MATHEMATICAL MODELING OF THE PROCESS OF CEMENTATION OF THE LEAD ACETATE SOLUTION WITH IRON

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În lucrare sunt prezentate rezultatele modelării matematice a procesului de cementare a plumbului din soluţii de acetat de plumb, obţinute prin prelucrarea deşeurilor sulfato-oxidice din acumulatori plumb-acid scoşi din uz. Folosind un program activ de cercetare şi anume un program ortogonal de ordinul doi (PO2), s-au stabilit condiţiile optime de desfăşurare a procesului care să conducă la obţinerea unui randament maxim de extracţie a plumbului.

The paper presents the results of a mathematical modeling of the process of cementation of lead in lead acetate solution, obtained by processing waste sulfato-oxide of lead-acid batteries removed from service. Using an active research program and a program that is orthogonal of order two (PO2), optimal conditions were established to conduct the process leading to obtaining of a maximum yield of extraction of lead.

Keywords: mathematical modeling, recycle batteries, lead

1. Introduction

In an effort to comply with regulations, namely that the product will be treated in a manner that provides the highest level of safety, a *vision of green lead* that emphasizes the need to follow sustainable industry lead-acid batteries [1] is on the work to be developed. Increased demand for lead-acid batteries due to the increasing number of vehicles with more stringent environmental regulations, has created the need to move, upgrade and reconvert both production processes and recycling of lead batteries in order to minimize their environmental impact. Currently, recovery of lead from exhausted lead-acid batteries is done by a thermal method, causing environmental problems due to emissions of lead particulates and sulfur dioxide [2]. Because laws becoming more stringent for these types of emissions, there was a large research effort to find a hydrometallurgical method to replace the procedures for lead-acid battery recycling [3]. In particular, electro-hydrometallurgical method of recovering metallic lead has been extensively studied and in this direction several pilot plants

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were designed. Lead electrolytic extraction techniques take place either in acidic or alkaline environments applied as yet fail to overcome many technological

problems or to prevent the formation of the passive lead dioxide anode [1.4]. Recovery of lead from lead hydroxide can be done through a two stage process (leaching and cementation in separate procedure) or one step procedure (leaching and cementation in a single proceeding). Cementation benefits include: high efficiency of the process, almost complete removal or detoxification of heavy metals, high speed process, simplicity of treatment facilities, reclamation of metals in pure metallic form and relative absence of sludge.If you use cheap scrap metal the costs of the functional processes can be maintained at a low level. Most of the industrial processes of cementing are using metal powder in the reactor agitator in the tank. Major interests are: low power requirements, ability of easly control, products obtained in the form of metal.

2. Experimental data

In a single step procedure (solubilization + cementation), all reagents were loaded into the reactor simultaneously, in the working conditions listed in Table 1.

Table 1

Workload and working conditions for cement pastes using lead batteries, remove from service

Load	Quantity	Working conditions
$Pb(OH)_2$ Urea Acetic Acid	70 g (0,2904 mol/l Pb) 8,33 mol/l 2,8668 mol/l	Temperature: 50,60,70ºC Response time: 2 h Molar ratio Fe/Pb: 1,3/1…1,9/1 d_m= -1mm Stirring: 100 rpm

All reaction steps were performed in a reaction carried out in a Pyrex flask of 500 ml double necked round base equipped with a condenser to condense the vapor released. During the reaction the solution was stirred with a magnetic stirrer at about 100 rpm and heated in a thermostatic bath. In a single step procedure, compounds of lead and iron were added simultaneously to the reactor and the reaction progress was monitored from time to time by atomic absorption spectroscopic analysis of samples of the solution. Lead hardened, together with unreacted iron were collected, rinsed with distilled water and dried.

Studies and preliminary investigations revealed the following parameters which have a significant influence on process performance (*yield of extraction - y): temperature (z1), the process (z3) and the molar ratio of Fe / Pb (z2*), the other parameters - *solution concentration acetate (M), reducing the average diameter of*

particles (dm) and stirring speed (rpm), who have not a significant influence, are maintained at constant values.

