

# Recovery of zinc and manganese from spent batteries by different leaching systems

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In this paper different leaching systems for the recovery of zinc and manganese from spent alkaline and zinc-carbon batteries have been studied. The experimental tests for the recovery of zinc and manganese present in the powder have been carried out by two acidic-reductive leachings: (1) sulphuric acid/oxalic acid and (2) sulphuric acid/hydrogen peroxide. For each system the analysis of variance (ANOVA) has been performed to evaluate the behaviour of the manganese and zinc extraction yields. Afterwards a hydrometallurgical process has been proposed for the recycling of alkaline and zinc-carbon batteries.

## 1. Introduction

Disposal of spent batteries represents an increasing environmental problem in terms of heavy metals content when these devices are disposed off in inadequate way. This environmental problem is closely related to the battery market evolution: in 2003 the total portable battery weight in the East and West Europe was about 164,000 tons, of which 50,197 and 99,138 tons were zinc-carbon and alkaline batteries respectively (30.5% and 60.3% of the total annual sales).

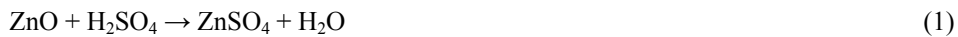
Several processes for the recycling of batteries were proposed, mainly in Europe, and the pyrometallurgical processes are the most used (Espinosa et al., 2004a and Espinosa et al., 2004b). As for secondary raw material exploitation, in the literature there are different patented processes for manganese and zinc recovery from exhausted cells. Pyrometallurgical and hydrometallurgical processes can be used with different energy consumption and environmental impact that generally favour the application of the second ones. Hydrometallurgical processes are generally characterised by different steps of pretreatment followed by leaching and metal separation. The main differences among the patents lay just in the methods used to recover metals from leach liquor (Salgado et al., 2003).

This research group also developed a patented process for the recycling of all cell components and the production of new cells (named as "green cells" for the zero-waste approach adopted) (Toro et al. 2004).

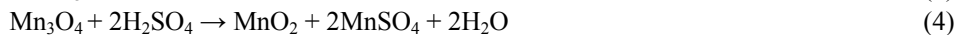
## 2. Aim of the work

The aim of this paper is the optimization of the leaching section with regard to a hydrometallurgical process for the recovery of zinc and manganese compounds from zinc-carbon and alkaline spent batteries. This process doesn't take into consideration other kinds of batteries.

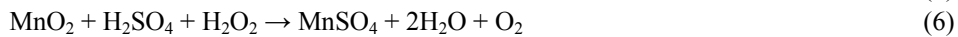
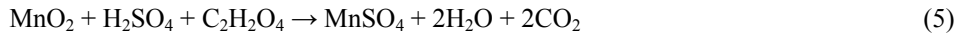
Two different acidic-reductive leaching systems have been investigated: (1) sulphuric acid – oxalic acid and (2) sulphuric acid – hydrogen peroxide. Tests have been designed according to a full factorial design (4 factors 2 levels for the first system, 3 factors 2 levels for the second system). Zinc and manganese oxides can be quantitatively dissolved by sulphuric acid, according to Eq. (1) and (2).



On the other hand, dissolution of manganese oxides such as  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$  is partial because  $\text{MnO}_2$  produced is insoluble, as we can see in Eq.(3) and (4).



Therefore it must be used a reducing agent to leach all manganese contained in the powder. The reduction between manganese dioxide and oxalic acid or hydrogen peroxide in acidic solution can be given as follows:



Because of the technical and economical feasibility, one of these leaching systems has been chosen for simultaneous dissolution of zinc and manganese oxides in a pilot-scale plant process simulated by using a commercial software.

