# Hydrometallurgical processing of dumped lead paste for lead acid batteries

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The present work represents an analytical survey of experimental results from conducted investigations, regarding desulphurization of dumped Pb-paste and the possibilities for the realization of the process. The aim is to compare and evaluate the results that we have obtained, with already existing data in the literature of leading technologies. Here are examined the kinetic relationships of the processes that take place and the related problems. The optimal conditions of the desulphurization process, developed by our team, are determined when using the following reagents – $Na_2CO_3$ and NaOH, depending on the working reactor (reactor with a laboratory stirrer and rotational reactor of drum type). The content of impurities in the solutions of our technology is investigated and compared with others of that type in order to obtain sufficiently clean crystalline $Na_2CO_3$ for the industry.

**Key words**: lead paste, Pb-paste desulphurization, lead accumulators processing.

## INTRODUCTION

The main aspects regarding chemistry and conduction of the process of desulphurization are targets of many investigations and publications of different authors [1−8]. In the industry there exist installations and technologies for the realization of the process in different hydro-metallurgical schemes [9−13].

Dumped lead acid batteries can be characterized like complicated secondary products because their processing causes many difficulties [14].

Lead acid batteries consist of three basic fractions and electrolyte [1−15]:

- Metalic (combs, poles, lattices and others) with Pb content of 93−95% and Sb content of 0.1−0.3%.

- Oxysulphatic (positive and negative paste), which has 68−76% Pb and 0.1−0.3% Sb.

- Not metallic – organic (boxes made from either ebonite, polypropylene or polyethylene, polyvinyl chloride separators and others).

During the production of the metal fraction lead and antimony or lead and calcium [1, 16] are mainly used, which causes reduction of impurities in the metal.

On the other hand the oxysulphatic fraction is divided into two categories: waste and dumped lead paste [1, 17]. Waste lead paste is obtained during the production of lead acid batteries and it consists of 79−86% Pb, mainly as oxide phase and 0.1−0.3%

Sb. Redeemed (positive and negative) paste has 68−76% Pb in the form of $PbSO_4 \sim$ 50–60%, $PbO_2 \sim$ 30–35%, PbO $\sim$ 10–15% and Sb $\sim$0.2–0.7%.

Many authors have investigated the pyrometallurgical processing of the lead pastes [18−21]. During these methods the extraction of lead reaches 98% and it can be conducted at relatively low temperatures 500−600°C under the condition that no lead sulphates are present. The presence of lead sulphate requires increasing of the temperatures of the process above 900°C, which leads to decreasing the degree of lead extraction and causes technological and ecological problems.

The necessity of desulphurization of pastes prior to pyrometallurgical processes of melting and refining is theoretically predicted and experimentally proved [22].

The preliminary desulphurization of lead paste contributes to the decreasing of the melting temperature, decreasing of the amounts of fluxes and caustic soda, slag and dusts, reduces the content of $SO_2$ in the gases and the quantity of chemical reagents used in the refining cycle, enhances the degree of lead extraction and so on [5, 11, 22].

The essence of the desulphurization process consists in taking the sulphate ions out of the paste into the solution and generating chemical compound of the lead, which does not cause any difficulties during following pyrometallurgical treatment [22].

Physicochemical and technological investigations of the main aspects of the desulphurization

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process of the lead sulphate have been published in the literature [22].

The basic chemical and kinetic principles like: stoichiometry of the reaction and diffusion kinetics, are thoroughly examined by Laidler *et al.* [23].

The most commonly used reagent for desulphurization of dumped lead pastes is the sodium carbonate [1−11, 24−26]. The desulphurization process is accomplished by treating the paste with solutions of sodium carbonate according to the reaction:

$$PbSO_4 + Na_2CO_3 \rightarrow PbCO_3 + Na_2SO_4 \quad (1)$$
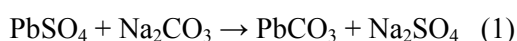
The sulphur goes into the solution in the form of sodium sulphate. The obtained solutions, after separation of the liquid and solid phase, can be subjected to evaporation and centrifuging in order to obtain waterless sodium sulphate [2, 27].

In the presence of electrolyte in the paste - $H_2SO_4$, a complete neutralization of the acid in the solution of $Na_2CO_3$ takes place, with molar proportion $Na_2CO_3:H_2SO_4 > 1$, according to the following reaction:

$$Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + CO_2 \quad (2)$$
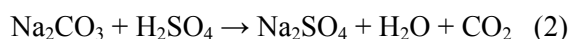
This explains the generation of $Na_2CO_3$:

$$2Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2NaHCO_3 \quad (3)$$
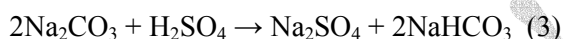
In view of the conditions during the desulphurization process – concentration of sodium carbonate, ratio of liquid to solid mass, temperature, duration of the process, *etc.*, it is possible to have parallel reactions.

When the consumption of the reagent exceeds the stoichiometrically corresponding to the reaction (1), actually in excess of sodium carbonate, the following reactions take place:

$$PbSO_4 + 4Na_2CO_3 + 2H_2O \rightarrow$$
$$\rightarrow 2PbCO_3.Pb(OH)_2 + 3Na_2SO_4 + 2NaHCO_3 \quad (4)$$

$$3PbCO_3 + Na_2CO_3 + 2H_2O \rightarrow$$
$$\rightarrow 2PbCO_3.Pb(OH)_2 + 2NaHCO_3 \quad 5)$$
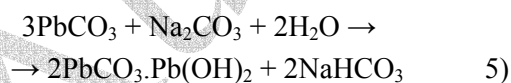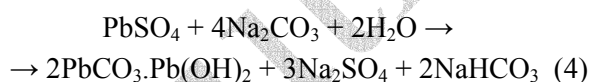
The interaction between the lead sulphate and sodium carbonate has been studied by many authors [1, 2, 8, 28, 29], and according to them reaction (1) describes accurately enough the process of desulphurization. Investigations of the chemistry of the process prove the generation of complex compound of the lead, incorporating in itself sodium and sulphatic ions of the type: $Pb_3(CO_3)_2(OH)_2$, $NaPb_2(CO_3)_2OH$, $Pb_{10}O(CO_3)_6(OH)_6$, $Pb_4(SO_4)(CO_3)_2(OH)_2$ [24, 30].

The nature of the compounds in solid phase depends on several factors, in particular on the pH and on the concentration of sodium carbonate and

sodium sulphate in the solutions [24]. The formation of these compounds causes increase of the reagent consumption and difficulties during further treatment and usage of the ready product.

It is established that during desulphurization of Pb paste with $Na_2CO_3$, 2−3% of the Sb, contained in the paste, can pass into the solution [22].

