

# Desulphurization of the damped lead battery paste with potassium carbonate

Veneta P. Yanakieva, Georgi Al. Haralampiev, Nedialko K. Lyakov \*

*Department of Non-ferrous Metallurgy, University of Chemical Technology and Metallurgy, 8 Kliment Ohridski Boulevard, 1756 Sofia, Bulgaria*

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## Abstract

The present study is devoted to processing of scrap batteries and more particularly, to desulphurization of the battery pastes. The sulphate ions are removed from solution by a salting out processing potassium carbonate. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Scrap batteries; Desulphurization; Potassium carbonate; Salting out

## 1. Introduction

Secondary lead raw materials are contributing on increasing fraction of lead production. This is due to both running out of ore, and the damaging effect of lead on environment.

Scrap batteries are the main source of secondary lead. According to Ref. [1], they account for 80% of the whole quantity of secondary lead raw materials.

Two fundamental methods are used for processing scrap batteries:

1. Direct pyrometallurgical processing without preliminary separation, which causes a series of technological and environmental difficulties [2];
2. Preliminary separation followed by processing of the fractions [1,2].

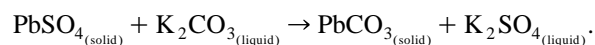
Lead paste is one of those fractions. It is an oxide–sulphate product with the following approximate composition: 50–60% of lead sulphate, 20–30% of lead dioxide and 5–15% of lead monoxide [2]. Sulphur content in the pastes is about 6%, which causes difficulties in the case of direct pyrometallurgical processing. This requires preliminary desulphurization of the paste.

Existing world practice technologies use as a desulphurization reagent sodium hydroxide [3,4], sodium carbonate

[5] or ammonium carbonate [6]. The problems that usually occur in these technologies arise in connection with precipitation and utilization of the soluble salt. The evaporation of solutions is most frequently in use [7]. The possibility for regeneration through partial crystallization [5] or by removal of the sulphur as insoluble sulphate is investigated, too.

The purpose of this study is to investigate the possibility for desulphurization of the paste with potassium carbonate; to verify the possibility for removal of sulphur ions in the form of potassium sulphate by salting out process; to recycle the residual solutions for desulphurization.

The interaction between potassium carbonate and lead sulphate goes according to reaction:



The transition of sulphate ions into the liquid phase is based on the difference between ion products of lead sulphate and lead carbonate [9]. According to handbook data [8]:

$$L_{\text{PbSO}_4} = 2.8 \cdot 10^{-8}; L_{\text{PbCO}_3} = 1.5 \cdot 10^{-13}.$$

The theoretical basis for the salting out process is the examination of the system  $\text{K}_2\text{CO}_3\text{--K}_2\text{SO}_4\text{--H}_2\text{O}$  [9]. An isothermal section of the phase diagram for this system is presented in the Fig. 1. In the case of potassium carbonate addition, the potassium sulphate solubility is reduced. This is giving a possibility for removing from the solution the

\* Corresponding author.

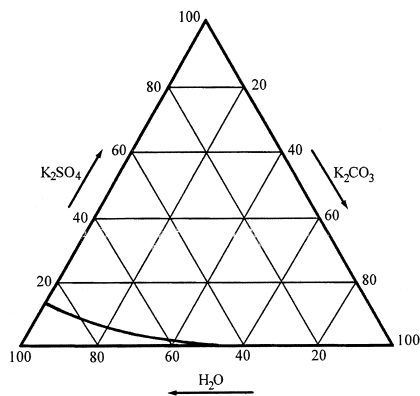


Fig. 1. Isothermal section of the phase diagram for the system  $K_2CO_3$ – $K_2SO_4$ – $H_2O$ .

sulphate ions, as potassium sulphate, by a salting out process and multiple use of the residual solutions.

## 2. Experimental

The experimental investigation includes a series of preliminary experiments that concerns the specifying of optimal parameters for the desulphurization process and a series of experiments based on the technological scheme.

Preliminary experiments include investigations on the influence of the liquid–solid phase ratio and the influence of the temperature and duration on the desulphurization process. The tests were carried out with 100 g of paste with sulphate ion content of 17.22%. The potassium carbonate quantity is 15% more than stoichiometrically needed (28 g instead of 24.75 g). The degree of desulphurization is calculated from analysis of the paste.

The influence of the liquid–solid phase ratio is investigated at ambient temperature and a duration of 3 h. Tested ratios are 2:1, 3:1, 3.5:1, 4:1 and 5:1. Results are shown in Fig. 2.

The extraction of sulphate ions into solution is sufficiently complete at a liquid–solid ratio 2:1. From the standpoint of the salting out process, the assumption for an optimal ratio is 3:1.

The influence of temperature is investigated at the liquid–solid phase ratio of 3:1 and a duration of 3 h.

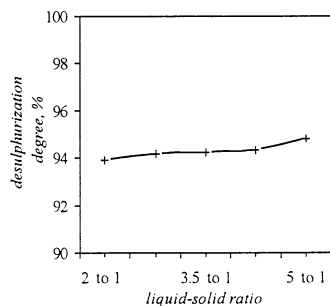


Fig. 2. Influence of liquid–solid phase ratio on desulphurization degree.

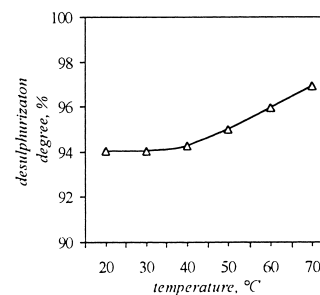


Fig. 3. Influence of temperature on desulphurization degree.

