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Dissolution of pastes in lead–acid battery recycling plants

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The dissolution of the active materials of lead–acid batteries in fluoboric electrolyte has been studied. The use of redox couples such as Ti^{3+}/Ti^{4+} is proposed for an efficient and quick dissolution of lead and lead dioxide mixtures. For PbO_2 and Pb electrodeposited on platinum electrodes the rate of dissolution in HBF_4 ($200\,g\,dm^{-3}$) containing Ti ions (0.3 M) corresponds to a current density of $400\,A\,cm^{-2}$ and $160\,A\,cm^{-2}$, respectively. Dissolved oxygen has a marked influence on lead dissolution acting as an oxidizer of Ti^{3+} to Ti^{4+}. It has also been shown that the Fe^{2+}/Fe^{3+} couple can be used, although with lower benefits. For industrial applications, a concentration of Ti ions of about 0.05 M and the use of a counter-current electrolyte flow in the electrolysis cell can advantageously accomplish the leaching process of pastes and slimes in a batteries recycling plant.

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1. Introduction

The problem of lead recovery from spent lead–acid batteries has received increasing attention in recent years. Electrochemical processes have been proposed as an alternative to pyrometallurgical methods with the aim of both reducing operating costs and meeting environmental requirements.

Some of these processes [1, 2] include a preliminary stage in which the batteries are crushed, followed by the separation of the metals, plastic material and the active mass, which is mainly composed of lead, lead sulphate and lead dioxide. Because of the very slow spontaneous dissolution of lead sulphate, the active mass is treated with ammonium or sodium carbonate solutions to transform sulphates into carbonates (desulphurization process).

The desulphurized mass so obtained is leached with the acid solution coming from the lead electrolysis cells. For the unleached mass, chemical reagents are used to complete the dissolution of the pastes. At the end of the process, the residual solids are generally treated with a pyrometallurgical method.

In another electrochemical process [3] the batteries, which have been previously subjected to a bottom cutting operation, after an activation stage to eliminate a part of the sulphates, are inserted by means of suitable frames as anodes in cells for lead deposition. In this case the dissolution of the metals and active material is nearly complete. The small amount of residual undissolved materials consists of the muds contained in the spent batteries and the anodic slimes from the electrolysis cells. They are treated in a small section of the plant [4] where desulphurization and leaching are carried out.

Antimony, as Sb_2O_5, and some other elements, are also present in the slimes. These come from the alloys used to manufacture the grids and the internal connections of the batteries. In the pyrometallurgical process these elements are lost in the slags, or remain as impurities in the produced lead. Conversely with the hydrometallurgical process, antimony and the other elements can be recovered from the unleached solids with the electrochemical method.

In the present work the dissolution of lead and lead dioxide mixtures in fluoboric solutions has been studied in order to determine appropriate conditions to decrease the leaching time.

2. The problem

The dissolution of Pb–PbO_2 mixtures in acid media occurs spontaneously when the lead and lead dioxide particles are in contact, as in a short-circuited cell, according to the reaction

$$Pb + PbO_2 + 4H^+ \rightarrow 2Pb^{2+} + 2H_2O \qquad (1)$$

From a practical standpoint, the electric contact between particles is rather poor, due to the presence of a thin layer of poorly conductive oxides and, consequently, Reaction 1 is quite slow.

In industrial applications, Reaction 1 can be used as a first step in the dissolution process. When the processing time becomes too long, chemical reagents [7–12], can be added to the electrolyte for the specific dissolution of lead and lead dioxide. These reagents should be easily regenerated and must not be dangerous. Despite the cost, hydrogen peroxide is currently used [5].

From an electrochemical point of view, any redox couple (e.g. Ti^{3+}/Ti^{4+}, Fe^{2+}/Fe^{3+}), with a standard potential ranging between that of Pb/Pb^{2+} and that of PbO_2/Pb^{2+}, can be used. The redox couple reacts with single particles of the slimes also in fissures and macropores of the scarcely conductive oxide layers, so that it can be effective even when Reaction 1 cannot occur.

The mass balance for the leaching process with an electrolyte containing a redox couple indicates that the molar ratio of reduced and oxidized species at the end of the dissolution depends on the ratio between the masses of lead and lead dioxide initially present in the pastes. No change in the molar fraction of redox reagents can occur under the stoichiometric conditions of Reaction 1. Moreover, the amount of leached mass does not depend on the concentration of the redox couple active species, such concentration being continuously restored. The active species of the couple provide the transfer of electrons from Pb to PbO_2. The redox couple concentration mainly affects the rate of the process.

