Study Concerning PbO Solubility in NaOH Solution for the Treatment of Sulfate-oxide Pastes Obtained from Dismantling used Lead-acid Batteries

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Growing of waste lead-acid battery quantity, collected from processors, means the growing demand for secondary lead as raw material for car batteries, both needed for increased cars production and for replacing of waste batteries for increased number of automotive in service. During operation of accumulator batteries due to the chemical reaction that occurs during their recharging and unloading, lead sulfate is forming, therefore, if in the initial paste the major component is PbO, then in accumulator paste the main component is $PbSO_4$. *Finally, sulfuric acid concentration decreases at 10 %. Leaching method with sodium hydroxide solutions is one of the most recent initiatives for lead obtaining, attempting a double win: the environment pollution control and processing of secondary resources such as volatile dust resulted from lead extractive metallurgy of primary resources. This method consists in leaching with sodium hydroxide solutions followed by electrolytic extraction of lead and regeneration of sodium hydroxide solution.*

Keywords: waste lead-acid battery; lead sulfate; sodium hydroxide; leaching; electrolytic extraction

The data presented in the literature [1- 7] showed that hydrometallurgical methods processing for oxide-sulfate paste obtained from disassembling of spent battery accumulators are in the laboratory research stage, pilot and functional way without being promoted on an industrial scale.

Generally, these methods are different by the way systems and techniques are used for performing of lead leaching process from oxide-paste.

Depending on the solvent used are known the following methods for lead leaching, namely:

- in chlorides solutions (NaCl, $CaCl_2$);
- in acidic solution;
- in alkaline solution (NaOH);
- in amines.

From all these lead leaching methods we considered that a real chance to promote at industrial scale has:

- Leaching method of lead in acidic solutions [8, 12];
- Leaching method in sodium hydroxide solutions [9].

Lead leaching, especially lead sulfate, in sodium chloride solutions and calcium chloride occurs almost selectively dissolving in addition to lead solution, only silver and copper.

Leaching of lead sulfate in sodium chloride solutions occurs according to reaction:

$$PbSO_4 + 2NaCl = PbCl_2 + Na_2SO_4 \qquad (1)$$

The best results for leaching of these compounds are given by EDA and DETA. These compounds at room temperature are totaling soluble in water in any proportion. Leaching of lead compounds occurs according the following reactions:

$$PbSO_4 + 2EDA \rightarrow [Pb(EDA)_2]SO_4 \qquad (2)$$

$$PbO + EDA + EDA\ H_2SO_4 \rightarrow [Pb(EDA)_2]SO_4 + H_2O \quad (3)$$

Lead extraction from lead complex is performed by treatment with carbon dioxide, resulting, lead carbonate, ethylenediamine sulfate and ethylenediamine carbonate according to chemical reaction.

$$2[Pb(EDA)_2]SO_4 + 3CO_2 + 5H_2O \rightarrow PbCO_3Pb(OH)_2 + 2EDA\ H_2CO_3 + 2EDA\ H_2SO_4 \qquad (4)$$

Solvent regeneration from mother solution is performed by treatment with chalk which decomposed the sulfuric acid complex.

$$2EDA\ H_2SO_4 + Ca(OH)_2 \rightarrow CaSO4 \rightarrow 2H_2O + EDA \quad .(5)$$

Fluosilicate solutions is a chosen alternative in most of lead refining installations, but also, are used electrolyte solutions by fluoborat and sulphamate type. From all lead complexes present in oxide-sulfate paste only PbO is soluble in hexafluosilicic acid. For that, in first stage is necessary to reduce $PbSO_4$ to $PbCO_3$ or PbO.

General reactions that are involved in leaching with hexafluosilicic acid are:

$$PbO + H_2SiF_6 = PbSiF_6 + H_2O \qquad (6)$$

$$PbCO_3 + H_2SiF_6 = PbSiF_6 + H_2O + CO_{2(g)} \qquad (7)$$

Lead extraction from hexafluosilicic acid solutions is performed by electrolysis.

The method with sodium hydroxide solutions is a part of the most new initiatives for lead obtaining, attempting a double win: the environment pollution control and processing of secondary resources such as volatile dust resulted from lead extractive metallurgy of primary resources.