3. Mathematical modeling

To determine the optimal conditions for conducting the oxidation process a program of active experimentation, namely an orthogonal second-order program (PO2) was used. As indicated by Box and Wilson since 1951, such a program is obtained by adding a program for first-order type 2n EFC (EFC = full factorial experiment) with certain points of the factorial space.

It follows

$$N = N_c + N_\alpha + N_0 \tag{1}$$

where:

- represents the total number of points in the program PO2; N_c - number of experments in a *EFC* 2^n program $(N_c = 2^n)$ or in a *EFF* 2^{n-p} subprogram if $n > 4$ $(N_c = 2^{n-p})$; N_α - the number of so-called "*star points*" $(N_\alpha = 2n)$; N_0 - number of determinations in the heart of the program (or multiple parallel determinations) (was chosen $N_0 = 5$).

As: $n = 3$ we get :

$N_c = 2^3 = 8$, $N_\alpha = 2 \cdot 3 = 6$, $N_0 = 5$ and therefore $N = 19$. (2)

PO2 steps in designing the program were:

a) Based on the results obtained in previous experiences of the experiment the point of the factorial space coordinate: $z_1^0 = 60^0 C$; $z_2^0 = 1{,}6$; $z_3^0 = 90$ *min*, and sizes and ranges as: $\Delta z_1 = 10^0 C$, $\Delta z_2 = 0{,}8$, $\Delta z_3 = 30$ *min*, was chosen as a base.

b) With these values the size of the factors in the 8 points of 2^3 EFC program, were determined and further used in PO2, using equations:

$$z_i^{(-1)} = z_i^0 - \Delta z_i; \qquad z_i^{(+1)} = z_i^0 + \Delta z_i. \tag{3}$$

c) Coordinates of the six "*star points*" $(z_i^{(-\alpha)}, z_i^{(+\alpha)})$ were determined using the parameter α (*„star arm"*), whose value was determined with Eq:

$$\alpha^4 + 2^n \alpha^2 - 2^{n-1}(n + 0{,}5N_0) = 0, \tag{4}$$

that

$$\alpha^4 + 8\alpha^2 - 22 = 0. \tag{5}$$

Experimental data and matrix work are presented in Table 1 and detailed calculations, PO2 schedule are presented below.

3.1. Model developement

$N := 19$ $i := 0..N-1$ $n := 3$ $l := 0.5\cdot(n+1)\cdot(n+2)$ $j := 0..l-1$

$r_0 := 5$ $\alpha := \sqrt{-4+\sqrt{38}}$

$x_{i,0}$:=	$x_{i,1}$:=	$x_{i,2}$:=	$x_{i,3}$:=	y_i :=
1	–1	–1	–1	49.8
1	1	–1	–1	60.24
1	–1	1	–1	51.79
1	1	1	–1	61.08
1	–1	–1	1	59.71
1	1	–1	1	87.94
1	–1	1	1	62.12
1	1	1	1	89.67
1	0	0	0	83.52
1	0	0	0	83.14
1	0	0	0	86.88
1	0	0	0	82.74
1	0	0	0	85.98
1	–α	0	0	58.68
1	α	0	0	86.22
1	0	–α	0	70.71
1	0	α	0	77.22
1	0	0	–α	69.01
1	0	0	α	90.12

Calculation of α

$f(\alpha) := \alpha^4 + 2^n\cdot\alpha^2 - 2^{n-1}\cdot(n + 0.5\cdot r_0)$

$r := \text{root}(f(\alpha), \alpha)$

$r = 1.471$

Calculation of coefficients

$x_{i,4} := x_{i,1}\cdot x_{i,2}$ $x_{i,5} := x_{i,1}\cdot x_{i,3}$

$x_{i,6} := x_{i,2}\cdot x_{i,3}$

$$x_{i,7} := (x_{i,1})^2 - \frac{1\cdot\left[\sum_i (x_{i,1})^2\right]}{N}$$

$$x_{i,8} := (x_{i,2})^2 - \frac{1\cdot\left[\sum_i (x_{i,2})^2\right]}{N}$$

$$x_{i,9} := (x_{i,3})^2 - \frac{1\cdot\left[\sum_i (x_{i,3})^2\right]}{N}$$

$$b_j := \frac{\sum_i (x_{i,j}\cdot y_i)}{\sum_i (x_{i,j})^2}$$

$b =$

	0
0	73.504
1	9.411
2	1.342
3	8.726
4	-0.229
5	4.506
6	0.164
7	-7.497
8	-6.797
9	-4.21

