

# The dismantling of the spent alkaline zinc manganese dioxide batteries and the recovery of the zinc from the anodic material

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## Abstract

The existing plants for the recovery of exhausted alkaline zinc manganese dioxide batteries adopt an initial heat treatment and then a grinding. The last operation intermixtures the components of the batteries and consequently the successive recovery process proves to be rather complicate and needs a large scale plant. An initial dismantling and separation of the anodic, cathodic and packing components allow a successively easier recovery process and a small scale plant. This possibility has been assumed in this work and a simple recovery process has been proposed for the anodic material, consisting of an initial leaching step to separate and recover the unconverted metallic zinc and a successive step of cathodic deposition to recover the converted ionic zinc. A highly efficient zinc recovery has been obtained at the cathodic deposition step by adopting a heat treatment of the anodic material before its leaching process. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Alkaline batteries; Battery dismantling; Zinc recovery; Zinc electrodeposition

## 1. Introduction

Alkaline zinc manganese dioxide batteries are widely used as they have a good ratio of discharging characteristics/price. The great quantity and diffusion of exhausted batteries of this type imposes a suitable waste management, which is easier now than in the past due to the introduction of ‘mercury free batteries’ [1].

The two compartments of exhausted batteries of this type contain different chemical species. The anodic compartment contains unconverted metallic zinc, electrolyte — usually potassium hydroxide — gelling agents and zinc converted in the ionic form during the discharging of the batteries. The cathodic compartment contains graphite, unconverted manganese dioxide ( $\text{MnO}_2$ ), converted manganese oxides ( $\text{Mn}_2\text{O}_3$  and  $\text{MnO}$ ) plus small quantities of zinc ions, that have been transferred from the anodic compartment during the discharging of the batteries [2].

The great quantity of both metallic and ionic zinc in the anodic compartment and of manganese oxides in the cathodic one imposes a proper landfill disposal or a suitable recovery process [3–5]. The existing processes propose an

initial heat pre-treatment of the exhausted batteries to eliminate humidity and to transform and separate organic species; then the batteries are subject to grinding [6–11]. The mixing, which takes place during the grinding increases the complexity and the cost of the successive separation and recovery of the various species. Large scale plants are needed for the recycling process and this is probably why only a small number of plants operate in this recycling field.

A preliminary dismantling and separation of the principal components of the batteries has not been used in the existing process even as this preliminary process seems to be easy to carry out [12]. The actual standard size of these kinds of batteries combined with a more suitable arrangement of the active components inside the battery can allow the principal components of the exhausted batteries to be easily dismantled and separated mechanically. The separation of the cathodic and anodic material through the dismantling of exhausted batteries makes the successive recovery process easier than the existing ones. This preliminary treatment offers new recovery methods in the field of exhausted batteries and some of them are probably easier and more convenient than the existing ones and need smaller plants, which are more suitable for a local treatment.

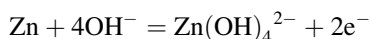
In this paper we study the treatment of the anodic exhausted material. The simple process reported here consists of separating the fraction of unconverted metal

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zinc by a suitable leaching, followed by the recovery of the converted ionic zinc into zinc metal form by cathodic deposition.

## 2. Zinc recovery from the anodic compartment

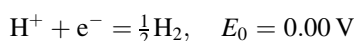
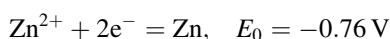
The active species of the anodic compartment of alkaline zinc manganese dioxide batteries is metallic zinc. As the discharging of the battery proceeds, the metallic zinc in this compartment decreases, due to the anodic reaction:



According to the above reaction, the quantity of ionic zinc in this compartment increases and only a small quantity of ionic zinc is transferred through the separator to the cathodic compartment [2]. It is evident that, as the degree of discharging increases, the ratio of ionic to metallic zinc increases. Previous studies in this field indicate that the portion of metallic zinc in the anodic compartment of exhausted batteries is more than 30%, while the rest of the zinc is in ionic form [13]. The exhausted anodic compartment contains also organic gelling agents and other species which help avoid the hydrogen evolution in the anodic compartment during the discharging of the batteries [14].

The separation by leaching of the unconverted from converted zinc is a simple method to recover both metallic and ionic zinc. In previous studies, due to the initial grinding, the leaching process of all the active components has considered, while in this work the leaching of the anodic material is proposed. A leaching stage with two different types of leaching solutions has been used in this study: (1) a solution that contains EDTA as chelating agent, which dissolves preferentially ionic zinc and (2) a solution of sulphuric acid, which dissolves ionic zinc and zinc oxide and small quantities of metallic zinc. The first leaching solution of EDTA probably allows a higher recovery of metallic zinc, but this solution contains organic species and is more expensive. The solution of sulphuric acid allows a lower recovery of metallic zinc than the previous one, due to the partial dissolution of metallic zinc, but this solution principally contains inorganic species and is less expensive.

