Mathematical Modelling for Optimisation of Lead Electrodeposition from Alkaline Solutions

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The paper presents the results of mathematical modelling for the electrolytic process of lead deposition from alkaline solutions. Using an active program of research, a 2nd order orthogonal program (PO2), the optimal conditions for the process development have been established so that to obtain a maximum yield of current without exceeding an imposed energy specific consumption.

Keywords: lead electrodeposition, mathematical modelling, factorial program, electrolysis yield

The drastic reduction of classical raw materials supply, correlated with stringent needs to elaborate ecologically efficient technologies imposed to search for new resources among which a very important one is waste materials with lead content from used batteries of accumulators.

At present, these waste materials are processed either by pyrometallurgical technologies that are high consumers of energy and environmental damaging or by combined pyro-hydro metallurgical technologies. In this context, the present research intends to develop a new technology based only on hydrometallurgical operations, consisting mainly on the following operation step (fig.1):
- reduction of PbO₂ to PbO;
- sulphate removal from the oxide –sulphate paste;
- lead leaching and purifying of solutions;
- separation and recovery of lead from solution either as PbO or as metallic Pb.

In the oxide sulphate paste resulting from batteries scrap of used accumulators, lead is found as oxide, as dioxide, as sulphate and, in a very small portion as metallic lead. The average content of lead in this paste is about 79-73%. A short description of the operations to be made is presented.

- Reduction of PbO₂ to PbO: is carried out by treating the paste with lead sulphide in weak acid medium, at pH=1.

-Sulphate removal from the paste: removal of SO₄²⁻ ion is carried out by treating the paste with solution of sodium hydroxide, at pH = 11-11.5, when the lead sulphate converts into lead oxide. To regenerate the sodium hydroxide and to obtain the hydrated calcium sulphate, the solution of sodium sulphate is treated with a solution of calcium hydroxide:

\[ Na₂SO₄ + Ca(OH)₂ + 0.5H₂O = 2NaOH + CaSO₄ \cdot 0.5H₂O \]

- Lead leaching and solutions purifying: lead oxide from paste is leached in solutions of sodium hydroxide 5-6 M NaOH and the obtained solution is purified in presence of metallic lead.

- Lead recovery from the alkaline solution: lead is separated from solution either as crystals of PbO by vacuum crystallisation, or as lead sponge by electrolytic deposition; the solution coming to electrolysis contains 40 – 50g/L Pb and is diluted to 30g/L Pb.

In this work, the steps of mathematic modelling of the lead electrolysis process from alkaline solutions are presented. The modelling was done by using an active research program, an order two orthogonal program PO2 [1-4].
Results and discussions

The modelling program

Rough research emphasized that the electrolysis performance expressed by the current yield \( y_1 \) and the energy consumption \( y_2 \) are mainly influenced by three parameters: current density \( z_1 \), A/m², concentration of NaOH solution \( z_2 \), moles/L, and concentration of lead in used electrolyte \( z_3 \), g/L. Other parameters like electrolysis time (2 h), distance between electrodes (30 mm), initial concentration of lead in solution (30 g/L), temperature (30-35°C) and additions of gelatine (1 g/L), having no significant influence, were maintained constant at the respective values.

To determine the optimal conditions for the electrolysis process development, an active program of experiments was employed, namely an order two orthogonal program (PO2), obtained by adjusting a first order program type \( EFC \) \( 2^3 \) (EFC = complete factorial experiment) with certain points in the factorial space. It results:

\[
N = N_c + N_a + N_0
\]  

(1)

\( N \) - represents the total number of points in the program \( PO2 \);

\( N_c \) - number of experiments in a \( EFC \) \( 2^n \) (\( N_c = 2^n \)) program;

\( N_a \) - number of determinations in the centre of the program (parallel or repeated determinations) (a value of \( N_a = 3 \) was chosen). For \( n = 3 \), the partial values are:

\[
N_c = 2^3 = 8, \quad N_a = 2 \cdot 3 = 6, \quad N_0 = 3 \quad \text{and, therefore, it results: } N = 17
\]  

(2)

The steps to elaborate the PO2 program have been the following:

a) based on the results obtained in previous experiments, we chose as basis of the experiment, the point from the factorial space having coordinates:

\[
z_i^0 = 750 \text{ A/m}^2; \quad z_i^0 = 6 \text{ M}; \quad z_i^0 = 15 \text{ g/L}
\]

and as variation intervals, the values: \( \Delta z_i = 150 \text{ A/m}^2, \quad \Delta z_i = 1 \text{ M}, \quad \Delta z_i = 3 \text{ g/L} \).

b) with these values, we determined the values of factors in the eight points of the \( EFC \) \( 2^3 \) program entering into the composition of PO2, using relations:

\[
z_i^{(+1)} = z_i^0 + \Delta z_i; \quad z_i^{(-1)} = z_i^0 - \Delta z_i.
\]  