$b^T =$

	0	1	2	3	4	5	6	7	8
0	73.504	9.411	1.342	8.726	-0.229	4.506	0.164	-7.497	-6.797

Ymax= 97.98

$z1_0 := 60$ $z2_0 := 1.6$ $z3_0 := 90$

3.2. Statistical analysis of the model

$Y_i := \sum_j \left(b_j \cdot x_{i,j}\right)$ $a := \frac{1}{N} \cdot \sum_i \left(x_{i,1}\right)^2$ $a = 0.649$

$v\_repetat := \begin{pmatrix} 83.52 \\ 83.14 \\ 86.88 \\ 82.74 \\ 85.98 \end{pmatrix}$ $D0 := Var(v\_repetat)$ $D0 = 3.438$ $Dcon := \frac{1 \cdot \left[\sum_i \left(y_i - Y_i\right)^2\right]}{N - 1}$

Dcon = 6.897

$Fc := \frac{Dcon}{D0}$ $Fc = 2.006$ $FT := qF(0.95, N - 1, 4)$ $FT = 5.821$

Fc<FT, so the mathematical model is appropriate and can be used for optimization

3.3. Canonical form of regression equation

$B11 := \begin{pmatrix} b_7 & 0.5 \cdot b_4 & 0.5 \cdot b_5 \\ 0.5 \cdot b_4 & b_8 & 0.5 \cdot b_6 \\ 0.5 \cdot b_5 & 0.5 \cdot b_6 & b_9 \end{pmatrix}$ $B1 := \begin{pmatrix} b_1 \\ b_2 \\ b_3 \end{pmatrix}$ $Xc := -0.5 \cdot B11^{-1} \cdot B1$

$b0 := b_0 - a \cdot \left(b_7 + b_8 + b_9\right)$

$B11 = \begin{pmatrix} -7.497 & -0.114 & 2.253 \\ -0.114 & -6.797 & 0.082 \\ 2.253 & 0.082 & -4.21 \end{pmatrix}$ $B1 = \begin{pmatrix} 9.411 \\ 1.342 \\ 8.726 \end{pmatrix}$ $Xc = \begin{pmatrix} 1.118 \\ 0.1 \\ 1.637 \end{pmatrix}$

$Dy_i := W_i + Q_i$

$Dy_i := W_i + Q_i$

$b0 = 85.51$

$Ymax := b0 + B1^T Xc + Xc^T \cdot B11 \cdot Xc$

$Dy_i := W_i + Q_i$

$a1 := eigenvals(B11)$ $\quad a1 = \begin{pmatrix} -3.064 \\ -8.653 \\ -6.787 \end{pmatrix}$ $\quad \Delta z1 := 10$ $\quad \Delta z2 := 0.3$ $\quad \Delta z3 := 30$

$K(x1, x2, x3) := b0 + b_1 x1 + b_2 x2 + b_3 x3 + b_4 x1 \cdot x2 + b_5 \cdot x1 \cdot x3 + b_6 x2 \cdot x3$

$L(x1, x2, x3) := b_7\left(x1^2 - a\right) + b_8\left(x2^2 - a\right) + b_9\left(x3^2 - a\right)$

$\eta(x1, x2, x3) := K(x1, x2, x3) + L(x1, x2, x3)$

3.4. Calculation of the error of the performance (δ_y)

$Db_j := \dfrac{D0}{\sum_i \left(x_{i,j}\right)^2}$ $\quad Db0 := Db_0 + 3 \cdot a \cdot Db_8$ $\quad Db0 = 0.895$

