

OBTAINING Na_2SO_4 FROM SODA SMELTING SLAG FROM THE RECYCLING OF LEAD ACID BATTERIES

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ABSTRACT

Soda smelting slag is generated during the processing of desulphurized paste from recycling of waste lead acid batteries and other lead containing secondary materials in tilting rotary furnaces, and it represents about 9.5 % of the mass of the charge entering the furnace. This type of slag is very reactive. It contains toxic substances (lead, arsenic and antimony) and because of the presence of alkaline compounds it is corrosive. In addition, it decomposes in contact with air, forming dust. Therefore, such hazardous product cannot be disposed without preliminary stabilization.

The aim of the present work is to investigate the possibility for environmentally utilization of this slag. The conducted experiments have shown the possibility of extracting the sodium sulfate from the soda slag only by grinding in an aqueous medium with subsequent filtration. The resulting solution is subjected to sulfide purification from heavy non-ferrous metals and subsequent crystallization for obtaining a commercial product sodium sulfate. These processes could be easily implemented in companies that have applied Engitec's technology for recycling spent lead-acid batteries and production of sodium sulfate from desulfurization of the lead paste. Implementation of these processes will eliminate the need for slag stabilization and prevent environmental problems.

Keywords: lead soda slag, spent lead-acid batteries, Engitec's technology, sodium sulfate.

INTRODUCTION

The main source for the production of secondary lead is waste lead batteries. One of the most effective and intelligent technologies for their recycling involves preliminary desulfurization before pyrometallurgical treatment. This process leads to reducing the consumption of reagents, increased productivity, reduction of lead losses with slag, increasing the lead content in the charge subject to pyrometallurgical treatment [1].

The first step in secondary lead processing is the breaking and separation of scrap batteries. In this step, batteries are shredded or disintegrated, then the battery components are separated by physical methods into metallic components, pastes containing lead oxides

and lead sulfate, plastics from battery cases and plate separators, and waste battery acid, which is usually neutralized with lime to form gypsum or is utilized for other purposes. Polypropylene recovered from cases is a valuable material and can be recycled for reuse.

The second step in this technology is the desulfurization of the lead paste, which is based on the lower solubility of lead carbonate (PbCO_3) compared to lead sulfate (PbSO_4). Lead sulfate converts to lead carbonate by addition of either a solution of sodium carbonate (NaCO_3) or ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$).

The third step is to process the desulphurized lead paste together with lead containing materials, fluxes (caustic soda or carbonated soda), reducing anthracite coal and iron in rotary furnaces.

Traditionally, a high sodium slag has been used since it had the characteristics of a relatively low melting point and low viscosity, allowing for good separation of slag and bullion. It also provided a means of capturing sulfur into the slag rather than reporting to the smelter gas and the need for costly gas scrubbing. However, there are significant costs in the use of soda ash and there are environmental problems with the disposal of soda slags.

Although soda slags provide a ready means of capturing sulfur and provide a low viscosity slag/matte at relatively low temperature for the efficient separation from bullion, there are significant associated problems, which may be listed as follows:

- Soda ash is a costly reagent.
- Soda slags are very aggressive to chrome magnesite brickwork and to steel if exposure occurs.
- Soda slags are hygroscopic and can expand and break down in landfill. Under these conditions the FeS can be oxidised to Fe_2O_3 and S^0 , generating heat and raising the temperature sufficiently to ignite the sulfur and the remaining sulfides [2].
- The slags contain water soluble heavy metal compounds, which can be leached in landfill situations, particularly when breakdown occurs as above.

EXPERIMENTAL

Because of the above mentioned, disposal of soda slags is classified as hazardous wastes with significant disposal difficulties and are unacceptable in many locations.

The main ingredients of soda slag are iron, lead and coke. Iron is in the form of magnetite - Fe_3O_4 , wustite - FeO and pyrite - FeS_2 . Lead exists as metallic lead, sulfate - (PbSO_4) and sulfide - PbS [3, 4]

The purpose of the present work is to investigate the possibility of utilizing the slag obtained as a result of the recycling of waste lead batteries using the ENGITEC technology.

The chemical composition of the used real sample of industrial soda slag is presented in Table 1.

