

STUDY OF A PILOT PLANT FOR THE RECOVERY OF METALS FROM SPENT ALKALINE AND ZINC-CARBON BATTERIES WITH BIOLOGICAL SULPHURIC ACID AND POLYTHIONATES PRODUCTION.

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Abstract— The recovery of Zn and Mn from spent alkaline and Zn-C batteries with a biohydrometallurgical process was studied in a pilot plant that consists in an *air lift* bio-reactor with a sulfur packed bed where *Acidithiobacillus thiooxidans* produces an acid-reducing medium; a leaching reactor where the acid-reducing medium is mixed with the battery powder and a recovery reactor where metals are recovered from the leaching liquor by electrolysis. Results shows that with a 350 mM in proton medium produced in 12 days by *Acidithiobacillus thiooxidans* in the bio-reactor, an extraction of the 100% of Zn and 67% of the Mn present in the battery powder was reached. The presence of polythionates in the medium produced in the bio-reactor allows the dissolution of the manganese. The solid remaining after bioleaching is a manganese oxide. The electrolysis of the leaching liquor produced a cathodic deposit of metallic Zn and an anodic deposit of a high surphase manganese oxide in one step at room temperature.

Keywords— batteries, biohydrometallurgy, *Acidithiobacillus thiooxidans*, metal, recovery.

I. INTRODUCTION

There are several approaches at the international level to address the problem of spent batteries though none of them has been universally accepted. There are different alternatives to the final destination of batteries: landfill, stabilization, incineration or recycling (Bernardes *et al.*, 2004). In the last years many technologies for battery recycling have been developed in several countries, such as pyrometallurgy, acid leaching, alkaline leaching, combined acid-reductive leaching, solvent extraction, electrolysis and chemical precipitation (Bernardes *et al.*, 2004, Provazi *et al.*, 2011). Many patented processes have already been applied mainly for treatment of dry cell batteries as BATENUS for a batteries mixture, PLACID for mercury recovery, RECYTEC for simultaneous recovery of zinc and manganese dioxide, HYDROMETAL SPA for lead-acid, REVABAT/REVATECH for alkaline and zinc-carbon, RECUPYL for all types of batter-

ies. (Ferella *et al.*, 2008; Sayilgan *et al.*, 2009). Ecorecycling SRL and University La Sapienza of Rome have patented the first recycling plant of spent alkaline and zinc-carbon batteries in Italy (Toro *et al.*, 2011). The European Union Battery Directive Extended Impact Assessment reports that each year, approximately 800,000 tonnes of automotive batteries, 190,000 tonnes of industrial batteries and 160,000 tonnes of portable batteries are placed on the community market. The total weight of portable batteries sold in Eastern and Western Europe in 2003 was about 164,000 tonnes, of which 50,197 and 99,138 tonnes were zinc-carbon and alkaline batteries, respectively (30.5% and 60.3% of the total annual sales) (Sayilgan *et al.*, 2009; EPBA, 2006). Xin *et al.* (2012a) reported that the Zn-Mn batteries occupy over 90% of the total annual sales of portable batteries due to their low prices, especially in developing countries like China. Legislation in many countries regulates the fabrication, commerce and final disposal of spent batteries, in the European Union and USA, there are already industrial plants for battery recycling. In Latin America, there are some new regulations about fabrication and final disposal of batteries, but there is still a lot to do about recycling. In Argentina, in particular, spent batteries are sent to the landfills with the domestic garbage (Directive 2006/66/EC; Argentinean Law 26184 ;Espinosa *et al.*, 2004). Spent batteries represent a valuable resource, since this kind of waste contains high levels of metals whose prices are rising worldwide. The benefits of recycling materials from an economic, environmental and technical point of view depend on many factors, including transport, recycling process and material to be treated. Recycled nickel and cadmium, for example, require 46% and 75% less primary energy (respectively) than the extraction and refining of the virgin metal (Ridh and Karlstrom, 2002). For zinc, the relation between the energy needed for recycling and the energy needed for extraction from primary resources is 2.2 to 8. These figures are particularly important given the fact that the primary production of metals is the source of approximately 10% of global CO₂ emissions (EU, 2003).