The cathodic deposition was applied in this work to recover the ionic zinc from the leaching solution. The main reactions that occur at the cathode during the electrochemical zinc recovery and affect its current efficiency are the following:



The above reactions indicate that, as both values of pH and zinc concentration of the leaching solution decrease the current efficiency decreases. The mass-transfer condition close to the cathode and the other species present in the electrolyte solution have some effect on the current

efficiency, especially when the zinc concentration reaches very low values at the end of the recovery process.

The current efficiency during the zinc recovery from the leaching solution also depends on the other dissolved organic and inorganic species, i.e. gelling agents of the electrolyte and other species, such as bismuth in very little quantities, to avoid the hydrogen evolution in the anodic compartment during the discharging of the batteries [15]. It is known from the plating field that additives such as gelatine are absorbed on the deposited metal, because of the formation of carbon metal bonds and inhibit the metal deposition probably by a simple blocking action [16]. It is evident that, while at a low concentration additives improve the quality of plating, at a higher concentration additives have an inhibiting effect on the metal deposition.

A heat pre-treatment has therefore been applied on the anodic material, before its leaching process, to eliminate the organic species and to improve the current efficiency during the zinc recovery of the leaching solution.

## 3. Experimental

Spent alkaline zinc manganese dioxide batteries size AA of the local municipal collection were dismantled to determine the constituents of the exhausted batteries: (1) the metallic, plastic and paper material of the packing, (2) the anodic and cathodic material of the two compartments and (3) the principal components of the anodic and cathodic compartment. A sufficient quantity of exhausted anodic material was obtained by this dismantling for successive treatments. The concentration of the zinc in the anodic material was determined by the use of a Perkin-Elmer Plasma emission spectrometer.

The previously proposed mechanical cutting and dismantling of the exhausted batteries allows the separation of the main components: anodic and cathodic material, metallic material, plastic and paper. After the separation, the various components were dehydrated by heating at 105°C for 5 h and then weighed. In particular the anodic material was ground after heating for 3 h and then the ground material was heated for two more hours. Some sample were also treated at 650°C for 4 h, in order to remove from them the organic species contained. Similar operating conditions have also been adopted for the initial heat treatment of the whole active material of the exhausted batteries [17].

An EDTA (Merck, 0.5 M) solution was used for the leaching process of the anodic material; the EDTA concentration was diluted to 0.23 mol dm<sup>-3</sup>, a small quantity of acetic acid was added (0.5 × 10<sup>-3</sup> dm<sup>-3</sup>), the solid to liquid ratio was 0.075. A magnetic stirring was used, the temperature was 50°C, the pH of the solution, at the end of the treatment, was between 4 and 5, and a process time of 30 min was adopted, as first attempt.

A second leaching solution of sulphuric acid was used for the anodic material. The concentration of the sulphuric acid

was  $0.9 \text{ mol dm}^{-3}$  while the assumed ratio of solid to liquid was 0.10. A magnetic stirrer was used while the temperature was of  $50^\circ\text{C}$ , the pH of the solution at the end of the leaching was between 1.3 and 2.4, and a process time of 30 min was adopted.

A series of cyclic voltammeteries have been carried out to establish the optimum cathodic conditions and to point out the effect of the contaminants on the cathodic deposition process. A potentiostat/galvanostat EC&C Model 273A and the EC&C Echem software was used, as well as the EC&G Model 636 disk rotating system; a zinc plated brass was used as a working electrode with  $0.31 \text{ cm}^2$  of active surface. Two different solutions with the same pH (2.4) and specific conductivity value ( $48 \text{ mS cm}^{-1}$ ), were used: (1) the leaching solution after the treatment of the anodic material containing zinc ions ( $26 \text{ g dm}^{-3}$ ), plus other contaminants and (2) a synthetic solution containing the same concentration of zinc ions plus potassium sulphate and sulphuric acid.

The limiting current density was calculated by using the following equation:

$$i_l = 0.62zFD^{2/3}v^{-1/6}C$$

where  $i_l$  is the limiting current density ( $\text{A m}^{-2}$ );  $z$  the number of electrons;  $F$  the Faraday constant ( $\text{C mol}^{-1}$ );  $D$  the diffusion coefficient ( $\text{m}^2 \text{ s}^{-1}$ );  $v$  the kinematic viscosity ( $\text{m}^2 \text{ s}^{-1}$ ), and  $C$  is the bulk concentration of the reacting species ( $\text{mol m}^{-3}$ ).

