

Clean Technology of Lead Recovery from Spent Lead Paste

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Abstract: - This paper focuses a hydrometallurgical process for recovering lead from lead paste form of tribasic lead sulfate (TBLS), which constitutes 60 % (wt %) of battery weight. The alkaline leaching process investigated in this paper present some distinct advantages over the pyrometallurgical processes routes. Optimum conditions were determined on the extraction efficiency of lead. Temperature and sodium hydroxide concentration were the variables tested. The temperature has a considerable effect on the yield of the lead extraction. This is valid for each liquid / solid ratio being studied. Since an increase of the quantity of the processed paste causes the reduction of the lead yield, the concentration of sodium hydroxide (or the L/S ratio) is the second important factor for the lead extraction. The most significant result obtained was a 75 % lead recovery after conventional alkaline leaching for 1 h with a 6M NaOH solution, at a temperature of 80⁰ C.

Key -Words: - Lead acid battery, battery paste, alkaline leaching, reprecipitation, tribasic lead sulfate

1 Introduction

Removal of spent batteries represents an environmental problem because of heavy metals that can be dispersed in the environment; as a matter of fact, some types of batteries, like the alkaline and zinc-carbon ones, can be thrown away together with unsorted municipal wastes. Current community legislation is Council Directive 91/157/EEC (and subsequent amending acts of Directives 93/86/EEC and 98/101/EC) on batteries and accumulators containing certain dangerous substances [1].

Drastic of legislation on production and consumption the lead changed character of its consumption caused by the need to recycle lead products. As a result, the degree of recycling of materials containing lead is growing. About 85 % of commercial products containing lead can be recycled [2].

The lead recycling battery industry uses various technological schemes. Most plants (80 of 190) have capacities on battery scrap is smelted due to processing the entire battery including its organic parts (casing, PVC separators in older battery types), inadequate removal of gases and vapors during the smelting and refining process absent

or inadequate flue gas treatment smelting of secondary lead in rotary furnaces; however, their contribution to the total output does not exceed 30 % because of a large number of small-output production capacities [3]. The lead-bearing components of a battery are: grid metal, poles, bridges (44 %), lead paste (56%), and lead paste contains: PbSO₄ (60 %), PbO (PbO₂) 19 %, Pb (21 %) [4]. Pyrometallurgical processing of lead paste involved the potential health and environmental risk when processing battery scrap is very high. Depending on the level of mechanization and environmental standards, the following environmental hazards can arise [5]: soil and groundwater contamination by acid spilled when batteries are emptied, wind dispersal of lead dust if crushed battery scrap is stored without protection, substantial atmospheric emissions (e.g. lead-containing dust, soot, SO₂, chlorides, dioxins, etc.).

The percentage value was transformed into a linguistic descriptor [16]. Therefore, it appears that the adoption of cleaner technologies at the pre-processing stage in secondary smelter operations can significantly improve the smelter performance from both economic and environmental perspectives. Consequently, future research should pursue these

options among secondary lead smelters.

The issue of battery paste by means of hydrometallurgical approaches has been described recently in the literature. These methods leaching in the lead paste to soluble sulfates by reacting with reagents such as NaOH, Na₂CO₃, K₂CO₃ solutions or acid citric and citrat salt [6-13]. As a significant clean technology, a hydrometallurgical processing facility is sulfate paste is highly efficient and produces a significantly lower amounts of emissions compared to pyrometallurgical systems. The use of a hydrometallurgical system to increased leads production, flux / energy savings, and significant reduction in SO₂ and slag. The desulfurization process is employed in quite a number of flowsheet of the processes in Western countries, its environmental advantages being indubitable. The best suitable reagents for the desulfurization process are aqueous solutions of sodium hydroxide [14]. Primary barriers to implementing improved environmental technologies and practices are economic factors [15]. The one-time capital cost investment was converted into an annual basis by dividing the value by 4 years to be able to compare it on equal level with annual benefits (a 4-yr normalization value was selected because it corresponds to the payback period for hydro-metallurgical units). Consequently, the obtained value was converted to a percentage level relative to the smelter's estimated.

The objective of this paper is to develop a novel process for recovering lead as tribasic lead sulfate (TBLS) from lead paste via chemical conversion by leaching, purification by precipitation with sulfuric acid and converted into TBLS by water ammonia.

TBLS is the most widely used thermal stabilizer for PVC plastics with strong ability of cohesion with hydrogen chloride, good long-term thermal stability, as excellent electrical insulation. It has the ability of white pigment with strong covering power, tolerate weather-resistant property and mainly used in non-transparent soft and hard products and cable material.

