Experimental Research on Lead Extraction from Alkaline Solutions by Electrolysis

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The hydrometallurgical processing technologies of the oxide-sulfate paste resulting from the dismantling accumulator batteries are still belonging to a research process (level- laboratory, pilot, functional mode), nowadays. Lead solubilization can be carried out in lead chloride solutions (with NaCl, $CaCl_2$), in acidic solutions (acetic acid, nitric acid, hexafluosilicic acid) and in alkaline solutions (NaOH) or amines. Leaching with sodium hydroxide solutions represents the most recent lead recovery initiative. The method is considered interesting due to its environmental pollution control and to the processing of both the oxide sulfate paste and other secondary resources such as volatile powders resulted in the extractive metallurgy of lead from primary resources. The lead extraction from alkaline solution by electrolysis, can be achieved with current efficiency of over 98%. The following initial conditions represent the starting point: the lead concentration in the electrolyte supplied: 17-30 g/L Pb, the electrolysis time: 2 h and the distance between anode and cathode: 40 mm. Under these conditions a maximum current efficiency and minimum energy consumption were obtained for the following values of the parameters taken into account: the cathodic power density 600 Am^{-2}; the NaOH solution concentration 6 M; the process temperature, 35^0 C.

Keywords: lead recovery, battery, hydrometallurgy, electrolysis, alkaline solution

Although the waste batteries processing can be achieved in the conventional equipment specific to lead metallurgy (melting in shaft furnace or blast furnace (Imperial Smelting Process)), this is usually done separately through direct melting [1-3]. The processing cost is not decisive in choosing the processing scheme, but the environmental protection expenses are. Theoretically, the pyrometallurgical processing of waste batteries includes the following operations: the batteries dismantling; the metallic fraction sorting, the oxide-sulfate paste sorting and organic fraction sorting (polypropylene, ebonite, polyvinyl chloride); the metallic fraction melting and the oxide-sulfate paste melting; the gas filtration. The processes based on melting in either Isasmelt / Ausmelt furnaces or in electric ovens are estimated to be the most appropriate.

In order to overcome the disadvantages of the waste accumulator batteries the pyrometallurgical processing, recent research has focused on two directions either pure hydrometallurgical processes or a combination of hydrometallurgical and pyrometallurgical processes.

The hydrometallurgical processes consist of the lead solubilization in depleted electrolyte solutions (solutions of hexafluosilicic acid, fluoboric acid, sodium hydroxide), the metallic lead being recovered as pure electrolytic lead. Variants of these industrial processes have not been applied in an industrial way, but they were investigated during either the pilot phase or the demonstration plant.

Hydro and pyrometallurgical combined processes [4-6], aiming to minimize the Pb and SO_2 emissions in the atmosphere and to obtain metallic lead through melting at lower temperatures. This is achieved during two stages of processing:

- The hydrometallurgical stage that converts $PbSO_4$ into $PbCO_3$;
- The pyrometallurgical melting stage of $PbCO_3$ at lower temperatures of approximately 800-900° C.

Variants of these processes have found their application in the industrial phase.

The main methods presented within this field of interest are the following:

- lead electrochemical extraction from waste accumulator batteries;
- lead extraction process from sulphate paste through solubilisation using amides;
- lead extraction process from the paste through solubilisation in hexafluosilicic acid;
- sulphate paste processing method - PLINT;
- paste processing method - CLEAN LEAD;

The method of lead solubilization of oxide-sulphate paste with sodium hydroxide solutions is a part of the latest initiative in obtaining lead, in an attempt to get a double win: on the one hand, the environmental pollution control and on the other hand, the other secondary resources processing such as volatile powders resulted in the extractive metallurgy of lead from primary resources [7,8].

This consists in the solubilization with sodium-hydroxide solutions followed by the electrolytic lead extraction and the regeneration of the sodium-hydroxide solution.