Some preliminary tests indicated the advantage of employing the Ti^{3+}/Ti^{4+} couple which has a standard potential of 100 mV vs NHE ranging between the Pb/Pb^{2+} and PbO_2/Pb^{2+} potentials, −200 and 1450 mV/NHE, respectively. In fact fluoboric acid solutions containing tri and tetravalent titanium ions quickly dissolve lead and lead dioxide according to the reactions:

$$Pb + 2HBF_4 + 2Ti^{4+} \rightarrow Pb(BF_4)_2 + 2Ti^{3+} + 2H^+ \qquad (2)$$

$$PbO_2 + 2HBF_4 + 2Ti^{3+} + 2H^+ \rightarrow Pb(BF_4)_2 + 2Ti^{4+} + 2H_2O \qquad (3)$$

For nonequimolar Pb/PbO_2 mixtures, the ratio [Ox]/[Red] between the concentrations of the redox couple active species changes with time and the composition of the leaching solution has to be restored by the addition of Pb or PbO_2. If the initial PbO_2/Pb molar ratio is greater than one, a part of the lead produced in the electrochemical plant must be recycled to reduce Ti^{4+} according to Reaction 2. By contrast, lead dioxide must be used to oxidize Ti^{3+}, Reaction 3, when the ratio PbO_2/Pb is lower than one.

The electrochemical reaction

$$Ti^{3+} \rightarrow Ti^{4+} + e^- \qquad (4)$$

must also be taken into account. It occurs as a secondary process in the lead electrolysis cells, affecting the [Ox]/[Red] ratio of the leaching solution.

3. Experimental details

The effect of the addition of titanium ions on the dissolution of lead and lead dioxide has been investigated by means of various electrochemical and leaching tests carried out by using: (i) electrodeposited lead and lead dioxide on a platinum substrate; (ii) mixtures of Pb/PbO_2 powder; (iii) industrial slimes. The Pb and PbO_2 mixtures were prepared from active materials of spent and fresh batteries. Some fresh negative pastes prepared in the laboratory using sodium stearate as an antioxidizer and vanisperse as an expander were also tested to study the organic compounds effect. The composition of the tested slimes from an industial plant [4], before and after desulphurization, is given in Tables 1 and 2.

Table 1. Composition of industrial slimes before desulphurization

Components	*Wt %*
Humidity	14.2
Sulphates	59.4
Lead	11.6
Lead dioxide	12.9
Inert*	1.9
Sb	1.0

*Black carbon, barium sulphate, plastic, glass fibre and oxides of Sb, Sn, Bi, etc.

The electrodes used in the electrochemical tests were platinum or lead foils with a surface area of $1.5\,cm^2$. The counter electrode was a platinum gauze and the reference electrode was a saturated sulphate electrode (SSE). Voltammetric curves were obtained with an Amel System 5000 apparatus connected to an IBM computer. All tests were carried out at 25° C.

Electrolytes were prepared using analytical grade reagents and bidistilled water. Ti^{3+} solutions were obtained by dissolving titanium metal in $200\,g\,dm^{-3}$ HBF_4. (Ti^{4+} ions by the oxidation of Ti^{3+}).

Dissolution of Pb/PbO_2 mixtures was carried out both in a stirred glass reactor and in a glass column having a diameter of 24 mm. In the stirred reactor the material (10–150 g) was treated with $1\,dm^3$ of $200\,g\,dm^{-3}$ HBF_4 solution containing different amounts of titanium ions.

The column was mainly used for the positive active material of the battery plates due to the high reaction rate. The column was of the fixed bed type and the thickness of the bed, consisting of the material to be leached, was 20 mm. The solution flow rate was varied in order to achieve different contact times.

In some tests nitrogen bubbling was employed to deoxygenate the leaching solution.

The analyses of solutions and slimes were carried out using a Perkin–Elmer atomic absorption spectrophotometer.

4. Behaviour of Pb and PbO_2 electrodes

The voltammetric behaviour of a platinum electrode in an acid lead fluoborate solution is illustrated in

Table 2. Composition of industrial slimes after desulphurization

Components	*Wt %*
Carbonates	50–53
Sulphates	2.5–4
Lead	5–7
Lead dioxide	14–16
Lead oxide	11–12

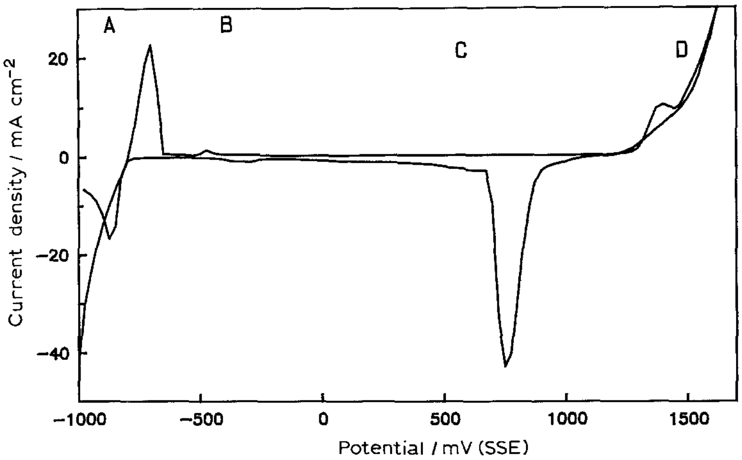

Fig. 1. Voltammetric curves (50 mV s^{-1}) for a platinum electrode in HBF_4 (200 g dm^{-3}) and Pb^{2+} (20 g dm^{-3}).