In this work, a biohydrometallurgical process for the

recovery of metals from spent batteries is proposed. Biohydrometallurgy can be defined as the field of applications resulting from the control of natural (bio-chemical) processes of interactions between microbes and minerals to recover valuable metals (Morin *et al.*, 2006). Biohydrometallurgical processes are a robust emerging technology with some advantages over pyrometallurgical systems and chemical leaching processes namely: less energy consumption, less atmospheric emissions, small, safe and versatile plants, simplicity and low cost of the process, applicability to low grade sources, low costs of installation and possibility of on-site treatment (Morin *et al.*, 2006; Brierley and Brierley, 2001, Brierley, 2010). In the field of biohydrometallurgy, three different processes can be defined: bioleaching, bio oxidation and indirect acid bioleaching using acid production by acidophilic bacteria cultivated in bioreactors or bioheaps. In the last few years several works about bioleaching of metals from solid waste have been reported (Cerruti *et al.*, 1998; Bosio *et al.*, 2008; Zhao *et al.*, 2008; Xin *et al.*, 2009; Xiang *et al.*, 2010). Cerruti *et al.* (1998) studied the bioleaching of Ni-Cd spent batteries with *Acidithiobacillus thiooxidans*. Previous works reported studies, at laboratory scale, about bioleaching of spent alkaline batteries (Xin *et al.*, 2012(a);2012(b)) and Li-ion batteries (Xin *et al.*, 2009) with acidophilus bacteria like *Alicyclobacillus sp.* (sulfur-oxidizing bacteria) and the *Sulfobacillus sp.* (iron-oxidizing bacteria). However, no pilot plant scale studies of biohydrometallurgy for battery recycling have been found in the literature. On-site sulphuric acid production has multiple advantages, since it eliminates the manipulation of concentrated sulphuric acid, the pollution of its industrial production and the costs of transporting it (Brierley, 2010). Despite of the lot of literature on bioleaching of sulphide metals and arsenopyritical gold only a few publications are dedicated to biologic production of sulphuric acid and intermediate sulphur compounds for industrial applications. *Acidithiobacillus thiooxidans* (*At*) is a chemolithotrophic bacterium able to catalyse the oxidation of elemental sulphur and other reduced sulphur compounds to polythionates and sulphuric acid, and to use it as his energy source. It requires a minimal mineral medium and is easily cultivated in laboratory. It has a remarkable tolerance to heavy metals and low pHs.

In this paper a pilot plant for the bioleaching of spent alkaline and zinc-C batteries was studied. This pilot plant consists in a packed bed *air-lift* bio-reactor with attached *At* cells for acid and polythionates production, a bioleaching reactor where metals are extracted from the battery powder with the acid-reducing medium produced in the bio-reactor, and a recovery reactor where Zn and Mn are recovered from the leaching liquor by electrolysis. Advantages of this indirect bioleaching are the possible optimisation of the acid production in one reactor and the leaching of metals in the other. This indirect mechanism also makes unnecessary to adapt the cells to high metal concentrations.

II. METHODS

A. Process flowsheet:

In fig. 1 there is a scheme of the pilot plant for the recovery of metals from spent batteries. The batteries are opened and steel can, plastic and paper are separated. The battery powder is washed several times with water in order to eliminate the electrolyte. In the *air-lift* bioreactor with a sulphur- packed bed, *At* produces sulphuric acid and polythionates. This product is mixed with the battery powder in the bioleaching reactor which is a stirred-tank reactor. The resulting leaching solution is filtered and send to the recovery reactor which is an electrolytic cube where metallic zinc and a manganese oxide are deposited simultaneously. The solid remained after leaching is a manganese oxide. The basic electrolyte, separated in the washing step, can be used for the neutralization of the liquid acid residue after metal electrodeposition.