The main chemical reactions are the following [9]:

$$PbSO_4 + 4NaOH = Na_2PbO_2 + Na_2SO_4 + 2H_2O \quad (1)$$
$$PbO + H_2O + NaOH = Na_2PbO_2 \quad (2)$$
$$Pb + 2NaOH = Na_2PbO_2 + H_2 \quad (3)$$

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All these three reactions generate sodium salts [10]. The lead extraction from solutions is achieved by electrolysis with stainless steel anodes in order to obtain a sponge-shaped cathodic deposit, which is easy to be removed and which needs then to be melted in order to obtain metallic lead.

The alkaline solutions electrolysis

The lead in alkaline solutions of purified 6M sodium hydroxide is recovered in the form of sponge lead by electrolysis with insoluble anode and stainless steel cathode in an electrolytic cell. The mechanism of the electrodeposition process of lead from NaOH solution takes place in the following sequence:

$$HPbO_2^- + H_2O + 2e^- \rightarrow Pb + 3OH^- \text{ at a potential of } Ec = -0.889\ V \qquad (4)$$

$$Pb(OH)_4^{2-} + 2e^- \rightarrow Pb + 4OH^- \quad Ec = -0.910\ V \qquad (5)$$

At more negative polarization the hydrogen evolution takes place:

$$2H^+ + 2e \rightarrow 2H_2 \quad Ec = -1.3\ V \qquad (6)$$

During the electrolysis process undesired side reactions also take place, such as high valent lead oxidation and the oxide deposition on the anode.

$$HPbO_2^- + H_2O \rightarrow PbO_3^{2-} + 3H^+ + 2e^- \quad E_e = -0.005\ V \qquad (7)$$

$$HPbO_2^- \rightarrow PbO_2 + H^+ + 2e^- \quad E_e = -0.018\ V \qquad (8)$$

$$3HPbO_2^- + H^+ \rightarrow Pb_3O_4 + 2H_2O + 2e^- \quad E_e = -0.077\ V \qquad (9)$$

$$Pb_3O_4 + 2H_2O \rightarrow 3PbO_2 + 4H^+ + 4e^- \quad E_e = -0.011\ V \qquad (10)$$

$$2Pb_3O_4 + H_2O \rightarrow 3Pb_2O_3 + 2H^+ + 2e- \quad E_e = -0.112\ V \qquad (11)$$

Experimental part

The electrolysis set-up description

For experimental research in a laboratory the electrolysis set-up presented in figure 1 was used.

1. Electrolysis cell; 2. Stabilized DC source, type I 4115, with voltage control from 0 to 40 V, connected with measuring devices -DC ampermeter and voltmeter ; 3. Peristaltic pump for recirculating solution; 4. The peristaltic pump for supplying the electrolytic solution into the cell; 5. Solution supply vessel with V = 500 mL; 6. Collection vessel for solutions with V = 500 mL, where the electrolyte is discharged from the electrolysis tank; 7. Electric heating plate; 8. Control device Multimeter type UN-7T, accuracy class 2.5. to measure the voltage drop in the electrolysis cell; 9. Control device Digital Multimeter type MAS-830B to measure the current intensity

The electrolysis cell is made of polypropylene 140x105x80 mm dimensions and 1.2 L working volume.

The components of set-up are the followings: a stabilized DC source type I 4115, with voltage adjustment from 0 to 40 V, fitted with measuring devices; an ampermeter and voltmeter DC; two stainless steel anodes with 1 mm thickness and surface of 80x32 mm; a stainless steel cathode with 1mm thickness and surface of 80x32 mm, the electrodes being placed on two copper power bars; a peristaltic pump for solution recirculation and a peristaltic pump for supplying solutions in the electrolytic cell; a solution supply vessel - type Berzelius bottle of V = 500 mL and a solution collecting tank - type Berzelius bottle of V = 500 mL, in which the electrolyte from the electrolysis tank is discharged; a heating plate; a control device - Multimeter type UN-7T, accuracy class 2.5 for measuring the voltage in the electrolysis cell; a control device - MAS-830B Digital multimeter to measure the current intensity.