Fig. 1. The peaks for lead (A,B) and lead dioxide (C,D) deposition and dissolution are evident.

The effect of trivalent titanium ions on the dioxide dissolution is shown in Fig. 2. The intensity of the reduction peak decreases if, for a fixed amount of electrodeposited lead dioxide on platinum, the electrode is maintained at the rest potential for progressively increasing times before the reduction.

The effect of tetravalent titanium ions on lead dissolution is shown in Fig. 3. Again, for a fixed amount of lead deposited on the platinum electrode, the intensity of the oxidation peak decreases when the waiting time at the rest potential is increased. These results indicate that, at the rest potential, Reactions 2 and 3 partially dissolve the electrodeposited material.

Both reactions appear to be very fast. Some potential measurements at zero external current were performed to determine their kinetics and the effect of the lead ion concentration. For these measurements platinum electrodes, covered with lead dioxide or lead, were dipped in a nonstirred fluoboric acid solution containing Ti^{3+} or Ti^{4+} ions. The results are shown in Fig. 4.

At 25° C the kinetic constant for PbO_2 reduction corresponds to a cathodic current density of 400 A m^{-2} independent of the lead ions concentration. A slight influence of the Pb^{2+} concentration was found for lead oxidation; the dissolution rate decreases from 170 to 150 A m^{-2} when the Pb^{2+} concentration is increased from 0 to 30 g dm^{-3}.

As far as the effect of tetravalent titanium ions in lead deposition is concerned, the voltammogram of Fig. 5 shows that the peak for lead deposition occurs at higher potentials than the Ti^{4+} reduction peak. In spite of this, the current efficiency for lead deposition decreases with increasing Ti^{4+} concentration. So, the ratio between Pb^{2+} and Ti^{4+} concentrations in the electrowinning solution must be carefully selected to obtain high cathodic current efficiencies. The tests indicated an efficiency above 90% for $[Pb^{2+}]/[Ti^{3+}]$ greater than 50.

5. Paste dissolution

Figure 6 is relative to mixtures prepared from negative

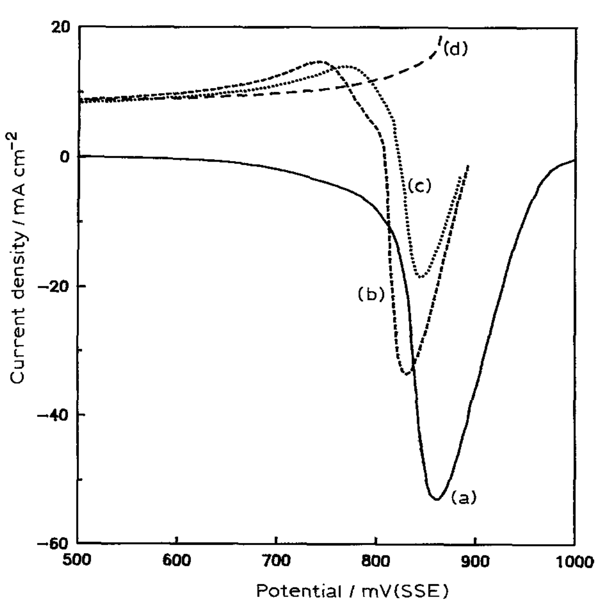

Fig. 2. Influence of $[Ti^{3+}]$ on the dissolution of PbO_2 electrodeposited on platinum (2000 mC cm^{-2}); $[Ti^{3+}] = 0.3$ M, HBF_4 = 200 g dm^{-3}, sweep rate = 5 mV s^{-1}. Curve (a) without Ti^{3+}, (b), (c) and (d) with Ti^{3+} after 0 min, 0.5 min and 1 min of dip at rest potential.

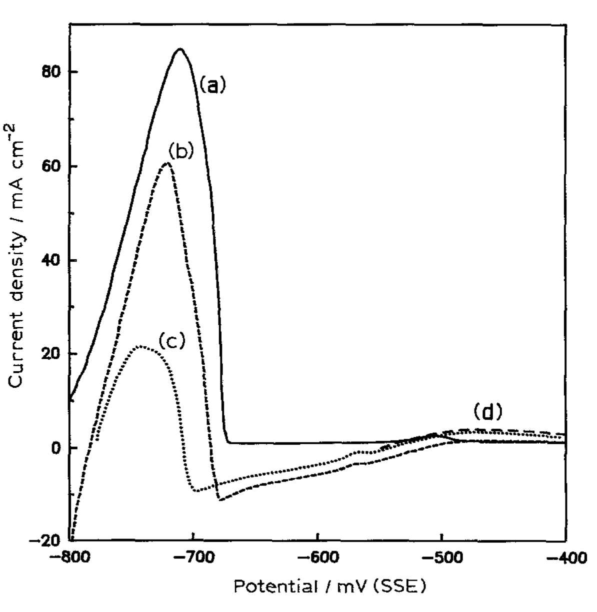

Fig. 3. Influence of $[Ti^{4+}]$ on the dissolution of Pb electrodeposited on platinum (2000 mC cm^{-2}); $[Ti^{4+}] = 0.3$ M, HBF_4 = 200 g dm^{-3}, sweep rate = 5 mV s^{-1}. Curve (a) without Ti^{4+}, (b), (c) and (d) with Ti^{4+} after 0 min, 1 min and 2 min of dip at rest potential.