Many technologies for processing of dumped lead paste use sodium base for the desulphurization process [7, 9, 10, 30−34].
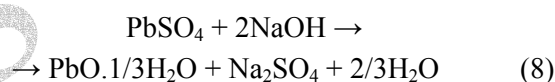
Also during this method a reaction of neutralization of the $H_2SO_4$ contained in the paste initially takes place:

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O \quad (6)$$

The transformation of $PbSO_4$ into $Pb(OH)_2$ is typical for the process of desulphurization and it takes place according to the reaction:

$$PbSO_4 + 4NaOH \rightarrow Pb(OH)_2 + Na_2SO_4 \quad (7)$$

The desulphurization using NaOH can be accomplished at room temperature. Increasing of the temperature may lead to changes in the solid phase of $Pb(OH)_2$ to $3PbO.2H_2O$ (or $PbO.1/3H_2O$), according to the reactions:

$$PbSO_4 + 2NaOH \rightarrow$$
$$\rightarrow PbO.1/3H_2O + Na_2SO_4 + 2/3H_2O \quad (8)$$

$$PbSO_4 + 2NaOH \rightarrow PbO + Na_2SO_4 + H_2O \quad (9)$$

An excess of NaOH ~10−20% of the stoichiometrically needed for the reaction (7) is necessary, for a complete desulphurization process in the technological practice [7, 22].

Part of the lead is transferred into the solution in the form of $Na_2PbO_2$, according to the reaction:

$$PbSO_4 + 4NaOH \leftrightarrow Na_2PbO_2 + Na_2SO_4 + 2H_2O \quad (10)$$

There is a direct relationship between the concentration of NaOH and the content of $Na_2PbO_2$ in the solutions. The concentration of $Na_2PbO_2$ increases at higher excess of NaOH [7, 29].

The solution of $Na_2SO_4$, obtained after desulphurization process, can be subjected to purifying from the lead using neutralization with $H_2SO_4$, according to the reaction:

$$Na_2PbO_2 + H_2SO_4 \rightarrow PbSO_4 + Na_2SO_4 + 2H_2O \quad (11)$$

The separated $PbSO_4$ in the form of deposit, again returns into stage for desulphurisation, and the solution of $Na_2SO_4$ is good for obtaining crystalline $Na_2SO_4$ which is free of impurities.

Many authors suggest that the regeneration of the $Na_2SO_4$ is to be conducted using $Ca(OH)_2$ [25, 38−42] and $Ba(OH)_2$ [42].

The degree of desulphurization is determined by the content of $PbSO_4$ in the treated paste. The bigger that percentage content in the initial product is, the higher is the consumption of NaOH (the concentration in the solution), which leads to increases in the concentration of Pb in the solutions [7, 29].

During desulphurisation with NaOH almost no Sb passes into the solutions, and no insoluble sodium salts are created [7, 29, 43].

There exists also technology for desulphurization of lead pastes with NaOH, during which the solutions of $Na_2SO_4$ are subjected to electrolysis for regeneration of NaOH. The ratio of liquid to solid phase, when using this method, is 10−15:1 [33].

In many technologies the desulphurisation of lead pastes with NaOH is followed by treatment with $NBF_4$ [44−46]. The insoluble remainder is treated with concentrated $H_2SO_4$. Because of that $PbO_2$ is transferred in the electrolyte and proceeds as electrolysis with insoluble anode.

Desulphurization of Pb paste can be successfully accomplished with ammonium carbonate, as well [47−52]. The chemical reaction takes place according to the reaction:

$$PbSO_4 + (NH_4)_2CO_3 \rightarrow PbCO_3 + (NH_4)_2SO_4 \quad (12)$$
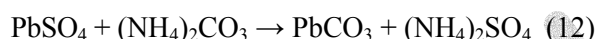
Data in the literature, concerning the usage of ammonium carbonate as a desulphurisation agent, is mainly connected with the investigation of kinetic and technological parameters. According to data by the authors, when the process lasts 30 minutes, the degree of desulphurization reaches 90%. Further increasing of the duration of the process does not affect significantly the degree of desulphurization. Increasing of the temperature in the range of 22−60°C is insignificantly accelerating the process.

Many authors are also investigating the possibility to use $K_2CO_3$ [2, 53−55] as a desulphurization agent, which reacts with $PbSO_4$ according to the reaction:

$$PbSO_4 + K_2CO_3 \rightarrow PbCO_3 + K_2SO_4 \quad (13)$$

High degree of desulphurization reached ~95%. The process proceeds at temperature ~60°C, ratio of liquid to solid 3:1, excess of $K_2CO_3$ 10−15% and duration of 60 minutes [2].
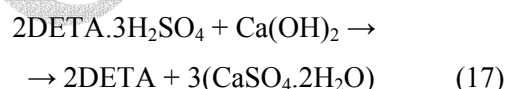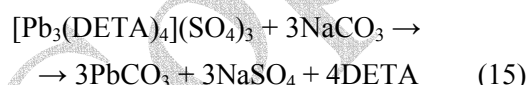
In the literature there exist data on the influence of the basic factors in the process (degree of desulphurization and utilization of the reagent). The authors have also investigated possible schemes for continuous process, which are followed by evaporation and taking out the salts from the solutions with the aim to obtain crystalline $K_2SO_4$ [2].

The hydrometallurgical treatment of the lead-containing raw materials can also be done with the use of amines. There also exists a technology for desulphurization of dumped lead pastes using the organic solvent diethylenetriamine (DETA) [1, 8, 56, 57]. The method is based on the formation of metallic complex compound, in which the metal-amine bond is stronger than the metal-water bond.

When the liquid phase is being treated with $Na_2CO_3$ pure compounds can be obtained: $PbCO_3$ and $PbSO_4$, and when it is treated with $H_2SO_4$ – pure $PbSO_4$ for the needs of lead acid battery industry. Soft lead can be obtained from the solid phase, when melted at relatively low temperatures, [1, 8].

The chemistry of the process comprises the following reactions:

$$3PbSO_4 + 4DETA \rightarrow [Pb_3(DETA)_4](SO_4)_3 \quad (14)$$

$$[Pb_3(DETA)_4](SO_4)_3 + 3NaCO_3 \rightarrow$$
$$\rightarrow 3PbCO_3 + 3NaSO_4 + 4DETA \quad (15)$$

$$[Pb_3(DETA)_4](SO_4)_3 + 2DETA + 3H_2SO_4 \rightarrow$$
$$\rightarrow 3PbSO_4^- + 2DETA.3H_2SO_4 + 4DETA \quad (16)$$

$$2DETA.3H_2SO_4 + Ca(OH)_2 \rightarrow$$
$$\rightarrow 2DETA + 3(CaSO_4.2H_2O) \quad (17)$$

On the basis of the above literature review concerning the methods for desulphurization of dumped lead pastes from lead batteries, the aims of the present investigation are formulated as follows:

- to determine the influence of the basic kinetic factors (concentration of $Na_2CO_3$ (NaOH) and the ratio of liquid to solid phases as a function of the temperature and duration of the process), that influence the parameters of the process of desulphurization of Pb-pastes − degree of desulphurization and utilization of the reagent;

- to specify the optimal conditions for accomplishing desulphurization of Pb-pastes with $Na_2CO_3$ or NaOH, depending on the type of the reactors used;

- investigation of the content of impurities in the solutions in order to obtain sufficiently pure crystalline sodium sulphate for further use in the industry;

- the results from the conducted experimental researches on both samples will be compared with each other and with the existing experimental and technological data in the literature.