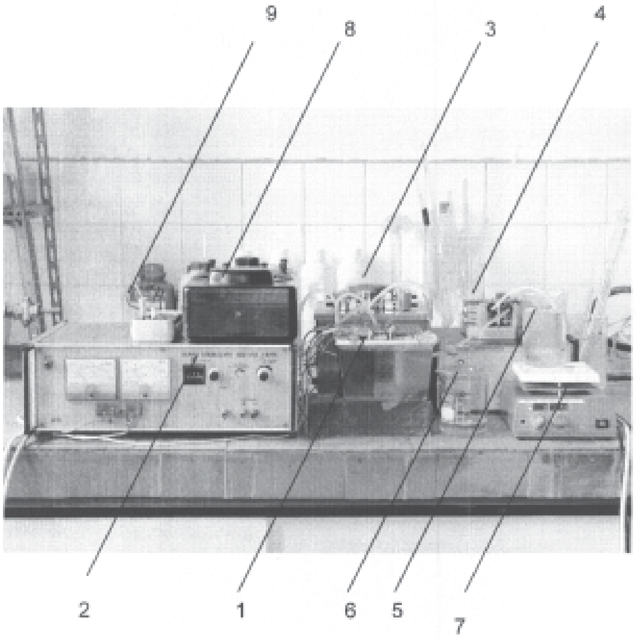

Fig.1. The electrolysis plant.

The experimental technique

A paste with the following composition: Pb_{total} = 72.01%; PbO = 5.71%; PbO_2 = 20.24%; $PbSO_4$ = 44.01% ; Pbmet = 2.05% was used.

The leaching paste (without preliminary desulphation) in NaOH solutions [11,12], led to the solution with chemical composition shown in table 1.

During the electrolysis process, the electrolysis cell was continuously fed with rich electrolyte provided by the peristaltic pump at a well established flow rate. The depleted electrolyte was evacuated from the cell into a Berzelius beaker through overflow.

Also, the solution in the cell was continuously recycled at a rate of aproximately 2 Lh^{-1}, being sucked from the bottom of the tank and re-introduced in the opposite side at the surface, thus ensuring the solution homogeneity regarding the lead content. The solution feeding was followed by both the current intensity adjustment to values between 2 and 4.5 A and the cell voltage control.

The lead in solution was deposited on the cathode in the shape of sponge, which was removed every 10 min and kept in the water to prevent it from oxidizing. After the experiment completion which lasted 2 h, the lead sponge was briquetted and weighed. The samples of solutions and lead were collected and were chemically analyzed.

Table 1
CHEMICAL COMPOSITION OF ALKALINE SOLUTION CONTAINING LEAD SPECIES

Elements	***Pb***	***Sb***	***Sn***	***Cu***	***As***
gL^{-1}	17-35	0.001-0013	0.032-0.088	0.001-0.002	0.018-0.056

Experiment no.	Working parameters							
	Dc, [Am^{-2}]	NaOH concentration [M]	Temp., ^0C	Time, h	Addition of gelatin, [gL^{-1}]	Cathode surface, [m^2]	Intensity, [A]	Cell voltage [V]
1	600	**4**	35	2	1	0.00495	3.0	1.80
2	600	**5**	35	2	1	0.00495	3.0	1.88
3	600	**6**	35	2	1	0.00495	3.0	2.01
4	600	**7**	35	2	1	0.00495	3.0	2.38
5	**450**	6	35	2	1	0.00495	2.25	1.84
6	**600**	6	35	2	1	0.00495	3.0	2.01
7	**750**	6	35	2	1	0.00495	3.7	2.06
8	**900**	6	35	2	1	0.00495	4.5	2.22
9	600	6	25	2	1	0.00495	3.0	2.07
10	600	6	35	2	1	0.00495	3.0	1.94
11	600	6	45	2	1	0.00495	3.0	1.85

Table 2.
EXPERIMENTAL RESULTS ON ELECTROLYSIS OF ALKALINE SOLUTIONS CONTAINING LEAD SPECIES

Results and discussions

The experimental research carried out for lead extraction from alkaline solutions through electrolysis with insoluble anodes had the purpose to establish the optimal working conditions as well as their influence on both the current efficiency and the specific electric power consumption.

The following parameters were studied: NaOH solution concentration, current density and electrolyte temperature.

The following parameters were maintained constant during the experiments:

- the electrolysis time: 2 h;
- the distance between the anode and the cathode: 40 mm.

Alkaline solutions synthetically prepared were used in these experiments.

