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STUDY OF $PbSO_4$ SOLUBILISATION IN NaOH SOLUTION, FOR THE TREATMENT OF OXIDE-SULPHATE PASTES OBTAINED FROM DISMEMBERED LEAD-ACID BATTERIES

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The paste from dismemberment of discarded lead-acid batteries contains mostly lead sulphate and lead oxide. Both can be solubilized with high yielding sodium hydroxide, the result being sodium with lead that can ultimately be exposed to electrolysis. A small quantity of insolubilized paste, which remains in the form of solid residue, is recycled to a classification phase. Using this procedure, no residue is to be generated during the hydrometallurgical process. The method of sodium hydroxide solution solubilisation belongs to a recent initiative of obtaining lead, while attempting a double win: the control for the pollution of the environment and the processing of other secondary resources, such as the volatile dusts resulted from the metallurgical extraction of lead from primary resources. This work presents the experimental results regarding the solubility of the lead sulphate. The parameters considered were the NaOH concentration, the S:L ratio, and the temperature under the working circumstances: concentrations 2;4;6 and 8M NaOH, S:L,ratios of 1:10, 1:30, 1:50, at temperatures 40°C, 60°C and 80°C.

Keywords: lead wastes, solubilisation, hydrometallurgical process, discarded lead-acid batteries

1. Introduction

Metal recycling is the most mature and most developed of all the recycling industries. The intense development of lead recycling during the second half of

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the 20-th century has raised the problem regarding the use of "environmentally friendly" new technologies [1,2] in order to process this secondary raw material, by eliminating the toxin-generating processes, for as accurately as possible.

The DIRECTIVE no. 2006/12/EC from 05.04.2006 concerning waste, approved by the European Parliament and the European Union Council, was published in the Official Journal of the European Union and which came into effect as soon as the old Waste Directive no.75/442/EEC was abolished (which had been amended by the Directive no 91/156/EEC).

This new directive establishes the basis for waste management, made up-to-date concerning: technology, terminology, definitions, principles, basic demands for collecting, transporting, depositing, recycling, organising and environmental aspects.

Among the general provisions concerning recyclable waste, also applicable for the acid-lead based discarded batteries, there are some aspects worth mentioning:

- applicable recovery operations: metal or metal compounds recycling is to be achieved without endangering human life and without adopting environmentally harmful processes or methods ;
- the organisations and economical agents which organise waste collections or professional waste transportation, as well as waste recovery for their own benefit or for third parties, need to be authorized and registered by the competent national authorities in conformity with the national legislation of the country members;

Besides the general aspects of the directive concerning the acid-lead based discarded batteries, there are also some specific provisions such as the ones which classify this kind of waste as the Q6 category of waste –parts (ex: discarded batteries, exhaust catalytic converters etc.).

In order to ignore the disadvantages involved using pyrometallurgical procedures for processing discarded batteries, research has been made for applying hydrometallurgical procedures which consist of lead solubilisation in sodium hydroxide solution as long as the resulting lead is electrolytic pure lead obtained through the electrolysis of these solutions.

The alkaline solubilisation

The paste contains mostly lead oxide and lead sulphate [3], table 1-3; it is leached with sodium hydroxide, the result being $PbNa_2(OH)_4$ which is afterwards subjected to in electrolysis:

$$PbSO_4 + 2NaOH \rightarrow PbO + Na_2SO_4 + H_2O \quad (1)$$

$$PbO + 2NaOH + H_2O \rightarrow PbNa_2(OH)_4 \quad (2)$$

The compound is denoted as sodium plumbite, $Na_2Pb(OH)_4$.

A small quantity of non-leached paste remains as solid residue and it is recycled to the classification phases for separating dismantled batteries components. This way no residue is generated in the hydrometallurgical process.

In order to prevent impurities from going through the process of electrolysis or from falling out on the cathode along with the lead, the process of leaching is to be made against the current. The impurities that might get into the electrolyte are the amphoteric ones such as antimony, copper, arsenic or tin. Working against the current, the dissolution of the impurities when the solution becomes saturated in lead becomes limited.

The electrolytic deposition

The soluble species of lead existing in the solution is electrodeposited on the cathode as a Pb layer similar to a sponge, and afterwards, through the melting process lead ingots can be obtained.