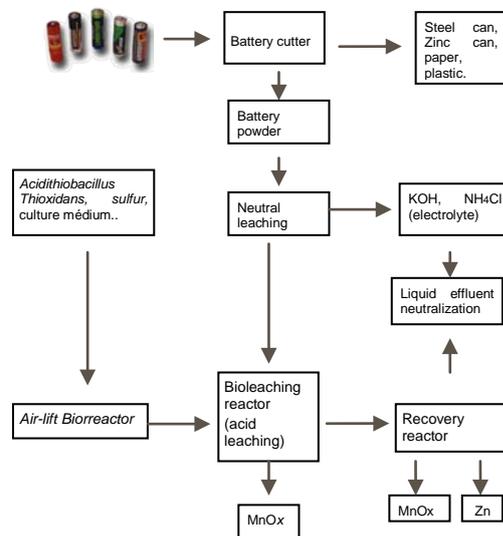


Figure 1. Process flow sheet.

B. Bacteria

An *Acidithiobacillus thiooxidans* (*At*) strain DSM 11478 was used. The organism was routinely maintained in a minimum mineral medium (1g/L $\text{SO}_4(\text{NH}_4)_2$, 0.5g/L K_2HPO_4 , 0.5g/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.0145 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 0.1 g/L ClK). The pH was initially adjusted to 2.5 and sulphur powder was added as the energy source (1% m/V). The organism was cultured in Erlenmeyer flasks and incubated at 30°C on a rotary shaker at 180 rpm.

C. Sulphuric acid and polythionates production:

The experiments were carried out using the reactor showed in fig.2. The *air lift* reactor used was built in acrylic, 3 mm width. Inside the *downcomer* section, sulphur (+3.5 ; -5 mesh) was added. This sulphur constituted the support media and the substrate for *At*. The gaseous phase was air in every experience. Airflows ranging from 75 to 240 L/h were fed continually to the reactor by the *riser* section. The reactor was maintained at 30°C by a temperature control system. The total

volume of the reactor was 26.5 liters. The reactor was inoculated once with a culture of *At* in the exponential stage of growth. When proton concentration reached the settled value, the same volume of fresh mineral medium without new inoculation replaced the entire medium. This acidified medium was used afterwards to leach the metals contained in the batteries.

To characterise the reactor we evaluated the oxygen volumetric transference coefficient (K_{La} , Sulphite method (Bu'Lock, 1995)). Periodically, samples were taken to evaluate proton (titration with NaOH) and sulphate concentration (turbidimetric method), pH (potentiometric), polythionates (UV spectrophotometry (Shirihari *et al.*, 1993), and cells/ml (direct counting, Burkholder chamber). The sulphuric acid/sulphur yield was calculated weighting sulphur before and after a certain amount of acid production. Here, the cell mass adhered to the sulphur surface is considered negligible (Konishi *et al.*, 1995). We define as a step in the reactor, every time new liquid medium is added.

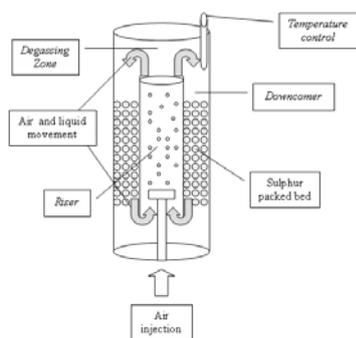


Figure 2. Air-lift bioreactor scheme.

D. Batteries:

A mixture of Zn-C and alkaline batteries, size AA, from different trade marks were used in this work. They are primary cells, so they can be fully discharged once and then discarded. Its principal components are zinc, manganese dioxide, NH_4Cl or KOH electrolyte and a steel can. (Energyzer, 2001, 2008).

E. Battery pre-treatment:

Batteries are cut by the battery cutter (equipment specially designed in our laboratory) and opened. The battery powder is separated from the can and all the ferrous parts, plastic and paper. The powder is washed with several portions of distilled water to eliminate the electrolyte, and then dried at 150° overnight.

F. Bioleaching of batteries:

Spent alkaline and zinc-carbon battery powder are treated with the biological acid-reducing medium to transfer the metals from the solid to the leaching liquor. The bioleaching experiments were carried on a 50 L polypropylene reactor mechanically stirred by a marine propeller at 200 rpm. 2 kg of battery powder was placed in the leaching reactor with 28 L of acid medium (pH

near 0.4). When pH reached a plateau and metals in solution did not increase, the entire medium was replaced by fresh acid medium in order to continue metal dissolution if it was necessary.