The results of the X-ray diffraction qualitative analysis show the presence of compounds such as PbSO₄ (68 %), PbO (PbO₂) 12 %, Pb (20 %). Other phases, which, on the basis of the chemical analysis, could be present, are probably below the detection limit. In order to exploit lead paste through sieve granulometric analysis was determined using a set of vibrating sieves with mesh size of 45-250 mm according to EN 24497/1994. Real assessment of the size of sulfate paste particle is shown in Table 2.

2. Experimental

2.1. Reactants and raw materials

Lead paste used in these experiments provided by Romplumb Co., Ltd, Romania, a company for recovery of spent lead acid-battery. The samples were washed with distilled water to remove remaining sulfuric acid until de pH value above 6.5. The chemical composition of the lead paste from the spent lead acid-battery given in Table 1, was determined by the inductively coupled plasma emission spectrometry (ICP-OES).

Table 2. Particle size analysis of lead paste

Class (µm)	250	100 -250	70-100	63-70	45- 63
Rest (%)	1	3,3	10	65,7	20

Its size distribution suggests that the reaction kinetics for the material that engages the paste should be fast, due to the prevailing fine particle sizes, which suggest that leaching may be an attractive route to treat this material, when lead recovery is of interest. The hydrometallurgy route is possible provided that the treatment process for the extraction of lead from the pulp, given the low sulfur content. It is interferred from the particle size distribution in Figure 1, that the proportion of the lead paste particles finer than 63 µm is higher than 85 vol.%.

Table 1. Chemical composition of the lead paste

Elem.	Pb	Cu	Sb	Fe	As	S
wt (%)	95-97	0.5-0.9	0.4-0.6	0.3-0.5	0.1-0.2	0.2-0.3

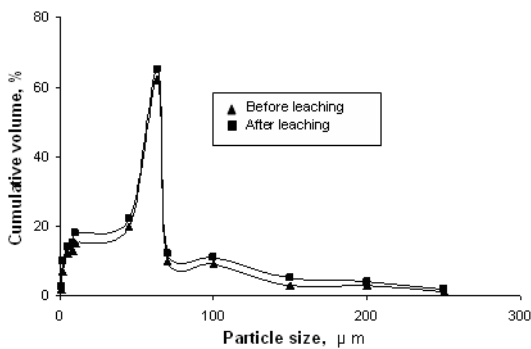


Fig.1 Particle size distribution of the before and after leaching

Lead paste particles, coarser than 63 μm , are therefore present in proportion less than 15 vol.% in these sulfate paste, before and after leaching for 1 h at 80 $^{\circ}\text{C}$.

2.2. Experimental set-up and procedure

Experimental facility (Figure 2) consists of the following components: stirrer engine, water thermostat, thermometer, feeder charge, and propeller. Alkaline leaching experiments were conducted in a glass reaction vessel Pyrex[®] of 1000 ml equipped with a teflon cap heated by a thermostatically controlled heating mantle. Stirring was done by variable-speed electric motor. Openings are located within the perimeter cap mercury thermometer, liquid sampling, and lead paste into powder.

The reactor has double walls with controlled water which acts as a thermostat which to perform the leaching at the desired temperature.

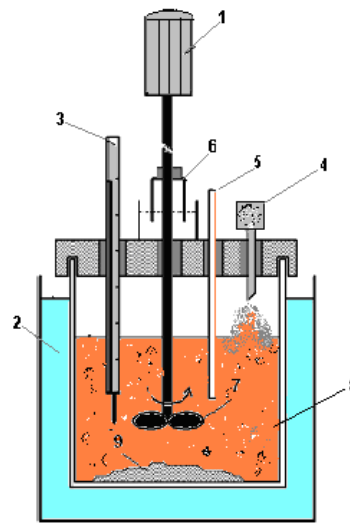


Fig.2 Device setup of the alkaline leaching lead paste: 1- stirrer engine; 2 -water thermostat; 3 – thermometer; 4 – feeder charge; 5 – sampling; 6 – water gasket; 7 – propeller; 8 – sulfate pulp suspension; 9 – sulfate paste; 10 – teflon cap.

Alkaline leaching tests are carried with a solution of 1000 mL of aqueous solution 6M NaOH Sample weight was set in the range of 30 - 80 g.

Three different ratios L / S of between 3 and 6 were used in the experiment, and the optimal value of selectivity was obtained by the L/S ratio of 1/6. The temperatures being used are 20, 40, 60, and 80⁰ C. The samples were collected after setting periods of time, and analyzing for Pb by ICP/AES. The samples are filtered into test tubes, and necessary to obtain a clear solution.

