

## Lead electrowinning in an acid chloride medium

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### Abstract

The results of an investigation of the electrowinning of lead employing a chloride medium are reported. The electro-deposition lead reaction was studied by voltammetric methods and scanning electron microscope (SEM) microphotographs of the electro-deposited lead were taken. The effects of current density, temperature, catholyte flow and  $H^+$  concentration were investigated at laboratory scale to optimise operating conditions in order to found adequate values for industrial purposes of the parameters energetic cost and production. For a working current density of  $100 \text{ mA/cm}^2$  the current efficiency, energy consumption and production were 90%,  $1.32 \text{ kW h/kg Pb}$  and  $83.4 \text{ kg Pb/m}^2$  per day, respectively. © 2001 Elsevier Science B.V. All rights reserved.

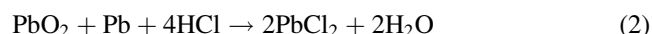
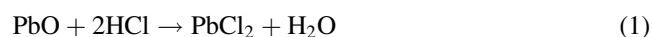
*Keywords:* Lead; Electrowinning; Chloride bath; Voltammetric study

### 1. Introduction

Within the next few years, the percentage of recycled lead acid batteries in the European Union must increase to almost 100% in agreement with new regulations. At the moment, the recovering of lead from batteries is carried out by pyrometallurgical processes [1]. However, these processes have important drawbacks. First, emissions of lead and  $SO_2$  fumes during pyrometallurgical smelting are very hard to control being difficult and expensive to meet the emission levels promulgated by environmental laws. Second, the lead obtained must be of high purity to be suitable for manufacturing maintenance free batteries [2].

For these reasons, in the last two decades there has been an increasing effort to recycle lead from scrap batteries using electrolytic methods [3–8]. These processes consist in a three-step treatment. After a first step for breaking the batteries and separating the plastic compounds and grids, the next one is the hydrometallurgical processing of these scrap batteries. At the end of this stage a solution with a high concentration of  $Pb^{2+}$  ions is obtained. Fluoboric, fluosilicic and hydrochloric acids have been used as leaching solutions. The last step is the electrowinning of lead. A typical bath for lead electrowinning is the fluoborate one and the deposition process of lead in this electrolyte has recently been studied [9].

The lead recovery from lead oxide secondaries (LERE-FLEOS) process [10] has been developed for the recovering of lead from scrap batteries. In this process, the leaching step is carried out at  $80^\circ\text{C}$  in a solution containing  $HCl$  and  $NaCl$  at high concentration. During the leaching step, the general reactions taking place are [10]:



Lead chloride is a relatively slightly soluble salt. In presence of high concentrations of chloride,  $Pb^{2+}$  ions can form different soluble complexes such as  $PbCl^+$ ,  $PbCl_3^-$  and  $PbCl_4^{2-}$  [11].

Impurities in solution such as  $Cu$ ,  $Bi$ ,  $As$ ,  $Sb$ , etc, can be removed by reduction using powder lead according to reaction (4):



The next step, electrowinning, is carried out in a tank reactor with compartments separated by a cationic membrane in order to avoid lead dioxide formation and chlorine evolution at the anode. The anolyte is a sulphuric solution and a dimensionally stable anode for oxygen evolution (DSA- $O_2$ ) anode is employed. The LEREFLEOS process uses a scrapper to remove the lead deposit from the cathode. The deposit must have negative buoyancy because is collected at the bottom of the tank by a mechanic system. To avoid positive buoyancy the hydrogen evolution must be

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low. Ti metal was selected as cathode because the lead deposit is not strongly adhered on the surface and can be easily removed by mechanical scrapping. Moreover on this electrode the hydrogen evolution at the beginning of the deposit is not high,

The aim of this paper is to study the electrodeposition of lead in an acid chloride medium from both fundamental and applied points of view. First, the deposition process is studied by means of cyclic voltammetry and after that a more applied study in which parameters such as current efficiency (CE) and physical properties of the lead deposit are optimised is carried out.