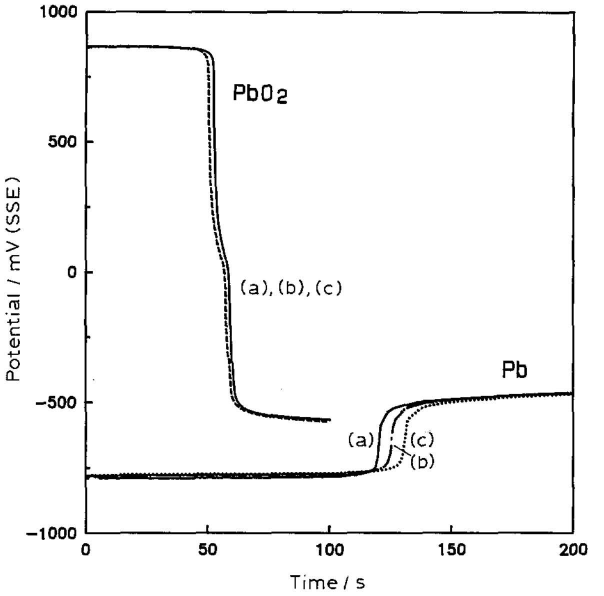

Fig. 4. Rest potential versus time for Pb and PbO_2 electrodeposited on platinum (2000 mC cm^{-2}); [Ti^{4+}] = 0.3 M for Pb and [Ti^{4+}] = 0.3 M for PbO_2, [HBF_4] = 200 g dm^{-3}. [Pb^{2+}] effect: curve (a) 0 g dm^{-3}, (b) 10 g dm^{-3}, (c) 30 g dm^{-3}..

and positive active material of spent batteries. These mixtures dissolve very slowly in pure fluoboric acid. In HBF_4 containing titanium ions, the dissolution rate is quite high and the chemical analyses showed that all metallic lead and lead dioxide is dissolved; the inerts and lead sulphate do not react. In pure fluoboric acid the decrease in the dissolution rate is mainly due to the loss of contact between Pb and PbO_2 particles, while, in the presence of titanium ions, the dissolution rate mainly depends on the active area of the solids. In the first case, taking into account the presence of 10 wt % of $PbSO_4$ and inerts, the reaction rate becomes very low after the dissolution of 30% of the soluble lead for an initial value of the solid/liquid ratio of 0.1. When titanium ions are present, the reaction slows down after the dissolution of more than 85% of the soluble lead. The present tests showed that a complete dissolution is achieved only in the presence of titanium ions.

Reactions 2 and 3 were separately studied by leaching both negative and positive active materials from spent batteries. The dissolution rate of active materials from the positive plates was found to be much higher than that from the negative ones; the rate was so high that it was possible to take measurements during the PbO_2 dissolution only using a leaching column with high electrolyte flow rate. The ratio between the kinetic constants for PbO_2 and lead dissolution is about four times the value found for electrodeposited lead and lead dioxide. The tests do not show a substantial effect of Pb^{2+} concentration on the leaching rate.

The increase in the ratio of the dissolution rates may be due either to a difference between the surface areas of the particles or to the inhibiting effect of the organic compounds commonly used in negative active material preparation. To obtain a deeper insight, pastes were prepared in the laboratory by using sodium stearate as an antioxidant and vanisperse as an expander or, in some cases, only sodium stearate. The results of the tests, performed on these pastes containing 3 wt % of sulphates and inerts, are shown in Fig. 7. Only a slight effect of sodium stearate was found, but this is not sufficient to explain the increase in the ratio between the Pb and PbO_2 dissolution rates, which should be mainly attributed to different specific areas.

The analysis of the results obtained from negative pastes of spent batteries, whose percentage of inerts and sulphates is about 11 wt %, revealed that lead dissolution can occur according to various kinetic mechanisms. As shown in Fig. 8, a remarkable influence of the oxygen dissolved in the electrolyte was observed.

In a titanium oxygen free HBF_4 solution lead cor-

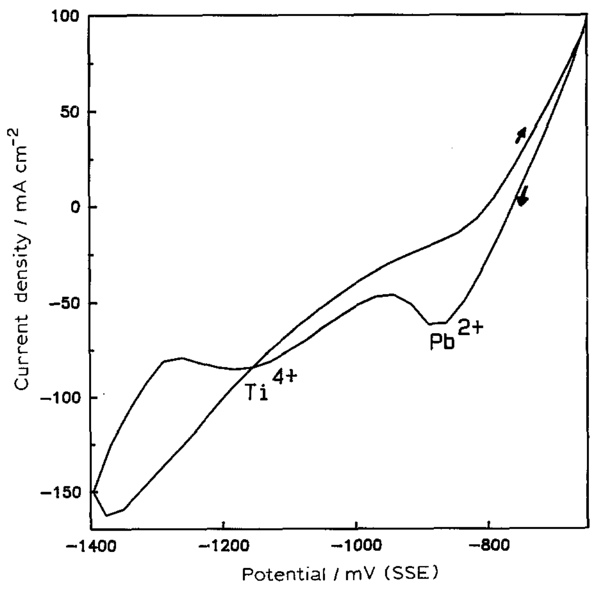

Fig. 5. Voltammetric curves for a lead electrode. [HBF_4] = 200 g dm^{-3} [Pb^{2+}] = 21 g dm^{-3} and [Ti^{4+}] = 0.3 M, sweep rate = 50 mV s^{-1}.

