STRUCTURAL AND PHYSICO-CHEMICAL ANALYSIS OF WASTE FROM USED LEAD –ACID BATTERIES

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Pasta sulfato-oxidică provenită din dezmembrarea bateriilor uzate a fost analizată din punct de vedere chimic, utilizând metodele clasice pentru concentraţii mari în elemente, sau metode instrumentale FAAS şi DCP (spectrometrie de absorbţie atomică în flacără şi spectrometrie de emisie atomică în plasmă de curent continuu) pentru concentraţii mici. De asemenea s-a efectuat studiul mineralogic pentru determinarea principalelor faze existente în material şi a conexiunilor lor morfologice, realizat prin difracţie de raze X şi microscopie optică.

The sulfato-oxide of paste dismembered batteries was chemically analyzed, using classical methods for high concentrations of elements, or instrumental methods and DCP FAAS (flame atomic absorption spectrometry and atomic emission spectrometry in plasma DC) for low concentrations. In order to determine the main mineralogical phases existing in the material and their morphological connections, X-ray diffraction and optical microscopy were used.

Keywords: waste, lead-acid batteries, characterization

1. Introduction

From statistical data released by the National Recycling Materials there are collected annually about 34.000 tons of waste lead-acid batteries and scrap metal, lead and alloys of lead.

The increase of quantities of lead-acid batteries used, taken by processors in the country signifies the growing demand for secondary lead as raw material for manufacturing automobile batteries, required by the increased domestic production of cars and for the replacement of the batteries to the big number of motor vehicles on the domestic market[1,2].

In order to facilitate the understanding of the processes of recycling of waste batteries together, the following is a brief and simplified description of them. Table 1 outlined the components of a new battery, with ebonite or polypropylene enclosure.

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With the possibility of a motivation, improve environmental pollution, and market requirements (polypropylene enclosures are significantly lighter), weight batteries with ebonite decreased enclosure for batteries with a polypropylene case. Currently it is estimated that the total battery, 90% are polypropylene case [3,4,5].

Table 1

Componentele unei baterii noi (%)

Components	Battery filled with acid		Battery without acid	
	Ebonite case	Polypropylene case	Ebonite case	Polypropylene case
Paste	31,2	35,7	41,6	49,8
Acid	25,0	28,6	0,0	0,0
Grids	19,5	22,3	26,0	31,4
Bridges+ terminals	5,2	5,9	6,9	8,3
Separators	2,2	2,5	2,9	3,5
Case	16,9	5,0	22,6	7,0
TOTAL	100,0	100,0	100,0	100,0

According to data presented it is noted that the batteries are composed of the following components:

• oxide paste (paste) consisting of PbO and PbO_2 Lead metal (for new batteries) and metallic lead and PbO, PbO_2, $PbSO_4$ (for used batteries)

• metal fraction: grids, bridges, terminals (polar head)

• non metallic fraction: ebonite Polypropylene, PVC

• H_2SO_4 solution concentration 32% (on fresh batteries) and 10% (in used batteries)

Table 2 gives the chemical composition of the components of a new battery, full of acid with polypropylene case (kg).

During the operation of the accumulator as a result of chemical reactions that occur when loading and unloading, lead sulfate forms:

at the anod:

$$Pb + HSO_4^- \rightarrow PbSO_4 + 2e^- + H^+$$

at the cathod:

$$\underline{PbO_2 + HSO_4^- + H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O}$$

$$Pb + PbO_2 + 2H^+ + 2HSO_4^- \rightarrow 2PbSO_4 + 2H_2O$$

For this reason, if the major component in the paste is initialy PbO, in the accumulators paste the main component is $PbSO_4$. Finally, the concentration drops to 10% sulfuric acid.

Tables 3 and 4 give the components resulting from manual dismantling of two types of batteries resulted from used accumulators.

Table 2

Phase composition of new battery of accumulators

Components	Amount	Pb_{tot}	Sb	H_2SO_4	H_2O	SO_4^{2-}	PVC	pp
Paste	5,7	5,3	-	-	-	-	-	-
Acid (32% H_2SO_4)	4,55	-	-	1,45	3,1	1,42	-	-
Grids	3,60	3,4	0,2	-	-	-	-	-
Bridges+ terminals	0,95	0,9	0,05	-	-	-	-	-
Separators PPV	0,4	-	-	-	-	-	0,4	-
Polypropylen Case	0,8	-	-	-	-	-	-	0,8
TOTAL (kg)	16,0	9,6	0,25	1,45	3,1	1,42	0,4	0,8
TOTAL (%)	100,0	60,0	1,60	9,00	19,0	8,0	2,5	5,0

2. Results and discussion

2.1. The microscopic study was performed with mineralogical a microscope with polarized light type Axiolmager A1m. The micrographs were recorded with a digital camera Canon Power Shot A type 640, 10X digital zoom. The samples for analysis was embedded in resin type EpoThin - Buehler, vacuum, and then prepared by grinding on emery paper and polishing on cloth soaked with a Lecloth type suspension α - alumina in water. Table 5 presents the complete chemical composition of pulp accumulators.