The reactions which take place during the electrolysis are as it follows:

At the cathode: $PbNa_2(OH)_4 + 2e^- \rightarrow Pb^0 + 2NaOH + 2OH^-$ (3)

At the anode: $2OH^- - 2e^- \rightarrow 1/2O_2 + H_2O$ (4)

the overall reaction: $PbNa_2(OH)_4 \rightarrow Pb^0 + O_2 + 2NaOH + H_2O$ (5)

The Regeneration of NaOH resulted from reaction (1) is achieved using whitewash, according to the following reaction:

$$Na_2SO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2NaOH \quad (6)$$

Table 1.

The components of discarded batteries [3].

No	Components of discarded batteries	wt. % (average value)	wt. % for dry material
1.	Electrolyte (conc. H_2SO_4 10-15%)	15-20 (17.5)	-
2.	Fraction of metal (lead - grids and terminals)	25 – 30 (27.5)	41
3.	Paste with about 70% Pb	40-50 (45)	47
4.	Light fraction: polypropylene PVC and ebonite	6 (3.5)	7 4
5.	Others	0.5	1 Get involved in the residual acid
	TOTAL amount	100	

We also determined by chemical analysis the lead compounds in the sulphate-oxide paste (table 6).

Table 2.

The Chemical composition of the sulphate-oxide paste [3].

Sample	Elements, %								
	Pb	Fe	Sb	Si	Sn	As	Cu	Sn	SO_4^{2-}
I	70.10	0.064	0.61	0.10	0.010	0.005	0.025	0.010	15.80
II	73.05	0.089	0.41	0.11	0.019	0.025	0.024	0.019	18.75

Table 3.

Phase analysis of paste, regarding lead species [3].

Sample	Pb_{tot}	Components (%)				
		$PbSO_4$	PbO_2	PbO	Pb_{met}	other
I	70.10	50.92	17.71	18.74	1.75	0.82
II	73.45	56.63	21.18	14.21	3.10	0.14

1.1. A theoretical study regarding the solubility of $PbSO_4$ in a NaOH solution

In general, the chemical reference data offer little information about the $PbSO_4 – NaOH – H_2O$ system regarding the solubility.

The data from the solubilisation of PbO in solutions of just under 100g/L NaOH are generally taken into account and commented on.

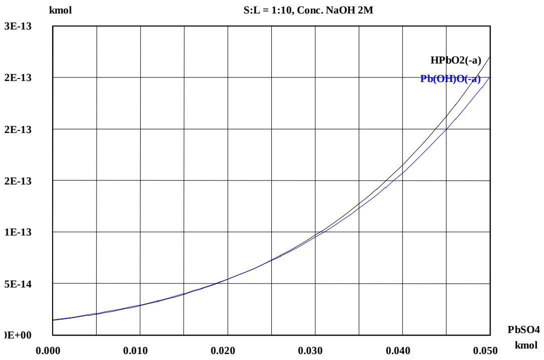

Fig.1

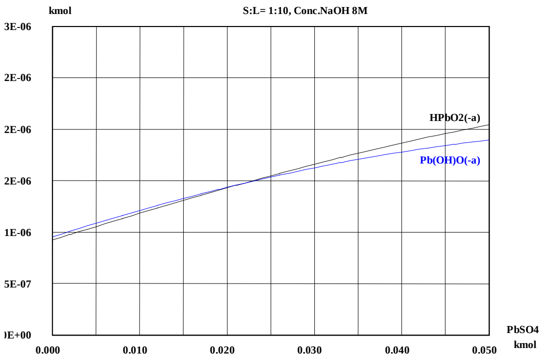

Fig.2

Fig.1. The solubility equilibrium diagram of the $PbSO_4$-$NaOH$-H_2O system with S:L=1:10 and a 2M NaOH concentration.

Fig.2. The solubility equilibrium diagram of the $PbSO_4$-$NaOH$-H_2O system with S:L=1:10 and a 8M NaOH concentration.

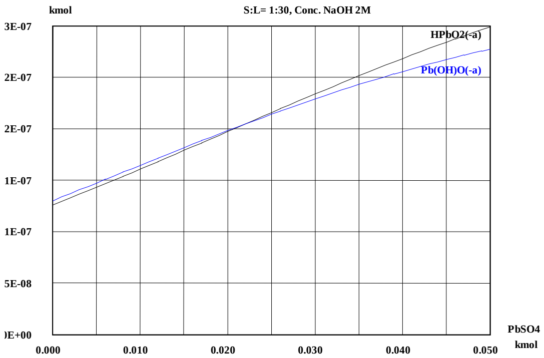

Fig.3

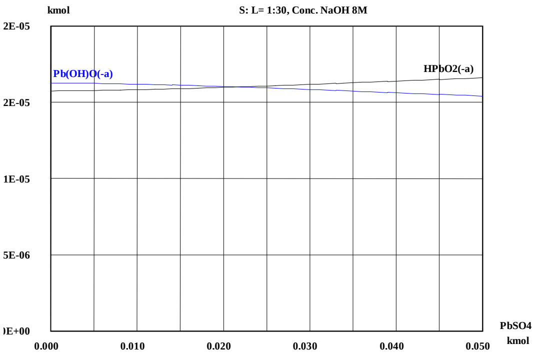

Fig.4

Fig 3. The solubility equilibrium diagram of the $PbSO_4$-NaOH-H_2O system with S:L=1:30 and a 2M NaOH concentration.