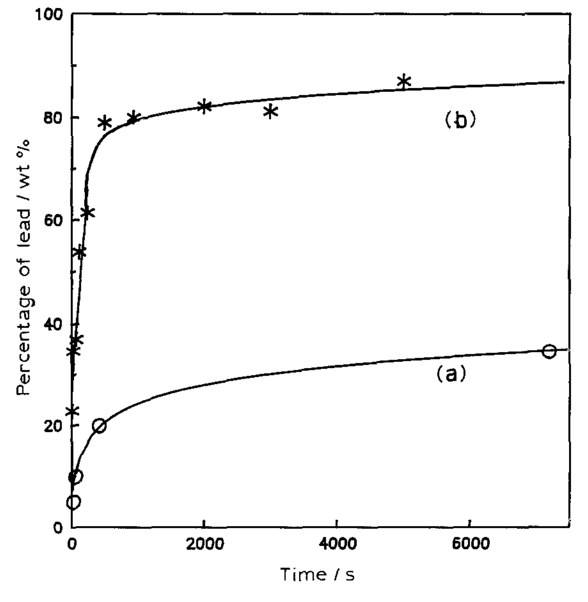

Fig. 6. Dissolution of equimolar Pb/PbO_2 mixtures, containing 10 wt % of $PbSO_4$ and inerts, in fluoboric solutions without (a) and with (b) titanium ions. HBF_4 200 g dm^{-3}, total titanium ions concentration = 0.3 M, mass ratio solid/liquid = 0.1.

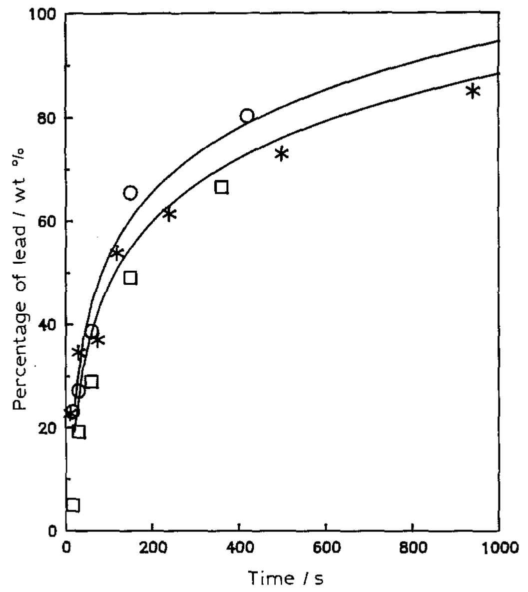

Fig. 7. Dissolution of negative active material, containing 3 wt % of $PbSO_4$ and inerts, prepared with or without organic compounds in aerated solutions. $[HBF_4] = 200\,g\,dm^{-3}$, $[Ti^{4+}] = 0.3\,M$, mass ratio solid/liquid = 0.1. (∗) With organic compounds, (○) without stearate, (□) without vanisperse.

rodes very slowly according to the mechanism:

$$4e^- + O_2 + 4H^+ \rightarrow 2H_2O \qquad (5a)$$

$$2Pb \rightarrow 2Pb^{2+} + 4e^- \qquad (5b)$$

Conversely, in oxygen free HBF_4 solution containing Ti^{4+} ions, the lead dissolves according to the reaction:

$$Pb + 2Ti^{4+} \rightarrow Pb^{2+} + 2Ti^{3+} \qquad (6)$$

In this case, chemical analyses showed that at the end of the reaction the amount of dissolved lead is equivalent to the amount of Ti^{4+} initially present in the electrolyte.

In aerated solutions containing Ti^{4+} the amount of dissolved lead is greater than the equivalent value of Ti^{4+} present. This can be justified by coupling Reaction 6 with Ti^{3+} oxidation, according to:

$$O_2 \rightarrow 2O_{ads}$$

$$2H^+ + O_{ads} + 2Ti^{3+} \rightarrow 2Ti^{4+} + H_2O \qquad (7)$$

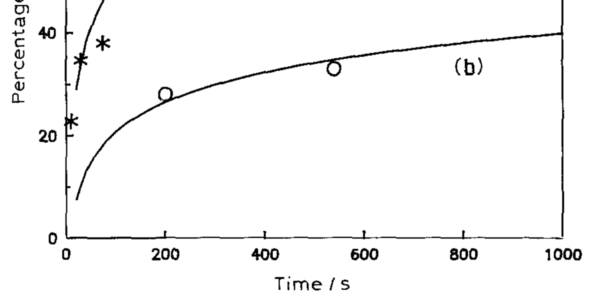

Fig. 8. Dissolution of negative active material, containing 11 wt % of $PbSO_4$ and inerts, in $HBF_4 = 200\,g\,dm^{-3}$, Ti^{4+} containing 0.3 M; (a) aerated and (b) deoxygenated solutions, mass ratio solid/liquid = 0.1.

