

Hydrometallurgical treatment of exhausted alkaline batteries

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Abstract

On a resource management level, batteries could be considered as a metal source of the secondary origin, ore of secondary raw materials, because of their high content in useful metals, such as zinc and manganese. Moreover, disposal of spent batteries constituted a serious environmental problem in terms of the heavy metals content, when these devices are disposed off in an inadequate way.

Main processes applied for the treatment of the batteries are based on pyrometallurgy, involving the high energetic consumption and pollution, and on hydrometallurgy, which is less expensive and lower energy demanding.

The experiments in the presented work were based on the technology well know in mineral processing and metal dissolution by the hydrometallurgical processes for Mn-Zn recovery from wastes, constituted by spent alkaline batteries.

The results have demonstrated the technical feasibility of the application of the mentioned technologies; in fact, high recovery of manganese and zinc dissolved in the solution were achieved (over 90 %).

Key words: hydrometallurgical processes, wastes, alkaline batteries, metals recover, Zn, Mn

Introduction

Disposal of spent batteries represents an increasing environmental problem in terms of the heavy metals content when these devices are disposed off in inadequate way (Vegliò et al., 2003).

On a resource management level, batteries could be considered as a metal source of the secondary origin. Valuable metals such as zinc and manganese can be recovered. The use of recycled metals in battery production instead of virgin metals has the positive environmental impacts through the reduced energy use and reduced pollution related to the mining of the virgin sources (Vatistas et al., 2001).

The topic is reflected in the current European legislation by the Council Directive 91/157/EEC on batteries and accumulators containing dangerous substances (Ubaldini et al., 2009). Many batteries and accumulators of the alkaline and zinc-carbon types are still deposited on landfills or incinerated, instead of being collected and recycled (Beolchini et al., 2009).

The purpose of the proposal of 21 November 2003 for a Directive of the European Parliament is to reduce the quantity of spent batteries and accumulators and to set

European targets for collection and recycling (Ubaldini et al., 2008a).

The proposal applies to all batteries and accumulators, unlike the current legislation (Directive 91/157/EEC). The ultimate disposal of industrial and automotive batteries and accumulators by incineration or landfilling is prohibited. Once this directive is in force, Member States will have more than five years for achieving a minimum average collection target equivalent to 160 grams per inhabitant per year for spent portable batteries and accumulators (Ubaldini et al., 2008b).

Several processes for the recycling of batteries were proposed, mainly in Europe, and the pyrometallurgical processes are the most used (Ubaldini et al., 2000). As for secondary raw material exploitation, in the literature different processes for manganese and zinc recovery from the exhausted cells have been reported (Vatistas et al., 2001; De Michelis et al., 2007; Ubaldini et al., 2008a; Ubaldini et al., 2008b; Ubaldini et al., 2009).

In this work, a complete flow-sheet for treatment of spent batteries has been outlined, starting from disassembling and physical separation of the component of the spent batteries. The attention of the investigation has been focused to the subsequent chemical dissolution

of the metals, purification and recovery, carried out by the hydrometallurgical processes.

Materials and methods

Characterization and physical process

The disassembly of the batteries was done with a cutting mill model Retsch RM 2000. The size fraction less than 2.5 mm was sent to the part of the process devoted to the recovery of components other than zinc and manganese, while the size below is directly air separated. For the separation of the magnetic materials, drum magnetic separator model Sala was used at a field intensity of about 0.2 T. The separation of the different specific gravity materials was carried out in a dry vertical elutriator, while Eriez eddy current magnetic separator was employed for separation of non-ferrous metals. The size fraction +2.5 mm was sent to the micronization step. In this phase a hammer mill was used.

The alkaline Zn/MnO₂ consists of Zn anode, MnO₂ cathode, KOH electrolyte solution and separators. The

cathode includes manganese dioxide, carbon (graphite) particles that enhance the conductivity of the cathode, and a binder. The anode can be formed of a gel including zinc particles. The separator (fibrous materials) is disposed between the cathode and the anode. Other constituents of the battery are an external plastic cover, steel needle and cap, a plastic disc and paper separators.