These consist in leaching with sodium hydroxide solutions, flowed by electrolytic extraction of lead and regeneration of sodium hydroxide solution. Principal chemical reactions involved are:

$$PbSO_4 + 4NaOH = Na_2PbO_2 + Na_2SO_4 + 2\ H_2O \qquad (8)$$

$$PbO + NaOH = Na_2PbO_2 + H_2O \qquad (9)$$

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$$Pb + 2NaOH = Na_2PbO_2 + H_2 \quad (10)$$

All three reactions generate sodium plumbite. Lead extraction from solutions is carried out by electrolysis with stainless steel OL anodes with obtaining of a cathode deposit in sponge form, which can be easily removed and must be melted for metallic lead obtaining. For establishing work conditions, there have been made tries to solubilize lead oxide with sodium hydroxide solutions, at different concentrations and L:S ratios, depending on temperature.

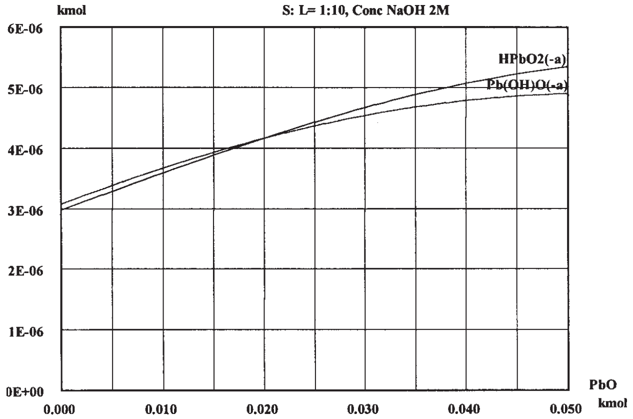

Fig.1. Equilibrium diagram of the PbO-NaOH-H_2O system at S:L=1:10 and concentration 2M NaOH

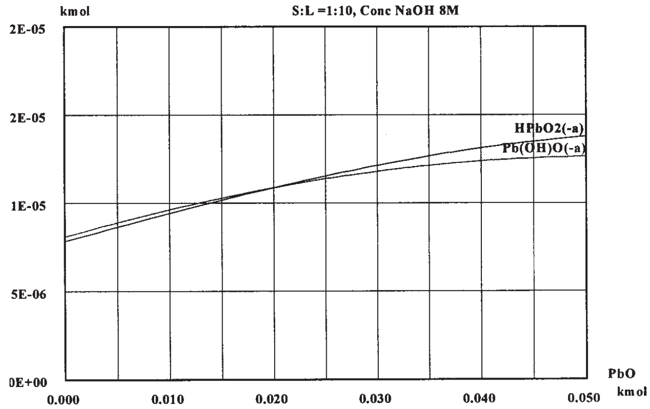

Fig.2. Equilibrium diagram of the PbO-NaOH-H_2O system at S:L=1:10 and concentration 8M NaOH

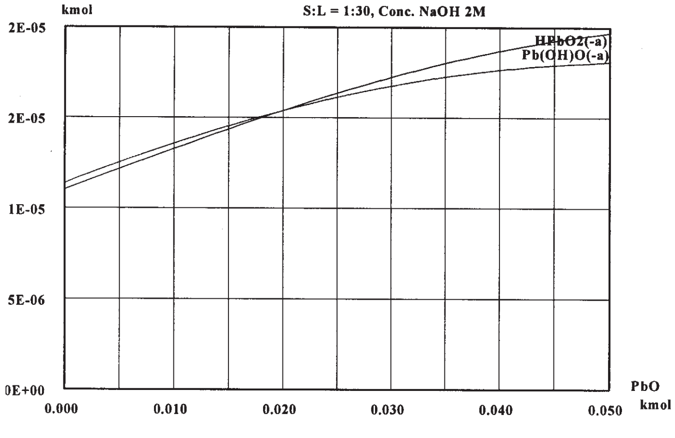

Fig.3. Equilibrium diagram of the PbO-NaOH-H_2O at S:L=1:30 system and concentration 2M NaOH

Experimental part

Experimental study on leaching of lead complexes in NaOH solutions

Literature data offer less information about PbO-NaOH-H_2O system. Generally are presented dates about the leaching of PbO in solutions until 100g/L NaOH. For this reason, to understand better the chemical process of lead leaching in alkaline media, were used the presented data from theoretical diagram performed with the help of HSC Chemistry Program (fig.1-6) at different NaOH concentration and ratio L:S.