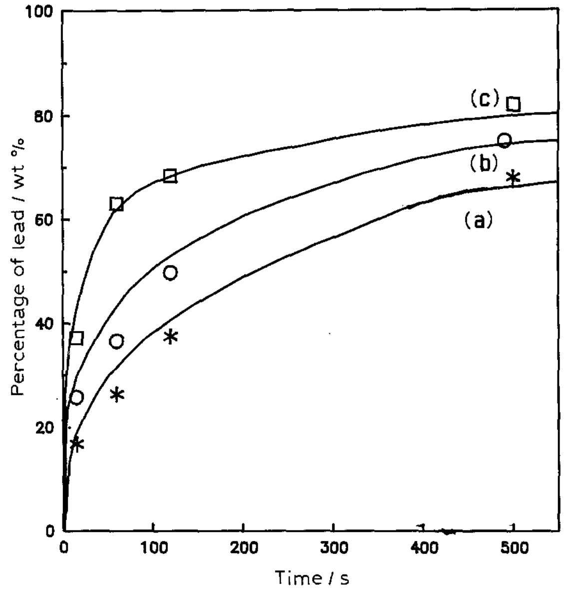

Fig. 9. Percentage of dissolved Pb^{2+} from an equimolar Pb/PbO_2 mixture, containing 11 wt % of $PbSO_4$ and inerts, in HBF_4 or in HBF_4 with various amounts of Ti^{3+}, mass ratio solid/liquid = 0.1. Curve (a) $[Ti^{3+}] = 0.03\,M$, (b) $[Ti^{3+}] = 0.1\,M$, (c) $[Ti^{3+}] = 0.3\,M$.

On the basis of these considerations it is possible to say that lead is dissolved in aerated fluoboric acid solutions by Ti^{4+} ions, which are continuously restored by the dissolved oxygen.

Some leaching tests have also been performed on an equimolar mixture of lead and lead dioxide with solutions which initially contain only Ti^{4+}. In this case, PbO_2 is dissolved by the action of Ti^{3+} ions produced on lead. The trend of the reactions is revealed by the colour change. The uncoloured initial electrolyte becomes brown due to Ti^{3+} ion formation. At the end of the process when all the mixture has been leached the electrolyte again becomes colourless because only Ti^{4+} ions remain in the solution.

Tests with various amounts of titanium ions were carried out to determine the effect of the concentration of the active species of the redox-couple on the leaching rate, Fig. 9. In the case of a mass ratio solid/liquid equal to 0.1, with a sulphate content of 11 wt % and under a high stirring of the solution, the rate values are almost proportional to the concentration of titanium ions. However, the choice of a suitable value of titanium ion concentration must be made taking into account its effect on current efficiency for lead electrodeposition.

Tests performed on a pilot plant with non-desulphurized industrial slimes, whose composition is given in Table 1, revealed that only about 40% of the material dissolves with a rate close to that of the previous findings. The remaining part dissolves very slowly: the processing time becomes two or three orders of magnitude higher, Fig. 10. This behaviour is due to the large amount of $PbSO_4$ contained in

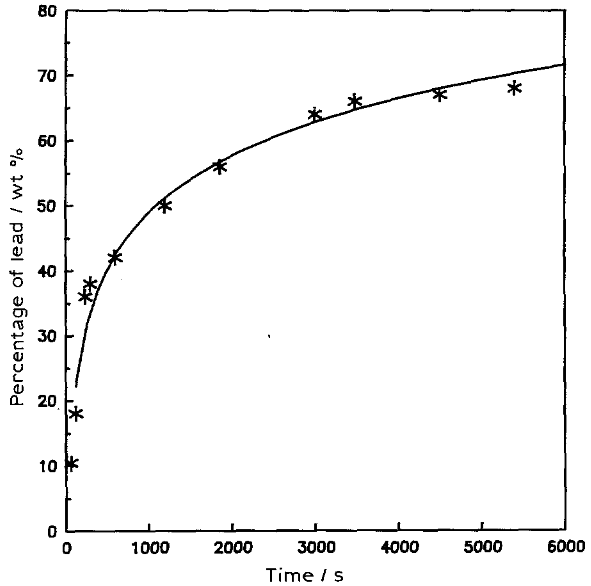

Fig. 10. Dissolution of non-desulphurized pastes, in a pilot plant, with Ti^{3+} ions 0.3 M in HBF_4 200 g dm^{-3} solution.

the pastes: the redox couple has no effect on $PbSO_4$. The tests carried out with desulphurized pastes, whose composition is indicated in Table 2, showed that almost all active material is dissolved.