## 2. Definition of parameters of interest

### 2.1. Current efficiency

Current efficiency is defined as the percentage of electrical charge used for the desired reaction related to the total charge passed.

$$CE\% = \frac{\text{Charge used for the deposit of lead}}{\text{Total charge passed}} \times 100 \quad (5)$$

### 2.2. Energy consumption (EC)

This parameter can be defined as the electric energy needed to obtain a given amount of product. Normally, it is expressed in kW h per kg of product obtained. For a reaction such as  $A + ne^- \leftrightarrow bB$ , EC is given as:

$$EC \left( \frac{\text{J}}{\text{kg B}} \right) = \frac{E_{\text{cell}} F}{M_B CE\%(b/n)} \times 10^3 \times 10^2 \quad (6)$$

where  $M_B$  is the molecular weight of B (g/mol),  $b$  the stoichiometric coefficient of B,  $n$  the number of electrons,  $F$  the Faraday's constant (96487 C/mol) and  $E_{\text{cell}}$  the cell voltage (V). If we substitute the value of  $F$ , and EC is given in kW h/kg B, the following equation is obtained:

$$EC \left( \frac{\text{kWh}}{\text{kg B}} \right) = \frac{2680.55 E_{\text{cell}}}{M_B CE\%(b/n)} \quad (7)$$

### 2.3. Production (P)

This parameter is defined for a given current density as the mass of product expressed in kilograms per day per  $\text{m}^2$ . For the reaction  $A + ne^- \leftrightarrow bB$ ,  $P$  is given as

$$P \left( \frac{\text{kg B}}{\text{m}^2 \times \text{day}} \right) = \frac{Q CE\% M_B}{F(n/b)} \times 10^{-2} \times 10^{-3} \times \frac{1}{A} \times \frac{j A^2 \times 3600}{Q} \quad (8)$$

$$P \left( \frac{\text{kg B}}{\text{m}^2 \times \text{day}} \right) = \frac{b}{n} CE\% j M_B 8.95 \times 10^{-6} \quad (9)$$

where  $j$  is given in  $\text{A}/\text{m}^2$  and  $M_B$  in g/mol.

## 3. Experimental

### 3.1. Voltammetric study

Electrochemical experiments were made using a VOLTALAB-32 RADIOMETER system. The scanning electron microscope (SEM) and energy dispersive X-ray (EDX) analyses were carried out with a Link X-Ray Analytical System model QX200. Solutions were prepared with ultra-pure water from a MilliQ system. The reactants employed were HCl 37%, NaCl and  $\text{PbCl}_2$  all from Merck p.a. All compounds were used without additional purification. Before each experiment, solutions were de-oxygenated by bubbling  $\text{N}_2$  quality N-50 from L'Air Liquide. The electrochemical cell was made in Pyrex glass without separated compartments. The cell temperature was controlled during the experiments, that were carried out at  $60^\circ\text{C}$ . The working electrodes were a Ti rod (Goodfellow, diameter 2.0 mm, purity 99.6%), and a Cu rod (Goodfellow, diameter 2.9 mm, purity 99.99%). Before each experiment, the electrode was polished and cleaned by standard procedures. Copper was used as cathode in a previous work on lead electrowinning in fluoborate medium [9]. Both metals are no very active for hydrogen evolution that is the competitive reaction for lead deposition in acid medium and show good mechanical and chemical stability at the working experimental conditions. The counter electrode was made of Pt and the reference electrode was a saturated calomel electrode, SCE, model TR-100 from Tacussel.

### 3.2. Laboratory scale plant

Schematic diagrams of the laboratory plant and the filter press reactor are shown in Figs. 1 and 2, respectively. The electrochemical reactor employed in all experiments was a filter press reactor with a geometric area of  $63 \text{ cm}^2$ . Although this reactor is not very convenient for its use in electrowinning, it was chosen because it has very uniform potential and current distributions and defined flow patterns. These facts allow us to obtain very reproducible results and high precision in the measurement of the volume of  $\text{H}_2$  evolved. Moreover, the multi-electrode tank cell developed in the LEREFLEOS European Project [10] has flow patterns very similar to those of a filter press.