Fig. 1 shows the characteristics of spent alkaline batteries utilized and the powder composition, analysed at the end of the physical process.

Basic sample for experimental texts has been analysed by the X-ray diffraction (XRD), utilizing an automatic diffractometer Bruker mod. D8 Advance. The results show that the following main crystalline mineralogical species are present, in order of decreasing abundance: zincite (ZnO), quartz (SiO₂), manganese oxide (Mn₂O₃), calcium manganese oxide (Ca₄Mn₂O₇), sylvite (KCl) and potassium oxide (KO₂).

Quantitative chemical analysis was conducted by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), using a Perkin-Elmer apparatus mod. Elan 6000. Results have shown that powder was composed mainly by 45 % MnO₂, 15 % Zn, 5.9 % K, 0.61 % Ni and 0.7 % Fe.

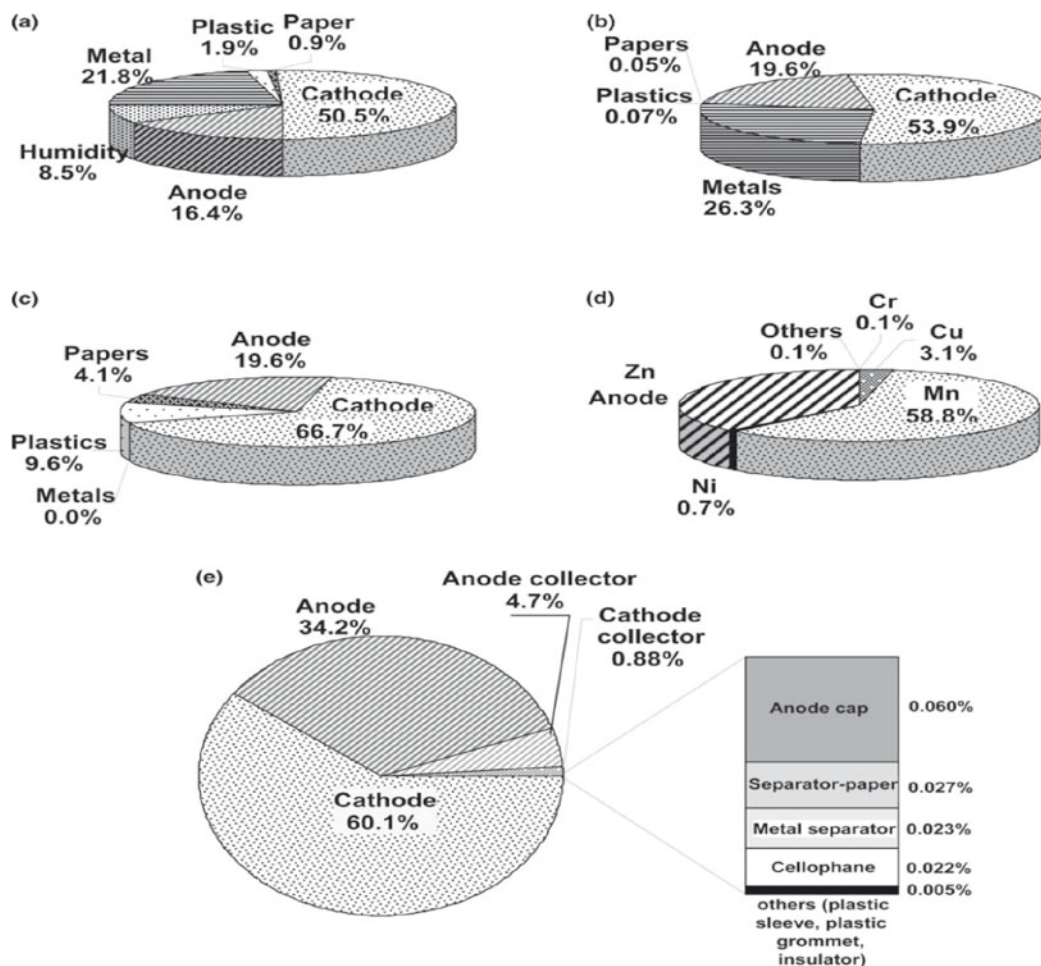


Fig. 1. Characteristics of spent alkaline batteries. (a) components and materials, (b) contribution of the components in the composition of the ash, (c) contribution of the components to lower heating value, (d) metal content. Other inclusions: As, Cd, Co, Hg, Pb, Sb, Si, Ti, V. (e) Heavy metals in the components (Ubal dini et al., 2009).

Hydrometallurgical process

Mixture of the cathode (manganese oxides) and the anode (zinc oxides and electrolytic solution) materials in form of the powder was extracted and treated, while the potassium contained was dissolved (Ubaldini et al., 2008a; Ubaldini et al., 2008b).

All the experimental tests shown in this paper were carried out with the washed powder. Leaching tests were conducted to evaluate the leaching behaviour of the metals under the different conditions of solid/liquid ratio, temperature, sulphuric acid concentration and oxalic acid concentration, according to previous studies (De Michelis et al., 2007), conducted by 2⁴ Factorial design. For each test the solution mixture was freshly prepared and washed battery powder in 100 ml of H₂SO₄ solution, by dissolving the required amount of analytical grade oxalic acid (OA) and adding washed battery powder in 100 ml of H₂SO₄ solution.

At the end of each test, pH was measured and the mixtures were filtered to separate undissolved material from solution, washed and put in the oven at 100 °C. After 24 h solid residues were recovered and weighed to evaluate the weight loss.