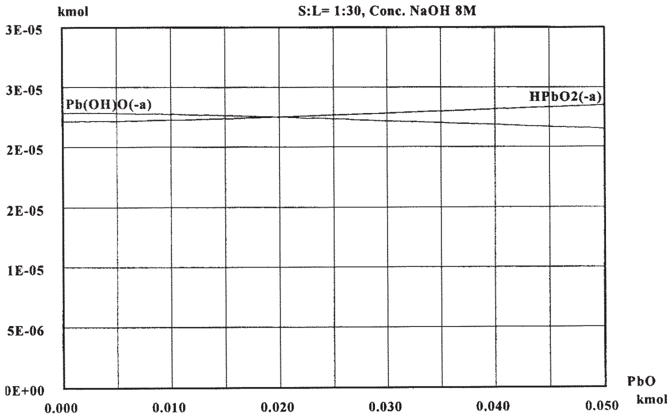

Fig.4. Equilibrium diagram of the PbO-NaOH-H_2O system at S:L=1:30 and concentration 8M NaOH

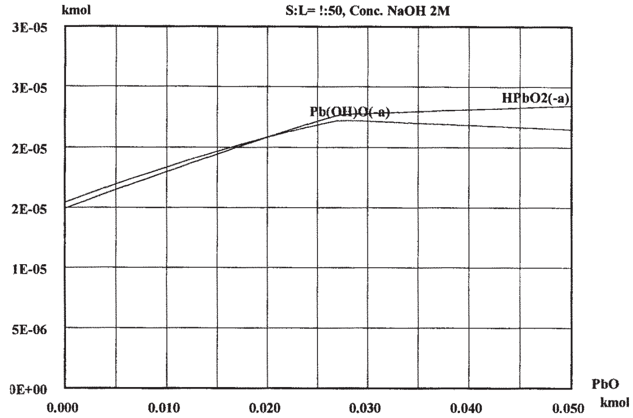

Fig. 5. Equilibrium diagram of the PbO-NaOH-H_2O at S:L=1:50 system at 2M NaOH

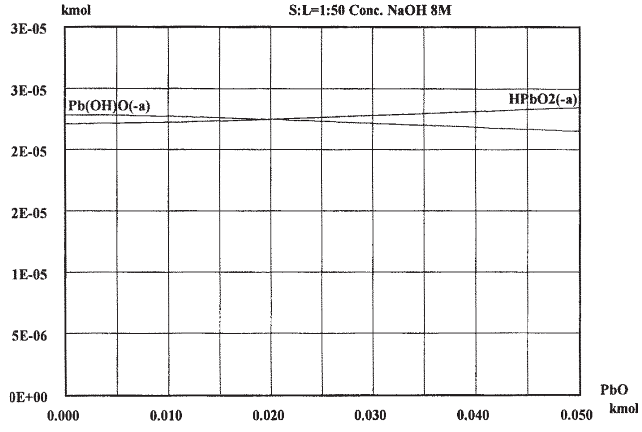

Fig. 6. Equilibrium diagram of the PbO-NaOH-H_2O at S:L=1:50 system and concentration 8M NaO

