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## Waste Management

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## Study concerning the recovery of zinc and manganese from spent batteries by hydrometallurgical processes

Traian Buzatu<sup>a</sup>, Gabriela Popescu<sup>a,\*</sup>, Ionela Birloaga<sup>a</sup>, Simona Săceanu<sup>b</sup>

<sup>a</sup> Department of Engineering and Management of Metallic Materials, Materials Science & Engineering Faculty, University "Politehnica" of Bucharest, Bucharest 060032, Romania

<sup>b</sup> The Romanian Ministry of Environment and Forests, Regional Environment Protection Association, Bucharest 060841, Romania

## ARTICLE INFO

## Article history:

Received 5 June 2012

Accepted 16 October 2012

Available online xxxx

## Keywords:

Zinc

Manganese

Alkaline leaching

Acid leaching

Extraction yield

## ABSTRACT

Used batteries contain numerous metals in high concentrations and if not disposed of with proper care, they can negatively affect our environment. These metals represent 83% of all spent batteries and therefore it is important to recover metals such as Zn and Mn, and reuse them for the production of new batteries. The recovery of Zn and Mn from used batteries, in particular from Zn–C and alkaline ones has been researched using hydrometallurgical methods. After comminution and classification of elemental components, the electrode paste resulting from these processes was treated by chemical leaching. Prior to the leaching process the electrode paste has been subjected to two washing steps, in order to remove the potassium, which is an inconvenient element in this type of processes. To simultaneously extract Zn and Mn from this paste, the leaching method in alkaline medium (NaOH solution) and acid medium (sulphuric acid solution) was used. Also, to determine the efficiency of extraction of Zn and Mn from used batteries, the following variables were studied: reagents concentration, S/L ratio, temperature, time. The best results for extraction yield of Zn and Mn were obtained under acid leaching conditions (2 M H<sub>2</sub>SO<sub>4</sub>, 1 h, 80 °C).

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### 1. Introduction

Spent batteries represent an increasing environmental problem due to the high content of heavy metals. Unlike large batteries used for vehicles, small, portable batteries are very diverse in terms of chemical composition and represent 80–90% of all portable batteries collected (Bernardes et al., 2004; Nogueira et al., 2012). The difference between various types of used battery is represented by the used materials such as electrolytes and electrodes (Bernardes et al., 2004). These batteries can be sorted by size, shape and chemical composition so that we can determine which metals can be recovered from each category.

The usage of recycled metals in batteries production instead of primary metals has a positive impact on the environment. Not only that lot of energy is saved, but pollution is also reduced as the chemical treatment of primary metals is not needed. Because portable batteries (alkaline MnO<sub>2</sub> and saline Zn–C) contain the same type of metals Mn and Zn respectively, and in high concentrations, Mn and Zn can be extracted together or separately from them. These nonferrous metals can be recovered and reused instead of being incinerated in municipal waste incinerators or stored on

landfills. In order to be processed by hydrometallurgical processes, portable batteries with Zn and Mn content require a pre-treatment before further chemical processing (Velooso et al., 2005). This pre-treatment consists in a physical separation process of spent batteries that involves: cutting–crushing, magnetic separation, dimensional separation (screening), ECS separation (using eddy currents) and powder fraction milling.

After the cutting–crushing process, the resulted material varies in terms of shape, and it is non-homogenous because an automatic crushing device is used. Therefore, this material will include all components that are used to produce the batteries. For the separation of components we could use pyro- or hydrometallurgical processes. The recycling processes that are implemented on industrial scale are generally based on pyro-metallurgical processes and on heat treatments. In terms of hydrometallurgical processes, in literature, there are various patents for the recovery of Mn and Zn from spent portable batteries, among these being: BATENUS, ZINCX, RECUPYL, REVABAT, BATMIX procedures and so on (Bernardes et al., 2004; DeMichelis et al., 2007; El-Nadi et al., 2007; Nogueira et al., 2012). Hydrometallurgical processes are directed mainly to the recover zinc by cathodic reduction and manganese recovery by precipitation (El-Nadi et al., 2007; Ferella et al., 2010; Sayilgan et al., 2009).

After the separation of ferrous metals and inert components (paper, plastic etc.) the result is a paste that contains mainly Mn, Zn and C, that represent 60%, and small amounts of other metals

\* Corresponding author. Tel.: +40 723850174.

E-mail addresses: [gabriela81us@yahoo.com](mailto:gabriela81us@yahoo.com), [gabriela.popescu@upb.ro](mailto:gabriela.popescu@upb.ro) (G. Popescu).

like: Cd, Cu and Ni, alkali metals (Na, K), alkaline earth metals (Ca, Mg), silicon dioxide (SiO<sub>2</sub>), and soluble salts that form electrolyte (NH<sub>4</sub>Cl, ZnCl<sub>2</sub>, KOH) As already demonstrated, by washing the paste with water, the soluble salts and a large part of chlorides, K, Na and NH<sub>4</sub><sup>+</sup> can be removed, (Veloso et al., 2005; Sayilgan et al., 2010)