Other redox couples can be employed for the dissolution of pastes. In this work the behaviour of the Fe^{2+}/Fe^{3+} couple was examined because iron ions can be present in the electrolyte as an impurity, from the corrosion of the metallic parts of the plant or from the electrolyte of spent batteries. The behaviour of the Fe^{2+}/Fe^{3+} redox couple on Pb and PbO_2, electrodeposited on platinum, is shown in Fig. 11. For the same concentration of the redox couple active species, the dissolution rate is about one order of magnitude lower with respect to the Ti^{3+}/Ti^{4+} couple.

6. Industrial plant

The findings led to the conclusion that it is possible to quickly dissolve the active materials of lead–acid batteries after their desulphurization, using fluoboric acid solutions containing titanium or ferrous ions. The rate of paste dissolution is determined by the lead oxidation according to Reaction 2 because the lead dioxide reduction is the fastest step. To discuss the industrial plant conditions, the behaviour of the redox couple in electrolytic cells for lead electrowinning must also be taken into account.

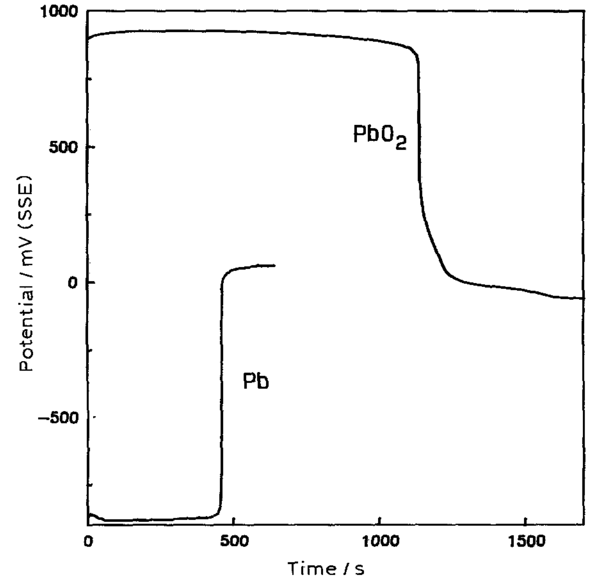

Fig. 11. Rest potential versus time for Pb and PbO_2 electrodeposited on platinum (2000 mC cm^{-2}). $[Fe^{3+}] = 0.3$ M for lead and $[Fe^{2+}] = 0.3$ M for PbO_2, $[HBF_4] = 200$ g dm^{-3}.

The active species of the redox couple react at the cell electrodes lowering the current efficiency. As far as electrowinning of lead solution containing titanium ions is concerned, the cathodic current efficiency decreases with increasing Ti^{4+} concentration. Thus it is advisable to keep the concentration of tetravalent titanium ions in the electrolyte inlet as low as possible, for example by feeding the cell with an electrolyte containing only Ti^{3+} ions. For this purpose, an appropriate value of the molar ratio PbO_2/Pb in the material to be leached must be selected; this ratio can be varied over a wide range by changing the working parameters of the battery components separation process.

If the molar ratio PbO_2/Pb is lower than one, only Ti^{3+} is present in the electrolyte at the end of the leaching and no secondary reaction occurs at the cathodes of the lead cells. Conversely, if the molar ratio PbO_2/Pb is greater than one, Ti^{4+} is produced during the leaching. In this case a reactor constituted by a tower filled with lead chips should be placed before the electrolytic cells to reduce Ti^{4+} ions, according to Reaction 2.

Since tetravalent titanium ions are produced at the anode of the lead cells, it is necessary to design a nonconventional electrolytic cell in which a countercurrent flow of solution, from cathodes towards anodes, maintains the proper fluodynamic conditions, hindering Ti^{4+} motion towards the cathodes.

Since the value of the counter-current flow depends on Ti^{3+} ions concentration is is necessary to maintain the total titanium concentration as low as possible. Electrolytic cells with Nafion membranes can also be used; studies on this possibility are currently in progress.

In the case of a molar ratio PbO_2/Pb lower than one, all the metallic lead may be dissolved if, in the leaching solution, there is an appropriate Ti^{4+} concentration. For this, the Ti^{4+} produced in the lead cells should be sufficient.

The ratio between the concentrations of active species of the redox couple in the solution entering cells or leaching reactors can be easily controlled by regeneration towers filled with lead chips or lead oxide to produce the required amount of Ti^{4+} or Ti^{3+} according to Reactions 2 and 3. For a given amount of pastes to be treated the volume of the leaching solution only depends on the lead concentration of the inlet and outlet electrolyte of the cell and on the cathode surface.

