

## EVALUATION OF DIFFERENT LEACHING SOLUTIONS FOR LEAD RECOVERY FROM LEAD-ACID BATTERIES

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### ABSTRACT

Lead recovery from non-metallic portion of the active material of exhausted lead-acid batteries, also called sludge was investigated using the electrohydrometallurgical process. Among thirteen aqueous solutions studied, only the following three were used in the electrowinning processes: tetrafluorboric acid (200 g/L), glycerol (92 g/L) + sodium hydroxide (120 g/L) and sodium and potassium tartarate (150 g/L) + sodium hydroxide (150 g/L). The tetrafluorboric acid showed an attractive performance as leaching electrolyte, due to its low cost and reasonable strenght of leaching. By leaching the desulfated sludge with this acidic electrolyte, compact, adherent and high-purity (99.989%) lead deposits were produced in the electrowinning process.

### INTRODUCTION

The annual production of automotive batteries in Brazil is approximately 15 million units, from which *ca.* 150,000 tonnes of lead can be recovered. With the new Brazilian government regulations<sup>1</sup> for collection and recycling of discarded batteries, most of the producers of lead-acid batteries established the goal of increasing the usage of lead from recycled batteries to almost 100%. Nowadays, the recovery of lead from exhausted batteries is carried out by the pyrometallurgical route, which causes environmental problems like the emission into the atmosphere of considerable amounts of dust containing lead particulates and sulfur oxides<sup>2</sup>. An alternative route is the electrohydrometallurgical one, as it might meet the environmental requirements<sup>3</sup> and also reduce operating costs. Consequently, a number of pilot plants based on this route have been proposed and investigated<sup>4</sup>.

The electrohydrometallurgical route comprises a preliminary stage in which the exhausted lead-acid batteries are crushed, followed by a separation into sulfuric acid and the plastic, metallic and non-metallic portions. The plastic portion is submitted to reprocessing, the metallic portion is cast into anodes for electrorefining, while the non-metallic portion, also called battery sludge, consists of distinct lead compounds, basically metallic lead, lead dioxide (PbO<sub>2</sub>), lead sulfate (PbSO<sub>4</sub>) and also lead oxide (PbO). Small amounts of glass, synthetic fibers, carbon, rubber, paper, separators and granular silica may also be present. Due to the low solubility of lead sulfate in acidic media, the battery sludge is treated with ammonium (or sodium) carbonate or sodium hydroxide solutions to transform the lead sulfate into lead carbonate or hydroxide (desulfuration process)<sup>5,6</sup>. After the sludge desulfuration, the remaining residue is leached using a suitable electrolyte to solubilize the lead compounds; lead is then recovered from solution by electrowinning using insoluble anodes. The major problem associated with lead electrowinning in acidic media is that lead is deposited in the dendritic form on the cathode simultaneously with the parasitic formation of PbO<sub>2</sub> on the anode<sup>3</sup>. An alkaline electrolyte has also been proposed for lead electrowinning, giving a stable electrolysis process<sup>7,8</sup>.

Most of the works reported in papers and patents concerning the recovery of lead from lead-acid batteries start from a sludge with metallic lead and antimony contents of 13%<sup>9</sup>. This is very important because during the acidic leaching these metals react spontaneously with dioxide lead also present in the sludge, reducing most of the Pb<sup>4+</sup> ions to Pb<sup>2+</sup>. The sludges used by Brazilian battery companies contain less than 5% of metallic lead<sup>10</sup>. Thus, the electrohydrometallurgical processes described in the literature are not totally appropriate for the Brazilian case. In the present experimental work, carried out at laboratory scale, the main objective was to develop a

suitable and competitive process for lead recovery from sludge obtained from Brazilian lead-acid batteries. Leaching and electrowinning processes using aqueous alkaline and acidic electrolytes were investigated.

## EXPERIMENTAL

### Sludge origin and treatment

The investigations were carried out with samples of an industrial sludge provided by Plajax Indústria e Comércio de Plásticos Ltda. (Bauru, SP, Brazil). The lead oxide (PbO), lead dioxide (PbO<sub>2</sub>), lead sulfate (PbSO<sub>4</sub>) and metallic lead (Pb) contents in the sludge were determined by EDTA titrations. Mineralogical characterization was carried out using a Siemens D5000 X-ray diffractometer.