A leaching solution containing 30 g · dm⁻³ Mn and of 70 g · dm⁻³ Zn, after precipitation and cementation phase (data not reported here) has been utilized for electrowinning tests (Ubaldini et al., 2008a, b; 2009).

A cylindrical glass laboratory cell of 200 cm³ in volume has been used. The cell was equipped by a thermostatic water jacket connected with the thermostatic bath, magnetic system for stirring and three electrodes: as cathode, a platinum mesh; as an anode, a spiral of platinum wire; as a reference, a saturated calomel electrode (SCE).

During MnO₂ deposition, the working electrode (W) was the anode and the cathode was the counter electrode (C). During Zn deposition, the W was the cathode, while the anode was the C. In both processes, the reference electrode was constituted by SCE, to permit an electrolytic process at controlled potential.

The cell was connected to a potentiostat-galvanostat (AMEL mod. 555B), equipped with an instrument system for automatic control of the process parameters at the constant potential conditions. By analysing the residual solution with ICP-MS, the purity of the MnO₂ and Zn deposition was monitored, while the deposit was analysed by XRD.

Electrowinning experiments were carried out in potentiostatic operations at constant anodic potential and stirring conditions.

Results

Results of the leaching experiments, elaborated by the analysis of the variance (ANOVA), demonstrate the high efficiency of the studied process. In any case, 70 % of manganese and 100 % of zinc were extracted after 5 h, at 80 °C with a 20 % of pulp density, 1.8 M sulphuric acid concentration and 59.4 g/L of OA.

Tab. 1
Main experimental levels of the parameters obtained for MnO₂ recovery

Parameters	Levels
Cathode Vs. SCE (V)	1.5 – 2.0
Cell voltage (V)	-2.5/-3.3
Current intensity (mA)	1 000 – 1 800
pHi	0.5 – 0.6
Bath temperature (°C)	90 – 95
Electrolysis time (h)	6 – 8
Stirring conditions (rpm)	200 – 250

Tab. 2
Main experimental levels of the parameters obtained for Zn recovery

Parameters	Levels
Cathode Vs. SCE (V)	-1.40/-1.5
Cell voltage (V)	3.5 – 3.9
Cell voltage (V)	1 300 – 1 600
pHi	2 – 3
Bath temperature (°C)	30 – 40
Electrolysis time (h)	6 – 8
Stirring conditions (rpm)	200 – 250