As cathodes a Cu sheet, a Ti sheet and a Ti mesh were employed. In all experiments the anode was a DSA- $\text{O}_2$  supplied by Metakem. The separator was a perfluorinated cationic membrane Nafion 117 and the reference electrode was a SCE model TR-100 from Tacussel.

Solutions were prepared with deionized water from a Osmo BL6 system. The products employed for preparing the different solutions were NaOH (99.5%), NaCl (99%) and  $\text{PbCl}_2$  (99%) all of PRS quality and from Panreac and HCl 37% from Merck p.a. Analyses of  $\text{Pb}^{2+}$  solutions were made with an ICP Perkin-Elmer Optima 3000.

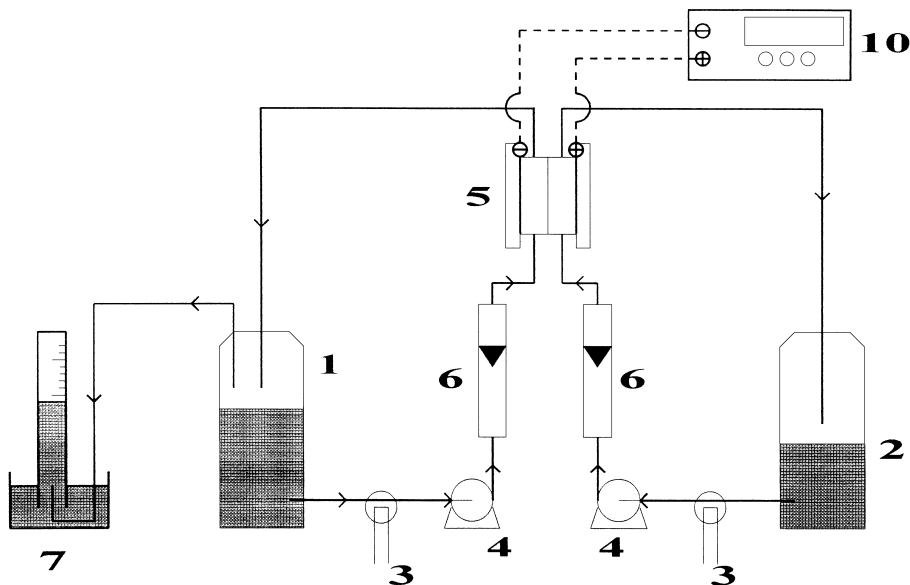


Fig. 1. Schematic illustration of the electrochemical assembly. 1, Catholyte reservoir; 2, anolyte reservoir; 3, heat exchanger; 4, pump; 5, filter press reactor; 6, flowmeter; 7, hydrogen measurement system; 8, power supply.

#### 4. Results

The first step in our work was to carry out a voltammetric study of the lead deposition reaction. The composition of the solution was 4.3 M NaCl + 0.1 M HCl + 0.048 M  $\text{Pb}^{2+}$  and the sweep rate 0.05 V/s. Because the low solubility of  $\text{PbCl}_2$ , the working temperature was 60°C. Fig. 3 shows a voltam-

mogram obtained using a Cu electrode. After starting the sweep at  $-0.30$  V, and during the negative potential going sweep, a reduction peak appears at  $-0.58$  V approximately. This peak corresponds to lead electro-deposition and is controlled by diffusion ( $j_p$  varies linearly with lead concentration and  $v^{1/2}$ ). Hydrogen evolution does not appear until potentials more negatives than  $-1.2$  V, showing that even at