EXPERIMENTAL

Object of the first part of our investigations [7] is dumped lead paste from lead acid batteries imported from Romania - Sample № 1 given to us by "KCM-Plovdiv", Bulgaria.

The second part of the investigations is done with dumped lead acid battery paste imported from Poland (Sample No. 2) given to us by the same company.

The pastes have the following chemical composition (%):

Sample No. 1: Pb 59.85; Sb 0.73; As 0.042; Cl 0.33; Cu 0.13; Zn 0.10; $S_\Sigma$ 7.20; $S_{SO_4^{2-}}$ 6.45.

Sample No. 2: Pb 73.05; Sb 0.053; As 0.015; Cl 0.01; Cu 0.007; Zn 0.009; $S_\Sigma$ 7.15; $S_{SO_4^{2-}}$ 6.38.

It should be pointed out that Sample No. 2 is purer than Sample No. 1 with respect to impurities.

Before subjecting to desulphurization process, the Pb-paste is dried and sifted in a sieve of mesh 5.0 mm.

Sample No. 1: The fraction (< 5.0 mm) is 80% and the fraction (> 5.0 mm) is 20%.

Sample No. 2: The fraction (< 5 mm) is 95%, and the fraction (> 5 mm) is 5%.

Sample № 1 is contaminated, which may be due to ineffective separation technology.

A laboratory stirrer type ER 10 and mass of the paste 200 g are used for the laboratory work and the temperature is maintained constant by thermostat type Ultra NBA. When treating in rotational reactor of drum type VEB Elmo Hartha DDR, the mass of the paste is 400 g. In this case the amount of paste is higher because of the larger working volume of the equipment and the related difficulties. These difficulties concern maintaining constant working temperature in this type of reactor under laboratory conditions, as with increasing the amount of material the rate of cooling under atmospheric air decreases.

The lead paste 200 (400) g is added to solutions of specified $Na_2CO_3$ (NaOH) concentration and at definite liquid-solid phase ratio (at preset temperature and duration of the desulphurization process).

The analyses are realized using analytical chemical methods. Upon accomplishment of the chemical treatment, the pulp is filtered and the solid phase is washed with water on the filter, dried to constant weight and analyzed for content of $SO_4^{2-}$. The liquid phases are analyzed for content of $Na_2CO_3$ (NaOH) and $SO_4^{2-}$. The determination of $SO_4^{2-}$ in the solid phase is done using weighting method. Initially the sample is decomposed with solution of $Na_2CO_3$ and after that from the obtained solutions $SO_4^{2-}$ is precipitated using $BaCl_2$ in the form of $BaSO_4$. The analysis of $SO_4^{2-}$ in liquid phase is identical (precipitation with $BaCl_2$). The

data from it in this case can be used for verification of the results from the analysis for $SO_4^{2-}$ in solid phase (balance with respect to sulphur).

The remaining concentration of uncombined $Na_2CO_3$ and NaOH in the liquid phases (filtrates) is determined by titration with 0.1 M HCl and *Methyl orange* as indicator.

The content of sulphatic sulphur $S_{SO_4^{2-}}$ in the non-desulphurized paste and the chemical composition is determined by phase analysis.

The desulphurization degree α (%) is calculated by the formula:

$$\frac{Ds(initial) - Ds(final)}{Ds(initial)} \cdot 100 = \alpha,$$

where: $Ds_{(initial)}$ and $Ds_{(final)}$ are initial and residual $SO_4^{2-}$ concentration.

The reagent utilization degree β (%) is calculated by the formula:

$$\frac{C(initial) - C(final)}{C(initial)} \cdot 100 = \beta,$$

where: $C_{(initial)}$ and $C_{(final)}$ are initial and residual reagent concentrations, $g \cdot L^{-1}$.

## RESULTS AND DISCUSSION

### *Desulphurization of Pb-paste with $Na_2CO_3$ in a reactor with a laboratory stirrer*

For the purposes of the present research, regarding the desulphurization of the paste, an examination regarding the influence of the basic kinetic factors is conducted: initial concentration of $Na_2CO_3$ (consumption of $Na_2CO_3$), ratio of liquid to solid phase, duration of the desulphurization process with set temperature interval, which is connected with the properties of the reagent and the products from the reaction.

Based on the conducted preliminary experiments [7, 28, 29] and data from the literature [2] it is determined that the temperature does not affect significantly the parameters of the desulphurization process (degree of desulphurization α, degree of utilization β of the $Na_2CO_3$), because the work is done in an environment of diffusion control [23]. The coefficients α and β have highest values in the range 30−40°C, above that temperature the solubility of $Na_2CO_3$ and $Na_2SO_4$ in water decreases [58−60].

The solubility of $Na_2CO_3$ and $Na_2SO_4$ and of the compounds, obtained from them, are directly connected with the indexes of the process – degree

of desulphurization and degree of utilization of the reagent and the stoichiometric realization of the filtration process, as well [5, 6].

Fig. 1 presents the results from the desulphurization of Pb-paste – Sample No. 2 with ratio of liquid to solid phase $m = 2.25$ ($m = 2.25:1$), temperature 38−40ºC and different initial concentrations of $Na_2CO_3$:
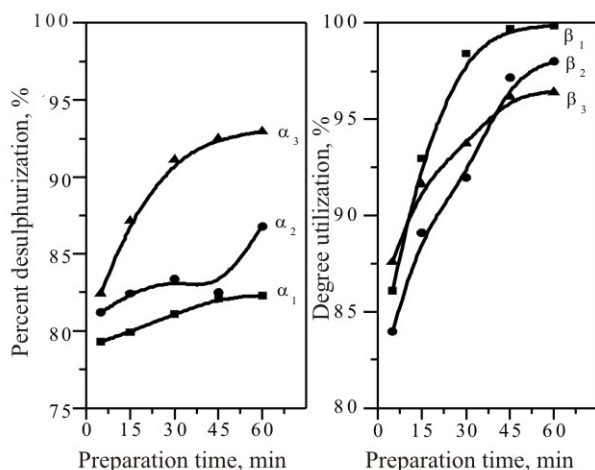


Fig. 1. Dependence of the percentage of desulphurization ($\alpha$) and $Na_2CO_3$ utilization degree ($\beta$) on the treatment time ($\tau$) when stirring with laboratory agitator ($m = 2.25$; $t = 38−40°C$): $C_{initial(1)} = 84.51$ g·L−1 ($\alpha_1$, $\beta_1$), $C_{initial(2)} = 93.93$ g·L$^{-1}$ ($\alpha_2$,$\beta_2$) and $C_{initial(3)} = 103.33$ g·L$^{-1}$ ($\alpha_3$, $\beta_3$); a −$\alpha_1$, $\alpha_2$, and $\alpha_3$; b − $\beta_1$, $\beta_2$ and $\beta_3$.

