

Short communication

## Desulphurization of damped battery paste by sodium carbonate and sodium hydroxide

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This paper is in memory of Prof. Nedialko K. Lyakov.

### Abstract

The paper treats investigation of the desulphurization process of damped Pb-paste by  $\text{Na}_2\text{CO}_3$  or NaOH. There is determined the effect of  $\text{Na}_2\text{CO}_3$  (NaOH) concentration and the liquid–solid phase ratio on the process parameters (degree of desulphurization and degree of  $\text{Na}_2\text{CO}_3$  (NaOH) utilization in function of the temperature and process duration). The optimum conditions for carrying out desulphurization of Pb-pastes by  $\text{Na}_2\text{CO}_3$  or NaOH are determined in dependence of the used reactors (common reactor with laboratory agitator and rotary reactor of drum type). The content of inclusions in the solutions is examined with the purpose of producing sufficiently pure crystalline  $\text{Na}_2\text{SO}_4$  for the industry.  
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**Keywords:** Lead paste; Desulphurization of Pb-paste; Processing of Pb damped batteries

### 1. Introduction

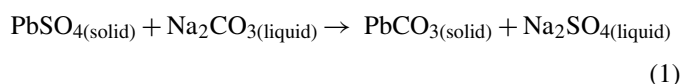
Damped batteries are a complex in composition waste product that in its quality of raw material creates many difficulties in the subsequent processing. In relation to the inclusions contained, this raw material is comparatively pure because in the production of batteries mainly Pb and Sb or Pb and Ca are used [1].

The amortized Pb-paste (oxide–sulfate fraction) in the conventional batteries is  $\approx 40$ –50% [1,2]. The quantity of the paste depends on the electrolyte content in the damped batteries and on the relative share of the batteries in ebonite boxes. It contains  $\approx 68$ –76% Pb, which is in the form of  $\text{PbSO}_4$  (50–60%),  $\text{PbO}_2$  (30–35%), PbO (10–15%) and Sb (0.2–0.7%) [3,4].

The necessity of paste desulphurization before its melting [5] is proved in scientific and experimental respect.

The sodium carbonate is the most frequently used reagent for desulphurization of damped Pb-pastes [6–11]. The process

is performed by treatment of the paste with  $\text{Na}_2\text{CO}_3$  solution according to the reaction:



The produced saturated solution is subjected to evaporation, centrifuging and precipitation of the crystalline  $\text{Na}_2\text{SO}_4$  [12,13].

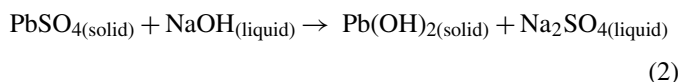
From the studies performed on the chemistry of the processes occurring between  $\text{PbSO}_4$  and  $\text{Na}_2\text{CO}_3$ , it is found out that Eq. (1) describes sufficiently accurately the interactions running [13–19]. The same authors prove also the formation of a number of intermediate compounds of the type  $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ,  $\text{Pb}_{10}\text{O}(\text{CO}_3)_6(\text{OH})_6$ , etc. There are convincing proofs that they increase the reagent consumption and create difficulties in the subsequent processing and use of the final products. These compounds contain in them  $\text{Na}^+$ - or  $\text{SO}_4^{2-}$ -ions:  $\text{NaPb}_2(\text{CO}_3)_2\text{OH}$ ,  $\text{Pb}_4(\text{SO}_4)(\text{CO}_3)_2(\text{OH})_2$ , their chemical composition depending on many factors, particularly on pH and on  $\text{Na}_2\text{SO}_4$  concentration in the solutions [17,18].

Many technologies suggest processing of Pb-paste by NaOH, the  $\text{PbSO}_4$  being transformed into  $\text{Pb}(\text{OH})_2$  [20,21]. The sulfur

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goes in the solution in the form of NaSO<sub>4</sub>:



In case of excess of the reagent  $\approx 10$ – $20\%$  then  $\approx 95\%$  degree of desulphurization is achieved and the content of S in the product does not exceed  $0.6\%$ . The lead may go in the solution also as Na<sub>2</sub>PbO<sub>2</sub>. Its quantity grows when the excess of NaOH grows [5]. The sodium sulfate is extracted from the solution through evaporation.

Detailed results concerning the physical-chemical and technological aspects of the process of PbSO<sub>4</sub> desulphurization have been reported in the specialized publications [5].