Tab. 3
Main results achieved by the hydrometallurgical process (leaching-electrowinning tests)

Species	Leaching y (%)	Electrowinning y (%)	η (%)	E (kWh/kg)
MnO ₂	95.05	94.35	43.00	4.63
Zn	98.10	95.50	67.43	5.59

y – extraction yield (leaching) and electrodeposition yield (electrowinning)

η – faradic current yield

E – energetic consumption

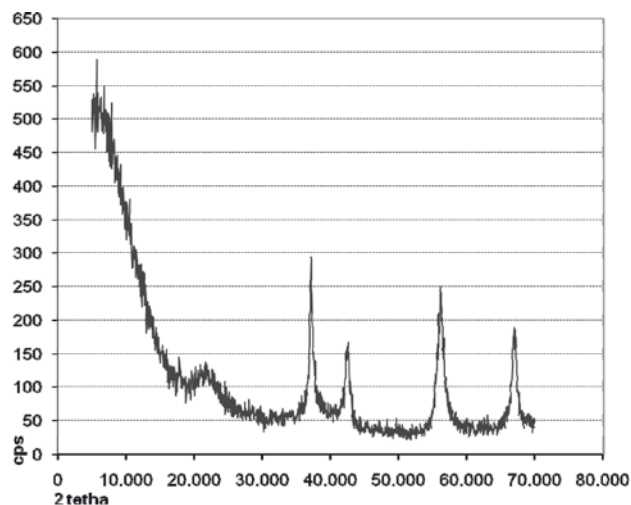


Fig. 2. The main identified peaks of MnO₂ were as follows: 294, 167, 250 and 190 cps.

At the end of the leaching process, a manganese and zinc sulphate solution has been obtained ($30 \text{ g} \cdot \text{dm}^{-3} \text{ Mn}$ and of $70 \text{ g} \cdot \text{dm}^{-3} \text{ Zn}$), together with the other dissolved metals (Fe, Si, Cr, Al and other trace elements).

Tabs. 1 and 2 show the best experimental level of the parameters obtained during Mn and Zn electrolysis.

Main results attained by the hydrometallurgical process (leaching-electrowinning) have been reported in Tab. 3.

Such as demonstrated by the X-Ray Diffraction Spectrum reported in Fig. 2, MnO_2 and Zn deposit at the high degrees of purity was achieved ($> 92 \%$).

Discussion

The removal of potassium permits the elimination of the interference during electrowinning and the reduction of consumption of sulphuric acid in the leaching step.

The experimental results of leaching stage showed that the maximum extraction yields of zinc and manganese cannot be reached simultaneously: in fact, the high OA concentration required to dissolve manganese oxides causes the precipitation of zinc oxalate.

If the manganese reduction is carried out after the zinc leaching/electrowinning, manganese recovery was higher (increasing from 70 to about 95 % MnO_2). In this case, after the Zn-electrodeposition, finalized to the Zn recovery, the solution can be recirculated to the leaching stage to added OA for Mn reduction.

Processing of the experimental data by ANOVA indicates that for the Mn extraction yield, the most significant combinations are three: oxalic acid concentration, that has a strong positive effect on dissolution of insoluble Mn, sulphuric acid concentration (positive) and the combination of oxalic acid concentration with the temperature that has a negative effect on the extraction yield (precipitation of dissolved Mn as oxalate).

Also 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.

Purification before electrowinning has been carried out by the precipitation-cementation, with the aim to eliminate other dissolved metals. Iron represents the major impurity when Zn and MnO_2 are deposited in the electrowinning step, so it has been precipitated by an alkaline reagent.

Conclusions

Results have demonstrated the technical feasibility of the application of hydrometallurgical technologies for Zn and Mn recovery from exhausted batteries.

A quantitative recovery of manganese (about 90 % MnO_2) and zinc (about 94 % Zn) has been achieved at the end of the complete leaching-electrowinning circuit.

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