I experiment – with shortage of 10% with respect to the stoichiometric ratio $C_{initial(1)} = 84.51$ g·L$^{-1}$ $Na_2CO_3$; II experiment – $C_{initial(2)} = 93.93$ g·L$^{-1}$ $Na_2CO_3$ (stoichiometric ratio); III experiment – $C_{initial(3)} = 103.33$ g·L$^{-1}$ $Na_2CO_3$ (10% excess).

A satisfactory degree of desulphurization, corresponding to the technological requirements [10], is achieved after 30 minutes but it is desirable that $\tau > 45$, when the degree of desulphurization is $\alpha = 92.48$ % (content of $S_{SO_4^{2-}}$ in the desulphurizated paste 0.48%). With an excess of $Na_2CO_3$ 10% ($C_{initial(3)} = 103.33$ g·L$^{-1}$) and duration of the process 60 minutes, the degree of desulphurization is $\alpha_3 = 92.95\%$ ($S_{SO_4^{2-}} = 0.45\%$).

The obtained results are in accordance with the data from the literature [2, 7, 22] and are close to those for Sample No. 1. After 15 min treatment of Pb-paste with stoichiometric amount of $Na_2CO_3$ ($C_{initial(2)} = 94.95$ g·L$^{-1}$) the degree of desulphurization is $\alpha = 94.11\%$ (0.38% $S_{SO_4^{2-}}$ in the desulphurized paste) [7]. For Sample No. 1, even with 10% shortage of the $Na_2CO_3$ the degree of desulphurization is $\alpha_1 = 92.09\%$ (0.51% $S_{SO_4^{2-}}$ in

the desulphurized paste) [7].

The high degree of utilization of the $Na_2CO_3$ is noticeable. This imposed a series of two more experiments with Sample No. 2, to be conducted upon changing the ratio $m = 2.5$, temperature 37−40°C and increasing the initial concentration of $Na_2CO_3$:

I experiment – with $C_{initial(1)} = 93.00$ g·L$^{-1}$ $Na_2CO_3$ (10% excess);

II experiment – $C_{initial(2)} = 101.45$ g·L$^{-1}$ $Na_2CO_3$ (20% excess).
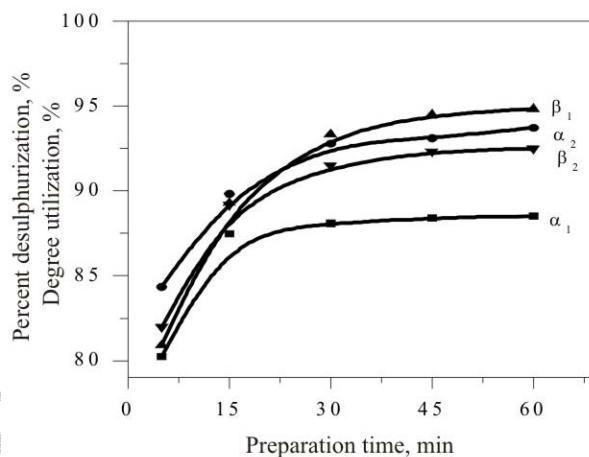
The results are presented in Fig. 2.



Fig. 2. Dependence of percentage of desulphurization ($\alpha$) and $Na_2CO_3$ utilization degree ($\beta$) on the treatment time ($\tau$) when stirring with laboratory agitator ($m = 2.5$; $t = 37−40°C$): $C_{initial(1)} = 93.00$ g·L$^{-1}$ ($\alpha_1$, $\beta_1$), $C_{initial(2)} = 101.45$ g·L$^{-1}$ ($\alpha_2$, $\beta_2$).

Satisfactory for the practice results [10] are obtained after $\tau = 30$ min, with initial concentration of $Na_2CO_3$ with 20% excess ($C_{initial(2)} = 101.45$ g·L$^{-1}$) – degree of desulphurization $\alpha_2 = 92.79\%$ ($S_{SO_4^{2-}} = 0.46$ % in the desulphurized paste), for 45 min and 60 min respectively 93.10% ($S_{SO_4^{2-}} = 0.44$ %) and 93.73% ($S_{SO_4^{2-}} = 0.40\%$).

These results correspond to existing data in the literature from laboratory experiment, during which the possibility for optimal running of the desulphurization process with excess of $Na_2CO_3$ − 20% is determined, duration 2 hours, temperature 55°C, <33% solid phase in the pulp and pH 8 [24].

Recommended conditions for desulphurization of Pb-paste – Sample № 1 with $Na_2CO_3$, when stirred with a laboratory stirrer, were established: excess of the reagent up to 10%; ratio of liquid to solid phase $m = 2.0−2.5$; temperature and duration of the process – t = 35−40ºC and $\tau = 15−30$ min respectively [7].

As optimal conditions in regard to degree of desulphurization and utilization of the reagent for Sample No. 2, can be accepted: initial concentration of $Na_2CO_3$ with 20% excess ($C_{initial(2)} = 101.45$ g·L$^{-1}$), $m = 2.5$ and duration of the process $\tau = 35-40$ min.

These minor differences in the obtained results for the different Pb-paste samples are due to the differences in their chemical composition.

The condition to work in excess of $Na_2CO_3$ not higher than 20% was observed during running this group of experiments, in order to avoid the formation of $NaHCO_3$ and the double salt $NaPb_2(CO_3)_2OH$ [24, 30], which increase the consumption of $Na_2CO_3$.

The results from investigations of the process pointed out by Yanakieva [2] are analogous. For optimal concentration, when working with a laboratory stirrer, the author recommends 20% excess of $Na_2CO_3$. The same methods of the experiment and the same analytical chemical analysis for determination of the results have been used.

The world leading company in desulphurization of dumped lead acid battery pastes is the Italian company "Engitec Impianti [10]" - installation "CX Compact".

When using the installation "CX Compact", dumped lead paste, after wet transportation on vibration sieve, is transferred into a precipitation device, and after compaction in it, is fed into one of two parallel working mechanical stirrers, where it is treated with solutions based on sodium carbonate or sodium hydroxide. During the process the pulp is heated, where upon the lead sulphate is transformed in either lead carbonate or lead hydroxide, and the sulphur passes into the solution as sodium sulphate. After the desulphurization process the pulp is fed into an automatic filter-press. The filtered solution is then sent for evaporation-crystallization, the solid desulphurizated paste, with humidity below 13% and sulphur content less than 0.8%, is collected in containers for revision.