The desulphurization of the Pb-paste in advance considerably eases the pyrometallurgical processing and that is expressed in the following: decrease of the temperature of the melting process, decrease of the amounts of used fluxes and soda, slag and powders, SO<sub>2</sub> in the gases and used chemical reagents in the refining cycle, increase of the level of lead extraction, etc.

To this effect the purpose of the present paper is:

- to determine the effect of the Na<sub>2</sub>CO<sub>3</sub> (NaOH) concentration and the liquid–solid phase ratio on the characteristics of the process “desulphurization of Pb-pastes” in function of the temperature and process duration;
- to determine the optimum conditions for carrying out the desulphurization of Pb-pastes by Na<sub>2</sub>CO<sub>3</sub> or NaOH in dependence of the type of the reactors used;
- to examine the content of inclusions in the solutions with the purpose to produce sufficiently pure crystalline sodium sulfate for the industry.

## 2. Experimental

Before to subjecting to desulphurization process, the Pb-paste is dried and sifted in a sieve of mesh 5.0 mm. The fraction ( $-5.0$  mm) is  $80\%$  and the fraction ( $+5.0$  mm) is  $20\%$ .

The paste has the following chemical composition [%]: Pb-59.85; Sb-0.73; As-0.042; Cl<sub>2</sub>-0.33; Cu-0.13; Zn-0.10; S<sub>Σ</sub>-7.20; S<sub>SO<sub>4</sub><sup>2-</sup></sub> – 6.45.

The paste composition is determined by chemical analysis and the content of sulphate sulphur S<sub>SO<sub>4</sub><sup>2-</sup></sub> by gravimetric analysis.

The desulphurization process is performed by the use of two types of agitators. Laboratory agitator ER 10 type and paste mass = 200 g are used while the temperature is maintained by means of thermostat Ultra-NBA type. In the case of treatment in drum type rotary reactor VEB Elmo Hartha (DDR) the paste mass = 400 g. The paste quantity for treatment in drum type rotary reactor varies because of the larger work volume of the facility. When the quantity of the material is increased the cooling rate by the air decreases as in laboratory conditions it is difficult to maintain constant temperature in the drum.

The lead paste 200 (400) g is added to solutions of specified Na<sub>2</sub>CO<sub>3</sub> (NaOH) concentration and liquid–solid phase ratio

(at preset temperature and duration of the desulphurization process).

On accomplishment of the chemical treatment, the pulp is filtered and the solid phase is washed with water on the filter, dried to stable weight and analyzed for content of SO<sub>4</sub><sup>2-</sup>. The liquid phases are analyzed for content of Na<sub>2</sub>CO<sub>3</sub> (NaOH) and SO<sub>4</sub><sup>2-</sup>. The SO<sub>4</sub><sup>2-</sup> content in the solid phase is determined by gravimetric method. The sample is first dissolved in Na<sub>2</sub>CO<sub>3</sub> solution. SO<sub>4</sub><sup>2-</sup> is precipitated by BaCl<sub>2</sub> in the form of BaSO<sub>4</sub>. The analysis of SO<sub>4</sub><sup>2-</sup> in the filtrates (after desulphurization) is analogical to the above one (precipitation by BaCl<sub>2</sub>), the data of it being used to check the results of the analysis of SO<sub>4</sub><sup>2-</sup> in solid phase (sulphur balance).

The content of free Na<sub>2</sub>CO<sub>3</sub> and NaOH in the liquid phases (residual concentration) is determined by titration with 0.1 M HCl and indicator methyl orange.

The desulphurization degree  $\alpha$  [%] is calculated by the formula:

$$\left( \frac{D_{S(\text{initial})} - D_{S(\text{final})}}{D_{S(\text{initial})}} \right) \times 100 = \alpha$$

where  $D_{S(\text{initial})}$  and  $D_{S(\text{final})}$  initial and residual SO<sub>4</sub><sup>2-</sup> concentration.

The reagent utilization degree  $\beta$  [%] is calculated by the formula:

$$\left( \frac{C_{(\text{initial})} - C_{(\text{final})}}{C_{(\text{initial})}} \right) \times 100 = \beta$$

where  $C_{(\text{initial})}$  and  $C_{(\text{final})}$  initial and residual reagent concentration, mol L<sup>-1</sup>.