The sludge was firstly treated with sodium hydroxide (NaOH) in order to convert all the lead sulfate (PbSO<sub>4</sub>) to lead hydroxide [Pb(OH)<sub>2</sub>]. For this desulfuration process, a mixture of sludge, sodium hydroxide and water in the mass ratio 100:18:75 was vigorously stirred during 1 h using a magnetic stirrer.

### Solubility tests

Samples (near 1 g) of original sludge, as well as pure PbO, PbO<sub>2</sub>, PbSO<sub>4</sub> and Pb analytical grade were submitted to qualitative solubility tests in 10 mL of the following aqueous electrolytes: **1** - concentrated sulfuric acid; **2** - tetrafluorboric acid (200 g/L); **3** - metanosulfonic acid (400 g/L); **4** - saturated oxalic acid; **5** - citric acid (384 g/L); **6** - glycerol (184 g/L); **7** - sodium hydroxide (120 g/L); **8** - glycerol (92 g/L) + sodium hydroxide (120 g/L) g; **9** - ascorbic acid (10 g/L); **10** - glycerol (92 g/L) + sodium hydroxide (120 g/L) + ascorbic acid (10 g/L); **11** - glycerol (92 g/L) + ascorbic acid (10 g/L); **12** - acetic acid (360 g/L); **13** - sodium and potassium tartarate (150 g/L) + sodium hydroxide (150 g/L).

### Leaching tests

From the solubility tests, only the aqueous electrolytes 2, 10 and 13 were used in the leaching tests. Thus, mixtures of the original or desulfated sludges with the mentioned electrolytes were prepared in the ratio 200 g of sludge per liter of electrolyte and stirred for different times. The content of Pb<sup>2+</sup> ions in the resultant solutions was determined by EDTA titration.

### Electrowinning tests

Firstly, the electrowinning tests were carried out using aqueous electrolytes obtained by dissolving analytical grade PbO in electrolytes 2, 10 and 13 (100 g/L).

The electrowinning tests were carried out under magnetic stirring in a glass cell of about 600 mL equipped with three electrodes: a strip from an AISI-304 stainless-steel foil (Acesita) as cathode (15 cm<sup>2</sup>) and two graphite bars as anodes (80 cm<sup>2</sup>), for the acidic electrolyte, and three strips from the same stainless-steel foil, one being the cathode (10 cm<sup>2</sup>) and two others the anodes (20 cm<sup>2</sup>), for the alkaline electrolytes. Phosphoric (1 g/L) and boric (10 g/L) acids were used as additive only in the acidic electrolyte. Animal gelatin (2 g/L) was also used as additive in both acidic and alkaline electrolytes. Different current densities (200, 250, 300, 350, 400, 450 and 500 A/m<sup>2</sup>) were used for a time necessary to consume approximately 60% of the initial Pb<sup>2+</sup> concentration in the electrolytic bath (200 mL of acidic or alkaline electrolyte in which the Pb<sup>2+</sup> concentration was 100 g/L). Current was applied using a Dawer PS3003D DC Power Supply and monitored with a Dawer DM-1010 multimeter. The cell voltage was monitored with a Minipa ET-20002 multimeter.

From the electrowinning tests, only the tetrafluorboric acid was chosen for leaching samples of desulfated sludge. The recovery of lead from the resultant acidic solution was carried out using the same experimental conditions above described. In order to evaluate the purity of the electrowinned lead, possible minor elements were analyzed using a Varian Spectrophotometer (SpectrAA 10 Plus). The quality of the lead deposit was evaluated using an Olympus Inverted Metallurgical Microscope (model PME).

## RESULTS AND DISCUSSION

According to Plajax Indústria e Comércio de Plásticos Ltda., after crushing and washing operations the solid components of lead-acid batteries are: grids (28%), polypropylene (8%), sludge (48%) and other residues such as PVC separators, rubbers, ebonite, fibers, organic additives etc. (16 %). The battery grids contain more than 90% of metallic lead and are readily remelted. The battery sludge, however, is more complex and is known to contain PbSO<sub>4</sub> in addition to a number of other lead compounds. X-ray diffraction analysis of the battery sludge showed the presence of PbSO<sub>4</sub>, PbO (litharge), PbO.PbSO<sub>4</sub>, α-PbO<sub>2</sub> and metallic Pb, which is in agreement with the literature<sup>6</sup>.