$e := 2^n + 2\alpha^2$ $\quad f := 2^n + 2\alpha^4$ $\quad H := 2 \cdot \alpha^4 \cdot \left[N \cdot f + (n-1) \cdot N \cdot 2^n\right]$ $\quad E := -2 \cdot H^{-1} \cdot e \cdot \alpha$

$G := H^{-1} \cdot \left(e^2 - N \cdot 2^n\right)$ $\quad cov\_b0bii := E \cdot D0$ $\quad cov\_biibjj := G \cdot D0$

$$W_i := Db0 + Db_2 \cdot \sum_{j=1}^{n} \left(x_{i,j}\right)^2 + Db_8 \cdot \sum_{j=1}^{n} \left(x_{i,j}\right)^4 + Db_5 \cdot \sum_{j=1}^{n-1} \sum_{k=j+1}^{n} \left[\left(x_{i,j}\right)^2 \cdot \left(x_{i,k}\right)^2\right]$$

$$Q_i := 2cov\_b0bii \cdot \sum_{j=1}^{n} \left(x_{i,j}\right)^2 + 2cov\_biibjj \cdot \sum_{j=1}^{n-1} \sum_{k=j+1}^{n} \left[\left(x_{i,j}\right)^2 \cdot \left(x_{i,k}\right)^2\right]$$

$Dy_i := W_i + Q_i$

$\eta(x1, x2, x3) := K(x1, x2, x3) + b_7 \cdot x1^2 + b_8 \cdot x2^2 + b_9 \cdot x3^2$

$x1op := Xc_0 \qquad x2op := Xc_1 \qquad x3op := Xc_2$

$z1op := z1_0 + x1op \cdot \Delta z1 \qquad z2op := z2_0 + x2op \cdot \Delta z2 \qquad z3op := z3_0 + x3op \cdot \Delta z3$

$z1op = 71.181 \qquad z2op = 1.63 \qquad z3op = 139.107 \qquad \eta(x1op, x2op, x3op) = 97.98$

$v_1 := Xc_0 \qquad v_2 := Xc_1 \qquad v_3 := Xc_2 \qquad j := 1..n$

$$T := Db0 + Db_2 \cdot \sum_{j=1}^{n} (v_j)^2 + Db_8 \cdot \sum_{j=1}^{n} (v_j)^4 + Db_5 \cdot \sum_{j=1}^{n-1} \sum_{k=j+1}^{n} \left[(v_j)^2 \cdot (v_k)^2 \right]$$

$$R := 2cov\_b0bii \cdot \sum_{j=1}^{n} (v_j)^2 + 2 \cdot cov\_biibjj \cdot \sum_{j=1}^{n-1} \sum_{k=j+1}^{n} \left[(v_j)^2 \cdot (v_k)^2 \right]$$

$Dy := T + R \qquad Dy = 6.492$

$tT := qt(0.975, N - 1) \qquad tT = 2.101 \qquad \delta y := tT \cdot \sqrt{Dy} \qquad \delta y = 5.353$

3.4. Practical Efficiency

$z1opt := 70 \qquad z2opt := 1.6 \qquad z3opt := 140$

$$x1opt := \frac{z1opt - z1_0}{\Delta z1} \qquad x2opt := \frac{z2opt - z2_0}{\Delta z2} \qquad x3opt := \frac{z3opt - z3_0}{\Delta z3}$$

$\eta(x1opt, x2opt, x3opt) = 97.786$

$\eta(x1opt, x2opt, x3opt) - \delta y = 92.433$

4. Results and discution

Based on calculations in Figs. 1-4 are presented the variations of extraction efficiency of lead from lead acetate solution with scrap iron mean diameter, dm =- 1mm, a stirring speed of 100 rpm and at different rates parameters taken into account.

All reaction steps were performed in a reaction carried out in a Pyrex flask of 500 ml double necked round base equipped with a condenser to condense the vapor released. During the reaction solution was stirred with a magnetic stirrer at about 100 rpm and heated bathroom temostatică.

The solution after filtration is recovered for recycling. Addition of sulfuric acid increases the recovery of the filtered solution of iron sulphate less soluble compounds (II).

The rezults are also summariszed in the Table 2.