The steel case extraction avoids excess Fe in solution and allows the direct recovery of steel for the siderurgy industry, as it reduces costs in acid consumption and pH control. Periodically samples were taken from the reactor to analyse metal concentration (atomic absorption in a Perkin Elmer 3110 spectrophotometer) and pH.

To evaluate if there was any difference between the metal extraction done by a commercial or biological sulphuric acid it was placed in one Erlenmeyer flask named S1 the battery powder in contact with commercial sulphuric acid at the same concentration than the biological one, and in another flask, named S2, the battery powder in contact with biological acid. Samples were taken periodically for pH and metal concentration determination.

G. Electrolysis:

A sample of 6.5 L of the leaching solution was transferred from the bioleaching reactor to an electrolytic cube with two stainless steel electrodes connected to a DC power source. The average current density was 100 A/m^2 and the distance between electrodes was 25cm. Experiments were carried at atmospheric pressure and room temperature, taking samples of the electrolytic bath to determine metal concentration by atomic absorption and pH with a combined electrode. The solid deposited in the electrodes was taken at the final of the experiment and characterized as we describe below.

H. Electrolytic MnO_x , Zn, battery powder, and residual leaching solid characterization:

Metal composition of all the solid samples was determined by acid digestion with HCl-HNO₃ (3:1) and atomic absorption in Perkin Elmer model 3110 spectrophotometer with the corresponding hollow cathode lamp. The BET surface areas of the samples were determined by nitrogen adsorption at 77 K using a Micrometrics ASAP 2020 analyzer. Crystal structures of the samples were analyzed by X-ray diffraction methods in a Philips Diffractometer using $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation at 2°min^{-1} scanning speed, in the $5 < 2\theta < 70^\circ$ range. Surface morphology and quantitative analysis of the composition of the samples were carried out with a scanning electron microscope provided with energy dispersive X-ray analysis (SEM-EDS) using a Philips SEM 505 microscope.

III. Results and discussion

A. Sulphuric acid and polythionates production.

a. *Biofilm development in the packed bed reactor.*

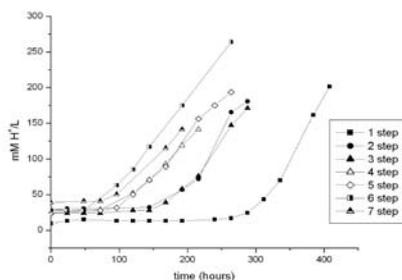


Figure 3. Production of acid by *At.* in the bioreactor

Proton concentration (mM) as a function of time is shown in fig. 3 for seven different steps and the same cycle (75 L/h airflow and 8.2 kg sulphur, end point of each step: 150 mM proton approximately). In the curves we might appreciate different phases: lag, exponential and linear in agree with previous results (Ceskova *et al.*, 2002). The short exponential phase followed by a lineal phase suggests a kinetic limitation: gaseous nutrients transfer or available sulphur surface. The curves move to the left in the successive steps without appreciable changes in their slopes. The reduction of the lag phase from 264 to 72 hours in four steps is probably due to the *biofilm* formation in the sulphur pearls. The proton production curves might be assimilated to the total biomass growth. Saturation of the sulphur available sites is probably reached since the fourth charge because we do not observe higher increases in proton productivity. The volumetric proton productivity (generated proton per unit of time and volume) increases as the lag phase reduces, reaching values between 13.4 and 16.8 mM/day in this cycle.

b. *Proton volumetric production as a function of sulphur mass:*

We evaluated proton productivity for two different sulphur mass and liquid media relations, namely 410 and 815 sulphur g/L, with a constant air flow of 75 L/h. When we used 410 g/L we obtained a productivity of 14.6 ± 1.5 mM proton/day (the error is the standard deviation for $n=4$, n representing steps in this case) and for the second relation a 47% better value of 27.7 ± 2.5 (n=2) mM proton/day. But it must be considered that an increase in sulphur mass diminishes the space available for the mineral medium (20 l. for the first, 13 l. for the second). Taking this into account, there is a net increase of 23% in the acid production (milimol proton/day) for a 50% increase in sulphur/medium relation.