Significant amount of lead could be recovered from sulfate paste by using a three-stage process that comprising (1) alkaline leaching of the followed by precipitation at lead sulfate (2) and (3) in dissolution of lead sulfate in water ammonia solution of ammonium hydroxide. A flow sheet was proposed by alkaline hydrometallurgical process for lead paste, and it shown in Fig. 3.

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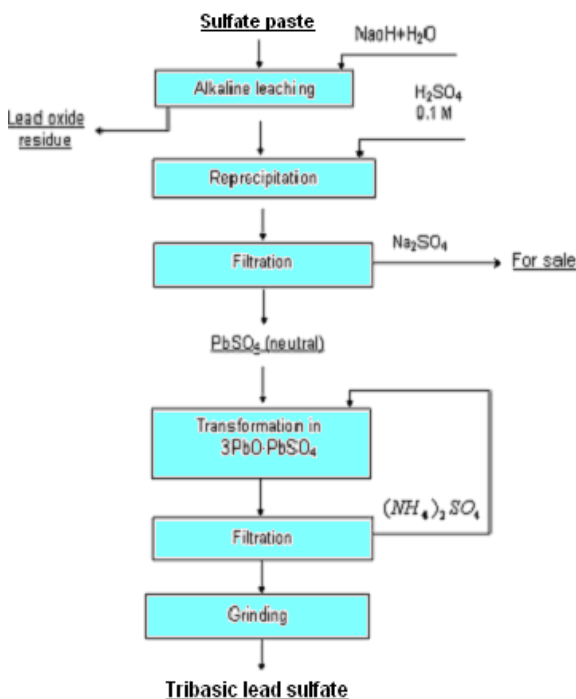


Fig. 3 A process flowsheet proposed for hydrometallurgical extraction of lead.

3. Results and discussion

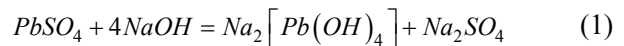
3.1. Desulfurization of lead paste

Lead oxides dissolve easily in alkalis, while zinc ferrite, silica and aluminum are very stable compounds and will dissolve only partially in alkalis. The solubility of certain amphoteric elements in strong alkaline solution decreases in the following sequence: Zn > Pb > Al > Cr(III) > Cu [17].

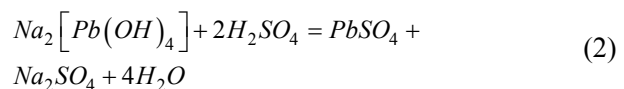
An aqueous solution of sodium hydroxide (NaOH, 99% purity, Lachema Czech Republic) was used as the desulfurizing agent to react with PbSO₄ in the paste. 6M NaOH while maintaining the stirring speed at 600 rpm was used as leaching agent, at a various solid / liquid ratio. The agent was added under constant agitation in a 1000 mL closed flask and a water-cooled condenser was used as flask cover in order to avoid solution loss by evaporation.

Aqueous alkaline solution was used to dissolve lead from the dust and was heated up to 80^o C and vigorously stirred, to avoid paste depositing on the bottom of the reactor.

The basic reaction that takes place in the reactor can be depicted as:

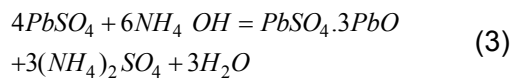


Alkaline leaching process lasted 1 h and the leaching mixture filtered was analyzed by atomic emission spectrometry. The second stage of the process consisted of the precipitation of lead neutral sulfate in sulfuric acid 0.1 M with density 1,10 g·cm³, given the reaction:



The process temperature was 25 ± 0.1 ^oC. Pure lead sulfate (PbSO₄) precipitates at the bottom of the reactor and the Na₂SO₄ is then crystallized from the remaining solution and can be sold off as a product.

The filter cake (PbSO₄) obtained in this stage detailed above would then be washed with water, and further treated by dissolution in ammoniacal solution of ammonium hydroxide by stirring at 400 rpm, when recast phase takes place in tribasic lead sulfate (TBLs):



The recast of lead sulfate in tribasic lead sulfate lasted 60 min, where S/L ratio ($PbSO_4 / NH_4OH$) was 1 / 3, at 25^o C temperature. After 3 h of drying the following amounts were found in TBLS: white powder with substances soluble in water, 0,1%; total lead oxide, 89%; lead oxide with 13% free lead, 57%; lead monoxide, 70%, and residue on sieve (250mesh)% \leq 0.80.

The solution, after TBLS filtering, is routed in the third stage.

However, the extraction efficiency of Pb is stable at 80^o C and at a 6 / 1 L/S ratio, when the Pb leaching rate reaches its maximum, around 75%.