Fig. 4. The solubility equilibrium diagram of the $PbSO_4$-NaOH-H_2O system with S:L=1:30 and an 8M NaOH concentration.

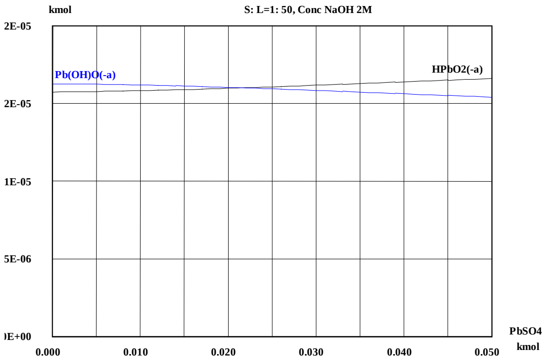

Fig.5

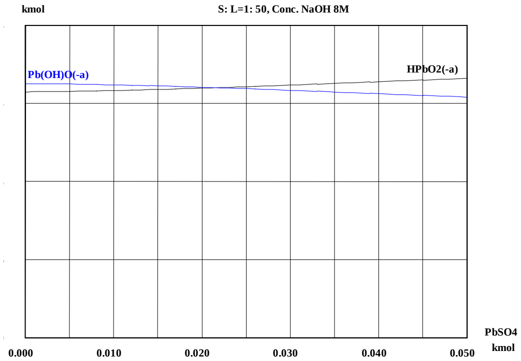

Fig.6

Fig. 5. The solubility equilibrium diagram of the $PbSO_4$-NaOH-H_2O system with S:L=1:50 and a 2M NaOH concentration.

Fig. 6**.** The solubility equilibrium diagram of the $PbSO_4$-NaOH-H_2O system with S:L=1:50 and an 8M NaOH concentration

Because of this, in order to better understand the chemical process of lead solubilisation in an alkaline environment we used data offered by the theoretical diagrams built by using the HSC Chemistry 6 programme [4] (fig.1-6) for different NaOH concentrations and S:L weight.

According to the study, the following conclusion can be drawn: lead sulphate can dissolve very well in relatively diluted sodium hydroxide solutions, at a low temperature. The study was achieved at 298K.

2. Materials, equipment and methods

In order to complete the experimental research for the lead sulphate-oxide solubilisation, at a laboratory level the following devices and equipment were checked and put into operation: 500-2000 ml – capacity Berzelius beaker, 250-1000 mL-capacity graduated cylinders, a mechanical agitator with the possibility to adjust the agitation speed from 0 to 2000 rot/min, an electrical stove type IKA RH GIGITAL KT/C, MZ 2C type vacuum pump, a Buchner funnel with a diameter of 110 and 195mm, blue band - type filter paper, a 1000ml Erlenmeyer beaker.

The sulphate-oxide paste resulted from dismantling used batteries was chemically analysed using either the classical analytical chemisty methods for great concentrations in elements, or the FAAS and DCP instrumental methods (flamed atomic absorption spectrometry and continuous current plasma atomic emission spectrometry) for small concentrations in elements.

Analysis was made using the BRUKER D8 ADVANCE diffract meter with the help of the DIFFRAC^{plus} XRD Commander (Bruker AXS) software, through the Bragg-Brentano diffraction method, with a $\Theta - \Theta$ coupling in a vertical configuration and the following parameters: power 40kV×40mA, radiation CuKα. Removal of the CuKβ component was done electronically using the SOL X detector.

The analysis for the solutions obtained through solubilisation was achieved with the atomic absorption spectrometry using an atomic absorption spectrometer with a flame, type GBC 932 AB plus.

3. Experimental results and discussions

The experiments were achieved by using analytically pure reagents as $PbSO_4$ and NaOH aqueous solution. The solubilisation was performed in thermostatic conditions and the phases were separated by a ceramic-void filter.