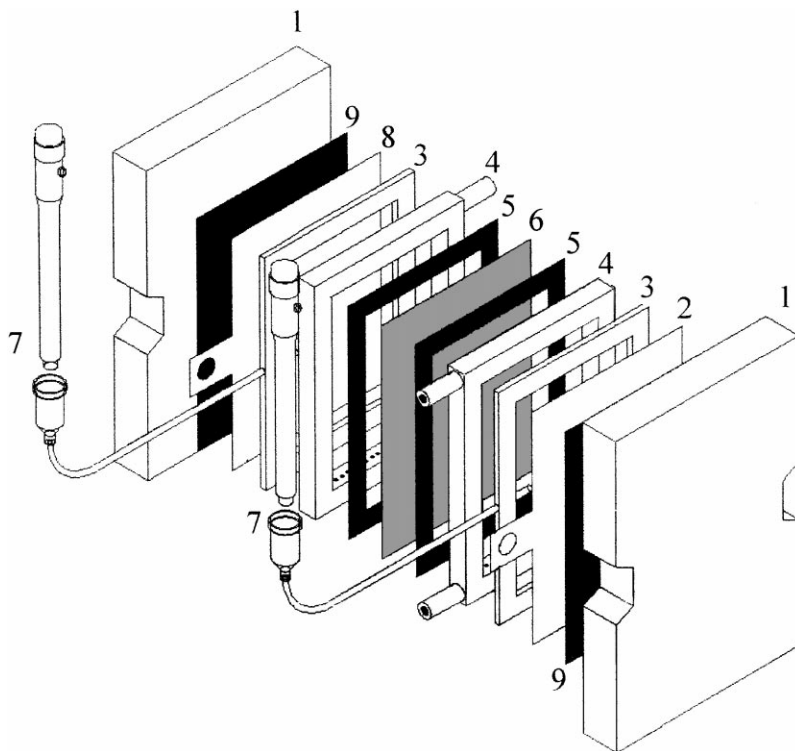


Fig. 2. Scheme of the filter press cell. 1, End plates; 2, cathode; 3, silicon gasket; 4, compartment frame; 5, rubber gasket; 6, cationic membrane; 7, reference electrode; 8, DSA-O<sub>2</sub> anode; 9, insulator gasket.

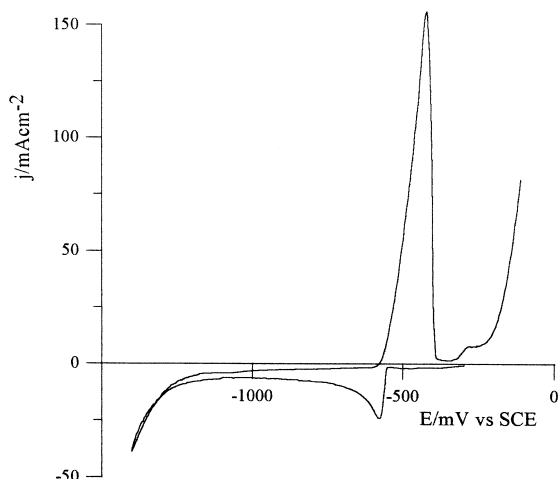


Fig. 3. Voltammetric curve of lead deposit on copper in acid chloride medium. Electrolyte composition and scan rate were 4.3 M NaCl + 0.1 M HCl + 0.048 M  $\text{Pb}^{2+}$  and 0.05 V/s respectively.

the initial stage of lead electro-deposition the current efficiency will be very high. On the other hand, in the positive potential going sweep, an oxidation peak appears at  $-0.42$  V related to the anodic stripping of the lead previously deposited. Approximately at  $-0.3$  V an anodic current that grows quickly appears. This current corresponds to the oxidation of the copper substrate.

