 tonnes of other type (EBRA, 2008). Concerning the Italian scenario, only batteries and accumulators covered by Directive 91/157/EEC are collected and recycled, while the zinc-carbon and alkaline ones are simply landfilled: in

2007 only 81 tonnes of portable batteries were recycled. Last European Directive 2006/66/EC clearly states that the ultimate disposal of portable, industrial and automotive batteries and accumulators by incineration or landfilling is strictly prohibited.

Member States shall achieve the following minimum collection rates: 25% by 2012 and 45% by 2016. Recycling processes shall achieve the following minimum efficiencies (European Union, 2008):

- recycling of 65% by average weight of lead-acid batteries and accumulators, including recycling of the lead content to the highest degree that is technically feasible while avoiding excessive costs;
- recycling of 75% by average weight of nickel-cadmium batteries and accumulators, including recycling of the cadmium content to the highest degree that is technically feasible while avoiding excessive costs;
- recycling of 50% by average weight of other waste batteries and accumulators.

An alkaline battery contains zinc powder as negative electrode (anode), a mixture of MnO_2 and graphite as positive electrode (cathode) and a highly conductive KOH solution as electrolyte.

In the literature there are different patented processes for manganese and zinc recovery from spent batteries for examples BATENUS (Lindermann, 1996); REVABAT (Serstevens, 2001); RECUPYL (Poinsignon et al., 1997). Pyrometallurgical and hydrometallurgical processes can be used with different energy consumption and environmental impact that generally favour the application of the second ones.

Many authors studied different ways to recover Mn and Zn from spent alkaline batteries (Devi et al., 1997; De Souza et al., 2001; Vatistas et al., 2001; Salgado et al., 2003; De Souza and Tenorio, 2004; Veloso et al., 2005; De Michelis et al., 2007).

In this work a process (Toro et al., 2007) for the treatment of spent alkaline batteries is presented. The hydrometallurgic process comprises the following stages:

- Pre-treatment (grinding and separation of the two fraction one coarse and one fine). The fine fraction undergoes the subsequent treatments.
- Acid-reducing leaching using carbohydrate as reducing agent
- Leach-liquor purification
- Separation and recovery of metallic Zn and MnO_2 (by electrowinning)

2. Materials and methods

2.1 Pre-treatment and characterization

Alkaline portable spent batteries of different size were crushed by a hammer mill recover the internal paste. All fractions obtained were separated by a sieve with 2 mm dimension. The fine fraction, composed by anodic and cathodic materials, was characterized by X-ray fluorescence (XRF) and X-ray diffraction (XRD). A quantitative analysis was also carried out by inductively coupled plasma (ICP). Quantitative analysis was performed dissolved the powder in aqua regia ($\text{HCl}:\text{HNO}_3 = 3:1$) in a digestion bomb.

2.2 Leaching tests

Leaching tests were carried out at room temperature and at 90°C under magnetic agitation, with sulphuric acid varying the stoichiometric ratio (g of solid/ g of acid).

2.3 Leach-liquor purification

Leach liquor purification was performed by iron precipitation and cementation with zinc power. Iron was precipitated as ferric hydroxide by using 2M solution of KOH. This test was carried out at room temperature adding KOH under stirring until pH 5 was reached. After half hour, the precipitate was filtered by vacuum pump and the solution was analyzed. Cementation was carried out by adding 400 mgL⁻¹ of Cu, Ni and Cd as sulphates in leach liquor coming from the iron precipitation stage (Ferella et al., 2008).

2.4 Electrowinning

Electrochemical cell for zinc recovery was formed as follows: glass cell, Zn plate cathode, Pt anode, and calomelan work reference. Operative conditions were: fixed potential -1.7V, temperature 45-50°C, pH 5, magnetic stirring; duration 2 h and 30 min. Two different starting solutions were used for electrowinning tests: the first solution contained Zn 2 gL⁻¹, Mn 0.8 gL⁻¹, K 5 gL⁻¹, as sulphate; the second solution contained the same concentrations of Zn and K with 3.8 gL⁻¹ of Mn. Zinc and manganese concentrations during electrowinning process were measured by an Inductively Coupled Plasma spectrophotometer.