(3)

c) then, the coordinates of six "star points" \( (z_i^{(+\alpha)}, z_i^{(-\alpha)}) \) were established with the aid of the parameter \( \alpha \) ("star

Table 1

<table>
<thead>
<tr>
<th>Exp</th>
<th>Process parameters (codified units)</th>
<th>Process parameters (natural units)</th>
<th>Yield of current % ( y_1 )</th>
<th>Energy consumption KWh/tone, ( y_2 )</th>
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</thead>
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<tr>
<td></td>
<td>( x_1 )</td>
<td>( x_2 )</td>
<td>( x_3 )</td>
<td>Density of current A/m²</td>
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Table 2

<table>
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<th>Exp</th>
<th>Factors of the process</th>
<th>Interactions</th>
<th>Yield of current %, ( y_1 )</th>
<th>Energy consumption, KWh/tone, ( y_2 )</th>
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<tr>
<td>16</td>
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<tr>
<td>17</td>
<td>0</td>
<td>0</td>
<td>-1,353</td>
<td>-0.686</td>
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</table>
whose value was determined with bi-squared equation
\[
\alpha^* + 2\alpha^* \alpha^2 - 2 \alpha^*(n + 0.5N_0) = 0,
\]
(4)

\[
z^*_{i(a)} = z^*_{i(a)} = \alpha \cdot \Delta z_i.
\]
(5)
d) since this elaborated mathematical model operates with another type of variables, the next step was to change variables from natural variables \(z_i, z_1, z_2, z_3\) to so called codified variables \(x_i, x_1, x_2, x_3\). For this purpose, the following relations were employed:

\[
x_i^{(a)} = \frac{z_i^{(a)} - z^*_{i(a)}}{\Delta z_i} = -1,
\]
(6)

\[
x_i^{(a)} = \frac{z_i^{(a)} - z^*_{i(a)}}{\Delta z_i} = +1,
\]
(7)
e) considering the present notations, the PO2 program employed in research has the aspect from the table 1.

The complete matrix of the program PO2, necessary to calculate coefficients of the regression equation, are as shown in table 2.

The significance of
\[
\hat{\alpha} = a = 0.686.
\]
(8)

According to PO2 program, the relations for computation as well as the values of the regression equation coefficients for the two considered performances are the followings:

- for the yield of current \((y_1)\):

\[
b_1 = \frac{1}{N} \sum_{i=1}^{N} y_i = 90.386,
\]
(9)

\[
b_2 = \frac{1}{N} \sum_{i=1}^{N} x_{ia}y_i = -2.229; \ b_1 = 1.739; \ b_2 = 7.263.
\]
(10)

\[
b_3 = \frac{1}{N} \sum_{i=1}^{N} (x_{ia})^2 = -1.45; \ b_3 = -0.405; \ b_3 = 0.252.
\]
(11)

\[
b_0 = \frac{1}{N} \sum_{i=1}^{N} x_{ia}y_i = \frac{1}{N} \sum_{i=1}^{N} (x_{ia})^2 = 0.319; \ b_2 = -0.424; \ b_3 = -2.33.
\]
(12)

- and for the energy consumption \((y_2)\):

\[
b_1 = 599.588; \ b_1 = 30.982; \ b_1 = 18.961; \ b_3 = -71.019.
\]

\[
b_3 = 9.125; \ b_3 = 1.375; \ b_3 = 6.625.
\]
(13)

The mathematical model, represented by two equations of regression of second order with three variables has the following form:

\[
\bar{y}_1 = 90.386 - 2.229x_1 - 1.739x_2 + 7.263x_3 - 1.45x_1x_2 - 0.405x_1x_3 + 0.252x_1x_3 + 0.319(x_1^2 - 0.686) - 0.424(x_2^2 - 0.686) - 2.33(x_3^2 - 0.686)
\]
(14)

\[
\bar{y}_2 = 599.588 + 30.982x_1 + 18.961x_2 - 71.019x_3 + 9.125x_1x_2 + 1.375x_1x_3 - 0.252x_1x_3 + 3.962(x_1^2 - 0.686) + 31.816(x_2^2 - 0.686)
\]
(15)

respectively:

\[
\bar{y}_1 = 90.386 - 2.229x_1 - 1.739x_2 + 7.263x_3 - 1.45x_1x_2 - 0.405x_1x_3 + 0.252x_1x_3 + 0.319(x_1^2 - 0.686) - 0.424(x_2^2 - 0.686) - 2.33(x_3^2 - 0.686)
\]
(16)

\[
\bar{y}_2 = 599.588 + 30.982x_1 + 18.961x_2 - 71.019x_3 + 9.125x_1x_2 + 1.375x_1x_3 - 0.252x_1x_3 + 3.962(x_1^2 - 0.686) + 31.816(x_2^2 - 0.686)
\]
(17)