The washing operation of the battery sludge led to a solution of pH 6 indicating the absence of sulfuric acid. The contents of the lead compounds in the original and desulfated sludges, determined by EDTA titrations, are summarized in Table 1. In both original and desulfated sludges a heterogeneous and pulverized residue was found; it consists probably of polypropylene, silica, PVC etc. As shown in Table 1, the battery sludge comprises major amounts of PbSO<sub>4</sub> and PbO<sub>2</sub> together with minor amounts of PbO and metallic Pb. Therefore, near 70% of the original sludge can be recovered as pure Pb. The PbSO<sub>4</sub> content in the desulfated sludge was negligible, demonstrating the efficiency of the desulfuration process used. The high PbO<sub>2</sub> content in both original and desulfated sludge represents the major problem for the leaching process. While PbO and Pb(OH)<sub>2</sub> are readily dissolved by most of the leaching electrolytes, PbO<sub>2</sub> requires the reduction of Pb<sup>4+</sup> to Pb<sup>2+</sup> prior to the leaching process.

Table 1 - Chemical composition of a typical sludge.

Compound	Sludge composition / %	
	Original	Desulfated
PbSO <sub>4</sub>	50	< 0.1
Pb(OH) <sub>2</sub>	-	52
PbO <sub>2</sub>	28	35
PbO	9	-
Metallic Pb	4	8

All the observations of the solubility studies of the original sludge in different aqueous electrolytes are summarized in Table 2. The following decreasing order of strenght of leaching was found: 2 ≅ 8 ≅ 10 ≅ 11 > 9 ≅ 12 ≅ 13 ≅ 7 >> 1 ≅ 3 ≅ 5. The sludge sample was completely leached in the ascorbic acid solution (9), but after 24 h the formation of undesirable solid residue was observed. The sludge and PbO samples were not leached in the saturated oxalic acid (4) and the glycerol (6) solutions. For most of the electrolytes used, a solid residue, probably of PbO<sub>2</sub>, was observed at the end of the solubility tests. This occurred due to the low content of metallic lead in the sludge, which does not favor the reduction of Pb<sup>4+</sup> to Pb<sup>2+</sup> during the solubility studies.

From the obtained results of the solubility tests, the following aqueous electrolytes were selected for the quantitative leaching tests of the original and desulfated sludges: (i) sodium and potassium tartarate (150 g/L) + sodium hydroxide (150 g/L), (ii) glycerol (92 g/L) + sodium hydroxide (120 g/L) and (iii) tetrafluorboric acid (200 g/L). The strenght of leaching was evaluated determining the Pb<sup>2+</sup> concentration and the weight of solid residue after the leaching tests (see Figures 1, 2

and 3). For the original sludge, electrolyte (i) presented the best strenght of leaching followed by electrolyte (iii). However, a large amount of solid residue was observed when electrolyte (iii) was used, due to the presence of the insoluble lead sulfate in the sludge. When solution (ii) was used, the amount of solid residue (white color) was increased as the leaching time increased. A possible saponification reaction may probably explain the formation of such residue. For the desulfated sludge the electrolytes (i) and (iii) presented similar strenght of leaching.

Table 2 - Solubility tests for original sludge and lead compounds.

solution	time	sludge	Pb	PbO	PbO <sub>2</sub>	PbSO <sub>4</sub>
1	1h	i	i	s	i	i
	1d	p	i	s	i	i
2	1h	p	i	s	i	i
	1d	p	i	s	i	i
3	1h	i	i	s	i	i
	1d	i	i	s	i	i
4	1h	i	i	i	i	i
	1d	i	i	i	i	i
5	1h	i	i	s	i	i
	1d	i	i	s	s	i
6	1h	i	i	i	i	i
	1d	i	i	i	i	i
7	1h	i	i	i	i	s
	1d	i	i	i	i	s
8	1h	p	i	s	i	s
	1d	s	i	s	p	s
9	1h	p	i	s	s	i
	1d	p	i	s	s	i
10	1h	s	i	s	s	s
	1d	s	i	s	s	s
11	1h	p	i	s	s	i
	1d	p	i	s	s	i
12	1h	i	i	s	i	s
	1d	p	i	s	i	s
13	1h	i	i	s	i	s
	1d	p	i	s	i	s

s: soluble; p: partially soluble; i: insoluble; h: hour and d: day.

The results obtained for the electrowinning of lead from electrolytes prepared by dissolving analytical grade PbO in the above three electrolytes [(i), (ii) and (iii)] are summarized in Table 3. Cathodic current efficiency (CCE), specific energy consumption (SEC), cell potential and the quality of the lead deposits were estimated and compared among the different electrolytes used.