## 3. Results and discussion

### 3.1. Desulphurization of Pb-paste by Na<sub>2</sub>CO<sub>3</sub>

#### 3.1.1. In common reactor with laboratory agitator

From the carried out preliminary experiments and published data it is found out that the temperature does not affect essentially the characteristics of the desulphurization process (degree of desulphurization  $\alpha$  and degree of Na<sub>2</sub>CO<sub>3</sub> utilization  $\beta$ ) because the operations are in the area of diffusion control. The coefficients  $\alpha$  and  $\beta$  are the highest in the temperature range  $30$ – $40$  °C [23–25], as above that temperature the solubility of Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> in water decreases.

Fig. 1 presents the results of Pb-paste desulphurization for liquid–solid phase ratio  $m=2$  ( $m=2:1$ ), at temperature  $t=40$  °C and initial Na<sub>2</sub>CO<sub>3</sub> concentration at stoichiometric ratio ( $C_{\text{initial}} = 1.01$  mol L<sup>-1</sup>).

After 15 min treatment of the Pb-paste the desulphurization degree is  $93.0\%$  (S<sub>SO<sub>4</sub><sup>2-</sup></sub> content in the desulphurized paste is  $0.45\%$ ). This result is satisfactory in respect of the pyrometallurgical processing of the paste in Engitec Impianti [21].

Fig. 2 presents the results of the performed series of two experiments with  $m=2.25$ ,  $t=38$ – $40$  °C and initial Na<sub>2</sub>CO<sub>3</sub> concentration at  $10\%$  shortage ( $C_{\text{initial}} = 0.81$  mol L<sup>-1</sup>) for the first experiment and stoichiometry ( $C_{\text{initial}} = 0.89$  mol L<sup>-1</sup>)—for the second experiment.

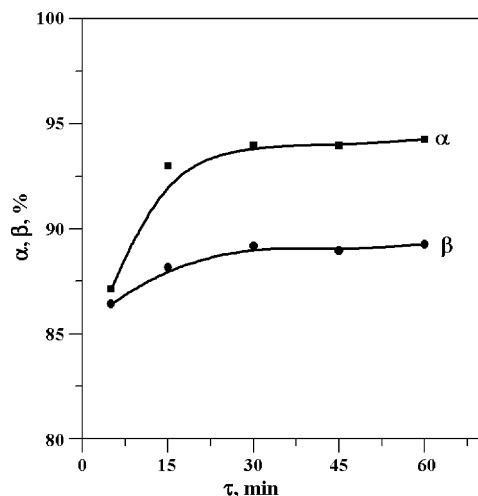


Fig. 1. Dependence between the desulphurization degree ( $\alpha$ ) and the utilization degree of  $\text{Na}_2\text{CO}_3$  ( $\beta$ ) on the treatment time ( $\tau$ ) at stirring with laboratory agitator:  $m = 2$ ;  $t = 40^\circ\text{C}$ ;  $C_{\text{initial}} = 1.01 \text{ mol L}^{-1}$ .

After 15 min treatment of the Pb-paste with stoichiometric quantity of  $\text{Na}_2\text{CO}_3$  ( $C_{\text{initial}} = 0.89 \text{ mol L}^{-1}$ ) the desulphurization degree  $\alpha_2 = 94.11\%$  (0.38%  $\text{S}_{\text{SO}_4^{2-}}$  in the desulphurized paste). Even at 10% shortage of  $\text{Na}_2\text{CO}_3$ —the desulphurization degree is  $\alpha_1 = 92.09\%$  (0.51%  $\text{S}_{\text{SO}_4^{2-}}$  in the desulphurized paste).

The process runs in the diffusion area, and Figs. 1 and 2 confirm increase of  $\alpha$  in function of the time  $\tau$  and with increase of the  $\text{Na}_2\text{CO}_3$  initial concentration. Fundamental chemical and kinetic principles are thoroughly presented by Laidler et al. [22].

Fig. 3 presents the results of performed experiment with  $m = 2.5$ ;  $t = 38\text{--}40^\circ\text{C}$  and initial  $\text{Na}_2\text{CO}_3$  concentration at 10% excess ( $C_{\text{initial}} = 0.89 \text{ mol L}^{-1}$ ).