## 3. Materials and methods

### 3.1 Battery pre-treatments and Powder characterization

Spent alkaline and zinc-carbon batteries were manually dismantled, and mixture of the cathodic (manganese oxides and graphite) and the anodic (zinc oxides and electrolytic solution) materials in form of powder was extracted. The powder, which was about 57% of the batteries total weight, was dried ground, sieved and washed with distilled water at 60°C (solid to liquid ratio 1:10) for 1 h. Finally the pH value of solution was 9.7, so the majority of potassium hydroxide was practically dissolved in water. The purpose of this washing was the removal of potassium (which interfere in the electrowinning) and the reduction the consumption of sulphuric acid in the leaching step.

Washed powder was dried for 24 h at 100°C, recovered and weighted: the weight loss was 5.7%. All the experimental tests showed in this paper were carried out with the washed powder.

Original and washed powders were analyzed by X-ray fluorescence (XRF) (Spectro Xepos). XRF data of the original powder were 33.59% Mn, 15.46% Zn, 0.50% Fe, 0.19% Cr, 0.36% Al, 3.26% K, 3.38% Cl, 0.27% Ti and 0.49% Si, while composition of the washed powder was 35.59% Mn, 18.58% Zn, 0.49% Fe, 0.20% Cr, 0.19% Al, 0.56% K, 0.13% Cl, 0.26% Ti and 0.42% Si.

Values of the washed powder show expressive amount of Zn and Mn, which represents about 54% of the total mass of the sample, according to the literature data (Veloso et al., 2005). Cl and K are due to the electrolyte of zinc-carbon and alkaline batteries, i.e. ammonium chloride and potassium hydroxide. Other trace elements are present, while graphite is not detectable by XRF. Metals are contained in the alloy of which outer casing is composed but in the anode rod structure too. It should be noted the potassium and chlorine reduction of about 83% and 96%, respectively: because of their solubility these elements are leached by water.

After all a quantitative analysis was carried out by atomic absorption spectrometry (AAS) (spectrometer SpectrAA 200, Varian) to evaluate the accurate percentages of manganese, zinc and iron. Iron represents the major impurity when Zn or MnO<sub>2</sub> are deposited in the electrowinning step, so it must be precipitate by an alkaline reagent. Results of the quantitative analyses showed that washed powder was composed by 40.8% Mn, 25.2% Zn and 0.45% Fe.

### 3.2 Leaching tests

In the present work, 2<sup>4</sup> factorial design was chosen for conducting the leaching tests when the investigated variables were quantity of pulp, oxalic acid concentration, sulphuric acid concentration and temperature. The levels of variables are given in Table 1.

Table 1  
2<sup>4</sup> factorial design for Zn and Mn leaching by oxalic acid in H<sub>2</sub>SO<sub>4</sub> solution.

Factor		Low level	Base level	High level
A	Pulp concentration	10%	15%	20%
B	Oxalic acid concentration <sup>(1)</sup>	-50%	0%	+50%
C	Sulphuric acid concentration <sup>(2)</sup>	0%	+25%	+50%
D	Temperature	40°C	60°C	80°C

<sup>(1)</sup> Referred to the stoichiometric quantity of manganese (without difference between soluble and insoluble form).

<sup>(2)</sup> Referred to the sum of stoichiometric quantities of zinc and manganese.

The leaching tests with the second acidic-reductive leaching system were performed on the basis of a 2<sup>3</sup> factorial design analogue to that of the first leaching system except for factor D which was fixed at room temperature. In these tests temperature was not investigated at larger values for the stability problem of the hydrogen peroxide. The levels of variables are given in Table 2. Leaching tests were performed in a 250 ml closed flasks immersed in a thermostatically controlled water bath equipped with a mechanical stirrer (Dubnoff Bath, ISCO). For each test the solution mixture was freshly prepared and washed battery powder in 100 ml of H<sub>2</sub>SO<sub>4</sub> solution, according to the experimental plan. During each test 1 ml of leach liquor was withdrawn after 1 h, 3 h and 5 h to measure the concentration of Mn, Zn and Fe by AAS. Each sample was

diluted 1:10 by an acidic solution of nitric acid (pH~2) to avoid precipitation of metals and stored at 5°C.