d. *Proton volumetric productivity as a function of oxygen volumetric mass transfer coefficient (K_{La}):*

Between 75 and 240 L/h airflow we observed a linear relationship with K_{La} . This indicates that we might increase even more the airflow to obtain higher K_{La} values. The K_{La} value indicates oxygen transfer in the reactor. *At.* is an aerobic microorganism which requires oxygen as an electron acceptor, so the culture might become limited in this transfer. To evaluate this limitation we correlated K_{La} with proton productivity in the range studied. We observed no increase in acid produc-

tivity over 138 L/h airflow in spite of the increase of K_{La} . This indicates that over a K_{La} value of 10.4 ± 0.8 1/h the system is no longer limited by oxygen transfer, so there is no reason to increase air flow and costs. However, in the oxygen limited zone we obtained a 30% increase in proton productivity by rising the air-flow between 75 and 138 L/h (29.9 ± 2.5 to 42.3 ± 0.6 proton mM/day).

e. *Sulphuric acid/sulphur yield ($Y_{A/S}$) as a function of the end point of the batch culture:*

Polythionates ($S_n(SO_3)_2^{-2}$) in water decompose and their solutions must be stabilised by adding OH^- . They are the intermediate products of the oxidation of sulphur catalysed by *At.* When the batch culture is finished they are present in the acid media (see fig. 4). If they are not readily oxidised, more sulphur is consumed than the stoichiometrically required reaching that level of acidity.

We studied the sulphuric acid/sulphur yield varying the end point of the batch culture (150 or 350 proton mM). This parameter is important since the sulphur consumption is one of the higher costs for the biological production of this acid (the other is energy for heating, but this can be solved by modifying some design parameters).

As *At.* might become inhibited by the product -though they resist high levels of acidity and sulphate- we evaluated free cells number in a culture that has reach a constant acidity level.

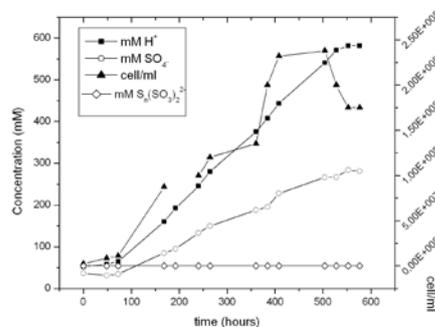


Figure 4. Sulphuric acid and polythionates production and *At.* free cell evolution in the *air lift* reactor.

In this test we found increases in cell population until 540 proton mM and 260 mM of sulphate (fig. 5). Over that concentration, cells begin to disappear. The final proton concentration stabilises in 600 mM approximately (pH = 0.2). Using these results we selected inferior proton concentrations for our experiments. The theoretical $Y_{A/S}$ is 3.0625 g/g (98 g sulphuric acid/32 g sulphur). Using an end point concentration of 150 proton mM we obtained a yield of 0.54 while incrementing the proton concentration to 350 mM, we increased this yield to 2.07 g/g.

B. Bioleaching

a. *Determination of battery powder composition:*

Acid digestion and atomic absorption spectrophotometry: Battery powder composition before leaching is quite different depending on the trademark, electrolytes are in general K(OH) or NH₄Cl, that were eliminated after washing with distilled water. See table 1.

SEM-EDS: In fig. 6 it can be seen that the most important components of the battery powder are Zn and Mn, a small quantity of Ni is also present, probably coming from the stainless steel case, and K from the electrolyte.

Table 1. Battery powder composition

M	Alkaline (% w/w)	Zn-C (% w/w)	Mixed battery powder (% w/w)	
			Without Zn can	With Zn can
Zn	24,56	19,85	14,84	30,43
Mn	38,73	22,26	31,82	21,87
Fe	2.35	0.002		
Pb	0.0064			
Hg	0.00001	0,00002	0,00001	0,00001
Cd	0.0006			
C	8.69			