Although the lead deposits had been compact for the three electrolytes used, high values of cathodic current efficiency (99%) were obtained only for tartarate and tetrafluorboric acid. Despite of lower specific energy consumption obtained for the tartarate electrolyte, only the tetrafluorboric acid one was chosen for the electrowinning tests at different current densities due to its low cost. The obtained results in these experiments are presented in Table 4. As the current density increased, the specific energy consumption and the cell potential increased while the cathodic current efficiency was practically constant. On the other hand, the quality of the deposits was strongly affected by the current density; good lead deposits were obtained only for current densities values lower than 350 A/m<sup>2</sup>. Coincidentally, the graphite anodes are less deteriorated for this same current density range.

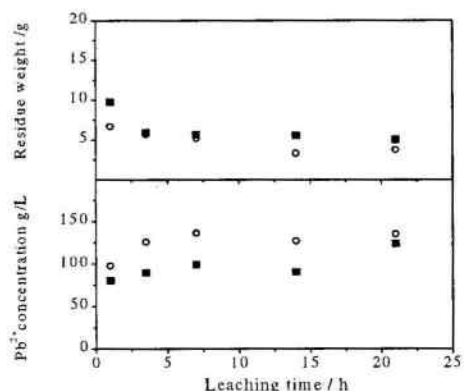


Figure 1 - Pb<sup>2+</sup> concentration and weight of solid residue for the leaching tests of (O) original and (■) desulfated sludges using sodium and potassium tartarate (150 g/L) + sodium hydroxide (150 g/L).

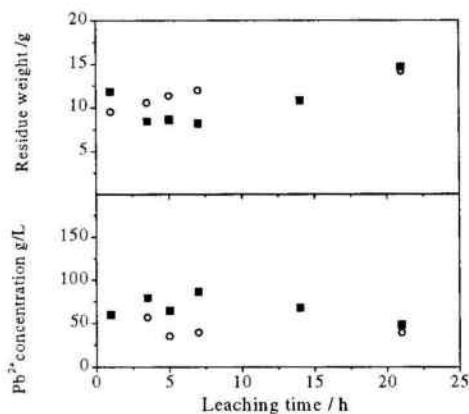


Figure 2 - Pb<sup>2+</sup> concentration and weight of solid residue for the leaching tests of (O) original and (■) desulfated sludges using glycerol (92 g/L) + sodium hydroxide (120 g/L).

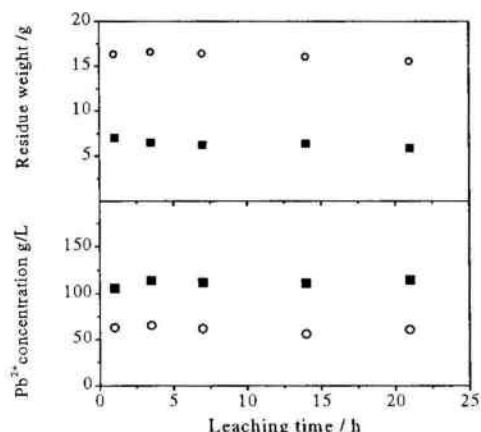


Figure 3 - Pb<sup>2+</sup> concentration and weight of solid residue for the leaching tests of (O) original and (■) desulfated sludges using tetrafluorboric acid (200 g/L).

Table 3 - Cathodic current efficiency (CCE), specific energy consumption (SEC), cell potential (*E*) and the quality of lead deposits for different electrolytes.

Electrolyte	CCE %	SEC W h / kg	<i>E</i> / V	Quality deposit
(i)	99 <sup>(a)</sup>	390	1.48 - 1.55	C
(ii)	90 <sup>(a)</sup>	430	1.43 - 1.70	C
(iii)	99 <sup>(b)</sup>	590	2.25 - 2.30	C

(i) sodium and potassium tartarate (150 g/L) + sodium hydroxide (150 g/L), (ii) glycerol (92 g/L) + sodium hydroxide (120 g/L) and (iii) tetrafluorboric acid (200 g/L); <sup>(a)</sup> *i* = 200 A/m<sup>2</sup>; <sup>(b)</sup> *i* = 250 A/m<sup>2</sup>; C: compact and adherent deposit.

Table 4 - Cathodic current efficiency (CCE), specific energy consumption (SEC), cell potential (*E*) and the quality of lead deposits for different current densities.