Change in the proportion  $m$  (Fig. 1,  $m = 2$ ; Fig. 2,  $m = 2.25$ ; Fig. 3,  $m = 2.5$ ) does not change significantly the process kinetic

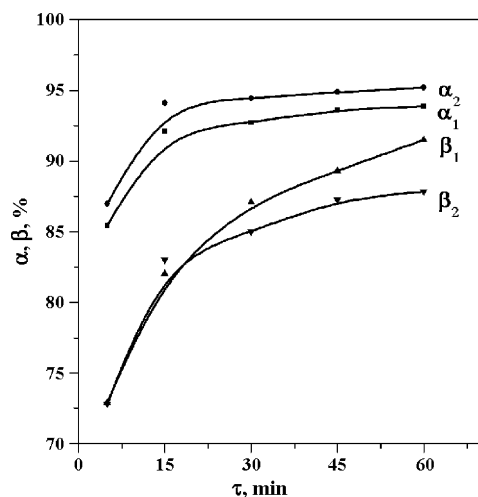


Fig. 2. Dependence between the desulphurization degree ( $\alpha$ ) and the utilization degree of  $\text{Na}_2\text{CO}_3$  ( $\beta$ ) on the treatment time ( $\tau$ ) at stirring with laboratory agitator ( $m = 2.25$ ;  $t = 38\text{--}40^\circ\text{C}$ ):  $C_{\text{initial}(1)} = 0.81 \text{ mol L}^{-1}$  ( $\alpha_1, \beta_1$ );  $C_{\text{initial}(2)} = 0.89 \text{ mol L}^{-1}$  ( $\alpha_2, \beta_2$ ).

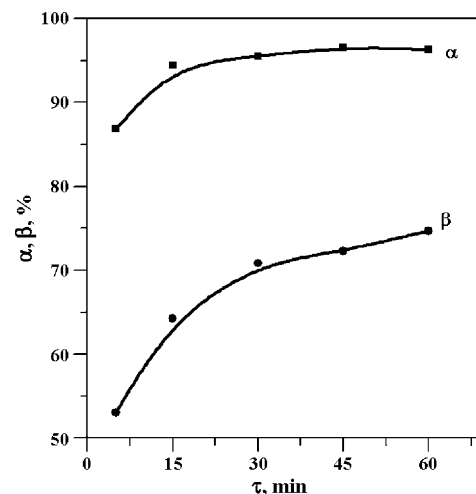


Fig. 3. Dependence between the desulphurization degree ( $\alpha$ ) and the utilization degree of  $\text{Na}_2\text{CO}_3$  ( $\beta$ ) on the treatment time ( $\tau$ ) at stirring with laboratory agitator:  $m = 2.5$ ;  $t = 38\text{--}40^\circ\text{C}$ ;  $C_{\text{initial}} = 0.89 \text{ mol L}^{-1}$ .

run. These data are in good agreement with the reported in publications by Yanakieva [11].

After 15 min treatment by  $\text{Na}_2\text{CO}_3$  the desulphurization degree reaches 94.42% (content of  $\text{S}_{\text{SO}_4^{2-}}$  in the desulphurized paste 0.36%), but the utilization degree of  $\text{Na}_2\text{CO}_3$  drops down below 70%.

From the investigation made on the paste desulphurization the effects of the main factors are determined: initial concentration of  $\text{Na}_2\text{CO}_3$  ( $\text{Na}_2\text{CO}_3$  consumption), solid-liquid ratio, operation duration at preset temperature range, which is related to the reagent properties and reaction products. When carrying out this group of experiments the condition to work with an excess of  $\text{Na}_2\text{CO}_3$  not higher than 20% is observed in order to avoid formation of  $\text{NaHCO}_3$  and the double salt  $\text{NaPb}_2(\text{CO}_3)_2\text{OH}$  in Morachevskii [14] that increase  $\text{Na}_2\text{CO}_3$  consumption. The recommended conditions for desulphurization of Pb-paste by  $\text{Na}_2\text{CO}_3$  in common reactor with stirring by laboratory agitator are: excess of the reagent up to 10%; liquid–solid phase ratio  $m = 2.0\text{--}2.5$ ; temperature and duration of the process  $t = 35\text{--}40^\circ\text{C}$  and  $\tau = 15\text{--}30$  min, respectively.

### 3.1.2. In rotary reactor

The investigations are carried out with the purpose to avoid some difficulties that accompany the agitators both in respect of stirring and in respect of emptying the installation. The inconvenience when using rotary reactor is the maintenance of constant temperature.