Based on this technology the following companies are working: Monbat AD - Bulgaria; Asarco; Doerun; GNB - USA; Metallgesellschaft - Germany, STCM - France, Metallum-Switzerland; Enirisorse - Italy, Tonolli - Canada, Brittania - England and others [8].

### Desulphurization of Pb-paste with Na$_2$CO$_3$ in rotational reactor of drum type

The investigations are conducted in order to avoid the difficulties, which are typical of stirrers: stirring of the materials and emptying the device. The inconvenience when working with rotational reactor is that it is not possible to maintain constant temperature. This disadvantage can be overcome by heating with sharp vapour in the volume of the device.

At temperature 56−28°C and $m = 2.25$ two experiments were conducted with $Na_2CO_3$ and Sample No. 2 (Fig. 3), with changed initial concentration:
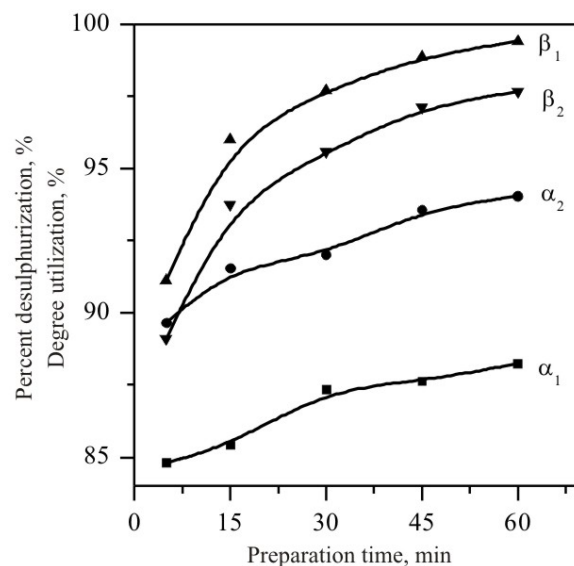


Fig. 3. Dependence of the percentage of desulphurization ($\alpha$) and the $Na_2CO_3$ utilization degree ($\beta$) on the treatment time ($\tau$) when using rotary reactor at t = 56−28ºC, $m = 2.25$: $C_{initial(1)} = 93.92$ g·L$^{-1}$ ($\alpha_1, \beta_1$), $C_{initial(2)} = 103.31$ g·L$^{-1}$ ($\alpha_2, \beta_2$).

I experiment − $C_{initial(1)} = 93.92$ g·L$^{-1}$ (stoichiometric ratio);

II experiment − $C_{initial(2)} = 103.31$ g·L$^{-1}$ (10% excess).

Good results, which correspond to the already mentioned technological requirements, were obtained with 10% excess of $Na_2CO_3$ ($C_{initial} = 103.31$ g·L$^{-1}$) and duration of the treatment $\tau = 30$ min – degree of desulphurization $\alpha_2 = 92.01\%$ ($S_{SO_4^{2-}} = 0.51\%$); when $\tau = 45$ and 60 min correspondingly 93.57% ($S_{SO_4^{2-}} = 0.41\%$) and 94.04% ($S_{SO_4^{2-}} = 0.38\%$).

The following parameters can be accepted as optimal for the process when working with rotational reactor: initial concentration of $Na_2CO_3$ with excess of 10% ($C_{initial} = 103.31$ g·L$^{-1}$), $m = 2.25$ and $\tau = 30-45$ min.

The obtained results supplement the previous data received for Sample № 1. Two experiments were conducted with it using $Na_2CO_3$, t = 55−28ºC and changing the ratio m [7], for the following conditions:

I experiment − $C_{initial} = 94.95$ g·L$^{-1}$ (stoichiometry); $m = 2.25$;

II experiment − $C_{initial} = 94.00$ g·L$^{-1}$ (10% ex-

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cess); *m* = 2.5.

For *m* = 2.25 and τ = 15 min the obtained degree of desulphurization is 92.40% (in the desulphurized paste $S_{SO_4^{2-}}$ = 0.49%); at τ = 30 min – α = 93.95% ($S_{SO_4^{2-}}$ = 0.39%);

For *m* = 2.5 and τ = 15 min − α = 92.87% ($S_{SO_4^{2-}}$ = 0.46%), when τ = 30 min. − α is 93.64% ($S_{SO_4^{2-}}$ = 0.41%).

The optimal conditions for desulphurization of Sample No. 1 are excess of $Na_2CO_3$ up to 10%; *m* = 2.25−2.50; t = 40−38ºC; τ = 15−30 min.

The obtained results are close to those obtained when working with an ordinary reactor equipped with a laboratory stirrer [7].

In order to optimize the influence of the initial concentration of $Na_2CO_3$ and m when using rotational reactor of the drum type, an experiment is conducted with Sample No. 2 (Fig. 4), under the following conditions: *m* = 2.5, t = 58−28°C and initial concentration $C_{initial}$ = 101.44g·L$^{-1}$ $Na_2CO_3$ (20% excess).

With 20% excess of $Na_2CO_3$ the process runs at higher speed. On the 15th minute the degree of desulphurization is 93.57% ($S_{SO_4^{2-}}$ = 0.41%).

As it has already been determined for the same sample (Sample No. 2 in the section above, when using laboratory reactor with a stirrer and initial concentration of $Na_2CO_3$ with 20% excess ($C_{initial(2)}$ = 101.45 g·L$^{-1}$), results which are satisfactory for the practice are obtained after τ = 30 min.
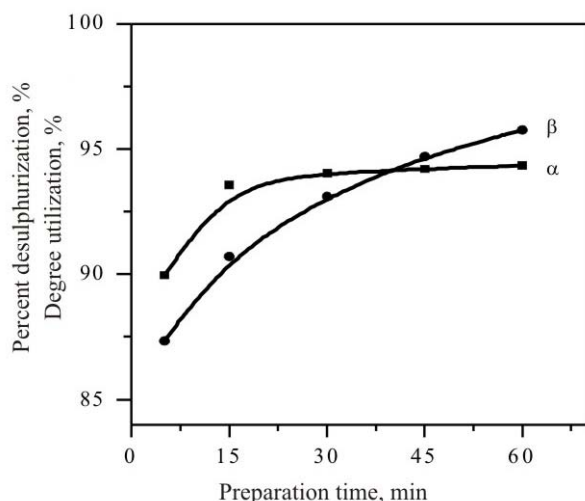


Fig. 4. Dependence of the percent desulphurization (α) and $Na_2CO_3$ utilization degree (β) on the treatment time (τ) when using rotary reactor at t = 58–28ºC, *m* =2.5, $C_{initial}$ =101.44 g·L$^{-1}$.