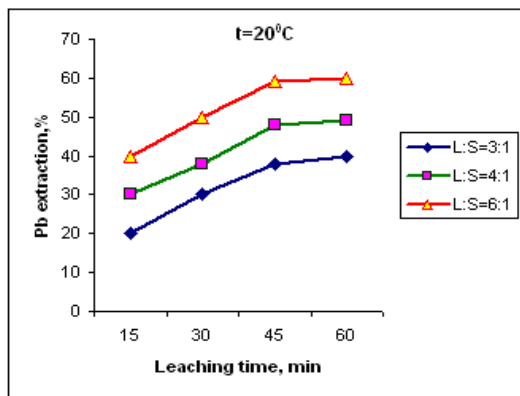


Fig. 5 Lead extraction vs. leaching time at different liquid-solid ratio (600 rot/min, 20^oC, 6M NaOH).

Increasing the amount of dust for leaching will lead to lower efficiency of lead extraction, because a large amount of solid will not be engaged and will remain unreacted. Optimum solid / liquid ratio was optimised to 1/6. Thus, increasing the quantity of the processed dusts causes the reduction of lead extraction yield.

3.4. Effect of temperature

On the other hand, temperature plays an important role in leaching. The temperature has a considerable effect on the yield of lead extraction.

Residue resulted after leaching and filtration in the first stage is a mixture of the ferrites, sulphides and sulphates consisting of 45 wt.% PbO, 20% PbO₂, 15% PbSO₄ and others, suitable for pyrometallurgical route. Separation of the residue from the leaching solution by decantation was fast and there was no need of using flocculants.

3.2. Effect of NaOH concentration

The major advantage with caustic soda leaching is its selectiveness in leaching lead compared to iron compounds. The concentrations of NaOH were 2, 4, 6, and 8M, while keeping the solution temperature at 20^o C, and stirring speed at 600 r/min. The leaching results are shown in Fig.4.

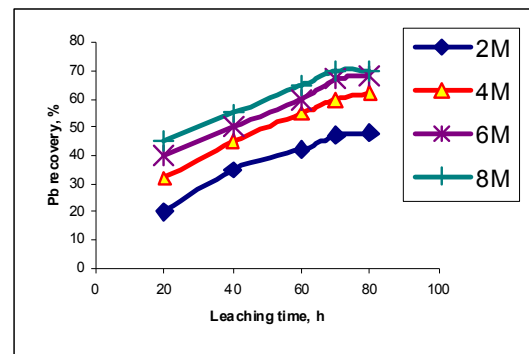


Fig. 4 Effect of NaOH concentration on lead extraction (600 rpm, 20^oC, 15% solid).

The rate of lead extraction increases as NaOH concentration rises up to 7 and 8 M, where about 70% Pb is extracted in 80 min. Additionally, the high NaOH concentration in solution increases its the viscosity, and will tend to reduce the diffusion rate of lead ions [18].

3.3. Effect of solid / liquid ratio

According to Fig. 5, results show that the ratio L / S as far as the lead extraction is concerned plays an important part in the dissolution process.

With different solid/liquid ratio, temperature has had a significant impact to the leaching time. Leaching temperature should lead to increased extraction of lead, but only at over 70^o C and after an hour. This is valid for each solid/liquid ratio studied, as illustrated in Fig. 6.

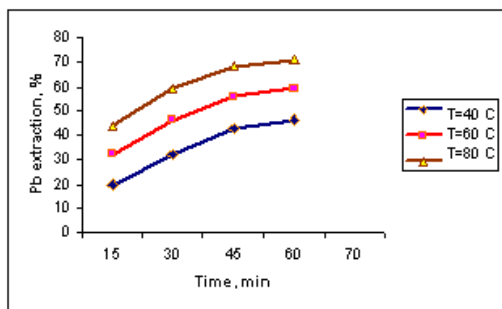


Fig. 6 Extraction of Pb by alkaline solution at different temperatures.

It was demonstrated that the high TBLS concentrations can be produced in the laboratory from pure lead sulfate mixed in water ammonia, within 4 h of drying at 80°C. Tribasic lead sulfate is mainly used as a heat stabilizer of PVC opaque or semi opaque products.

4. Conclusions

The main objective of this investigation was to propose an integrated method for the treatment, recovery and recycling of similar type of solid wastes. Specific emphasis was assigned to the efficient hydrometallurgical removal and subsequent recovery (after the appropriate precipitation) of main lead and content in the form of type lead compound ($3\text{PbO}\cdot\text{PbSO}_4$). According to the results obtained in this work, the hydrometallurgical recovery of lead from sulfate paste is feasible with a relatively high recovery yield, while mixture of oxides lead stays in solid phase. Regarding the management and minimization of residues, the alkaline treatment route is more favorable than the pyrometallurgical one.

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