Let G be the mass rate of the pastes to be leached, i the percentage of inert material, R the molar ratio

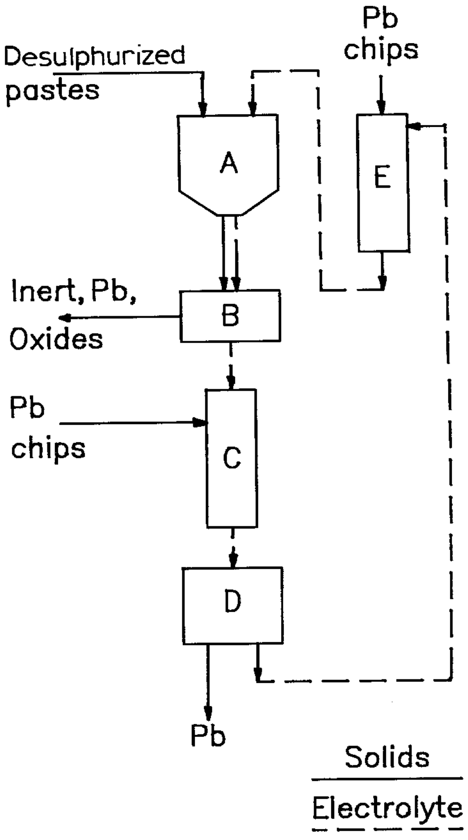

Fig. 12. Plant scheme for the leaching and electrolysis of pastes: (A) leaching reactor; (B) filtration; (D) lead cells; (C,E) regeneration tower.

PbO_2/Pb (assumed to be less than 1), δ the current density, Δc the difference between the lead concentration of the inlet and outlet electrolyte of the cell, S the total cathode surface, M_1 and M_2 the molar weight of lead and lead dioxide respectively. According to the mass balance of the electrolytic and leaching stages, the flow rate V of the solution is given by:

$$V = \frac{G}{\Delta c}\left[1 - \frac{i}{100}\right](1+R)\left[\frac{M_1}{RM_2 + M_1}\right] \qquad (8)$$

The cathode surface is given by:

$$S = 2\frac{F}{\delta}G\left[1 - \frac{i}{100}\right]\left[\frac{(1+R)}{RM_2 + M_1}\right] \qquad (9)$$

In oxygen free systems, the molarity of the titanium tetravalent solution necessary for a complete leaching is

$$[Ti^{4+}] = 2\left(\frac{1-R}{1+R}\right)\frac{\Delta c}{M_1} \qquad (10)$$

For a PbO_2/Pb molar ratio of 0.66, $\Delta c = 25\,g\,dm^{-3}$ the minimum titanium ion concentration is about 0.05 M; this concentration ensures a sufficiently high leaching rate, slight lead loss and good working conditions for the cell.

Finally the oxygen effect has to be considered. During filtration of the solids from the leaching, some Ti^{3+} may be oxidized by the oxygen contained in the air. As in the case of $Pb/PbO_2 > 1$, a regeneration tower must therefore be placed before the electrolytic cells to reduce the Ti^{4+} ions. In this case there is a lead loss and, if all the trivalent titanium is oxidized by the oxygen, the cycle efficiency, because of the recycled lead, can be expressed as:

$$\eta = \frac{2R}{1+R} \qquad (11)$$

As a consequence, to obtain an efficiency greater than 0.8, R has to be greater than 0.66.

Figure 12 shows a pilot plant for the treatment of pastes with a ratio $PbO_2/Pb < 1$. The scheme does not show the initial stage of paste desulphurization and dissolution without using redox couples.

As the electrolyte is never renewed, the amount of impurities present in the initial mixture increases with time until their oxides or insoluble salts precipitate. From this moment, the residual solids at the end of the leaching process will also contain such impurities. In fact, some tests have shown that residual non-leached solids are considerably enriched in antimony.

7. Conclusions

Cyclic voltammetry carried out in acid lead fluoborate solutions on platinum electrodes coated with lead and lead dioxide together with electrode potential measurements at zero external current, showed that lead and lead dioxide are quickly dissolved in the presence of Ti^{4+} and Ti^{3+} ions. The dissolution rates have been evaluated as corresponding to about $150\,A\,m^{-2}$ for lead and $400\,A\,m^{-2}$ for lead dioxide.

Thus the Ti^{3+}/Ti^{+4} redox couple can be advantageously used as a chemical reagent to increase the leaching rate of lead and lead dioxide mixtures in fluoboric acid solutions. This redox couple can be easily restored and it is preferable to H_2O_2, which is usually employed in electrochemical plants for the recovery of lead from spent lead–acid batteries.

On account of the fact that reduction of Ti^{4+} ions produced at the anodes of the lead electrolysis cells lowers the cathodic current efficiency for lead deposition, a counter-current flow of the electrolyte should be imposed and the titanium ion concentration should be kept as low as possible.

Tests carried out on a pilot plant indicate that advantageous conditions are met when the molar ratio PbO_2/Pb in the pastes to be leached is less than one and when the leaching solution contains only Ti^{4+} ions in a concentration equivalent to the excess of lead.

Due to the fact that in the presence of titanium ions, the dissolved oxygen markedly affects the corrosion of lead, reduction of Ti^{4+} by means of a regeneration tower containing lead chips should be accomplished to obtain a Ti^{4+} free solution to feed the electrolysis cell.

Acknowledgements

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