The process of desulphurisation takes place faster in a rotational reactor compared to that in a laboratory stirrer, which is due to improvement of the conditions for better contact with the reagent.

The obtained results clearly show the kinetic correlations described above, that is upon increasing of the concentration of $Na_2CO_3$ the degree of desulphurization increases but the degree of utilization of the reagent decreases because the process runs with diffusional difficulties [23].

The change in the ratio *m* does not affect significantly the kinetics of the process. The obtained data are in accordance with those mentioned in the literature [7, 22].

The correlations were determined also by Yanakieva [2] by indicating data regarding periodical and continuous process of desulphurization in rotational drum separator in a technological line No. 1 in department "Lead acid battery waste" of the company OCK-LTD in Kurdjali. It is established that when using 20% excess of $Na_2CO_3$ under industrial conditions, after washing the paste a higher degree of desulphurization is achieved (99%) than under laboratory conditions with a stirrer (95%).

*Desulphurization of Pb-paste with NaOH in a reactor with a laboratory stirrer*

These investigations were done in order to determine the influence of the initial concentration of NaOH and the ratio of liquid to solid phase at temperature 38−40ºC upon the parameters of the process, as a function of time: degree of desulphurization of the paste and degree of utilization of NaOH.

Here, similarly to the other groups of experiments, it was found out that the temperature above certain value does not affect significantly the parameters of the desulphurization process [7, 28, 29].

Four experiments with Sample No. 2 paste were done at t = 40°C and *m* = 2.25 (Fig. 5a, b) and the following conditions:

I experiment − $C_{initial(1)}$ = 63.80 g·L$^{-1}$ (stoichiometric ratio);

II experiment − $C_{initial(2)}$ = 67.00 g·L$^{-1}$ (5% excess);

III experiment − $C_{initial(3)}$ = 70.20 g·L$^{-1}$ (10% excess);

IV experiment − $C_{initial(4)}$ = 76.56 g·L$^{-1}$ (20 % excess).

On the 5th minute a very high degree of desulphurization is reached, at a stoichiometrical ratio ($C_{initial(2)}$ = 63.80 g·L$^{-1}$) the degree of desulphuri-

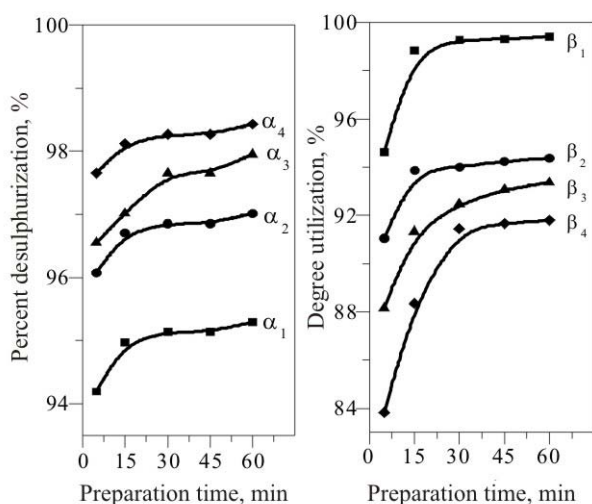zation is $\alpha_1 = 94.62\%$ ($S_{SO_4^{2-}} = 0.37\%$), and at 5% excess ($C_{initial} = 67.00$ g·L$^{-1}$) − $\alpha_2 = 96.08\%$ ($S_{SO_4^{2-}} = 0.25\%$).



Fig. 5. Dependence of the percentage of desulphurization (α) and Na$_2$CO$_3$ utilization degree (β) on the treatment time (τ) when stirring with laboratory agitator ($m = 2.5$; $t = 40°C$): $C_{initial(1)} = 63.80$ g·L$^{-1}$ ($\alpha_1$, $\beta_1$), $C_{initial(2)} = 67.00$ g·L$^{-1}$ ($\alpha_2$, $\beta_2$), $C_{initial(3)} = 70.20$ g·L$^{-1}$ ($\alpha_3$, $\beta_3$), $C_{initial(4)} = 76.56$ g·L$^{-1}$ ($\alpha_4$, $\beta_4$), a − $\alpha_1$, $\alpha_2$, $\alpha_3$ and $\alpha_4$; b − $\beta_1$, $\beta_2$, $\beta_3$ and $\beta_4$.

Analogous research works were done with NaOH and change in the ratio m with Sample No. 1 as well [7], at t = 38−40ºC, $m = 2.0$ and concentration:
I experiment – stoichiometric ratio ($C_{initial} = 80.62$ g·L$^{-1}$);
II experiment – 5% excess ($C_{initial} = 84.65$ g·L$^{-1}$);
III experiment – 10% excess ($C_{initial} = 86.68$ g·L$^{-1}$).

The indexes of the desulphurization process with NaOH were very good with Sample No. 1, as well [7]. On the 5th minute the degree of desulphurization at stoichiometric ratio is α = 92.10% (in the desulphurized paste $S_{SO_4^{2-}} = 0.51\%$). After 15 min degrees of desulphurization are achieved α = 93.64−94.88%, depending on the initial concentration of NaOH.

Decrease in the conversion of the reagent (β) is observed with the increase of the initial concentration (excess 5−10%), which is in complete correspondence with the kinetic laws.

When using a bigger excess of NaOH (Sample No. 2) – 10% and 20%, the desulphurization degree is: $\alpha_3 = 96.55\%$ ($S_{SO_4^{2-}} = 0.22\%$) and $\alpha_4 = 97.65\%$ ($S_{SO_4^{2-}} = 0.15\%$).

It is noticeable that the change in the ratio of liquid to solid phase for desulphurization with NaOH in the range m = 2−2.5, does not affect significantly the parameters of the process.

It can be accepted that m = 2.5 is optimal, because bigger ratio will increase the volume of the system and the amount of waste solutions and the consumption of the reagent respectively.

The optimal conditions for desulphurization in relation to α and β are: from 0 to 5% excess of NaOH ($C_{нач} = 63.8−67.00$ g·L$^{-1}$), m = 2.5, t = 40°C and τ = 5−15 min.

According to data from the technological practice of the desulphurization process, the need of ~10−20% excess of NaOH is determined, and the degree of desulphurization reaches ~95%, and the content of sulphate sulphur in the desulphurized paste does not exceeds 0.6% [22].