Fig. 4 shows the voltammogram of lead electro-deposition on a Ti electrode. The voltammetric profile is very similar to that obtained with the Cu electrode. On Ti, the cathodic peak of lead electro-deposition appears at  $-0.61$  V, and the stripping peak is found at  $-0.37$  V. Hydrogen evolution takes place at  $-1.25$  V approximately. On the other hand, the voltammogram shows that Ti substrate is stable in the working potential range. The voltammetric curves show the characteristic profile of an electro-deposition process. Due to the formation of a new phase, these processes have very peculiar voltammograms which were intensely studied in the 1980s [14–16]. The electro-deposition processes show four different stages: underpotential deposition (UPD), nucleation, diffusion control and dendritic growth. From a general point of view, the UPD is a process where approximately a monolayer of a metal M is deposited on a substrate  $M'$  at a more positive potential than the equilibrium potential  $M^{n+}/M$ . Given that the UPD is strongly influenced by specific interactions between the substrate and the metal to be deposited, we can easily conclude that this process does not appear on all substrates. In our experiments, an UPD process of lead on copper was registered. This result agrees with that obtained for lead electro-deposition on copper in fluoborate medium [9].

Fig. 5 shows a voltammogram obtained in the potential range  $-0.40$ – $0.57$  V on copper. The voltammogram has the characteristic profile corresponding to a metallic deposition process with UPD. It shows the UPD peaks of lead on copper at  $-0.43$  and  $-0.56$  V approximately. Bulk lead deposition

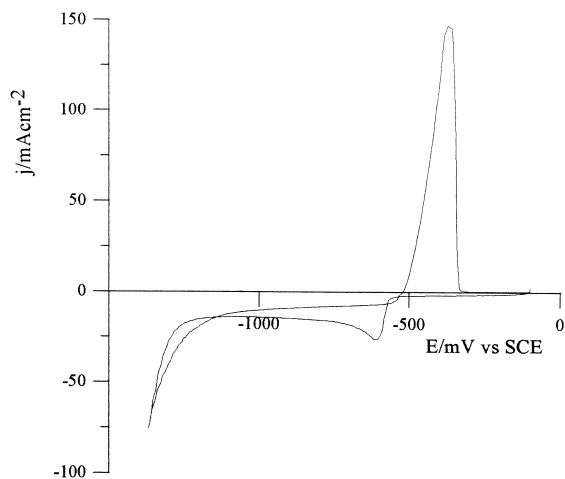


Fig. 4. Voltammetric curve of lead deposit on titanium in acid chloride medium. Electrolyte composition and scan rate were 4.3 M NaCl + 0.1 M HCl + 0.048 M  $\text{Pb}^{2+}$  and 0.05 V/s, respectively.

starts at  $-0.55$  V. The negative going scan is reversed at  $-0.57$  V, where a current loop appears. This unusual feature arises because of the need to form nuclei of the electro-deposited lead on the copper surface. The positive going scan shows a sharp anodic peak due to the stripping of the previously electro-deposited metal. The existence of a UPD process followed by a nucleation one has been previously reported [12,13,17].

Fig. 6 shows a microphotograph of a lead deposit on Ti corresponding to low potentials. The deposit was obtained during the negative sweep with an initial potential of  $-0.10$  V. The final potential was  $-0.57$  V. Small lead crystallites can be seen whose composition was confirmed by EDX analysis.

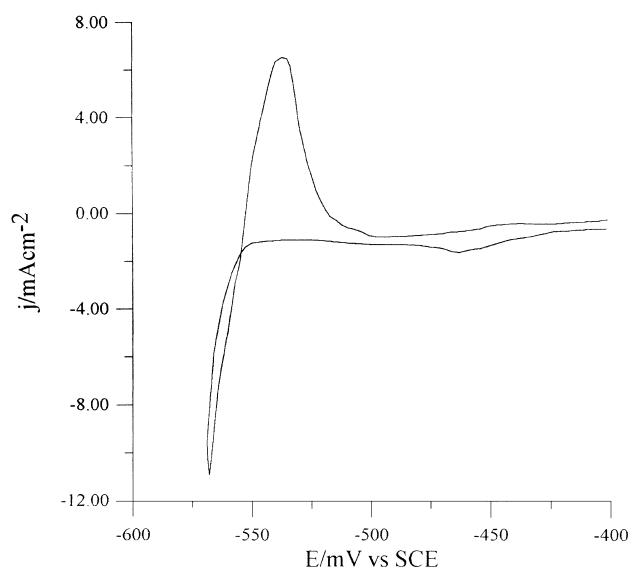


Fig. 5. Voltammetric curve registered in the nucleation controlled region. Electrolyte composition: 4.3 M NaCl + 0.1 M HCl + 0.048 M  $\text{Pb}^{2+}$ . Scan rate: 0.05 V/s. Working electrode Cu.