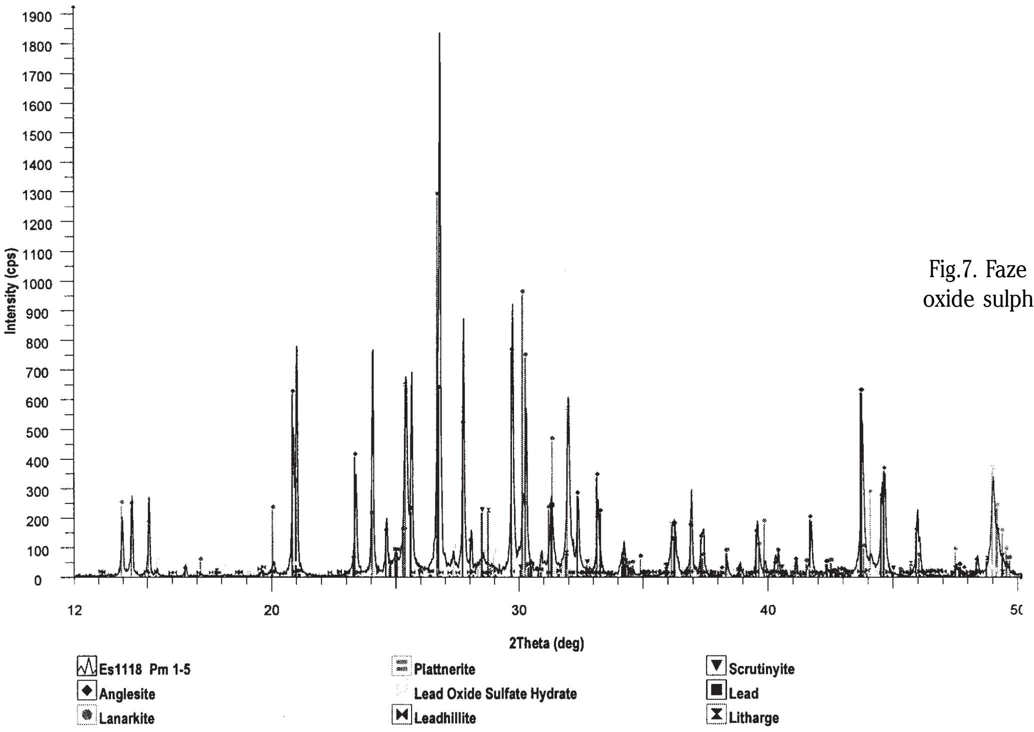

Fig.7. Faze analysis through DRX for the oxide sulphate paste from used batteries

Table 1
FAZE ANALYSIS OF THE OXIDE SULPHATE PASTE

Elements	Pb	Fe	Sb	Si	Ca	AS	Cu	S	O_2	Sn	Na	C	H_2O	Others	TOTAL
Compounds	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
PbO	13.190								1.020						14.210
PbO_2	18.350								2.837						21.187
$PbSO_4$	38.690							5.981	11.962						56.633
Pb met.	2.820														2.820
$Fe_2(SO_4)_3$		0.089						0.076	0.153						0.318
Na_2SO_4								0.016	0.032		0.023				0.071
$Sn(SO4)_2$								0.010	0.020	0.019					0.050
SiO_2				0.110					0.126						0.236
CaO					0.022				0.009						0.031
$CuSO_4$							0.032	0.016	0.032						0.080
As_2O_3						0.025			0.008						0.033
Sb_2O_3			0.410						0.081						0.491
C												0.880			0.880
H_2O													0.290		0.290
Others														2.671	2.671
TOTAL	**73.050**	**0.089**	**0.410**	**0.110**	**0.022**	**0.025**	**0.032**	**6.100**	**16.279**	**0.019**	**0.023**	**0.880**	**0.290**	**2.671**	100.000

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As we can see a passing of the lead into solution is possible through solubilisation of the lead oxide also at low solution concentrations and low temperatures, the diagrams being built at room temperature (298K).

Below are presented experimental data regarding the lead oxide leaching in sodium hydroxide solutions at different concentration by using pure substances.

Equipment and operating mode

Faze analysis [10] through X-ray diffraction of the pastes was done using the Bragg-Brentano diffraction method, on plane powdery samples.

Data acquisition was realized on the BRUKER D8 ADVANCE diffract meter with the help of the DIFFRACplus XRD Commander (Bruker AXS) software, using the Bragg-Brentano diffraction method, Θ–Θ in a vertical configuration.

Solution analysis: atomic absorption spectrometer with a GBC 932 AB plus type flame.

After analysis the following results have been obtained, concerning the faze composition of the oxide sulphate pastes (table 1 and fig. 7).

Results and discussions

In the following, leaching experiments for the lead oxide, one of the main components of the oxide sulphate paste, have been made. The results regarding the lead sulphate and the pastes will be presented in another paper.