*Desulphurization with NaOH when working with rotational reactor of the drum type*

In order to confirm and summarize the results three experiments were conducted with Sample № 2 (Fig. 6a, b), at t = 48−28°C, m = 2.5 and initial concentration of NaOH:
I experiment − $C_{initial(1)} = 63.80$ g·L$^{-1}$ (stoichiometric ratio);
II experiment − $C_{initial(2)} = 67.00$ g·L$^{-1}$ (5% excess);
III experiment − $C_{initial(3)} = 70.20$ g·L$^{-1}$ (10% excess).
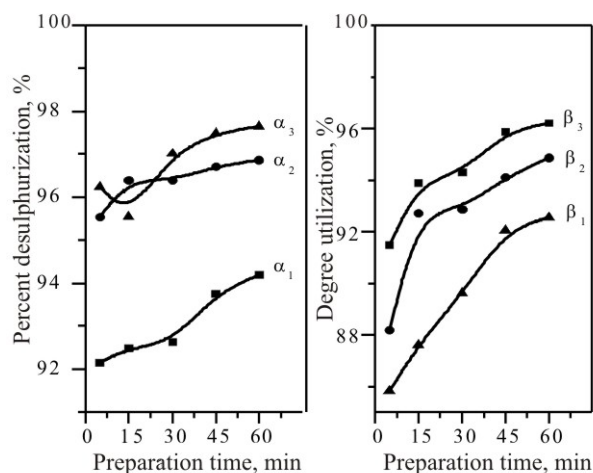


Fig. 6. Dependence of percentage of desulphurization (α) and Na$_2$CO$_3$ utilization degree (β) on the treatment time (τ) when using rotary reactor at t = 48−28°C, $m = 2.5$: $C_{initial(1)} = 63.80$ g·L$^{-1}$ ($\alpha_1$, $\beta_1$), $C_{initial(2)} = 67.00$ g·L$^{-1}$ ($\alpha_2$, $\beta_2$) and $C_{initial(3)} = 70.20$ g·L$^{-1}$ ($\alpha_3$, $\beta_3$); a − $\alpha_1$, $\alpha_2$ and $\alpha_3$; b − $\beta_1$, $\beta_2$ and $\beta_3$.

On the 5th minute and stoichiometric ratio

$C_{initial(1)} = 63.80$ g·L$^{-1}$: $\alpha_1 = 92.16\%$ ($S_{SO_4^{2-}} = 0.50\%$).

For 5% excess of NaOH ($C_{initial} = 67.00$ g·L$^{-1}$) we obtained $\alpha_2 = 95.55\%$ ($S_{SO_4^{2-}} = 0.28\%$), and for 10% excess ($C_{initial} = 70.20$ g·L$^{-1}$) – $\alpha_3 = 96.24\%$ ($S_{SO_4^{2-}} = 0.24\%$).

These data are also confirmed by three experiments conducted with Sample № 1 [7], under the following conditions: $m = 2$, t = 48−28ºC and initial concentration of NaOH: $C_{initial} = 80.62$ g·L$^{-1}$ (stoichiometric content) − I experiment; $C_{initial} = 84.65$ g·L$^{-1}$ (5% excess) – II experiment ; $C_{initial} = 86.68$ g·L$^{-1}$ (10% excess) − III experiment.

These results are similar to those obtained by treating the Pb-paste with NaOH in a reactor with a laboratory stirrer.

During desulphurization in rotational reactor of the drum type increase of the degree of desulphurization is observed after the 15th minute. On the 30th minute values of $\alpha = 95.50$−97.36% are reached.

These results exceed significantly the technological requirements [10]. Because of this, the following conditions can be accepted as optimal for both samples: up to 5% excess of NaOH, $m = 2$−2.5, t = 48−42°C and τ = 5−15 min.

Data, regarding desulphurization process with NaOH in rotational reactor of the drum type, were not found in the literature.

### Behaviour of the impurities during desulphurization of Pb-pastes

*Behaviour of the impurities during desulphurization of Pb-pastes with Na$_2$CO$_3$.* The results from analysing the liquid phase after desulphurization of the pastes with Na$_2$CO$_3$, using a laboratory stirrer, regarding the concentration of impurities are presented in Table 1.

It is also important to point out the fact that the solutions obtained after treating Sample No. 2 are 10−100 times purer than those from Sample No. 1, regardless of the fact that with it values of the degree of desulphurization above 90% are achieved with stoichiometric amount of Na$_2$CO$_3$ and the process of desulphurization is of shorter duration.

The value of pH of the solutions after desulphurization, is 9.20−9.40 for Sample No. 1 and 8.17−8.63 for Sample No. 2.

The concentration of Sb in the solutions is directly connected with the excess of Na$_2$CO$_3$. For 100% excess of Na$_2$CO$_3$ in the solution one can obtain up to 7% Sb [22]. This causes additional purification of the solutions, including also from Pb, which in the technological practice is done by adding iron salts.

Data by other authors were not found in the literature, concerning investigation of the concentration of impurities under the different conditions of conducting the desulphurization process. There exist only data regarding the content of lead in the crystalline Na$_2$SO$_4$ obtained after desulphurization of the pastes. Yanakieva [2] indicates data received by X-ray-structural (Röntgen-structural) analysis for the percentage content of Pb in the crystalline Na$_2$SO$_4$, which is in the range 0.0129−0.0099%.

*Behaviour of the impurities during desulphurization of Pb pastes with NaOH.* The results from analyzing the obtained liquid phase after desulphurization of the pastes with NaOH, using a laboratory stirrer and a rotational reactor of the drum type, concerning the concentration of impurities, are presented in Table 2.

In contrast to the solutions obtained after desulphurization of the pastes with Na$_2$CO$_3$, here the lead passes to a greater extent and the antimony to smaller degree.

**Table 1.** Concentration of impurities in the liquid phase of Na$_2$SO$_4$ when treating the pastes with Na$_2$CO$_3$ and a laboratory stirrer.

| No. | Condition of carrying out the process | Inclusion concentrations, mg·L$^{-1}$ | | | | | | | pH |
|---|---|---|---|---|---|---|---|---|---|
| | Sample No. 1 | Pb | Sb | Cl$_2$ | As | Cu | Zn | Fe | |
| 1 | stoichiometric; m = 2; τ = 30 min | 4.76 | 38.40 | 2160.0 | 51.00 | 4.30 | 0.22 | 1.5 | 9.42 |
| 2 | stoichiometric; m = 2.25; τ = 30 min | 2.90 | 28.44 | 2140.0 | 24.20 | 7.49 | 2.21 | 0.04 | 9.20 |
| 3 | 10% excess Na$_2$CO$_3$; m = 2.25; τ = 15 min | 6.80 | 13.40 | 1980.0 | 50.80 | 2.62 | 0.54 | 0.09 | 9.41 |
| 4 | 10% excess Na$_2$CO$_3$; m = 2.5; τ = 30 min | 6.10 | 15.90 | 1940.0 | 42.00 | 2.39 | 0.26 | 0.08 | 9.27 |
| | Sample No. 2 | | | | | | | | |
| 1 | 10% excess Na$_2$CO$_3$; m = 2; τ = 30 min | 0.40 | 32.40 | 170.0 | 0.47 | 0.07 | 1.16 | 1.20 | 8.63 |
| 2 | 10% excess Na$_2$CO$_3$; m = 2.5; τ = 30 min | 0.11 | 29.63 | 140.0 | 0.44 | 0.14 | 2.20 | 0.05 | 8.17 |
| 3 | 20% excess Na$_2$CO$_3$; m = 2.5; τ = 15 min | 1.20 | 15.30 | 170.0 | | 0.11 | 0.53 | < 0.01 | 8.48 |
| 4 | 20% excess Na$_2$CO$_3$; m = 2.5; τ = 30 min | 1.20 | 14.70 | 170.0 | 0.83 | 0.05 | 1.85 | < 0.01 | 8.22 |