Table 3

Components of a used batteries (%)

Component	Polypropylene batery 12V 66 Ah		Ebonite baterie 12V 70 Ah	
	Amount kg	% raported at acid batery	Amount kg	% raported at without acid batery
Bridges+ terminals	1,320	8,71	2,100	10,81
Grids	4,250	28,05	3,050	15,64
Paste	3,000	19,80	3,000	15,43
Grids with adherent paste	4,950	32,67	6,000	30,86
Separators	0,580	3,83	0,950	4,88
Case	1,050	6,94	3,650	18,78
Pitch + remains ebonite	-	0,00	0,700	3,60
TOTAL amount without acid	15,150	100,00	19,450	100,00
Acid	2,350		2,050	
TOTAL amount with acid	17,500		21,500	

2.2.Phase analysis by X-ray diffraction (XRD) was performed by Bragg- Bretano diffraction method on flat powder samples.

Data acquisition: bz means of BRUKER D8 diffractometer was performed by using the software ADVANCE XRD DIFFRACplus Commender (Bruker AXS) method Bragg-Brentano diffraction, coupling Θ - Θ vertical configuration with the following parameters: Power, 40kV×40mA; Radiation, Cu Kα; Primary radius (mm), 250; Secondary radius (mm), 250; Receiving slit width (mm), 0.2; Divergence slit width (mm) / angle (°), 1/0.5; Anti scatter slit width (mm) / angle (°), 1/0.5; Filament Length (mm), 12; Sample Diameter (mm), 15; Receiving Slit Length (mm), 12; Primary Sollers (°), 2.5; Secondary Sollers (°) , 2.5; 2Θ Region, $4 \div 74^0$; 2Θ Step, 0.02^0; Time (sec)/step, 3; Scan mode, Continous;
Scan type, Locked Coupled; Rotation speed (rot/min), 60; CuKβ component removal was done electronically with SOL detector X.

Table 4

Composition of used batteries

No	Components of used batteries	% Weight ratio (total amount)	% Weight ratio (dry material)
1.	Electrolyte (conc. H2SO4 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**	

Data processing: A DIFFRACplus program BASIC Evaluation Package, version EVA12, 2006 composition DIFFRACplus BASIC software package (Bruker AXS) and databases ICDD PDF-2 Release 2006 were used.

Table 5

Chemical composition of sulfato-oxide paste

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

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

Table 6

Phase analysis of lead

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

Table 7

Name of compounds	Chemical formula	S-Q, wt. %
Anglesite	$PbSO_4$	38
Lanarkite	Pb_2SO_5	36
Plattnerite	PbO_2	9
Lead Oxide Sulfate Hydrate	$(PbO)_3(Pb(SO_4))(H_2O)$	6
Leadhillite	$Pb_4(SO_4)(CO_3)_2(OH)_2$	4
Scrutinyite	PbO_2	3
Lead	Pb	2
Litharge	PbO	2