There are carried out two experiments with  $\text{Na}_2\text{CO}_3$  (Fig. 4) under the following conditions:

- I experiment:  $C_{\text{initial}} = 0.89 \text{ mol L}^{-1}$  (stoichiometric ratio);  $m = 2.25$ ;  $t = 55\text{--}28^\circ\text{C}$ ;
- II experiment:  $C_{\text{initial}} = 0.88 \text{ mol L}^{-1}$  (10% excess);  $m = 2.5$ ;  $t = 55\text{--}28^\circ\text{C}$ .

These results are close in value to those given in Figs. 1–3. For  $m = 2.25$  (Fig. 4a) and  $\tau = 15$  min—the desulphurization

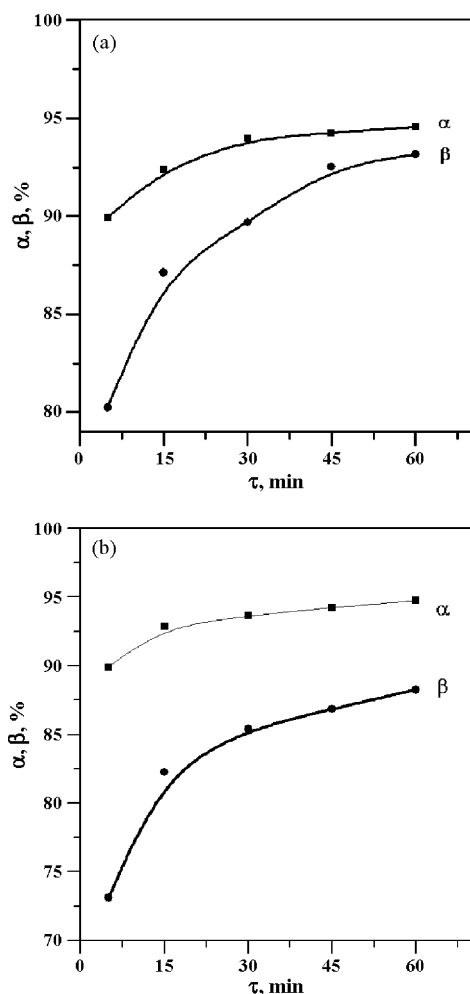


Fig. 4. Dependence between the desulphurization degree ( $\alpha$ ) and the utilization degree of  $\text{Na}_2\text{CO}_3$  ( $\beta$ ) on the treatment time ( $\tau$ ) when using rotary reactor at  $t = 55\text{--}28^\circ\text{C}$ : (a)  $m = 2.25$ ;  $C_{\text{initial}} = 0.89 \text{ mol L}^{-1}$ ; (b)  $m = 2.5$ ;  $C_{\text{initial}} = 0.88 \text{ mol L}^{-1}$ .

degree is 92.40% ( $S_{\text{SO}_4^{2-}}$  in the desulphurized paste is 0.49%); at  $\tau = 30 \text{ min}$ — $\alpha = 93.95\%$  ( $S_{\text{SO}_4^{2-}} = 0.39\%$ ); at  $m = 2.5$  and  $\tau = 15 \text{ min}$  (Fig. 4b)— $\alpha = 92.87\%$  ( $S_{\text{SO}_4^{2-}} = 0.46\%$ ) and for  $\tau = 30 \text{ min}$ — $\alpha = 93.64\%$  ( $S_{\text{SO}_4^{2-}} = 0.41\%$ ).

The results obtained clearly display the above-described kinetic dependences, i.e. with increase of the concentration the desulphurization degree grows but the degree of reagent utilization decreases.

Table 1

Inclusion concentrations in the liquid phase from  $\text{Na}_2\text{SO}_4$  during treatment of Pb-paste by  $\text{Na}_2\text{CO}_3$