Table 2
EXPERIMENTAL DATA REGARDING THE SOLUBILISATION OF PbO IN $NaOH$ SOLUTIONS

Sample	Conc. $NaOH$, M	Temp., °C	L:S Ratio	Pb in solution, g/l	Extraction Yield, %
1	2	40	1:10	26.45	28.47
2	4	40	1:10	40.08	43.40
3	6	40	1:10	40.87	46.65
4	8	40	1:10	30.06	30.05
5	2	60	1:10	33.09	24.52
6	4	60	1:10	42.42	36.33
7	6	60	1:10	43.87	39.79
8	8	60	1:10	33.41	33.34
9	2	80	1:10	39.82	31.64
10	4	80	1:10	48.02	36.13
11	6	80	1:10	54.85	40.87
12	8	80	1:10	51.79	41.17
13	2	40	1:30	26.03	74.98
14	4	40	1:30	32.87	97.07
15	6	40	1:30	33.88	97.88
16	8	40	1:30	33.03	95.77
17	2	60	1:30	29.19	81.62
18	4	60	1:30	30.08	83.68
19	6	60	1:30	29.97	97.85
20	8	60	1:30	33.89	95.69
21	2	80	1:30	34.16	93.03
22	4	80	1:30	35.09	93.93
23	6	80	1:30	36.02	97.48
24	8	80	1:30	34.01	95.05
25	2	40	1:50	19.87	93.01
26	4	40	1:50	21.32	97.76
27	6	40	1:50	22.48	97.11
28	8	40	1:50	21.40	94.82
29	2	60	1:50	20.08	99.42
30	4	60	1:50	18.23	99.14
31	6	60	1:50	19.86	99.13
32	8	60	1:50	17.72	97.43
33	2	80	1:50	23.12	96.10
34	4	80	1:50	21.71	96.05
35	6	80	1:50	21.08	95.45
36	8	80	1:50	20.09	96.93

The experiments were performed by using litharge and $NaOH$ of analytical purity. Leaching was carried out in thermostatic flask, phase being separated by ceramic vacuum filter. Reaction time was about 3600 s; reaction is reversible, relatively fast and is not necessary more than 300 s.

Is knew[11] that medium rate of PbO leaching in $NaOH$ solutions are:

- 1.44 g Pb/l. sec in interval 0 – 300 s;
- 0.01 g Pb/l. sec in interval 300 – 1800 s;
- 0.008 g Pb/l. sec in interval 1800 – 3000 s.

Results are showed in table 2 and figure 8-10.

The experimental data presented in table 2 were mathematically and statistically processed with the help of Jandel Scientific program, and the results are presented in figure 8 through figure 10.

L:S=1:10 Ratio

z=a+LOGNORMX(b,c,d)+LOGNORMY(e,f,g)+
LOGNORMX(h,c,d)*LOGNORMY(1,f,g) (11)

r2 Coef Det	DF Adj r2	Fit Std Err	F-value
0.8962841699	0.6197086231	5.2147112793	4.9381312623

Param	Value	Std Error	t-value	Trust	Limits
a	34.31534424	1.33336e+08	2.5736e-07	-3.7065e+08	3.70653e+08
b	15.63254269	1.64469e+08	9.50487e-08	-4.572e+08	4.57197e+08
c	5.13232549	0.232898013	22.03679381	4.48490555	5.779745431
d	0.27730852	0.0796392	3.482060606	0.05592404	0.498693001
e	8.56972503	1.28096e+08	6.69009e-08	-3.5609e+08	3.56086e+08
f	79.27476088	1.10752e+10	7.15789e-09	-3.0787e+10	3.07872e+10
g	0.20767245	1.10289e+08	1.88299e-09	-3.0658e+08	3.06585e+08
h	10.57068446	1.58005e+08	6.69009e-08	-4.3923e+08	4.39229e+08

```
    r2 Coef Det          DF Adj r2           Fit Std Err
    0.8962841699       0.6197086231        5.2147112793
Source   Sum of Squares       DF     Mean Square      F        P>F
Regr       939.98561                   7     134.28366       4.93813
Error    108.77285              4     27.193214
Total    1048.7585              11
```

From the data presented above we can see the value of r (the multiple correlation coefficient) is very close to 1, this meaning that between the objective function and the considered parameters there is a strong connection. The determination coefficient (r^2) shows that 90% of the extraction yield for the lead in the solution depending on the temperature and the NaOH concentrated solution is explained by equation 11. Because the value of F (Fisher's constant) is 4.93813, and the signification threshold P is 0.01096 (value which always has to be smaller than 0.05), the proposed regression model for the case variation studied is valid and can be used for the dependency analysis between variables.