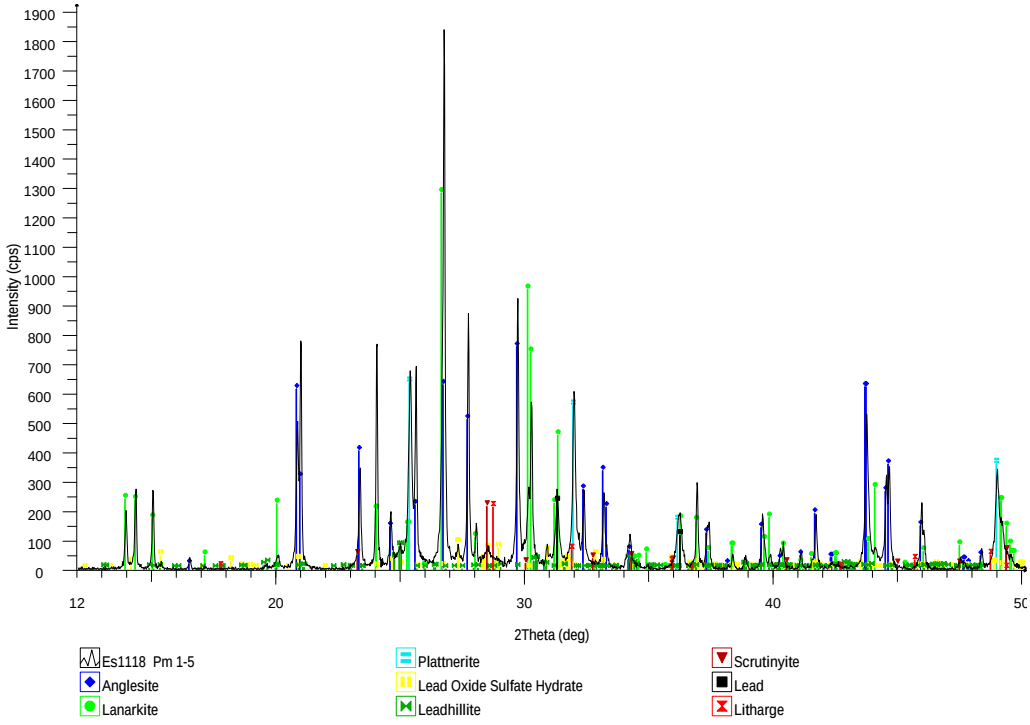

Fig. 1. XRD pattern for sulfato - oxide pasta in used batteries

These compounds in the paste of lead-oxide sulfate were put in evidence by mineralogical analysis (X-ray diffraction analysis and microscopic study) determining the main morphological phases and their connections.

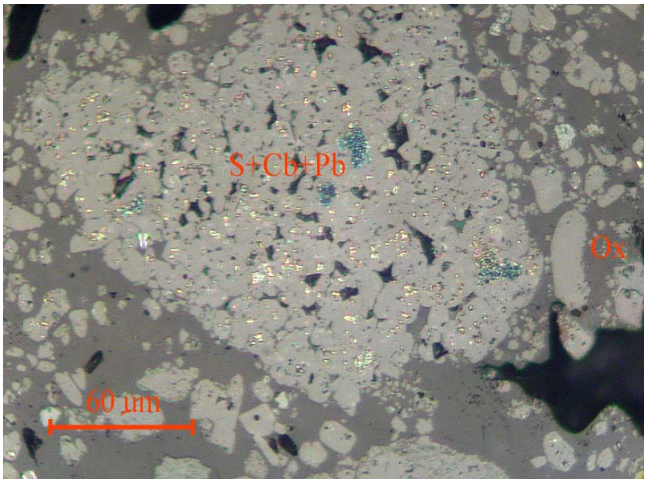

Fig. 2. Sample P1. X500, NII, reflected light. S-sulfate-carbonate Cb, Pb-lead, lead oxide-Ox

Phase analysis by X-ray diffraction (XRD) of the sample P2 highlighted the following phases (table 7 and Fig. 1).

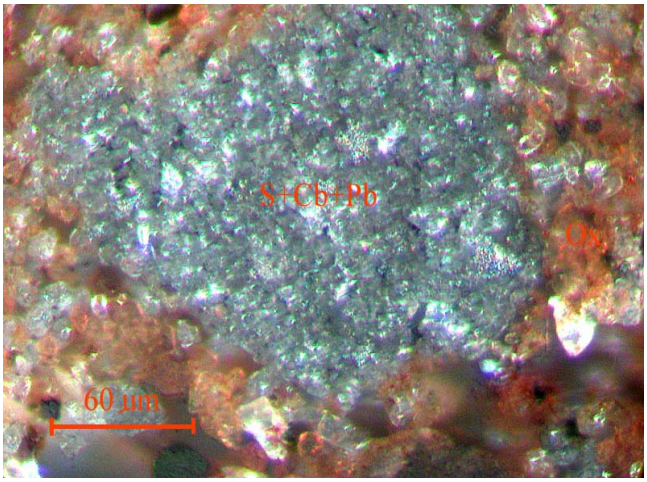

Fig. 3. Sample P1. X500, N +, reflected light. S-sulfate-carbonate Cb, Pb-lead, lead oxide-Ox

The microscopic study shows that the paste is composed of microcrystalline material in the form of aggregates. Studied in polarized light, the sample shows characteristic of white internal reflections for anglesite-PbSO4, yellow, characteristic of massicot - litharge PbO and characteristic of red - PbO and Minium - Pb3O4. In aggregate, metalic lead particles are trapped (see fig. 2-5).

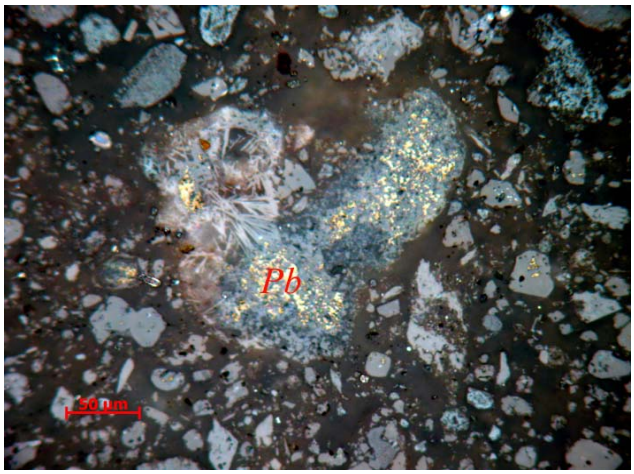

Fig. 4. P2 sample. X500, NII, reflected light
Microcrystalline aggregates of sulphate and metallic oxides containing lead fragments
S-sulfate-carbonate Cb, Pb-lead, lead oxide-Ox.