No	Conditions of carrying out the process in common reactor with laboratory agitator	Inclusion concentrations ( $\text{mg L}^{-1}$ )							pH
		Pb	Sb	$\text{Cl}_2$	As	Cu	Zn	Fe	
1	$C_{\text{initial}} = 1.01 \text{ mol L}^{-1}$ (stoichiometric), $m = 2$ , $\tau = 30 \text{ min}$	4.76	38.40	2160.0	51.00	4.30	0.22	1.5	9.42
2	$C_{\text{initial}} = 0.89 \text{ mol L}^{-1}$ (stoichiometric), $m = 2.25$ , $\tau = 30 \text{ min}$	2.90	28.44	2140.0	24.20	7.49	2.21	0.04	9.20
3	$C_{\text{initial}} = 0.99 \text{ mol L}^{-1}$ (10% excess), $m = 2.25$ , $\tau = 15 \text{ min}$	6.80	13.40	1980.0	50.80	2.62	0.54	0.09	9.41
4	$C_{\text{initial}} = 0.88 \text{ mol L}^{-1}$ (10% excess), $m = 2.5$ , $\tau = 30 \text{ min}$	6.10	15.90	1940.0	42.00	2.39	0.26	0.08	9.27

The optimum conditions for desulphurization are: excess of  $\text{Na}_2\text{CO}_3$ —up to 10%;  $m = 2.25\text{--}2.50$ ;  $t = 40\text{--}38^\circ\text{C}$ ;  $\tau = 15\text{--}30 \text{ min}$ .

### 3.1.3. Behavior of the inclusions in the solutions

The results of the chemical analysis of the liquid phase concerning the inclusion concentrations after desulphurization of Pb-pastes by  $\text{Na}_2\text{CO}_3$  in common reactor with laboratory agitator are presented in Table 1.

The inclusions  $\text{Cl}_2$ , As and Sb go in the solutions to the greatest extent and Pb—to a lower one. Desulphurization degree above 90% is reached with stoichiometric quantity of  $\text{Na}_2\text{CO}_3$ . After desulphurization the solutions have pH 9.20–9.40.

## 3.2. Desulphurization of Pb-paste by NaOH

### 3.2.1. In common reactor with laboratory agitator

This group of experiments is carried out in order to determine the effect of the initial NaOH concentration and the liquid–solid phase ratio at temperature range  $38\text{--}40^\circ\text{C}$  in function of time on the process parameters: degree of paste desulphurization and degree of NaOH utilization.

Here also, as with the rest of the investigation groups, it is found out that temperature above the specified value for the chemical treatment of the Pb-paste does not significantly affect the desulphurization parameters.

At  $t = 38\text{--}40^\circ\text{C}$  three experiments with NaOH are carried out (Fig. 5) under the following conditions:

- I experiment:  $C_{\text{initial}} = 1.01 \text{ mol L}^{-1}$  (stoichiometric ratio);  $m = 2.0$ ;
- II experiment:  $C_{\text{initial}} = 1.06 \text{ mol L}^{-1}$  (5% excess);  $m = 2.0$ ;
- III experiment:  $C_{\text{initial}} = 1.08 \text{ mol L}^{-1}$  (10% excess);  $m = 2.0$ .

The parameters of the desulphurization process with NaOH are very good. In the 5-th min the desulphurization degree is  $\alpha = 92.10\%$  (in the desulphurized paste  $S_{\text{SO}_4^{2-}} = 0.51$ ) at  $C_{\text{initial}} = 1.08 \text{ mol L}^{-1}$ ;  $\alpha = 92.88\%$  ( $S_{\text{SO}_4^{2-}} = 0.46\%$ ) at  $C_{\text{initial}} = 1.06 \text{ mol L}^{-1}$  and  $\alpha = 93.64\%$  ( $S_{\text{SO}_4^{2-}} = 0.41\%$ ) at  $C_{\text{initial}} = 1.08 \text{ mol L}^{-1}$ . After 15 min the same parameters achieve the following values, respectively:  $\alpha = 93.64\%$  ( $S_{\text{SO}_4^{2-}} = 0.41\%$ ),  $\alpha = 93.80\%$  ( $S_{\text{SO}_4^{2-}} = 0.40\%$ ),  $\alpha = 94.88\%$  ( $S_{\text{SO}_4^{2-}} = 0.33\%$ ).

There is observed a drop of the reagent utilization ( $\beta$ ) at increase of the initial concentration (excess of 5–10%).