Sieve analysis of waste slag

For the purposes of the research soda slag with a mass of 5 kg was used. The starting material was divided into three fractions: -1 mm; -1+5.5 mm and +5.5 mm and the results are presented in Fig. 1. The largest share is the fine fraction (-1 mm), which is half of the studied material.

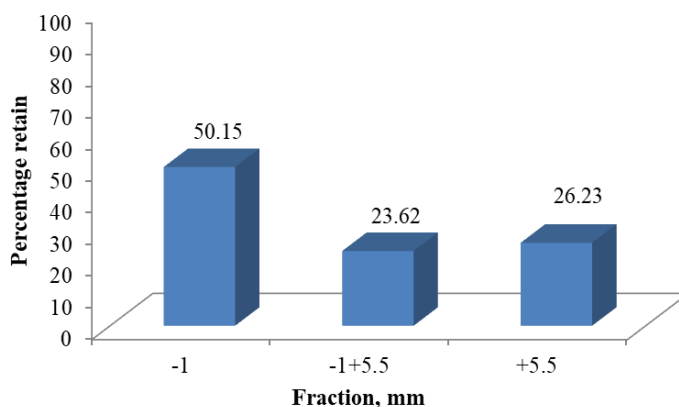


Fig. 1. Particle size distribution of soda slag.

Table 1. Chemical composition of soda slag, mass %.

Pb	Fe	Na	Zn	Ca	Cu	Sb	Si	Cr	Sn	S
12.09	22.71	11.98	0.4	1.02	0.45	0.12	0.16	0.020	0.86	10.52

Hydrometallurgical separation of slag

Water leaching of the three fractions was performed to determine the water-soluble components. The leaching was carried out for a period of 30 min, with a solid : liquid ratio of 1:10, at three different temperatures - room, 40°C and 60°C. The results of these experiments are presented in Fig. 2. As can be seen from the figure, the largest share of water-soluble components is the fine fraction (-1 mm), and the lowest share is the coarse fraction. Taking into account the percentage content of each of the fractions in soda slag, the total amount of water-soluble components in the studied sample is on average 23 %. Temperature does not significantly affect the degree of extraction of water-soluble components.

Since almost 25 % of the slag is larger than 5 mm, it is advisable to combine the leaching of the water-soluble components with grinding. For this purpose, a ball mill type reaction vessel was used, in which ceramic balls were used as grinding bodies.

One experiment was conducted with a slag mass of 500 g. The hydro separation was carried out at a ratio of one part slag and two parts of water at room temperature for a period of 2 hours. The mass of the used grinding bodies was 800 g. The mass of the remaining insoluble

residue is 385 g. This means that the mass of water-soluble is 23 %.

The chemical composition of the insoluble residue and the filtrate from this experiment is presented in Table 2.

Sulfide precipitation of heavy metals

The most effective way to remove heavy non-ferrous metals from the filtrate obtained from the soda slag hydro separation is the sulfide method. Arsenic and antimony sulfides, however, are soluble in alkaline media and in excess of sulfide ions. For the complete precipitation of these metals, it is necessary to reach a certain pH and a certain consumption of sodium sulfide. The sodium sulfate solution before crystallization should contain heavy non-ferrous metals < 5 ppm and lead < 1 ppm.

The starting solution is characterized by a high pH value ($\text{pH} > 12$). In addition to heavy non-ferrous metals, it also contains carbonates, which during the pyrometallurgical recycling of lead-containing waste did not react with lead sulfate and did not decompose. In order to neutralize the excess of carbonate, it is necessary to reduce the pH of the solution to a value of 4 - 4.5. The required pH is reached with the help of a

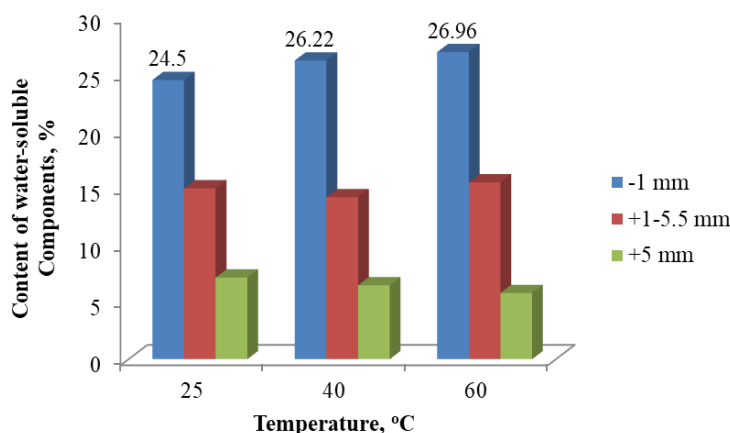


Fig. 2. Content of water-soluble components depending on the size of the slag particles, period of 30 min, solid : liquid ratio of 1:10.