Table 2

2<sup>3</sup> factorial design for Zn and Mn leaching by hydrogen peroxide in H<sub>2</sub>SO<sub>4</sub> solution: temperature = 25°C.

Factor		Low level	Base level	High level
A	Pulp concentration	10%	15%	20%
B	Hydrogen peroxide concentration <sup>(1)</sup>	-50%	0%	+50%
C	Sulphuric acid concentration <sup>(2)</sup>	0%	+25%	+50%

<sup>(1)</sup> Referred to the stoichiometric quantity of manganese (without difference between soluble and insoluble form).

<sup>(2)</sup> Referred to the sum of stoichiometric quantities of zinc and manganese.

After 5 h, when reactions were stopped, pH was measured and the mixtures were filtered, washed and put in the oven at 100°C. After 24 h solid residues were recovered and weighted to evaluate the weight loss.

## 4. Results and discussion

### 4.1 Leaching tests: factorial experiments with sulphuric acid – oxalic acid

The results of the factorial design of ANOVA analysis for Mn and Zn extraction are reported in Table 3. For the Mn extraction yield the significant combinations are three: oxalic acid concentration, that has a strong positive effect on dissolution of insoluble Mn, sulphuric acid concentration (obviously positive) and the combination of oxalic acid concentration with temperature has a negative effect on the extraction yield (precipitation of dissolved Mn as oxalate). When the oxalic acid concentration was +50% there is always a high Mn concentration but weight loss and zinc concentration are very low. For the Zn extraction yield the most significant combinations are three: oxalic acid concentration, which has a strong negative effect (precipitation of zinc oxalate), combination of temperature with oxalic acid concentration and finally the combination of acids with pulp percentage.

Table 3: Results of ANOVA analysis for Mn and Zn extraction after 5 hours.

Treatment	Mn extraction yield (%)	Effect (%)	Significance (%)	Zn extraction yield (%)	Effect (%)	Significance (%)
(1)	61.3			86.6		
a	60.1	0.0	2.6	96.1	-0.1	3.9
b	76.1	11.0	100.0	6.1	-89.9	100.0
ab	80.0	-1.3	65.6	4.3	-0.9	49.9
c	61.5	3.0	94.2	98.2	0.9	48.3
ac	62.8	-0.3	15.3	87.1	-2.9	92.6
bc	82.4	1.7	76.8	6.7	0.7	36.4
abc	81.4	-1.8	78.6	6.2	3.3	95.3
d	69.1	1.1	58.1	95.4	1.6	73.8
ad	69.8	-0.8	44.8	100.0	0.9	46.7
bd	72.1	-7.5	99.9	3.4	-3.7	96.9
abd	69.6	-2.0	83.0	2.2	-0.8	43.3
cd	68.5	0.3	19.2	96.7	-0.3	19.8
acd	72.7	0.3	18.9	97.2	2.0	81.2
bcd	79.2	0.5	28.8	5.1	0.7	37.4
abcd	73.4	0.1	4.5	4.3	-2.2	85.2

Temperature and pulp percentage seem to be not so important for the extraction yield of both metals, but probably this is due to the effect of the high concentration of oxalic acid that covers the effect of these factors.

#### 4.2 Leaching tests: factorial experiments with sulphuric acid – hydrogen peroxide

The results of the factorial design of ANOVA analysis for Mn and Zn extraction are reported in Table 4.

As expected Mn leaching is lower when the reducing agent is below the stoichiometric value.

Hydrogen peroxide is a strongly significant factor either for Mn and Zn extraction yield, but it acts in opposite direction: in fact it is positive for Mn and negative for Zn. Zn yield is also negatively affected by the pulp density. Another significant factor for Mn yield is the concentration of sulphuric acid (positive effect).

Table 4: Results of ANOVA analysis for Mn and Zn extraction after 5 hours.