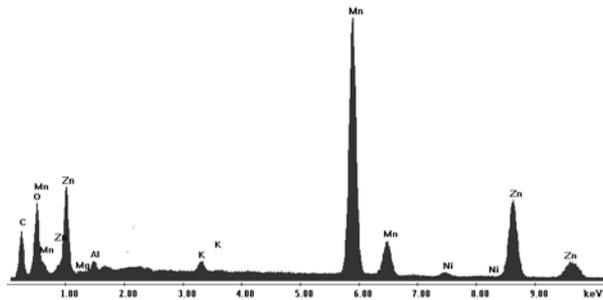
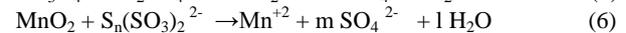
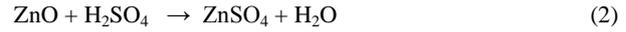
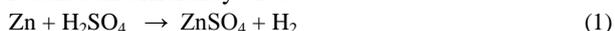


Figure 5. Battery powder EDS spectra before leaching.

b. *Leaching reactor:*

In two successive extractions it was observed that Zn is easier to extract compared to Mn, zinc and zinc oxide are totally dissolved by sulphuric acid, eq. (1) and (2), while manganese oxides are only partially leached by sulphuric acid, see eq. (3,4,5) (Sayilgan *et al.*,2009(b); Ferella *et al.*, 2010). But the leaching media produced in the biorreactor by *At* is composed for sulphuric acid and polythionates as intermediate compounds, those polythionates are reducing agents, in previous works it was used citric acid (Ferella *et al.*,2010) or the Fe(II) produced by an iron oxidizing bacteria (Xin *et al.*,2012(a)) as reducing agents to leach Mn (IV), in the present work reducing agent were polythionates, so a possibly reaction is eq. (6). The % of metals extracted are shown in fig. 7 , in two loads of fresh acid-reducing media, the 100% of zinc is extracted while manganese reaches an efficiency of 65% .



In the first load, pH reaches a stable value of 5 after 14 days of leaching, while in the second load the pH stabilizes at values below 2, meaning that there is an excess of acid in that step.

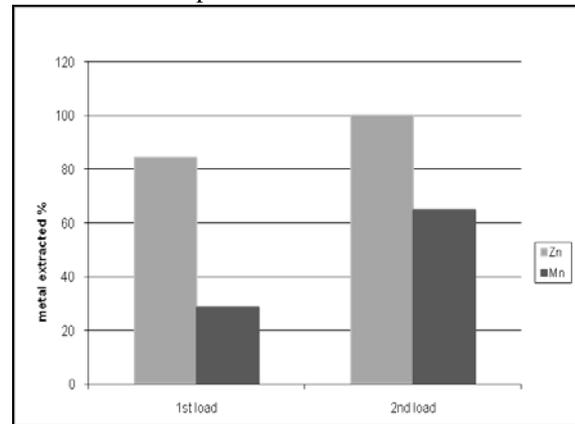


Figure 6. Concentration of Zn and Mn in the leaching reactor

c. *Comparison between commercial and biological acid media:*

Results from the analysis of samples from the S1 and S2 flasks indicates that the quantity of Mn extracted increases in a 60% in S2 (biological acid) in comparison with S1 (commercial acid), and for Zn, the increment of the extracted mass was 40%. This results shows a better metal extraction performance for the biological acid than the commercial one. The extraction of Mn in S2 increases because of the presence of reducer compounds in the biological leaching medium (see eq. 6).

d. *After-leaching solid characterization:*

From EDS spectrum of the solid leaving after the acid leaching step, it can be observed that two major intensity peaks belong to Mn and O, so it suggested that the principal component in the solid after leaching step is a manganese oxide. No other metals are present in the spectrum in significant concentrations. It indicates that the bioleaching solid residue is one of the reusable products from the process. X ray analysis of this solid calcined at 500°C shows the presence of Mn₂O₃. BET surface area was 7 m² g⁻¹.

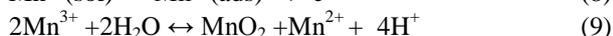
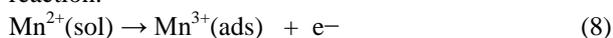
C. Metal recovery from leachate:

a. *Electrolysis:*

During electrolysis experiments, zinc metallic was deposited in the cathode, eq. (7), and a brown thin powder, which is supposed to be a manganese oxide, in the anode. It was also observed a change in the colour of the electrolytic bath, from uncoloured to green; it could be a consequence of electrode corrosion, especially in the anode, which showed a mass loss at the end of the electrolysis.