The experimental results are presented in tables 2 and 3 and figures 2-5.

During the first set of experiments (lines 1-4 in table 2) the NaOH solution concentration was varied from 4 M to 7 M, with a cathodic current density of 600 Am^{-2}, at a temperature in the tank maintained at 35°C. Under these conditions the current yields of 90-97% and the energy consumption of 490-685 $kWht^{-1}$ were obtained. The highest lead extraction yield was noticed for a concentration of 5-6 M in the NaOH solution figure 2.

For lower concentrations of NaOH there are conditions for the development of unwanted side reactions (reactions 7-11) such as the higher-valence lead oxidation and the lead oxide deposition at anode.

For current densities higher than 600 Am^{-2} (samples 5-8 in table 2), the yield decreases (fig.3) and the power consumption increases (table 2) due to both the lead detachment from the cathode surface and the current loss because of the “edge effect” (the non-uniform distribution of the current on the cathode surface and higher current densities on the electrode edges).

Related to the temperature adopted during the electrolysis process (set of experiments 9-11), better extraction yields were obtained at 35-45 °C (fig. 4). The selection is justified by Pourbaix diagrams recorded in figure 5-6. It is worth to mention that we have made a thermodynamic study on the solubilization of the oxide and lead sulfate into sodium hydroxide solution by using the HSC Chemistry 6.0 software. It may be seen from Pourbaix diagrams that the $HPbO_2^-$ ions existence domain was not too much enlarged. A higher increase of the temperature is not justified due to the fact that a significant increasing of the $HPbO_2^-$ processing yield is no longer obtained.

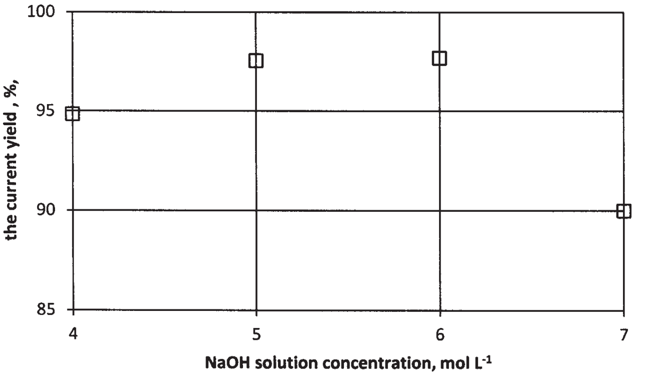

Fig.2. Influence of the NaOH solution concentration on the current yield at 35 °C, Dc = 600 Am^{-2}

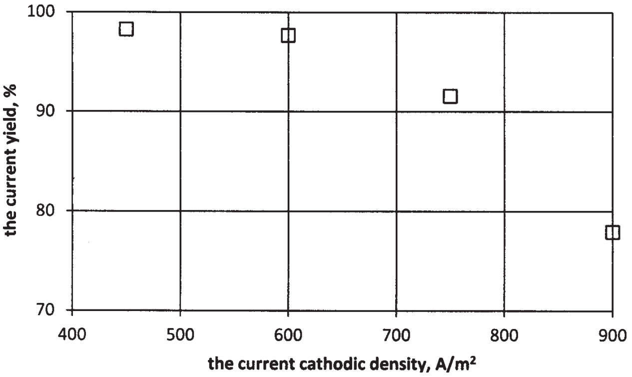

Fig.3. Influence of the current density on the yield power at 35 °C, 6 M NaOH solution.

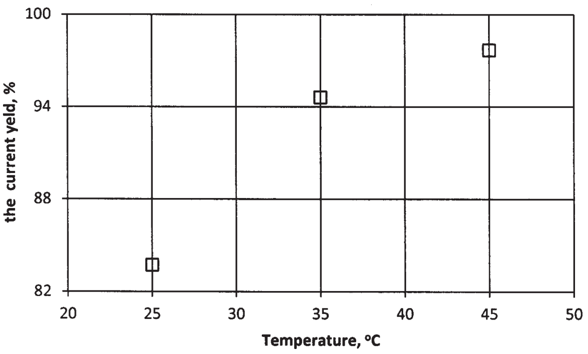

Fig.4. Influence of temperature on the current yield for 6 M NaOH solution, Dc = 600 Am^{-2}.