A constant current condition was applied during the zinc electrochemical recovery of leaching solutions. Anodic material subject or not to heat pre-treatment was separately leached and the zinc from both solutions was recovered. In order to obtain the galvanostatic conditions, a potentiostat/galvanostat AMEL Model 553 was used and a standard calomel electrode allowed us to measure the cathodic potential during this treatment. A volume of  $100 \text{ cm}^3$  was used for the electrochemical zinc recovery with initial value of the zinc concentration between 14 and  $27 \text{ g dm}^{-3}$ , pH value between 1.30 and 2.38, and temperature of  $35^\circ\text{C}$ . Small volumes of solution were drawn during the treatment to determinate the variation of the zinc concentration and then the current efficiency versus treatment time.

A zinc cathode with an active surface of  $18 \text{ cm}^2$  was used. Two equal lead anodes with 1% of silver and a total anodic surface of  $30 \text{ cm}^2$  were located symmetrically to the cathode in order to obtain a homogeneous zinc deposition on the cathode. The cathode was weighed before and after the treatment and the quantity of the deposit during the process was obtained. The same magnetic stirring was adopted during the electrochemical treatment.

## 4. Experimental results and discussion

### 4.1. Composition of the exhausted batteries

After being cut and dismantled, the exhausted batteries were separated in anodic, cathodic and metallic material

plus paper and plastic. The percentage of the above materials after drying is the following: (1) anodic material 18.8%, (2) cathodic material 52.8%, (3) metals 22.8% and (4) paper and plastic 3.6%. The determination of the zinc in the anodic material indicates that it contains a high quantity of converted and unconverted zinc (67.1% in weight).

### 4.2. Leaching treatments

The leaching with the use of the EDTA solution allows dissolution of 53% of the anodic zinc, while the rest of the zinc (47%) remains in the solid phase. The analysis of the solid phase indicates that the metallic zinc is the main constituent (95%); this result points out that the EDTA solution almost completely dissolves all the constituents of the anodic material, except the metallic zinc. It is important to point out that, during the leaching, the EDTA solution is contaminated by the other species present in the anodic material. This condition imposes a periodical renewal of the EDTA solution to replace the exhausted one.

The experimental results with a sulphuric acid solution point out that the dissolved zinc is higher than in the previous EDTA solution, in fact in this case 67% of zinc was dissolved compared to the 53% of the previous one. About 14% more of the metallic zinc was dissolved during the acid treatment and in this case the recovered metallic zinc by leaching was more pure than in the previous one (96%). In this case, as in the previous one, the solution is contaminated by the species of the anodic material and we have to consider that during the successive treatment only the zinc ions will be recovered.

A new series of experiments with the same sulphuric acid solution were carried out using an anodic material, which was previously subjected to the reported heat pre-treatment ( $650^\circ\text{C}$  for 4 h), in order to eliminate the existing organic species. In this case, a higher quantity of the zinc is dissolved (72.8%). This is probably due to the zinc oxide produced during the heat treatment in air which is more easily dissolved in the acid solution.

### 4.3. Cyclic voltammetry with rotating disk cathode

Experimental results of cyclic voltammetry at 800 rpm of the rotating disc electrode were reported in Fig. 1. The two diagrams concern the different solutions: (1) a sulphuric acid solution after the leaching of the anodic material and (2) a synthetic solution that contains the same zinc concentration plus potassium sulphate and sulphuric acid to reach the same values of conductivity and pH.

The two voltammetric diagrams (scanning rate  $5 \text{ mV s}^{-1}$ ) show a higher current for the laboratory solution with respect to the leaching solution. The contaminants of the last solution have an inhibiting effect on both cathodic reactions. The same figure indicates a high current, when the cathodic potential becomes lower than  $-1.25 \text{ V}$ . At these conditions, bubbles of gas are observed on the anode.