Table 2  
Inclusion concentrations in the liquid phase from Na<sub>2</sub>SO<sub>4</sub> during treatment of Pb-paste by NaOH

No	Conditions of carrying out the process	Inclusion concentrations (mg L <sup>-1</sup> )							pH
		Pb	Sb	Cl <sub>2</sub>	As	Cu	Zn	Fe	
(A) Common reactor with laboratory agitator									
1	C <sub>initial</sub> = 1.01 mol L <sup>-1</sup> (stoichiometric), m = 2, τ = 30 min	972.0	<0.1	1320.0	52.5	<0.01	13.93	1.8	12.55
2	C <sub>initial</sub> = 1.06 mol L <sup>-1</sup> (5% excess), m = 2, τ = 30 min	1602.6	<0.1	1640	65.3	<0.01	6.16	1.8	12.60
3	C <sub>initial</sub> = 1.08 mol L <sup>-1</sup> (10% excess), m = 2, τ = 30 min	2019.2	<0.1	1560.0	70.3	<0.01	5.10	1.7	12.60
(B) Rotary reactor of drum type									
4	C <sub>initial</sub> = 1.01 mol L <sup>-1</sup> (stoichiometric), m = 2, τ = 30 min	874.7	<0.1	1460.0	48.5	0.60	14.60	1.70	12.50
5	C <sub>initial</sub> = 1.06 mol L <sup>-1</sup> (5% excess), m = 2, τ = 30 min	1097.8	<0.1	1640.0	60.0	0.90	20.40	1.90	12.53
6	C <sub>initial</sub> = 1.08 mol L <sup>-1</sup> (10% excess), m = 2, τ = 30 min	1496.8	<0.1	1840.0	68.9	0.80	26.50	2.00	12.55

The optimum conditions for desulphurization are: excess of NaOH—up to 5%, m = 2, t = 38–40 °C and τ ≤ 15 min.

### 3.2.2. In rotary reactor

Three experiments are carried out (Fig. 6) under the following conditions: m = 2, t = 48–28 °C and initial concentration of NaOH C<sub>initial</sub> = 1.01 mol L<sup>-1</sup> (stoichiometric composition): I experiment; C<sub>initial</sub> = 1.06 mol L<sup>-1</sup> (5% excess): II experiment; C<sub>initial</sub> = 1.08 mol L<sup>-1</sup> (10% excess): III experiment.

The results obtained are close to those obtained when treating Pb-paste by NaOH in common reactor with laboratory agitator. Increase of the desulphurization degree is observed after the 15th min. In the 30th min the process parameters are as follows: α<sub>1</sub> = -95.50% (S<sub>SO<sub>4</sub><sup>2-</sup></sub> = 0.29%), α<sub>2</sub> = 96.90% (S<sub>SO<sub>4</sub><sup>2-</sup></sub> = 0.20%), α<sub>3</sub> = 97.36% (S<sub>SO<sub>4</sub><sup>2-</sup></sub> = 0.17%).

The optimum conditions for desulphurization are: excess of NaOH—5%, m = 2, t = 38–40 °C and τ = 15–30 min.

### 3.2.3. Behavior of the inclusions in the solutions

The results of the chemical analysis of the liquid phase concerning the inclusion concentrations after desulphurization of Pb-pastes by NaOH in common reactor with laboratory agitator and in rotary reactor of drum type are presented in Table 2.

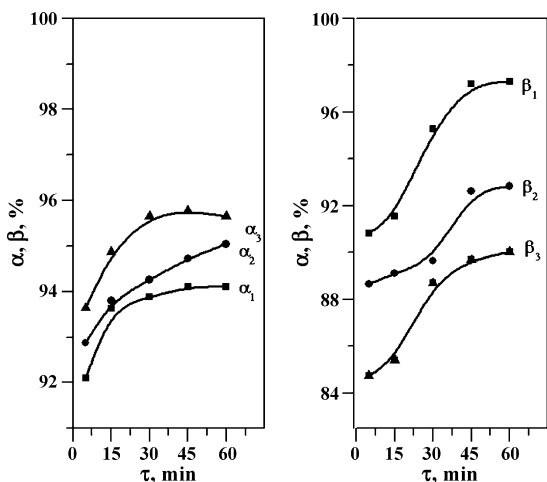


Fig. 5. Dependence between the desulphurization degree (α) and the utilization degree of NaOH (β) on the treatment time (τ) at stirring with laboratory agitator (m = 2; t = 38–40 °C): C<sub>initial(1)</sub> = 1.01 mol L<sup>-1</sup> (α<sub>1</sub>; β<sub>1</sub>); C<sub>initial(2)</sub> = 1.06 mol L<sup>-1</sup> (α<sub>2</sub>; β<sub>2</sub>); C<sub>initial(3)</sub> = 1.08 mol L<sup>-1</sup> (α<sub>3</sub>; β<sub>3</sub>).