In order to establish if the proposed model was adequate or not, the equations (16) and (17) have been submitted to a statistical analysis. For this purpose we calculated the following parameters:

- dispersions of the reproducibility (points 9-11 from tables 1 and 2)

\[
(s_{y1}^2) = \frac{1}{N-1} \sum_{i=1}^{N} (y_i - \bar{y}_1)^2 = 0.776;
\]
(18)

\[
(s_{y2}^2) = \frac{1}{N-1} \sum_{i=1}^{N} (y_i - \bar{y}_2)^2 = 74.333;
\]
(19)

- dispersions of concordance

\[
(s_{y1}^2) = \frac{1}{N-1} \sum_{i=1}^{N} (\bar{y}_1 - y_i)^2 = 5.208;
\]
(20)

\[
(s_{y2}^2) = \frac{1}{N-1} \sum_{i=1}^{N} (\bar{y}_2 - y_i)^2 = 81.99;
\]
(21)

- values of Fisher criterion

\[
(F_{1}) = \frac{(s_{y1}^2)}{(s_{y1}^2)} = 6.713; \quad (F_{2}) = \frac{(s_{y2}^2)}{(s_{y2}^2)} = 1.103
\]
(22)

Since the calculated values of Fisher criterion \((F)\) for both equations are smaller than its labelled value \((F_{0.05(n-2,n-2)} = 19.353)\) it results that the equations expressing the mathematical model are adequate for the studied process and they could be employed for optimisation.

The problem to be solved was to establish those values for the process parameters which maximise the yield of current \((y_1)\) and lead, in the same time, to an energy consumption below an imposed limit \(Y^*\) ≤ 500 kWh/t. In this case, we employed the method of Lagrange multipliers.

For this purpose, we adopted an auxiliary equation like:

\[
F(x_1, x_2, x_3, \lambda) = \bar{y}_1(x_1, x_2, x_3) + \lambda(\bar{y}_1(x_1, x_2, x_3) - Y^*)^2,
\]
(23)

where \(\lambda\) is the Lagrange multiplier.

By equaling with zero the first order partial derivatives of the function \(F(x_1, x_2, x_3, \lambda)\) with respect to variables \(x_1, x_2, x_3\) and \(\lambda\), we obtained a system of four equations with four unknowns. The solutions of this system were the optimal values of the process parameters:

\[
\hat{x}_1 = -0.85; \quad \hat{x}_2 = -0.985; \quad \hat{x}_3 = 1.24 \quad (\lambda = 0.059).
\]
(24)
Substituting the codified variables with natural values in relations (7), the following optimal values have been obtained:

\[
\hat{z}_1 = 622.517 \pm 620 \, A/m^2 \ ; \ \hat{z}_2 = 5.015 \pm 5 \, M \ ; \\
\hat{z}_3 = 18.721 \pm 18.7 ,
\]

for which \( \hat{y}_1 = 99.82\% \) and \( \hat{y}_2 = 500 \, \text{KWh/tone} \)

Since the error of calculation for the process performance in the considered regime is \( \delta = 2.047\% \) the maximum yield to be taken into consideration is \( \hat{y}_1 - \delta = 97.76\% \).

**Conclusions**

The studies and rough experimental research have emphasized three parameters with significant influence over the electrolysis performances: density of current \( (z_1) \), \( A/m^2 \), concentration of NaOH solution \( (z_2) \), moles/L and concentration of lead in used electrolyte \( (z_3) \), g/L. Other parameters, like time \( (2 \, h) \), distance between electrodes \( (30 \, \text{mm}) \), initial concentration of lead in solution \( (30 \, \text{g/L}) \), temperature \( (30-35 \, \text{°C}) \) and additions of gelatine \( (1 \, \text{g/L}) \), having no significant influence, were maintained constant at the respective values.

To determine the optimal conditions for the electrolysis process development, experiments were made according to an active program, an order two orthogonal program \( (PO^2) \). The mathematical model obtained with this program and presented as two polynomials of second order with three variables, was statistically analysed and, with Fisher criterion, the concordance between the model and the experimental data was ascertained.

Since the mathematical model was found as adequate, the following step was to establish the optimal regime, that is to determine the electrolysis parameters that lead to a maximum yield of current in conditions of energy specific consumption imposed to 500 KWh/t.

The optimal values found are: \( \hat{z}_1 \equiv 620 \, A/m^2 \ ; \ \hat{z}_2 \equiv 5 \, M \ ; \ \hat{z}_3 \equiv 18.7 \, g/L \) and, taking into consideration the error of calculation of the process performance \( \delta = \pm 2.047\% \), the prognosis for the maximum yield is \( \hat{y}_1 - \delta = 97.76\% \).

**References**


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