The aim of the paper was to analyse spent batteries containing zinc and manganese, in particular Zn–C and alkaline batteries. They contain primary Zn and MnO<sub>2</sub>, in an NH<sub>4</sub>Cl/ZnCl<sub>2</sub> electrolyte, KOH respectively, that impregnates mainly a coal support. In these batteries, the anode, formed by metallic zinc, is oxidised to ZnO and Zn(OH)<sub>2</sub> to produce energy. Commonly, Zn–C and alkaline batteries are not exhausted, and therefore they can contain some metallic zinc. The study was therefore focused on the simultaneous extraction of Zn and Mn from used batteries; Zn as a metal by cathodic reduction, and Mn as manganese electrolytic dioxide, of high quality, by anodic oxidation. These metals are used in the batteries production based on Zn/KOH, NH<sub>4</sub>Cl, ZnCl<sub>2</sub>/MnO<sub>2</sub> system. This type of recycling was also investigated by Provazi using a mixture of spent household batteries and two hydrometallurgical procedures selective precipitation with NaOH and a liquid–liquid extraction using CYANEX 272 as extracting agent (Provazi et al., 2011).

## 2. Materials and methods

Firstly, the spent batteries were cut and crushed with a disk crusher. The resulted paste with a 10 mm particle size has been transported by a conveyor belt, for magnetic separation, in order to remove the iron. The nonmagnetic fraction of the paste was subsequently sieved with a 1.25 mesh size standard sieve. The material with less than 1.25 mm particle size was used as raw

material in the experimental work. With the aim of Zn and Mn recovery from portable batteries, two methods were investigated: (i) Zn selective leaching in alkaline medium and (ii) Zn and Mn leaching in acid medium. Selective leaching of Zn in an alkaline medium using a NaOH solution and in an acid medium using a H<sub>2</sub>SO<sub>4</sub> solution has been investigated by many researchers (DeMichelis et al., 2007; El-Nadi et al., 2007; Ferella et al., 2010; Provazi et al., 2011; Sayilgan et al., 2009, 2010). All the used reagents were of analytical grade. The elements concentration was determined by X-ray fluorescence analysis (Table 1) with UV–VIS PG Instruments T90+ Spectrometer and X-ray diffraction (Fig. 1) with Bruker-AXS D8 ADVANCE Bragg–Brentano Diffractometer.

### 2.1. Selective leaching of zinc in alkaline medium

The presence of metallic zinc in alkaline batteries is confirmed by X-ray diffraction of the spent electrode paste of batteries (Fig. 1). The diffractogram presented in Fig. 1 shows the specific metallic zinc peak, and zinc oxide peak, so it is expected metallic zinc residues are to be found in the raw material used for the leaching process.

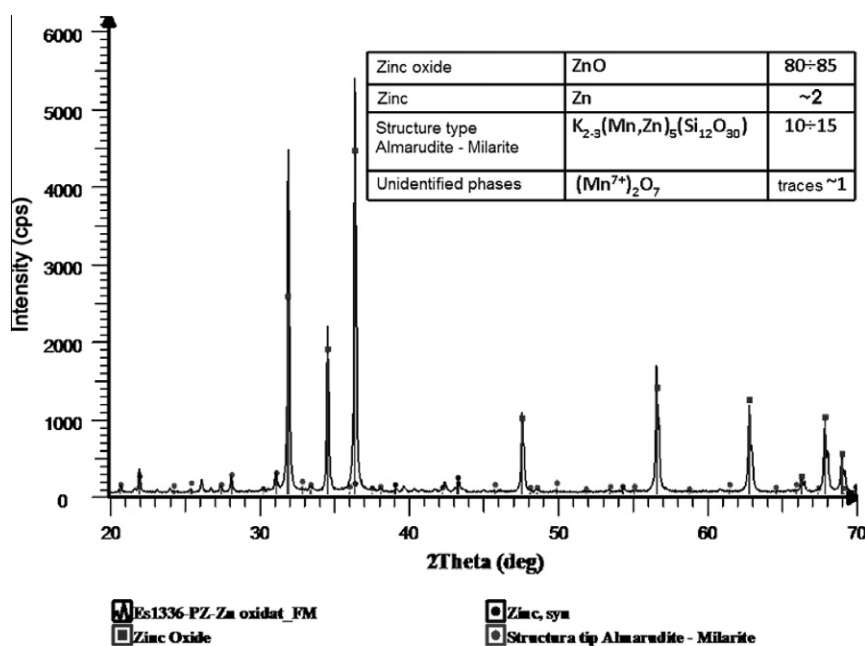
By using leaching in alkaline medium, zinc was selectively dissolved in sodium hydroxide solution, according to the following reactions, and iron and manganese remained in the waste:



The leaching in alkaline medium of the electrode paste of Zn–MnO<sub>2</sub> batteries was studied. The average composition of the batteries electrode paste is presented in Table 1. All tests performed

**Table 1**  
Average composition of electrode paste (fine fraction).

Electrode paste	Mn (%)	Zn (%)	Fe (%)	Cr (%)	Al (%)	K (%)	Ti (%)	Si (%)	Cl (%)	Pb (%)
Alkaline batteries	30.07	19.05	0.52	0.012	0.028	4.74	0.014	0.062	–	0.010
Zn–C batteries	22.44	20.86	0.39	0.017	0.050	–	0.004	0.13	5.14	0.050



**Fig. 1.** Diffractogram of anodic paste from alkaline batteries.

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