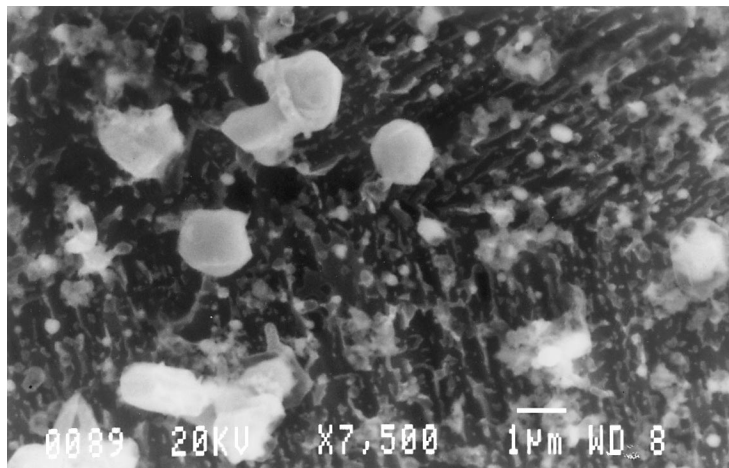


Fig. 6. Microphotography of a Pb deposit formed after the potential scan to  $(-0.575\text{ V at } 0.05\text{ V/s. Electrolyte composition: } 4.3\text{ M NaCl} + 0.1\text{ M HCl} + 0.048\text{ M Pb}^{2+}$ . Working electrode Ti.

In order to obtain lead deposits with good physical characteristics and at the same time high current efficiencies the deposition process was optimised at a laboratory scale. The experimental variables selected were: catholyte composition  $4.3\text{ M NaCl} + \text{XM HCl} + 0.048\text{ M Pb}^{2+}$ , temperature  $60^\circ\text{C}$ . The anode was a DSA- $\text{O}_2$  and the anolyte was a  $1\text{ M NaOH}$  solution.

#### 4.1. Influence of current density

Table 1 shows CE% values for lead deposition and  $\text{H}_2$  formation at three different current densities. It can be seen that, as expected, higher the current density lowers the current efficiency for lead deposition.

All deposits have an adequate adherence that allows to be removed by scrapping although their other physical characteristics were very different. Lead deposited at  $10\text{ mA/cm}^2$  is denser, showing metallic shine and strong adherence. Lead deposited at  $150\text{ mA/cm}^2$  is much spongy and does not present metallic shine. Once detached this deposit has a positive buoyancy. Because of the edge effect, the deposit grows preferentially at the edges of the electrode being this effect more important for higher current densities. Although

Table 1  
Influence of current density on CE% of lead deposit<sup>a</sup>

% Charge	10 mA/cm <sup>2</sup>		100 mA/cm <sup>2</sup>		150 mA/cm <sup>2</sup>	
	CE% <sub>H<sub>2</sub></sub>	CE% <sub>Pb</sub>	CE% <sub>H<sub>2</sub></sub>	CE% <sub>Pb</sub>	CE% <sub>H<sub>2</sub></sub>	CE% <sub>Pb</sub>
25	0	97	0	98	6	93
50	0	98	0	99	3	96
75	0	97	0	98	7	90
100	5	93	12	86	17	81

<sup>a</sup> Catholyte composition:  $4.3\text{ M NaCl} + 0.1\text{ M HCl} + 0.048\text{ M Pb}^{2+}$ , temperature:  $60^\circ\text{C}$ , cathode: Ti mesh and catholyte flow:  $100\text{ l/h}$ . % Charge is the percentage of charge passed related to the theoretical need for total lead deposition.

the highest CE% is obtained at  $10\text{ mA/cm}^2$ , the best working current density for our purposes is  $100\text{ mA/cm}^2$ . There are two main reasons for this choice. First, the production of lead at  $100\text{ mA/cm}^2$  is much higher. Second, the choice is based on the physical properties of the lead deposit. In an industrial electrowinning process, lead must be periodically and easily removed from the cathode and a working current density of  $100\text{ mA/cm}^2$  gives a lead deposit with the appropriate adherence and negative buoyancy.