$PbSO_4$ solubilisation takes place in two steps:

1. the removal of SO_4^{2-} by using weak base solutions, according to the following reaction:

$$PbSO_4 + 2OH^- = Pb(OH)_2 + SO_4^{2-} \tag{7}$$

2. for the next step, the following reaction takes place, resulting the plumbite anion:

$$Pb(OH)_2 + OH^- = Pb(OH)_3^- \tag{8}$$

which may be written as H_3PbO_3

During the experiments the following parameters were taken into consideration:

- The NaOH concentration;
- The S:L weight ratio;
- The temperature.

The results are presented in Table 4.

The experimental data presented in Table 4 were processed mathematically and statistically with the help of the Jandel Scientific program.The results are presented in Figures 7-9.

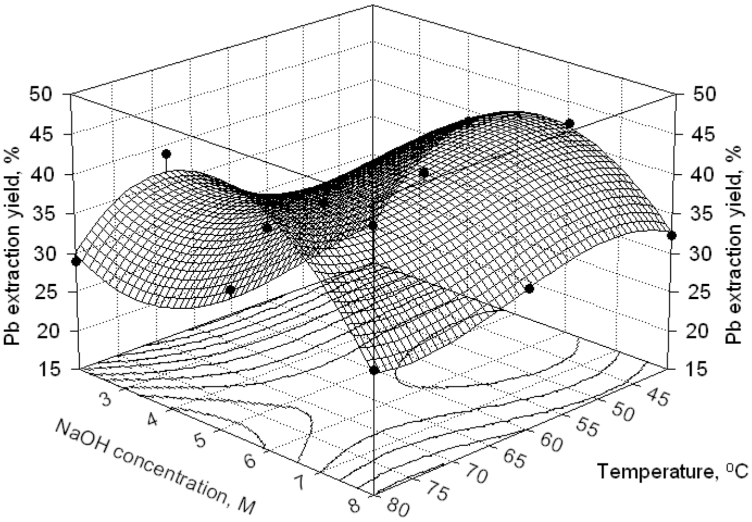

Fig.7. The extraction yield variation for the lead depending on temperature and the NaOH concentration at a S:L=1:10 weight.

Table 4.

Experimental data concerning the solubilisation of lead sulphate in a sodium hydroxide solution

Sample	Conc. NaOH, M	Temp., °C	S:L ratio	Pb conc. in solution,g/L	Pb extraction yield, %
1	2	40	1:10	24,95	20,05
2	4	40	1:10	33,11	38,48
3	6	40	1:10	35,09	42,23
4	8	40	1:10	22,44	32,32
5	2	60	1:10	20,02	18,29
6	4	60	1:10	25,08	34,18
7	6	60	1:10	32,26	42,36
8	8	60	1:10	24,91	32,62
9	2	80	1:10	21,83	28,97
10	4	80	1:10	27,93	46,81

11	6	80	1:10	30,02	42,19
12	8	80	1:10	23,73	30,09
13	2	40	1:30	20,07	94,12
14	4	40	1:30	21,91	93,05
15	6	40	1:30	22,03	93,10
16	8	40	1:30	22,88	98,43
17	2	60	1:30	19,87	90,06
18	4	60	1:30	21,76	88,43
19	6	60	1:30	22,83	94,96
20	8	60	1:30	23,02	98,26
21	2	80	1:30	22,43	99,03
22	4	80	1:30	23,05	97,32
23	6	80	1:30	23,93	98,52
24	8	80	1:30	22,76	92,15
25	2	40	1:50	13,64	96,12
26	4	40	1:50	13,02	92,58
27	6	40	1:50	13,08	91,07
28	8	40	1:50	13,19	95,16
29	2	60	1:50	13,48	96,06
30	4	60	1:50	13,30	94,44
31	6	60	1:50	13,32	94,93
32	8	60	1:50	13,32	95,66
33	2	80	1:50	13,85	96,78
34	4	80	1:50	13,38	91,27
35	6	80	1:50	13,24	94,92
36	8	80	1:50	13,26	95,52