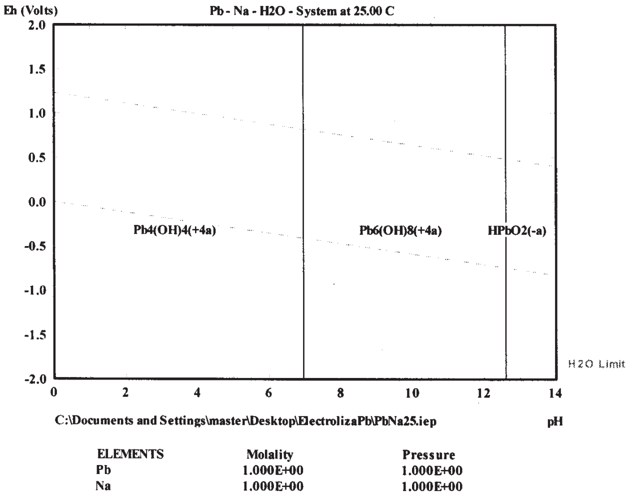

Fig.5. Pourbaix E-pH diagram for the Pb-Na-H_2O system at 25 °C.

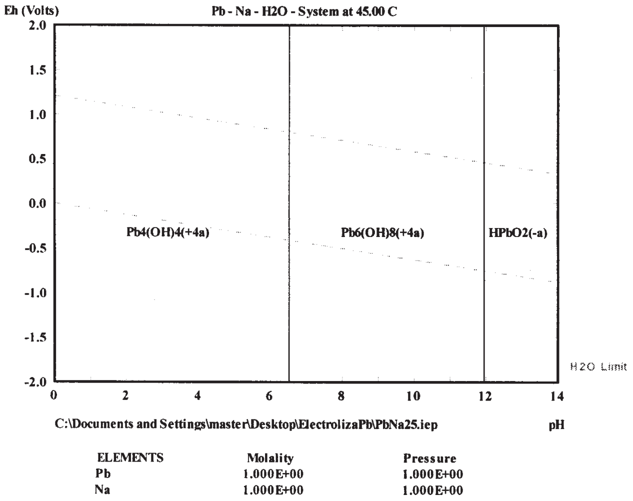

Fig. 6. Pourbaix E-pH diagram for the Pb-Na-H_2O system at 45°C

Table 3
BALANCE OF MATERIALS FROM ELECTROLYSIS

Experiment no.	Pb in solution* [gL^{-1}]	Metallic lead deposited on the cathode [g]	Performance	
			Current yield [%]	Power consumption [Kwh/t]
1	22.986	21.8	94.84	491
2	22.965	22.4	97.54	499
3	22.934	22.4	97.67	533
4	22.891	20.6	89.99	685
5	17.201	16.9	98.25	485
6	22.934	22.4	97.67	533
7	28.724	26.3	91.56	583
8	34.403	26.8	77.90	739
9	22.936	19.2	83.71	640
10	22.936	21.7	94.61	531
11	22.934	22.4	97.67	533

* Analysis of solutions was performed using a flame atomic absorption spectrometer GBC type AB 932 plus.

Conclusions

The waste recovery process of the sulfate oxide obtained from decommissioned car lead batteries, using sodium hydroxide solution is a promise in this field of interest. The gain is considered twofold: on the one hand, it improves the environmental pollution control and on the other hand, it makes possible to process other secondary resources such as the volatile powders resulted in the lead extractive metallurgy from primary resources.

The lead extraction from alkaline solution through electrolysis can be achieved with current efficiencies of over 98%.

The best results on the lead extraction through the alkaline solutions were obtained under the following initial conditions: the lead concentration in the electrolyte feed: 30 gL^{-1} Pb, the electrolysis time: 2 hours and the distance between the anode and the cathode: 40 mm. A maximum current efficiency and a minimum energy consumption have been obtained at the following values of parameters: the cathodic current density 600 Am^{-2}; NaOH solution concentration 6 M and the process temperature 35°C.

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