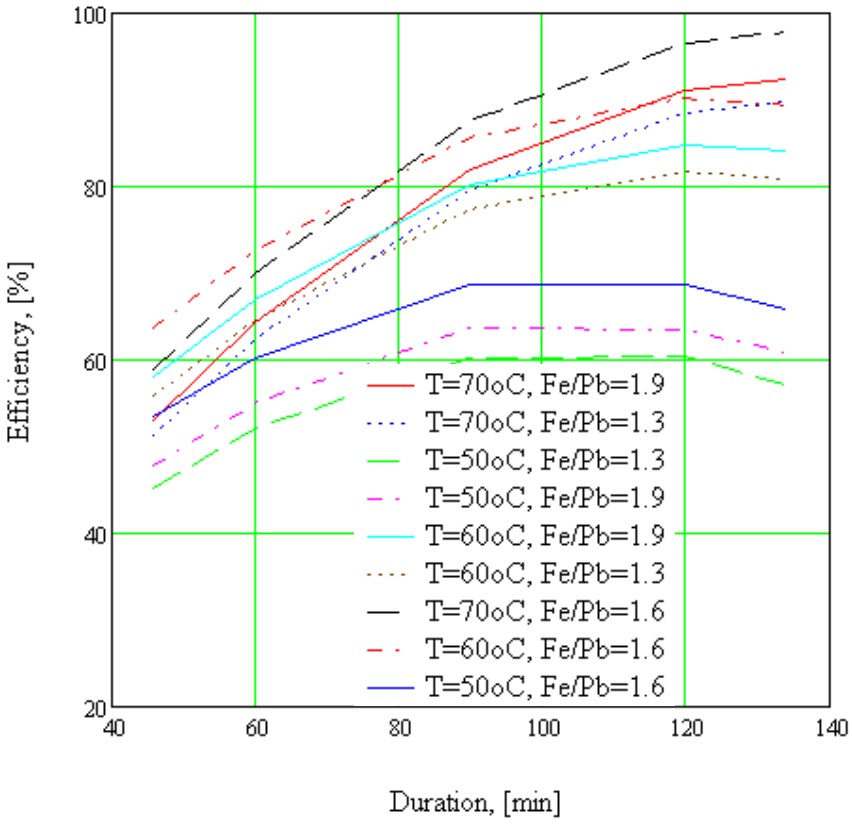

Fig. 1. Extraction yield depending on temperature and the amount of reducing.

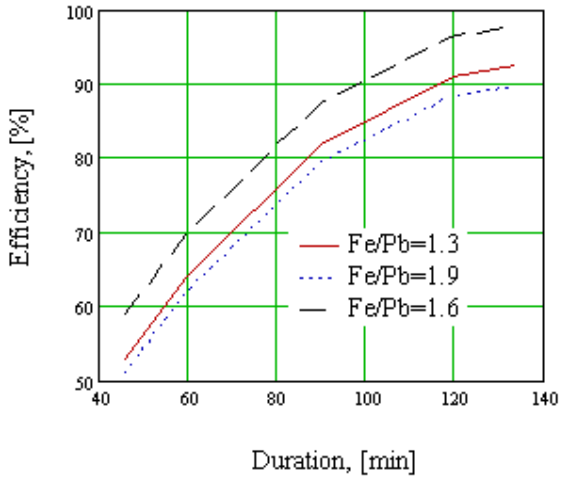

Fig. 2. Extraction yield versus the depends on the amount of reduction agent at 70 ° C

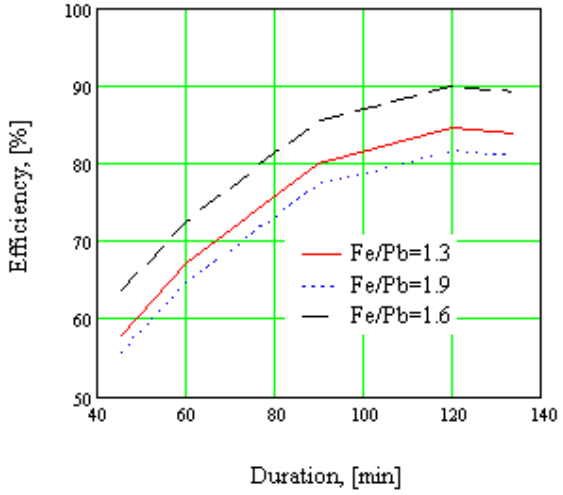

Fig. 3. Extraction yield versus the depends on the amount of reduction agent at 60^{O}C