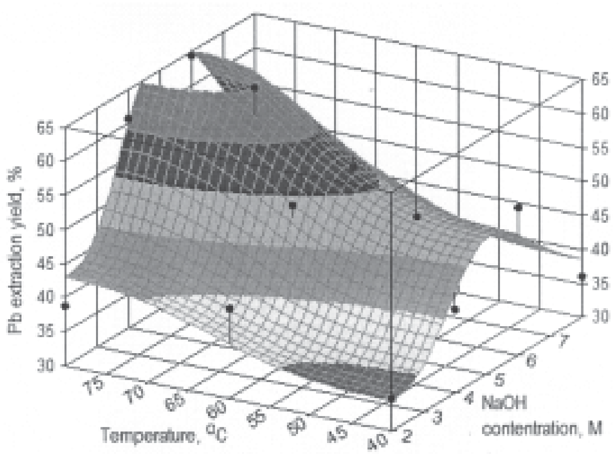

Fig.8. Extraction yield variation for the lead depending on temperature and NaOH concentration temperature at a L:S=1:10 ratio

L:S=1:30 Ratio

Rank 19 Eqn 151276347 lnz=a+bx2+cx3+d/lny+e/y0.5 (12)

```
r2 Coef Det      DF Adj r2      Fit Std Err      F-value
0.9330056806  0.8771770811  1.0375008139  24.371617701
```

Param	Value	Std Error	t-value	Trust	Limits
a	-342.307548	174.4238174	-1.96250462	-756.378663	71.76356684
b	-0.00737592	0.004250064	-1.73548368	-0.0174653	0.002713467
c	0.000922178	0.000493053	1.870343392	-0.0002483	0.002092654
d	2777.622732	1398.890465	1.985589867	-543.25479	6098.500254
e	-2578.54539	1295.292939	-1.99070443	-5653.48893	496.3981565

```
r2 Coef Det              DF Adj r2             Fit Std Err
0.9330056806           0.8771770811          1.0375008139
Source   Sum of Squares     DF    Mean Square      F          P>F
Regr        104.93521         4     26.233803      24.3716    2.11345.10-2
Error       7.5348556         7     1.0764079
Total        112.47007         11
```

From the data presented above we can see the value of r (the multiple correlation coefficient) is very close to 1, this meaning that between the objective function and the considered parameters there is a strong connection. The determination coefficient (r^2) shows that 93% of the extraction yield for the lead in the solution depending on the temperature and the NaOH concentrated solution is explained by equation 12. Because the value of F (Fisher's constant) is 24.3716, and the signification threshold P is $2.11345.10^{-2}$ (value which always has to be smaller than 0.05), the proposed regression model for the case variation studied is valid and can be used for the dependency analysis between variables.

L:S=1:30 Ratio

z=a+LOGNORMX(b,c,d)+LOGNORMY(e,f,g)+
LOGNORMX(h,c,d)*LOGNORMY(1,f,g) (13)

```
r2 Coef Det      DF Adj r2      Fit Std Err      F-value
0.7947539293  0.247431074  7.5859209561  2.2126859767
```

Param	Value	Std Error	t-value	Trust	Limits
a	80.37754949				
b	-3.5028123				
c	7.35263588	577.3301626	0.012735582	- 1597.53464	1612.23991
d	0.131538983	86.8710815	0.001514186	- 241.356438	241.6195163
e	-14.9905518				
f	54.76577423				
g	0.260031302				
h	45.22331603				

r2 Coef Det	DF Adj r2	Fit Std Err
0.7947539293	0.247431074	7.5859209561

Source	Sum of Squares	DF	Mean Square	F	P>F
Regr	891.32164	7	127.33166	2.21269	$1.2254.10^{-3}$
Error	230.18479	4	57.546197		
Total	1121.5064	11			

From the data presented above we can see the value of r (the multiple correlation coefficient) is very close to 1, this meaning that between the objective function and the considered parameters there is a strong connection. The determination coefficient (r^2) shows that 93% of the extraction yield for the lead in the solution depending on the temperature and the NaOH concentrated solution is explained by equation 13. Because the value of F (Fisher's constant) is 2.21269, and the signification threshold P is $1.2254.10^{-3}$ (value which always has to be smaller than 0.05), the proposed regression model for the case variation studied is valid and can be used for the dependency analysis between variables.