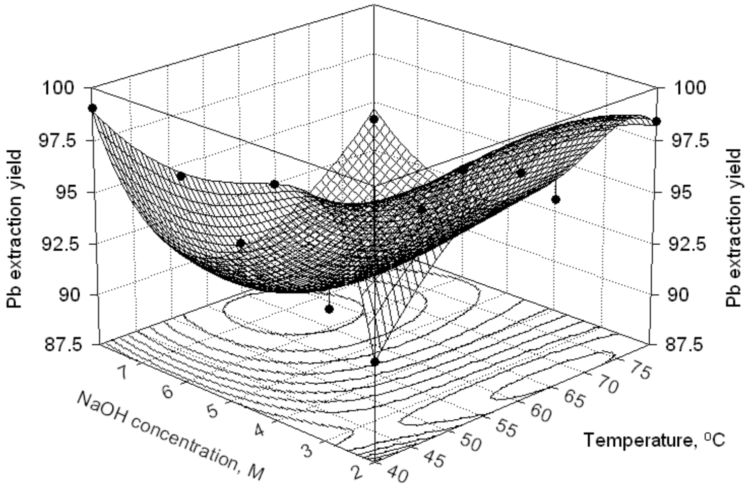

Fig. 8. The extraction yield variation for the lead depending on temperature and the NaOH concentration at a S:L=1:30 weight

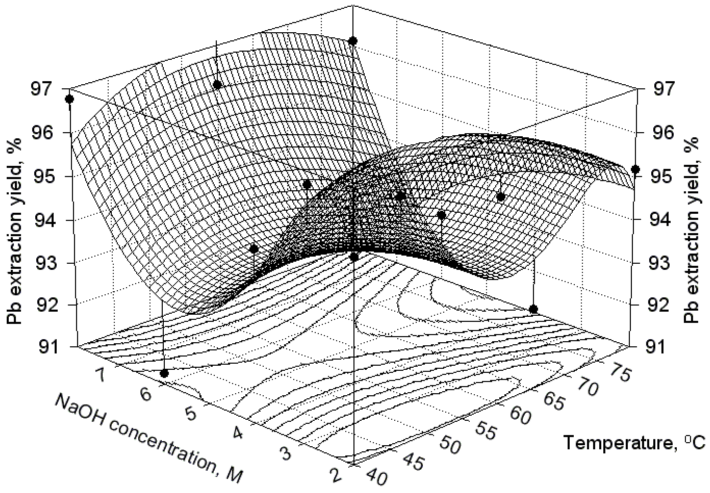

Fig.9. The extraction yield variation for the lead depending on temperature and the NaOH concentration at a S:L=1:50 weight.

During the experiments where the mixture exceeds in $PbSO_4$ (S:L = 1:10), the influence of temperature is significant. Only if is higher than 60°C at S:L ratio= 1:30 and S:L ratio= 1:50 this influence is smaller.

Also, for the ratio S:L = 1:10 (excess of $PbSO_4$) we noticed that for 8M NaOH solution, the lead solubilisation yield is smaller than at 6M NaOH. Thus, we appreciate that solutions of 8M NaOH have a strong oxidising character and convert a part of PbO into PbO_2, which has a smaller solubility in solutions. Also, the compounds of Pb^{2+} convert into compounds of Pb^{4+}.

According to experiments we noticed that at concentrations smaller than 2M NaOH the $Pb(OH)_2$ forms $PbO.H_2O$ (hydrated Pb oxide). The solution is opaque and very hard to be filterd.

The decrease of lead solubilisation in 8M NaOH solutions (noticed at PbO solubilisation) is visible in this case also. The lead concentrations in solution are lower for $PbSO_4$ and higher for the PbO solubilisation. In the solutions with 2 - 6M NaOH, the $PbSO_4$ solubilisation is done after an approximate linear dependence of function of concentration.

Experimental results show the highest yields of over 92% of the lead solubilisation from paste were obtained when the chemical process took place in the following working conditions:

- solubilisation agent	NaOH 6M solution
- temperature	60^0C
- reaction time	2 h
- L:S weight ratio	20 - 30:1

In these conditions we obtained a sodium hydroxide solution rich in lead, which may be subject to electrolysis to obtain lead.

4. Conclusions

The method of leaching with sodium hydroxide solutions with various concentrations and temperatures was tested.

The theoretical study conducted on equilibrium diagrams performed at room temperature revealed that the lead sulfate dissolves well in relatively diluted solutions of sodium hydroxide at a high enough speed. The experiments were carried out using the $PbSO_4$ and NaOH solutions of analytical grade.

For the $PbSO_4$ leaching with a ratio S:L=1:10, the temperature does not significantly influence the extraction yield, and values up to 50% were obtained. The yield of about 99% was obtained for S:L = 1:30 and temperature of 60-80^oC. Accordig to experiments, it was noticed that at a lower concentration of NaOH solution than 2M NaOH, the phenomenon of hydrolysis for the PbO takes place with the formation of $3PbO.H_2O$.

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