3. Results

3.1 Pre-treatment and characterization

X-ray diffraction analyses (experimental data reported elsewhere, De Michelis et al., 2007) showed that the most probable phases are ZnO, KO₂, Mn₂O₃, Ca₄Mn₂O₇ and graphite, whereas the content of the main metals is as follows: 440 mg/g Mn, 253 mg/g Zn, 2.7 mg/g K, 3.8 mg/g Fe (table 1). The powder obtained after sieving was washed by distilled water for the removal of soluble compounds, such as potassium. Once dried, it showed a weight loss of around 10%.

Table 1 Total metal concentration in spent battery paste

Metal	Conc. (mg/g)
Fe	3.8±0.2
K	2.7±0.1
Mn	440±70
Zn	253±7
Al	0.091±0.01
As	0.50±0.02
Cd	0.0010±0.0001
Co	0.0090±0.0001
Cr	0.04±0.01
Cu	0.20±0.05
Li	0.007±0.01
Ni	0.11±0.01
Pb	0.047±0.004

3.2 Leaching tests

In figure 1 experimental results of leaching tests at 90°C for different stoichiometric ratios were reported. Selectivity for zinc was calculated as %Zn extracted / %Mn extracted.

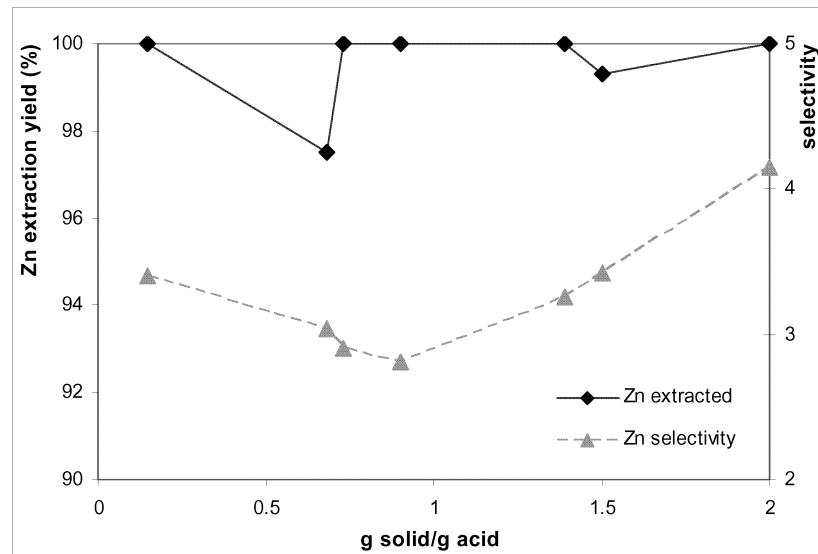


Figure 1. Zinc extraction yield (%) and selectivity at 90°C.

Zinc extraction was quantitative for all the investigated range of stoichiometric ratios while selectivity presented a non monotonic behavior. In figure 2 experimental results of leaching test at room temperature were reported.

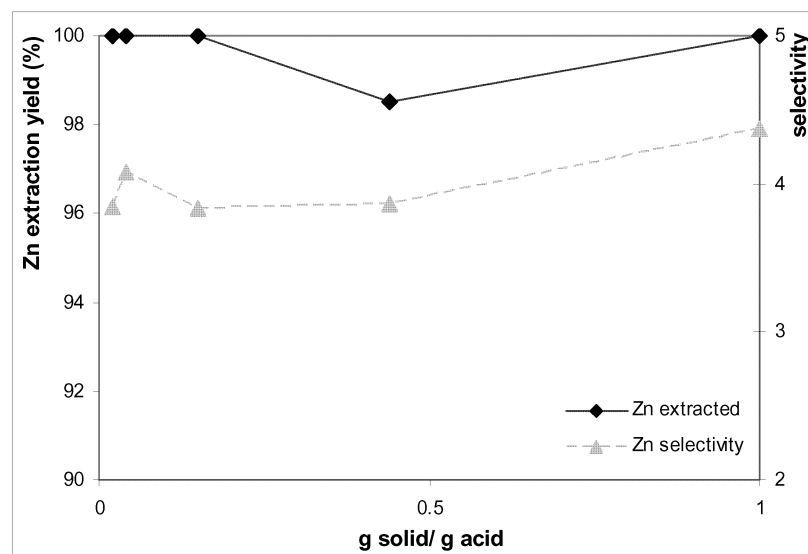


Figure 2. Zinc extraction yield (%) and selectivity at room temperature.