Table 2. Chemical composition of the insoluble residue obtained during the hydro separation of soda slag, mass %.

Pb	Fe	Na	Zn	Ca	Cu	Sb	Si	Cr	Sn	S
13.70	24.60	4.03	0.48	1.24	0.43	0.13	0.18	0.0131	0.77	5.67

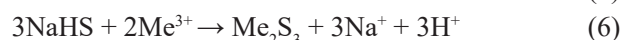
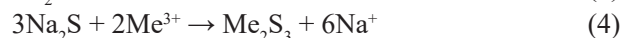
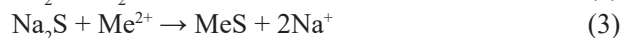
sulfuric acid solution ($\rho = 1.2769 \text{ g cm}^{-3}$). The acid is added slowly and the pH is continuously measured with a pH meter (Fig. 3).

The concentration of sodium sulfate in the test solution increases as a result of the reaction:



Sodium sulfide is a highly efficient precipitant that achieves high removal of heavy metal cations [5]. Precipitation of heavy non-ferrous metals is carried out using 65 g L^{-1} sodium sulfide. The following reactions

take place:



Sodium sulfide is added until pH = 8 is reached. And in this operation, the change in pH and potential is continuously monitored (Fig. 4). The consumption of $65 \text{ g L}^{-1} \text{ Na}_2\text{S}$ is 25 mL L^{-1} .

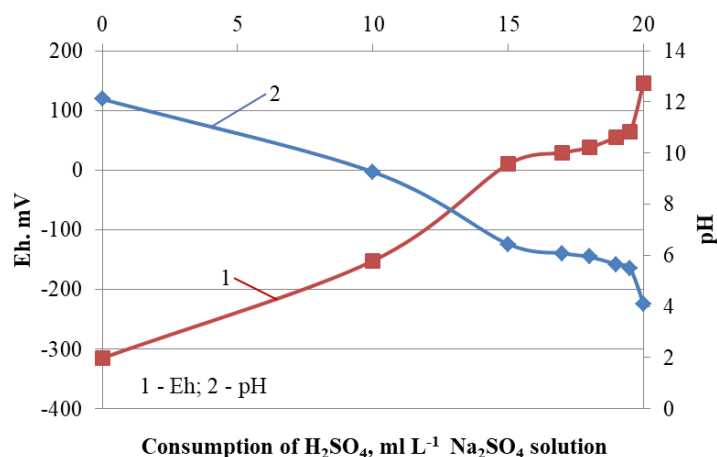


Fig. 3. Consumption of H_2SO_4 and change of pH and Eh during the neutralization of Na_2SO_4 solution.

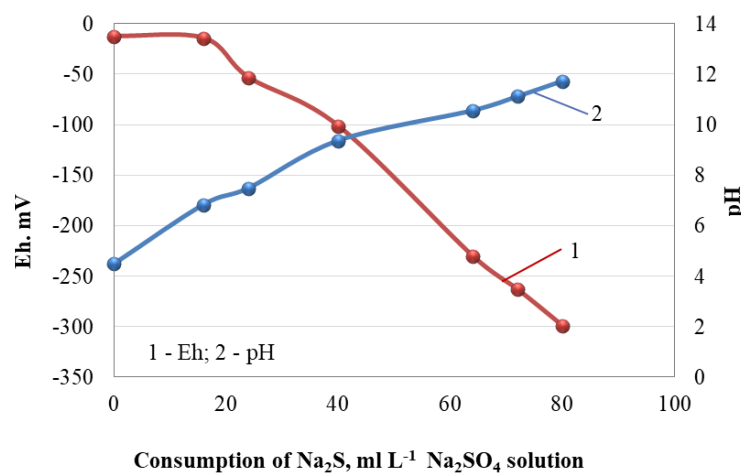


Fig. 4. Consumption of Na_2S and change of pH and Eh during the sulfide precipitation.