#### 4.2. Influence of cathode

In this paragraph, the influence of cathode material and geometry on CE% was studied. The influence of the cathode material was checked for Cu and Ti sheets. Ti mesh and Ti sheet were employed for studying the influence of the geometry of the electrode on current efficiency. Table 2 shows CE% values for the three cathodes.

The Ti mesh electrode shows the best value for CE%, and is the only cathode where does not exists evolution of hydrogen at the beginning of the experiment — this fact is important in order to avoid positive buoyancy. There are two main reasons to explain this behaviour. First, the real

Table 2  
Influence of cathode on CE% of lead deposit<sup>a</sup>

% Charge	Ti mesh		Ti sheet		Cu sheet	
	CE% <sub>H<sub>2</sub></sub>	CE% <sub>Pb</sub>	CE% <sub>H<sub>2</sub></sub>	CE% <sub>Pb</sub>	CE% <sub>H<sub>2</sub></sub>	CE% <sub>Pb</sub>
25	0	98	9	89	16	82
50	0	99	4	93	8	91
75	0	98	3	95	5	93
100	12	86	14	82	17	81

<sup>a</sup> Catholyte composition:  $4.3\text{ M NaCl} + 0.1\text{ M HCl} + 0.048\text{ M Pb}^{2+}$ , temperature:  $60^\circ\text{C}$ , cathode: Ti mesh, current density:  $100\text{ mA/cm}^2$  and catholyte flow:  $100\text{ l/h}$ . % Charge is the percentage of charge passed related to the theoretical need for total lead deposition.

Table 3  
Influence of catholyte flow on CE% of lead deposit<sup>a</sup>

% Charge	10 l/h		100 l/h	
	CE%H <sub>2</sub>	CE%Pb	CE%H <sub>2</sub>	CE%Pb
25	31	65	0	98
50	15	80	0	99
75	12	85	0	98
100	23	74	12	86

<sup>a</sup> Catholyte composition: 4.3 M NaCl + 0.1 M HCl + 0.048 M Pb<sup>2+</sup>, temperature: 60°C, cathode: Ti mesh and current density: 100 mA/cm<sup>2</sup>. % Charge is the percentage of charge passed related to the theoretical need for total lead deposition.

area of the mesh electrode is two times the geometric area i.e. the area of the sheet, and the real current density is decreased. Second, the mesh works as a very effective turbulence promoter increasing the mass transport of lead ions to the electrode surface.

#### 4.3. Influence of catholyte flow

Data of CE% for two catholyte flows are shown in Table 3. An increase in the catholyte flow increases the mass transport of the Pb<sup>2+</sup> ions to the electrode and consequently the value of CE% for the lead deposition reaction. The morphology of the deposit does not change with flow.

#### 4.4. Influence of catholyte pH

Table 4 shows CE% values for three different hydrochloric acid concentrations. As expected, the increase in HCl concentration causes an increase in H<sub>2</sub> generation. The H<sub>2</sub> evolved is occluded in the highly divided metal deposit giving a spongy deposit. Moreover, the occluded hydrogen could produce a positive buoyancy to the deposit and this is a big inconvenient for the industrial process.