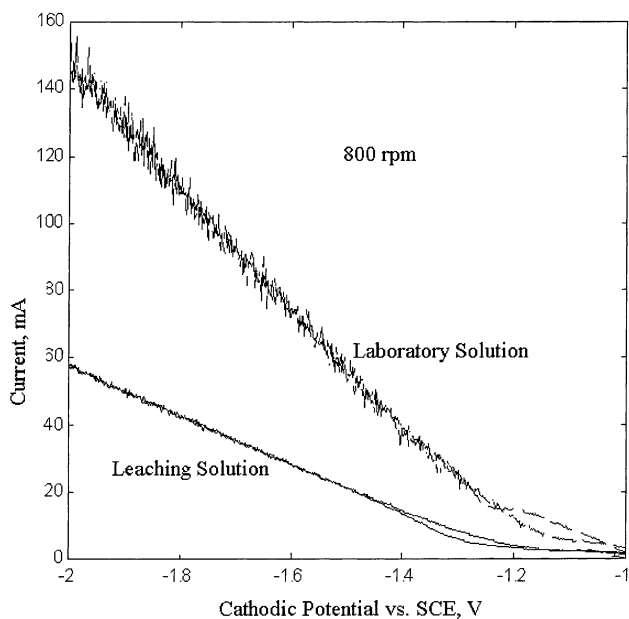


Fig. 1. Cyclic Voltammetry diagrams by using leaching and laboratory solution.

The current value observed at the beginning of the hydrogen evolution (16.5 mA), is lower than the limiting zinc deposition current (41 mA). This result indicates that as the cathodic potential decreases, the two reactions occur simultaneously.

Therefore the obtained voltammetric diagrams indicate that the cathodic recovery of the zinc from the leaching solutions depends on: (1) the previous pre-treatments of the anodic material and (2) the applied overpotential to avoid hydrogen evolution.

#### 4.4. Cathodic zinc recovery

The zinc concentration versus furnished specific charge is shown in Fig. 2 for two current densities with the same

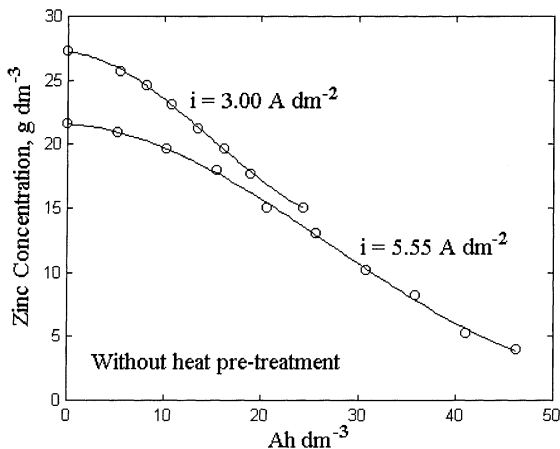


Fig. 2. Zinc concentration vs. specific charge, for two density currents, using a not pre-treated anodic material.

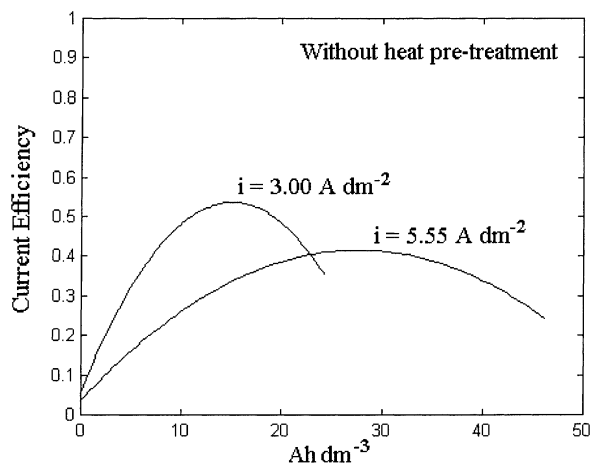


Fig. 3. Current efficiency vs. specific charge, for two density currents, using a not pre-treated anodic material.

anodic materials, which are not subjected to heat pre-treatment. The conditions concerning the electrochemical recovery of the electrolytes were: current density 3.00 and 5.55 A dm<sup>-2</sup>, temperature 35°C, initial zinc concentration 27.2 and 21.6 g dm<sup>-3</sup>, initial pH 2.35 and 1.3, final zinc concentration 15.0 and 3.92 g dm<sup>-3</sup>. The comparison of the two cases indicates a higher decrease of zinc concentration in the case of the lower applied current density. Fig. 3 reports the current efficiency versus specific charge, for the two leaching solutions previously indicated in Fig. 2. The obtained values of the current efficiency are not very different in the two cases, which means that the applied current density of the recovery process has a relatively small effect on the current efficiency. In both cases we observe that the current efficiency starts with a low value and successively increases to reach, after some time, its maximum; then a successive decrease is observed, at the end of the recovery process.