Treatment	Mn extraction yield (%)	Effect (%)	Significance (%)	Zn extraction yield (%)	Effect (%)	Significance (%)
(1)	64.0			59.1		
<i>a</i>	71.8	3.9	91.2	80.2	-5.3	99.9
<i>b</i>	75.7	14.5	99.2	54.0	-12.7	100.0
<i>ab</i>	86.4	-2.0	74.8	73.2	2.2	99.3
<i>c</i>	72.8	8.3	97.7	83.7	-2.0	99.1
<i>ac</i>	77.0	-5.3	94.7	87.3	0.5	86.7
<i>bc</i>	94.1	1.3	60.1	84.5	0.8	95.5
<i>abc</i>	87.4	-3.4	88.6	74.8	0.5	89.7

#### 4.3 Recycling process

A hydrometallurgical process is proposed for the recycling of zinc-carbon and alkaline batteries. This process comprises the steps schematically shown in Fig. 1: a preliminary treatment for the dismantling of batteries, followed by an acidic-reductive leaching. The solution obtained is then purified and, finally, zinc and manganese dioxide are recovered by electrolysis.

Zinc-carbon and alkaline batteries are manually separated from other types of batteries. In the dismantling section batteries are crushed by a hammer mill and the black powder, consisting of graphite and metallic oxides, is separated by screening from the coarse fraction (iron scraps, plastic films and paper pieces). Magnetic scraps are separated by a magnetic separation, and then non-ferrous materials are recovered by using an electrostatic separator. Remaining plastic films and papers are landfilled or incinerated. Metallic scraps can be recycled by a pyrometallurgical process for steel and ferro-alloys production. The battery powder is sent to a water washing for the removal of potassium hydroxide; resulting solution can be evaporated to obtain pure KOH or it can be neutralized by sulphuric acid to give potassium sulphate. Total dissolution of zinc and manganese oxides can be achieved by an acidic-reductive leaching by using sulphuric acid and hydrogen peroxide as reductant.

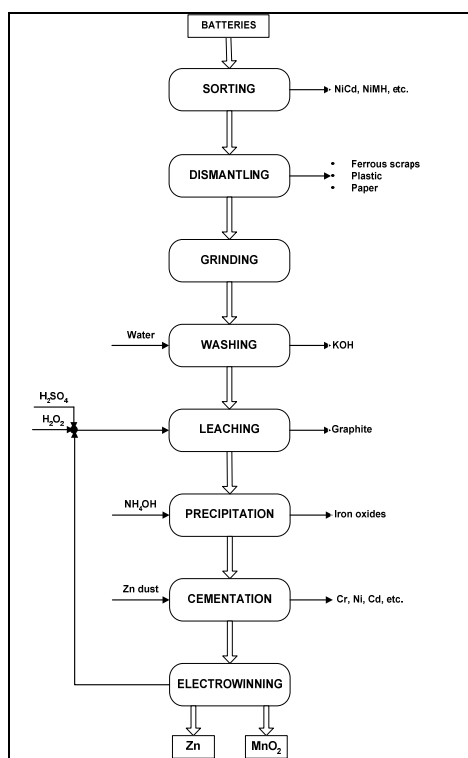


Fig. 1. Flow-sheet for the recycling of alkaline and zinc-carbon batteries.

In this section a manganese and zinc sulphate solution is obtained, together with other dissolved metals; for this reason solution must be purified before the electrowinning section.

The aqueous solution is sent to a precipitation step where iron is precipitated by ammonium hydroxide (pH = 4) and then some metallic ions are removed by zinc dust (reducing agent) during the cementation step. Purified Zn-Mn solution is then ready for the electrowinning, in which metallic zinc is plated on the cathode and manganese dioxide is deposited on the anode. The exhaust solution resulting from electrolysis is recycled back to the leaching reactor.

The research activity is in progress in the ambit of a MIUR (Italian Ministry of Education, University and Research) project (PRIN 2005), so these results are not conclusive.

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