**Table 2.** Concentration of impurities in liquid phase of $Na_2SO_4$, when the pastes are treated with NaOH.

| No. | Conditions of carrying out the process | Inclusion concentrations, $mg \cdot L^{-1}$ | | | | | | | pH |
|---|---|---|---|---|---|---|---|---|---|
| | Sample No. 1 | Pb | Sb | $Cl_2$ | As | Cu | Zn | Fe | |
| A | Common reactor with laboratory agitator | | | | | | | | |
| 1 | stoichiometric; $m = 2$; $\tau = 30$ min | 972.0 | < 0.1 | 1320.0 | 52.5 | < 0.01 | 13.93 | 1.8 | 12.55 |
| 2 | 5% excess of NaOH; $m = 2$; $\tau = 30$ min | 1602.6 | < 0.1 | 1640 | 65.3 | < 0.01 | 6.16 | 1.8 | 12.60 |
| 3 | 10% excess of NaOH; $m = 2$; $\tau = 30$ min | 2019.2 | < 0.1 | 1560.0 | 70.3 | < 0.01 | 5.10 | 1.7 | 12.60 |
| B | Rotary reactor of drum type | | | | | | | | |
| 4 | stoichiometric; m = 2; $\tau = 30$ min | 874.7 | < 0.1 | 1460.0 | 48.5 | 0.60 | 14.60 | 1.70 | 12.50 |
| 5 | 5% excess of NaOH; $m = 2$; $\tau = 30$ min | 1097.8 | < 0.1 | 1640.0 | 60.0 | 0.90 | 20.40 | 1.90 | 12.53 |
| 6 | 10% excess of NaOH; $m = 2$; $\tau = 30$ min | 1496.8 | < 0.1 | 1840.0 | 68.9 | 0.80 | 26.50 | 2.00 | 12.55 |
| | Sample No. 2 | | | | | | | | |
| A | Common reactor with laboratory agitator | | | | | | | | |
| 1 | stoichiometric; m = 2.5; $\tau = 30$ min | 0.12 | < 0.1 | 54.0 | < 0.01 | 0.05 | 0.1 | < 0.01 | 10.35 |
| 2 | 5% excess of NaOH; m = 2.5; $\tau = 30$ min | | < 0.1 | 40.0 | 10.8 | 0.04 | 4.12 | < 0.01 | 12.46 |
| 3 | 10% excess of NaOH; m = 2.5; $\tau = 30$ min | 43.84 | < 0.1 | 44.0 | 4.0 | 0.07 | 0.20 | < 0.01 | 12.22 |
| B | Rotary reactor of drum type | | | | | | | | |
| 1 | stoichiometric; $m = 2.5$; $\tau = 30$ min | 76.82 | < 0.1 | 64.0 | 0.77 | < 0.01 | 1.00 | 1.2 | 12.15 |
| 2 | 5% excess of NaOH; $m = 2.5$; $\tau = 30$ min | 30.4 | < 0.1 | 60.0 | 2.40 | 0.40 | 0.12 | 1.2 | 12.15 |
| 3 | 10% excess of NaOH; $m = 2.5$; $\tau = 30$ min | 20.4 | < 0.1 | 46.0 | 4.70 | 0.50 | 0.10 | 1.30 | 12.22 |

The lead passes into the solutions in the form of sodium plumbite ($Na_2PbO_2$).

Regarding the chlorine and arsenic, the purity of the solutions depends on the purity of the nonde-sulphurized paste and the presence of other lead-containing impurities or additives (for example lead powder). The latter also holds true to some extent for the arsenic and some of the other impurities in the paste.

The pH value of the solutions after desulphurization is: 12.50−12.60 for Sample No. 1 and 10.30−12.40 for Sample No. 2, respectively.

Based on the analysis of the results received from both paste samples, the increase in concentration of impurities is important when the process is done in rotational reactor of the drum type, which is due to the better conditions of contact between the paste and the reagent.

Data were not found in the literature, concerning investigations on the effect of the concentration of impurities in the solutions after desulphurization with both types of reactors.

CONCLUSIONS

- The process of desulphurization runs at higher speed when using NaOH, than using $Na_2CO_3$ for both types of reactors;

- The optimal conditions for desulphurization of Pb-paste with $Na_2CO_3$ in both reactors are: excess of $Na_2CO_3$ up to 10%, m = 2.0−2.5, t = 55−35ºC and $\tau$ = 15−30 min (the degree of desulphurization under these conditions is 92.4−94.4%, and $S_{SO_4^{2-}}$ = 0.49−0.36%);

- For the two reactors the optimal conditions for desulphurization of Pb-paste with NaOH are: excess of NaOH up to 10%, $m = 2$, t = 55−35ºC and $\tau$ = 15−30 min. (the degree of desulphurization under these conditions is 93.64−96.90%, and $S_{SO_4^{2-}}$ = 0.41−0.20%);

- After desulphurization with $Na_2CO_3$ greater amount of Sb goes into the solutions than of Pb, while when using NaOH into the solutions goes more Pb, and the amount of Sb in them is below 0.1 $mg \cdot L^{-1}$;

- The process of desulphurization of Pb-paste can be realized continuously when using rotational reactor of the drum type, and from the solutions significantly pure crystalline $Na_2SO_4$ can be obtained, which is suitable for the aims of the industry (Tables 1 and 2).

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# ХИДРОМЕТАЛУРГИЧНО ПРЕРАБОТВАНЕ НА АМОРТИЗИРАНА ОЛОВНА АКУМУЛАТОРНА ПАСТА

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(Резюме)

Настоящата работа представя анализ на експериментални резултати от извършени изследвания относно десулфатизиране на амортизирана оловна паста и възможностите за осъществяване на процеса. Целта е да се направи сравнителна оценка на получените резултати със съществуващи данни в литературата и водещи технологии. Разгледани са кинетичните зависимости на протичащите процеси и свързаните с това проблеми. Определени са оптималните условия на процеса на десулфатизиране, при използване на реагентите $Na_2CO_3$ и $NaOH$ в зависимост от типа на работния реактор (обикновен реактор с лабораторна бъркалка и ротационен реактор от барабанен тип). Изследвано е съдържанието на примеси в разтворите с цел получаване на достатъчно чист кристален $Na_2SO_4$ за промишлеността.