<i>i</i> A/m <sup>2</sup>	CCE %	SEC W h / kg	<i>E</i> / V	Quality deposit
250	99	590	2.25 - 2.30	C
300	99	610	2.30 - 2.50	C
350	99	600	2.30 - 2.40	C
400	99	625	2.30 - 2.45	C + D
450	99	622	2.30 - 2.45	C + D
500	99	650	2.50 - 2.70	D

C: compact and adherent deposit; D: dendrite deposit; C + D: compact in the center and dendrite in the corners.

Taking into account all the obtained results with the previous electrowinning tests and also the lower cost of the tetrafluorboric acid, the recovery of



lead from samples of desulfated sludge was carried out using only this acid. For these experiments, the leaching time used was always 1 h. The electrowinning tests were performed at a constant current density of 250 A/m<sup>2</sup>.

From various experiments, the values of cathodic current efficiency (CCE), specific energy consumption (SEC), cell potential (*E*) were very similar to those presented in the Table 4, for the same current density. Compact and adherent lead deposits were obtained in all cases. Moreover, a high-purity lead (99.989%) was produced with the electrohydrometallurgical process used, as shown by chemical analysis relating to possible trace element (see Table 5).

Table 5 – Composition (weight percent) of the metallic lead recovered from sludge of lead-acid batteries.

<b>Pb</b>	<b>Sb</b>	<b>Sn</b>	<b>Se</b>	<b>As</b>
99.989	0.001	0.002	<0.001	0.001
<b>Zn</b>	<b>Ni</b>	<b>Fe</b>	<b>Bi</b>	<b>Cu</b>
<0.001	<0.001	0.001	0.002	0.002

## CONCLUSIONS

Unlikely the case for other countries, Brazilian sludge obtained from exhausted lead-acid batteries contains a low content of metallic lead. Due to this fact, none of the leaching electrolytes investigated here totally dissolved such sludge. Lead dioxide was the majority component in the solid residues of the leaching tests.

Tetrafluoroboric acid showed an attractive performance as leaching electrolyte, due to its low cost and reasonable strength of leaching. When the desulfated sludge was leached with this acidic electrolyte, compact, adherent and high-purity (99.989%) lead deposits were produced in the electrowinning tests. Therefore, the electrohydrometallurgical process used presented a suitable and competitive performance for lead recovery from sludge of exhausted lead-acid batteries.

## ACKNOWLEDGEMENTS

The scholarships granted by RHAECNPq (contract no. 610044/98-2) to authors L. C. F., L. O. R., R. A. D. and D. J. C. and by CNPq to author A. R. F. are gratefully acknowledged.

## REFERENCES

- [1] CONAMA (Conselho Nacional do Meio Ambiente), Resolution No. 257, June 30<sup>th</sup>, 1999. Diário Oficial da União (DOU), July 22<sup>th</sup>, 1999. Reproduced in *Saneamento Ambiental*, **61**, 30, 1999.
- [2] H. Valdez, "Lead battery markets and recycling in Mexico and South America", *Journal of Power Sources*, **67**, 219, 1997.
- [3] M. Maja, S. Bodoardo, C. Serracane, R. Baudino, "Dissolution of pastes in lead-acid battery recycling plants", *Journal of Applied Electrochemistry*, **23**, 819, 1993.
- [4] R. D. Prengaman, "Recovering lead from batteries", *JOM*, **47**, 31, 1995.
- [5] A. G. Morachevskii, "New lines in lead battery scrap recycling", *Russian Journal of Applied Chemistry*, **70**, 3, 1997.
- [6] T. T. Chen and J. E. Dutrizac, "The mineralogical characterization of lead-acid battery paste", *Hydrometallurgy*, **40**, 223, 1996.
- [7] C. Weiping, T. Yizhunang, B. Kerun, Z. Yue, "Basic electrolytic method for recovery of lead from scrap batteries", *Transactions Nonferrous Met. Soc. China*, **6**, 47, 1996.
- [8] C. Weiping, C. Fancai, P. Yanbing, L. Qizhong, B. Kejun, Z. Yue, "Cathode electrodeposition of lead in Pb<sup>2+</sup>-OH-C<sub>4</sub>H<sub>4</sub>O<sub>6</sub><sup>2-</sup> system", *Transactions Nonferrous Met. Soc. China*, **7**, 154, 1997.
- [9] M. Maja, N. Penazzi, M. Baudino and M. V. Ginatta, "Recycling of lead/acid batteries: The Ginatta Process", *Journal of Power Sources*, **31**, 287, 1990.
- [10] Plajax Indústria e Comércio de Plásticos Ltda. (Bauru, SP, Brazil). Inner Report, August, 1999.