#### 4.5. Results

Once the lead deposition reaction has been optimised to get high current efficiencies and deposits with negative

Table 4  
Influence of HCl concentration on CE% of lead deposit<sup>a</sup>

% Charge	0.05 M		0.1 M		0.2 M	
	CE%H <sub>2</sub>	CE%Pb	CE%H <sub>2</sub>	CE%Pb	CE%H <sub>2</sub>	CE%Pb
25	0	97	0	98	4	95
50	0	99	0	99	2	97
75	0	98	0	98	2	95
100	5	93	12	86	16	82

<sup>a</sup> Catholyte composition: 4.3 M NaCl + HCl variable + 0.048 M Pb<sup>2+</sup>, temperature: 60°C, current density: 100 mA/cm<sup>2</sup>, cathode: Ti mesh and catholyte flow: 100 l/h. % Charge is the percentage of charge passed related to the theoretical need for total lead deposition.

Table 5  
V<sub>cell</sub>, CE%, P and EC values during the experiment made in the best experimental conditions<sup>a</sup>

% Charge	V <sub>cell</sub> (V)	CE%Pb	EC (kW h/kg Pb)	P (kg Pb/m <sup>2</sup> per day)
25	4.1	96	1.10	89.0
50	4.3	97	1.14	89.9
75	4.4	98	1.16	90.8
100	4.6	90	1.32	83.4

<sup>a</sup> % Charge is the percentage of charge passed related to the theoretical need for total lead deposition.

buoyancy, once detached from the electrode, an experiment using the best experimental conditions was carried out and the energy consumption of lead deposition and production were calculated. Table 5 shows the results obtained for different percentages of the theoretical charge passed.

## 5. Discussion

The results obtained clearly show that the deposition of lead is a process controlled by diffusion on the three electrodes used, smooth and mesh Ti and smooth copper. Under an adequate flow regimen the deposition can be carried out at constant current with high current efficiencies even for current densities as high as 150 mA/cm<sup>2</sup>. Due to its especial characteristics a mesh electrode behaves better than a smooth one, not only because the increase on real area for a given projected area is bigger than for a smooth electrode, but also because the mesh is a very good turbulent promoter. Ti should be chosen because the adherence of the deposit formed is not very high and can easily be mechanically scraped from the surface giving a deposit with negative buoyancy. This deposit can easily be collected at the bottom of the cell by mechanical means [10]. Obviously lower the current density lowers the potential needed for deposition (overpotentials plus ohmic drop) and the energy consumption of the process decrease with current density. However, lower current density means lower production of the cell and for currents lower than 50 mA/cm<sup>2</sup> the production rate is too low for industrial electrowinning of lead. For a current density of 150 mA/cm<sup>2</sup> the lead deposit is too spongy, non adherent and with positive buoyancy and this last point makes this current value unacceptable to be used in an industrial process even the current efficiency is not very low. Thus a current density of 100 mA/cm<sup>2</sup> is a very good candidate for industrial purposes: (i) current efficiency is high; (ii) production is high, 83.4 kg Pb/m<sup>2</sup> per day; (iii) energy consumption is not very high 1.32 kW h/kg Pb and could be improved very easily using a continuous process with a stirred tank reactor with recycle loop in such a way that the lead concentration be no lower than the 25% of the entrance concentration (energy cost 1.1 kW h/kg Pb); (iv) deposit can be easily detached from the surface by mechanical scrapping.

## 6. Conclusions

The current efficiency for lead deposition increases when the working current density and  $H^+$  concentration diminish and when catholyte flow increases. On the other hand, the mesh electrode is a more suitable cathode than smooth ones due to its higher real area and its behaviour as turbulent promoters. Ti is a more convenient material for industrial purposes than Cu because the deposit produced has an adequate adherence and is easily scrapped from the surface. On Cu electrodes the lead deposit is too strongly adhered. In spite of the fact that denser lead deposits can be obtained decreasing the working current density, a current density of  $100 \text{ mA/cm}^2$  has been chosen as the more adequate one for an industrial process, because the production of the cell is higher and the characteristic of the deposit are adequate i.e., it is a not very spongy deposit with negative buoyancy once detached from the electrode. Values of 90% in current efficiency with an energy consumption of  $1.32 \text{ kW h/kg Pb}$  and a production of  $83.4 \text{ kg Pb/m}^2$  per day have been obtained for this current density.

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