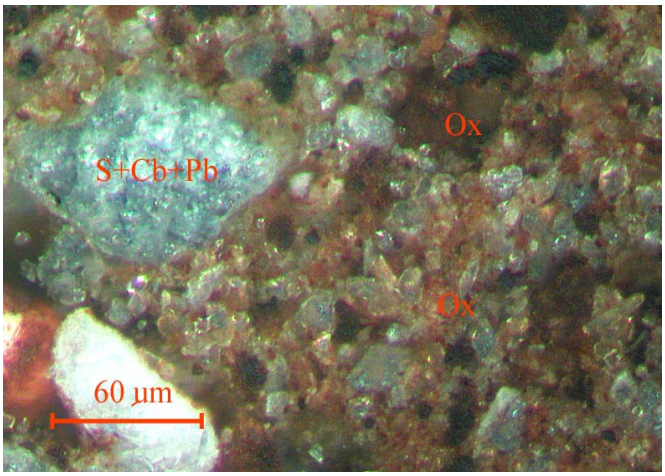

Fig. 5. P2 sample. X500, N +, reflected light
S-sulfate-carbonate Cb, Pb-lead, lead oxide-Ox

Table 8

Phasic composition of sulfato-oxide paste - part I

Elements	Pb	Fe	Sb	Si	Ca	AS	Cu
Compounds	%	%	%	%	%	%	%
PbO	13,190						
PbO_2	18,350						
$PbSO_4$	38,690						
Pb met.	2,820						
$Fe_2(SO_4)_3$		0,089					
Na_2SO_4							
$Sn(SO4)_2$							
SiO_2				0,110			
CaO					0,022		
$CuSO_4$							0,032
As_2O_3						0,025	
Sb_2O_3			0,410				
C							
H_2O							
Others							
TOTAL	**73,050**	**0,089**	**0,410**	**0,110**	**0,022**	**0,025**	**0,032**

Phasic composition of sulfato-oxide paste - part II

Elements	S	O_2	Sn	Na	C	H_2O	Others	TOTAL
Compounds	%	%	%	%	%	%	%	%
PbO		1,020						14,210
PbO_2		2,837						21,187
$PbSO_4$	5,981	11,962						56,633
Pb met.								2,820
$Fe_2(SO_4)_3$	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		0,126						0,236
CaO		0,009						0,031
$CuSO_4$	0,016	0,032						0,080
As_2O_3		0,008						0,033
Sb_2O_3		0,081						0,491
C					0,880			0,880
H_2O						0,290		0,290
Others							2,671	2,671
TOTAL	**6,100**	**16,279**	**0,019**	**0,023**	**0,880**	**0,290**	**2,671**	100,000

Metallic lead, mainly occurs as inclusions in $PbSO_4$ particles; most of the antimony is present in the paste form of solid solution Sb_2O_3 and PbO_2, Pb_2O, Pb_2O_3. Based on the chemical and mineralogical analysis it was established the phase composition of the paste, which is presented in table 8.

Particle size analysis of sulfato-oxide paste shows that particle sizes are <1mm (table 9).

Table 9

Particle size analysis

Sieve size (mm)	Sample 1 %	Sample 2 %
d > 1	0,1	0,1
0,5 < d < 1	11,7	11,7
0,1 < d < 0,5	26,8	26,4
0,063 < d < 0,1	15,2	15,2
d < 0,063	46,6	46,2
	100	100

3. Conclusions

We hawe determined chemical compounds existing in the lead-oxide sulfate paste, which proved to be $PbSO_4$, PbO_2, PbO, Pbmet. These compounds in were put in evidence by mineralogical analysis (X-ray diffraction analysis and microscopic study) the microscopic study shows that the paste is composed of microcrystalline material in the form of aggregates, microscopically indeterminate. Studied in polarized light, the sample shows characteristic of white internal reflections for Anglesite-PbSO4, yellow, characteristic massicot - litharge PbO and characteristic of red - PbO and Minium - Pb_3O_4. In the aggregate, metalic particles of lead are trapped. Metallic lead, mainly occurs as inclusions in most $PbSO_4$ particles, most of the antimony is present in the paste in the form of solid solution Sb_2O_3 and PbO_2, Pb_2O, Pb_2O_3.

R E F F E R E N C E S

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