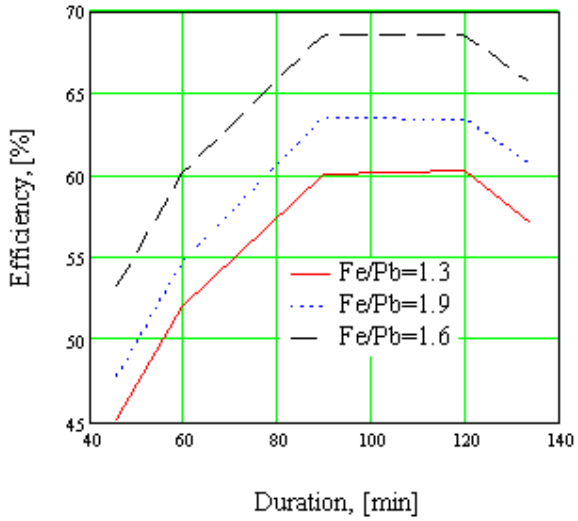

Fig.4. Extraction yield versus the depends on the amount of reduction agent at 50 ° C

Table 2

PO2 Program

Sample	Process parameters (coded units)			Process parameters (uncoded units)			Process Performance , η, %
	Temp. x_1	Molar ratio Fe/Pb x_2	Duration x_3	Temp. °C	Molar ratio Fe/Pb	Duration, min.	
1	-1	-1	-1	50	1.3	60	49.80
2	+1	-1	-1	70	1.3	60	60.24
3	-1	+1	-1	50	1.9	60	51.79
4	+1	+1	-1	70	1.9	60	61.08
5	-1	-1	+1	50	1.3	120	59.71
6	+1	-1	+1	70	1.3	120	87.94
7	-1	+1	+1	50	1.9	120	62.12
8	+1	+1	+1	70	1.9	120	89.67
9	0	0	0	60	1.6	90	83.52
10	0	0	0	60	1.6	90	83.14
11	0	0	0	60	1.6	90	86.88
12	0	0	0	60	1.6	90	82.74
13	0	0	0	60	1.6	90	85.98
14	-1.471	0	0	45.29	1.6	90	58.68
15	+1.471	0	0	74.71	1.6	90	86.22
16	0	-1.471	0	60	1.1587	90	70.71
17	0	+1.471	0	60	2.0413	90	77.22
18	0	0	-1.471	60	1.6	45.87	69.01
19	0	0	+1.471	60	1.6	134.13	90.12

It enables one to calculate the mathematical model, proved to be proper one the optimal conditions, and to determine the process parameters leading to maximum efficiency cement lead. These best values are: 70°C operating temperature, process duration-120 min, the molar ratio Fe/Pb 1.6, for which extraction yield is 97.78%. Since the error of calculation of the process for the regime considered is 5.35, maximum efficiency to be taken into consideration for designing industrial plant is 92.43%.

5. Conclusions

- Studies and preliminary investigations have taken account the folloiyng parameters which have a significant influence on process performance (*yield of solubilization - y*): *temperature (z_1), the duration of the process (z_2) and the ratio L / S (z_3)*; other parameters - *particle size reduction (dm)* and *stirring speed (rpm),* or they have a significant influence - case of stirring speed, or they are limited by cost; in this case they are kept constant.

- To determine the optimal conditions for conducting the process of hardening, experiments were conducted under an active experimental program that is active namely orthogonal second-order program (PO2).

- The mathematical model obtained with this program and presented as a polynomial of degree two of three variables, was subjected to statistical analysis and based on Fisher criterion correlation was found between the model and experimental data.

R E F E R E N C E S

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