During manganese dioxide electrodeposition in the leaching acid solution, the reactions are eq. (8) for the anodic oxidation, and eq. (9) for the disproportionation reaction.



Mn^{2+} ions produced returns into the solution leaving a cation vacancy on the deposit surface. In this oxidation, more H^{+} are formed, so acidity grows up in the electrolytic bath (Aldekani *et al.*, 2007).

After 68 hours of electrolysis, 36% of manganese and 66% of zinc could be recovered from the leaching solution. pH changed from 5 to 1.8. Low efficiency in the recovery of manganese could be a consequence of the regeneration of cation Mn^{2+} in the disproportionation reaction, equation (9), and the mass loss of the anodic deposit in the filtration step. Efficiency in the recovery of zinc could be affected by low pH (1.5) at the end of the electrolysis, metallic zinc can be dissolved in that acid medium.

Current efficiency was for both deposits, less than 10%, this parameter can be lowered by H_2 evolution caused by impurities in the solution; and by the low concentrations of both metals in the electrolytic bath (9000 ppm Zn and 4000 ppm Mn) (Souza and Tenorio, 2004).

b. Characterization of anodic and cathodic deposit:

X-Ray diagrams shows the presence of Mn_2O_3 in the solid calcined at 500°C .

BET surface areas of the sample calcined at 400°C was $442.4397 \text{ m}^2/\text{g}$, and for the sample calcined at 500°C , it was $44.04 \text{ m}^2/\text{g}$. That difference in the areas could be a consequence of a change of phases in the calcination step. Acid digestion and atomic absorption characterization of the deposits indicates a 90% of purity for the cathodic deposit (metallic Zn) and a 82% for the MnOx . The main impurity was Fe from the anodic corrosion. SEM micrograph (fig.8) shows that anodic deposit present a laminar morphology.

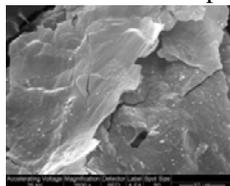


Figure 7. SEM micrograph for the anodic deposit.

III. CONCLUSIONS

The research demonstrated that biological sulphuric acid and polythionates allow the recovery of metals contained in alkaline and Zn-C batteries, with better efficiency than a commercial sulphuric acid of the same concentration (in particular for the manganese), due to the presence of polythionates in the first one. The optimised operation conditions of the biological reactor determined in this work are: 8 kg sulphur mass (-3.5 and +5 mesh), 10 L mineral medium, 138 L/h air flow, end point of the batch culture 350 proton mM. This bioreac-

tor was installed 5 years ago, and is still producing biological sulphuric acid and polythionates.

The biological production of sulphuric acid is under the cost of a commercial one and can be reduced even more (mineral medium composition optimisation, end point of the culture, design parameters of the reactor, incrementing available sulphur surface).

In the bioleaching reactor, extractions of 100% zinc and 65% manganese were reached and the manganese that was no leached remains as manganese oxide in the solid, one of the products of the process, so is not necessary to extract all the manganese contained in the battery powder. Steel cases firstly separated from the battery powder can be treated with pyrometallurgical process.

In the electrolysis of the leaching liquor, it was obtained in one step at room temperature metallic Zn (90% purity) as the cathodic deposit, and a high surface manganese oxide as the anodic deposit (85% purity) The main contaminant of both deposits is Fe that comes from the anodic corrosion. Low efficiency in this step may be caused by H_2 evolution during electrolysis, anode corrosion, impurities, and low concentration of metals in the electrolytic bath. The electrolytic reactor efficiency can be improved in next works, for example, using more concentrated leaching solutions and changing electrodes material.

It was demonstrated in this work that metallic Zn and manganese dioxide can be recovered from spent alkaline and Zn-C batteries in a biotechnological pilot plant with the economical and ecological advantages of the biological sulphuric acid and polythionates production.

The recycling costs could be paid in part by selling the metals obtained.

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