Fig. 4 shows zinc concentration versus specific charge at the same current density, by using leaching solutions

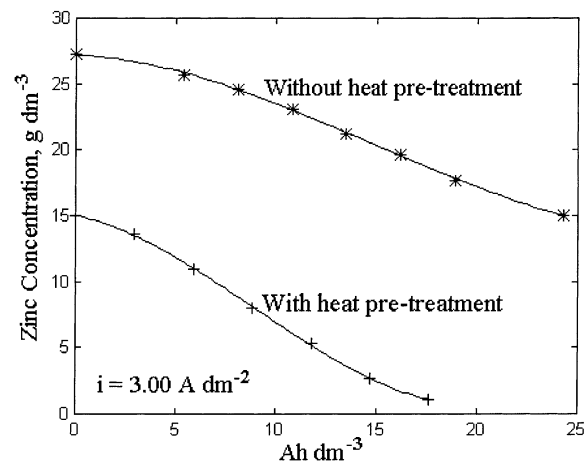


Fig. 4. Zinc concentration vs. specific charge, using treated and not treated anodic material.

Table 1  
Characteristic parameters of some experimental runs, concerning the zinc recovery from leaching solutions

| Initial heat treatment (yes/no) | Current density ( $\text{mA cm}^{-2}$ ) | Initial zinc concentration ( $\text{g l}^{-1}$ ) | Final zinc concentration ( $\text{g l}^{-1}$ ) | Initial pH | Final pH | Current efficiency (%) |
|---------------------------------|---|--|--|------------|----------|------------------------|
| No                              | 55                                      | 21.6   | 3.92   | 1.30       | 0.50     | 36                     |
| No                              | 30                                      | 27.2   | 15.0   | 2.35       | 1.67     | 41                     |
| No                              | 30                                      | 24.2   | 11.7   | 1.84       | 1.42     | 36                     |
| Yes                             | 30                                      | 15.0   | 1.08   | 1.76       | 0.90     | 65                     |

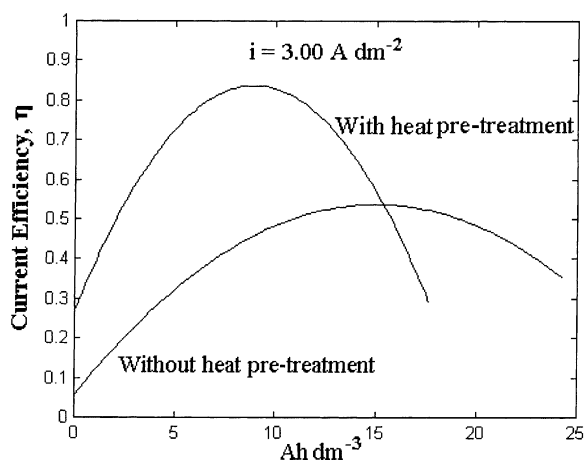


Fig. 5. Current efficiency vs. specific charge, using treated and not treated anodic material.

obtained from heated and not heated anodic material. The leaching solution of the thermally pre-treated anodic material shows a high decrease in zinc concentration. This is due to the higher current efficiency, as shown in Fig. 5. We observed that higher value of the current efficiency can be reached with the use of heat pre-treatment.

Table 1 reports the parameters of all experimental runs: current density, initial and final zinc concentration, pH value of the solution and the mean current efficiency of the process. This table shows that the heat pre-treatment and not the variation of the current density has an appreciable effect on the current efficiency. Furthermore, the increase of the pH initial value from 1.30 to 2.35 has a limited effect on the current efficiency (from 36 to 41%). In conclusion, the comparison of the various results reported in Table 1 confirms that the more efficient method to increase the current efficiency is the heat pre-treatment of the anodic material.

## 5. Conclusions

The dismantling of the exhausted alkaline zinc manganese dioxide batteries was assumed to separate the anodic, cathodic and packing material with the objective to make the successive species recovery from the previously separated

three components of the exhausted batteries easy and convenient.

The recovery of the zinc from the anodic compartment was studied and a simple method was proposed to separate and recover the unconverted metallic zinc by a leaching stage and, successively, recovering the converted ionic zinc by electrodeposition. Two different solutions have been proposed for the leaching stage: EDTA and sulphuric acid solutions. A single compartment cell was used for the cathodic zinc recovery.

The leaching experimental results indicate that a high portion of the unconverted metallic zinc is recovered in this form even when the anodic material is subjected to a heat pre-treatment. The current efficiency of the successive cathodic deposition of the ionic zinc has been improved by means of a suitable heating pre-treatment of the anodic material.

With the proposed recovery method of the anodic material, about 30% of the zinc was separated in the metallic form, by using a simple and economic leaching method, while the heat pre-treatment allows the recovery of the rest of the zinc (about 70%) with a high current efficiency.

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