Table 3. Chemical compositions of filtrates obtained after hydro separation of soda slag, g L^{-1} .

Pb	Fe	Zn	Ca	Cu	Ni
0.122	0.103	0.430	0.840	0.017	0.050

Table 4. Chemical composition of the Na_2SO_4 solution obtained from soda slag, mg L^{-1} .

Pb	Fe	Zn	Ca	Cu	Ni
0.122	0.103	0.430	0.840	0.017	0.050

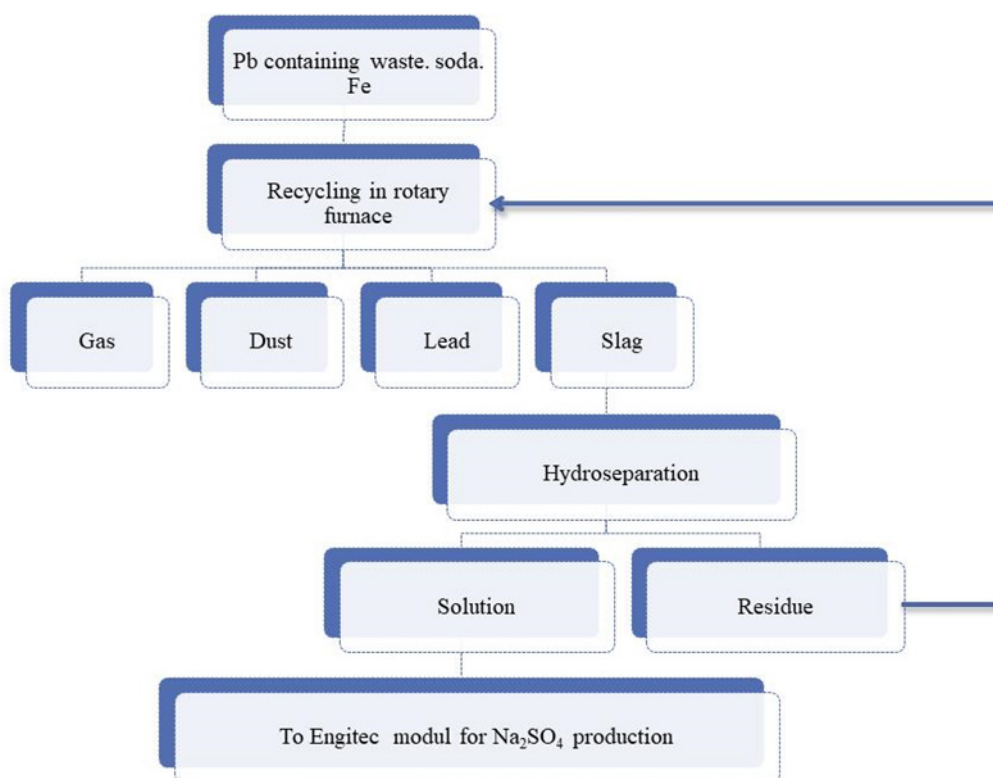


Fig. 5. Process flowsheet for managing of recycling process of waste lead-acid batteries.

Chemical composition of the Na_2SO_4 solution obtained from soda slag in mg L^{-1} is presented in Table 4.

Thus, the purified solution meets the requirements for the concentration of heavy non-ferrous metals < 5 ppm and lead < 1 ppm and can be subjected to crystallization. Therefore, in order to prevent the environmental problems with the disposal of soda slag and to utilize the sodium sulfate contained in it, the technological scheme for processing waste lead-acid batteries must include another technological stage of water leaching (Fig. 5).

CONCLUSIONS

The conducted experiments show the possibility of extracting the sodium sulfate from the soda slag only by grinding in an aqueous medium and subsequent

filtration. These processes can easily be implemented in companies that use Engitec's technology to recycle waste lead batteries and produce sodium sulfate from the desulfurization of the lead paste.

Implementation of these processes will eliminate the need for slag stabilization and prevent environmental problems.

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