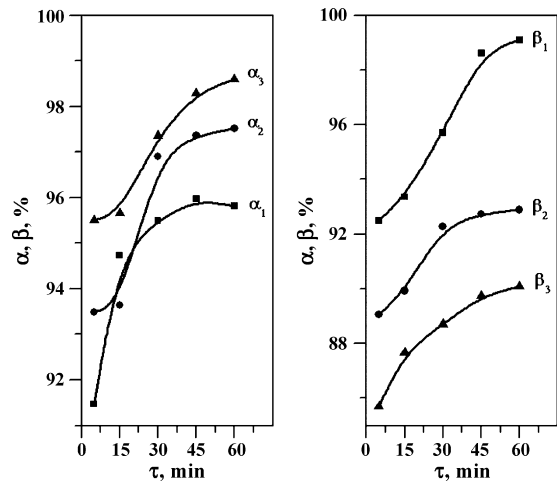


Fig. 6. Dependence between the desulphurization degree (α) and the utilization degree of NaOH (β) on the treatment time (τ) when using rotary reactor at t = 48–28 °C, m = 2: C<sub>initial(1)</sub> = 1.01 mol L<sup>-1</sup> (α<sub>1</sub>; β<sub>1</sub>); C<sub>initial(2)</sub> = 1.06 mol L<sup>-1</sup> (α<sub>2</sub>; β<sub>2</sub>); C<sub>initial(3)</sub> = 1.08 mol L<sup>-1</sup> (α<sub>3</sub>; β<sub>3</sub>).

Unlike the solutions produced after the desulphurization of Pb-pastes by Na<sub>2</sub>CO<sub>3</sub>, when NaOH is used the lead goes in the liquid phase to a much greater extent than with antimony.

The lead goes in the solutions in the form of sodium plumbite (Na<sub>2</sub>PbO<sub>2</sub>).

Considering Cl<sub>2</sub> and As, the purity of the solutions depends on the purity of the non-desulphurized paste and the presence of other Pb-containing inclusions or additives (e.g. Pb-powder). The latter is valid in a sense for As, as well as for some of the rest of the inclusions in the paste. The pH value of the solutions after desulphurization is: 12.50–12.60.

## 4. Conclusions

The thorough analysis of the examined dependences between the desulphurization degree α and utilization degree of Na<sub>2</sub>CO<sub>3</sub>(NaOH) β in dependence of the time of treatment τ shows that:

- the desulphurization process of Pb-pastes goes at higher speed when using NaOH than when using Na<sub>2</sub>CO<sub>3</sub>;
- the optimum conditions for desulphurization of Pb-paste by Na<sub>2</sub>CO<sub>3</sub> are: excess of Na<sub>2</sub>CO<sub>3</sub> up to 10%, m = 2.0–2.5,

$t = 55\text{--}35\text{ }^\circ\text{C}$  and  $\tau = 15\text{--}30$  min (the desulphurization degree under these conditions is 92.4–94.4%, and  $S_{\text{SO}_4^{2-}} = 0.49 - 0.36$ ); the optimum conditions for desulphurization of Pb-paste by NaOH are: excess of NaOH up to 10%,  $m = 2$ ,  $t = 55\text{--}35\text{ }^\circ\text{C}$  and  $\tau = 15\text{--}30$  min (the desulphurization degree under these conditions is 93.64–96.90%, and  $S_{\text{SO}_4^{2-}} = 0.41 - 0.20\%$ ).

The thorough analysis of the results presented in Tables 1 and 2 show that after desulphurization by  $\text{Na}_2\text{CO}_3$  much greater quantity of Sb goes in the solutions than Pb, while when using NaOH—it is the opposite: predominantly lead goes in the solutions and the antimony in them is below  $0.1\text{ mg L}^{-1}$ .

The results obtained in the study of the dependences  $\alpha(t)$  and  $\beta(t)$  provide the ground to assert that the desulphurization process of Pb-pastes can be also performed in continuous mode with application of rotary reactor of drum type and that crystalline, sufficiently pure  $\text{Na}_2\text{SO}_4$ , suitable for the purposes of the glass industry can be produced from the solutions (see Tables 1 and 2).

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