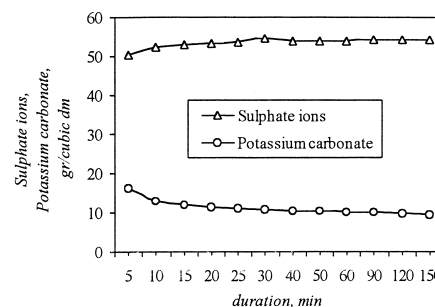


Fig. 4. Influence of process duration on the content of sulphate ions and potassium carbonate into solution.

Results are presented in Fig. 3. Some increase of the degree of desulphurization is seen at temperatures above 40°C. The temperature influence potassium sulphate solubility. According to handbook data [8], solubility potassium sulphate at 60°C is twice that at ambient temperature. In accordance with the subsequent salting out process, the temperature chosen is  $65 \pm 5^\circ\text{C}$ .

The influence of process duration is investigated at a liquid–solid phase ratio 3:1 and temperature  $65 \pm 5^\circ\text{C}$ . Results are presented in Figs. 4 and 5.

The following process parameters are chosen according to the results from preliminary experiments: liquid–solid phase ratio 3:1, temperature 60–70°C and duration 40 min. A series of experiments, based on technological scheme presented on Fig. 6, was implemented at those conditions.

Each series included six tests. 185 g of paste was inserted, at the desulphurization stage, for the first experiment. For later experiments, 100 g was used. For the first experiment, the paste quantity was more for saturating the

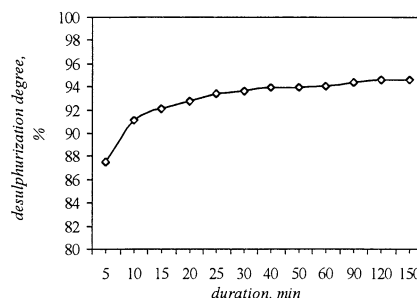


Fig. 5. Influence of process duration on desulphurization degree.

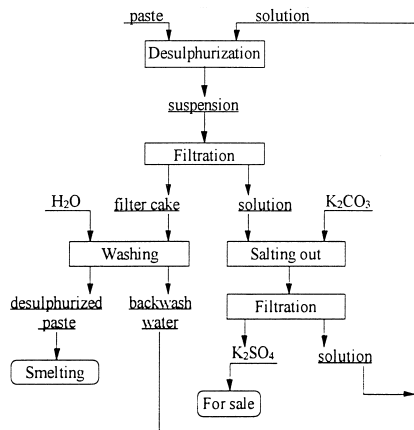


Fig. 6. Technological scheme.

solution by potassium sulphate. This condition is important for the salting out process. The starting and ending concentration of potassium carbonate at desulphurization stage was under observation.

Next is the separation of solid from the liquid phase by filtration. At this stage, the weight of moist cake and the volume of filtrate was measured. The obtained cake was washed with 50 cm<sup>3</sup> of water, dried, weighed and the content of sulphate ions determined. The temperature of filtrate was 55 ± 5°C. For the salting out process to obtain filtrate, 30 g of potassium carbonate was added. That is approximately 10% more than stoichiometrically needed for desulphurization of the paste portion. The suspension was stirred until complete dissolution of potassium carbonate and was cooled naturally to 20°C. Formatted crystals of potassium sulphate were separated from solution by filtration. The crystals, after drying, were weighed and analyzed for potassium sulphate, potassium carbonate and ions of lead. The solution, obtained after filtration, was concatenated with backwash water and was entered for desulphurization of the paste portion. In such a way, the full cycle of solutions in the technological process was organized.

### 3. Results

The initial concentration of potassium carbonate in the desulphurization process was average 118 ± 5 g/dm<sup>3</sup> and the final concentration was average (from number of tests) — 27 ± 6 g/dm<sup>3</sup>. The weight of moist cake was 90 ± 3 g. The filtrate volume after the separation of solid from liquid phase was 250 ± 5 cm<sup>3</sup>.

Table 1  
The content of SO<sub>4</sub><sup>2-</sup> into pastes after desulphurization

Test no.	1	2	3	4	5	6
SO <sub>4</sub> <sup>2-</sup> (%)	1.12	1.07	0.57	0.89	0.95	1.17

Table 2

Results from the analysis of potassium sulphate crystals

	Test no.					
	1	2	3	4	5	6
Weight (g)	28.63	27.22	28.9	27.25	28.51	28.40
K <sub>2</sub> SO <sub>4</sub> (%)	97.27	96.71	97.39	97.21	97.03	97.69
K <sub>2</sub> CO <sub>3</sub> (%)	2.50	3.23	2.57	2.75	2.85	3.23

The content of sulphate ions in the pastes was represented in Table 1. The averaged content of sulphate ions in desulphurized pastes was 0.92%, which corresponds to desulphurization degree of 94.66%.

The results from the analysis of potassium sulphate crystals are represented in Table 2.

Lead was not detected after atomic absorption spectrophotometry.

### 4. Conclusions

As a result of the experiments performed and the results received, the following conclusions are made:

1. The possibility for desulphurization of the paste with potassium carbonate is verified;
2. The possibility for removal of sulphur ions in the form of potassium sulphate by salting out process is proved;
3. The possibility for recycling of solutions without waste water receiving is proved;
4. A high degree of paste desulphurization is achieved — more than 94.5%.

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