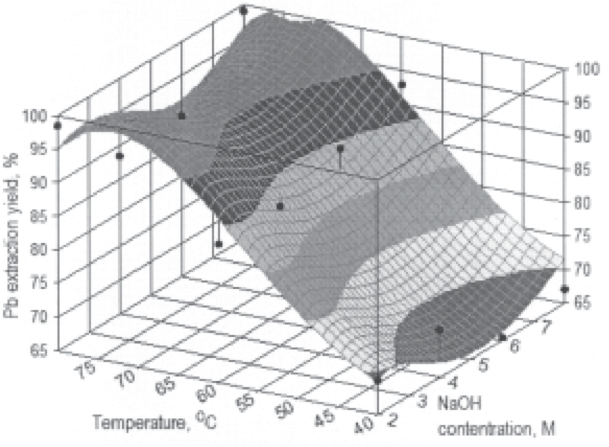

Fig.9. Extraction yield variation for the lead depending on temperature and NaOH concentration temperature at a L:S=1:30 ratio

It can be observed that in experiments with excess of PbO (S:L=1:10), temperature is important if is higher than 60°C. For S:L = 1:30 and S:L = 1:50 these differences are more less. Also, at ratio S:L = 1:10 (PbO excess) were observed that at 8M NaOH leaching efficiency for lead is more less than at 6M NaOH. We consider that 8M NaOH solutions have a strong oxidant character and transform a part of PbO in PbO_2 which have a little solubility in NaOH solutions.

From experiments it can be observed at a lower concentration of NaOH than 2M NaOH hydrolysis phenomenon is produced for PbO with formation of $3PbO.H_2O$. Solution is mat and very hard to filter.

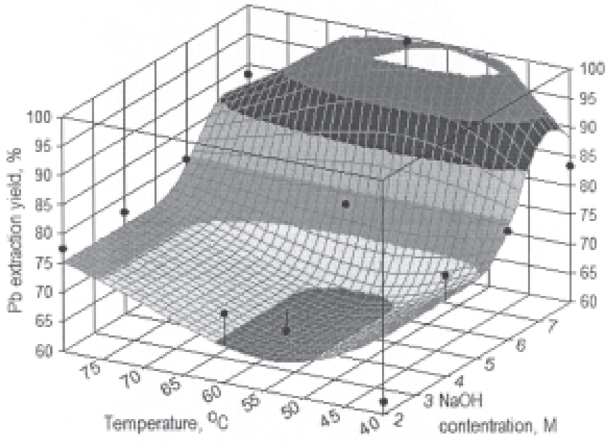

Fig.10. Extraction yield variation for the lead depending on temperature and NaOH concentration temperature at a L:S=1:50

Conclusions

The leaching with sodium hydroxide solutions method is one of the most recent initiatives for obtaining lead, attempting a double win: the environment pollution control and processing of secondary resources such as volatile dust resulted from lead extractive metallurgy of primary resources.

For a better understanding of chemical process for lead leaching in alkaline media, we used data presented in theoretical diagram performed with help of HSC Chemistry Program at different NaOH concentration and ratio L:S.

At PbO leaching to a ratio S:L=1:10, best results are obtained at a temperature higher than 60°C. At S:L=1:30 and S:L=1:50 influence of temperature is lower. Also, at S:L=1:10 (PbO excess) was observed that at a 8M NaOH concentration, Pb leaching efficiency is less than at 6M NaOH. We could not clarify this issue scientifically. We consider that 8M NaOH solutions have a strong oxidant character and transform a part of PbO in PbO_2 which have a little solubility in NaOH solutions.

From experiments can be observed at lower concentration of NaOH than 2M NaOH hydrolysis phenomenon is produced for PbO with formation of $3PbO.H_2O$.

Using these data were performed leaching tests on industrial waste and the results will be presented in another paper.

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