Under the same condition selectivity for zinc increase at room temperature with respect to 90°C.

3.3 Leach-liquor purification

Iron was quantitatively removed by precipitation with yields higher than 99%. In the same way the purification of the solution by cementation showed a removal higher than 99% for each metal (Ferella 2008).

3.4 Electrowinning

In the first type of experiment, recovery was 83% for zinc (purity 99.5%) and 1% for Mn with an electric energy requirement of 2.5 kWh kg⁻¹ and an efficiency of 35% (Figure 3).

In the second type of experiment with higher Mn concentration, recovered zinc was 64% (purity 97.6%) and Mn 7% with an energy efficiency of 46% and an electric energy requirement of 2.2 kWh kg⁻¹ (figure 4).

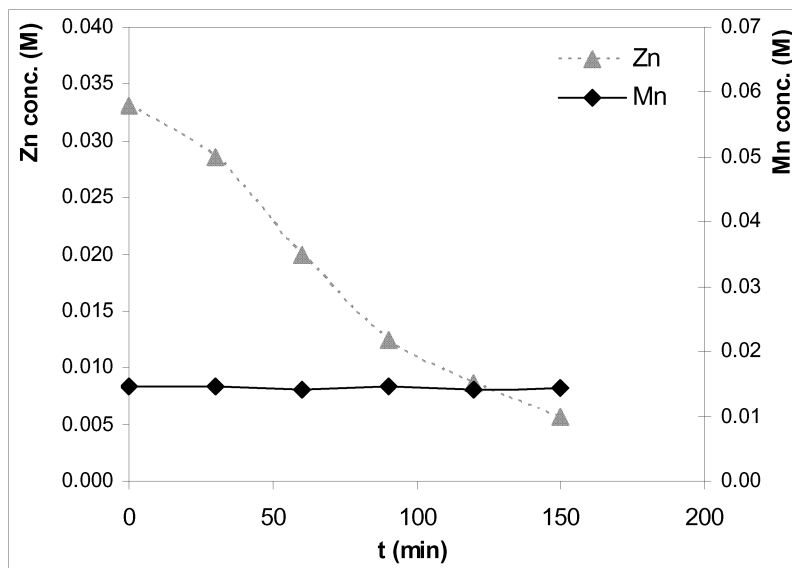


Figure 3. Zinc and manganese concentrations during electrowinning process.

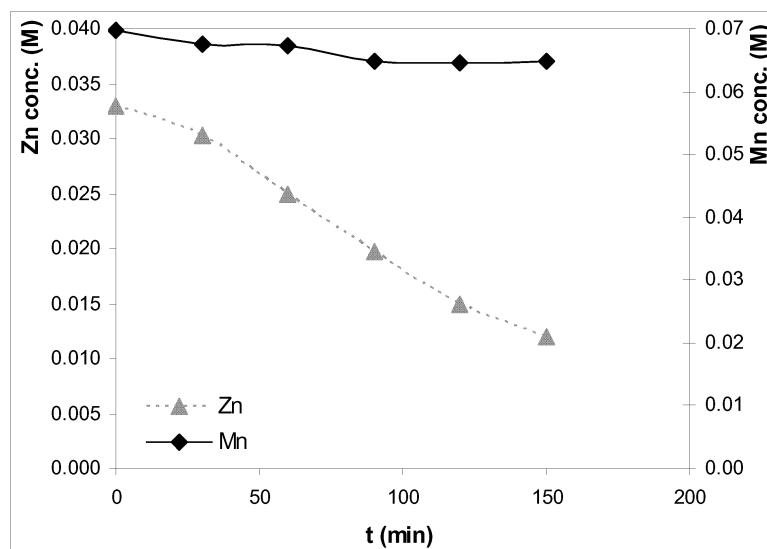


Figure 4. Zinc and manganese concentrations during electrowinning process.

Conclusions

Leaching at room temperature gave quantitative zinc extraction with selectivity higher than at 90°C. Leach-liquor solution after purification (iron precipitation and cementation) was used in electrowinning process for recovery of zinc which was obtained with 98-99% purity.

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