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Comparative analysis of two processes for desulphurization of battery paste

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ABSTRACT

Purpose: The paper touches the problem of recycling battery scrap and desulphurization methods. The aim of this paper is to compare sodium method and new amine method for desulphurization of battery paste. Also the comparison of this methods refers to environmental and technological aspects of lead smelting.
Design/methodology/approach: Base of the comparison of two different methods were tests of melting of desulphurized battery paste in a rotary-tilting furnace by BJ Industries Company.
Findings: Both methods of desulphurization allow to reduce amount of sulphur to less than 1%. The economic considerations determine the degree of desulphurization of battery paste. Amine method allows to reduce sulphur to a degree of about 0,5% maintaining favorable technical and economical parameters.
Research limitations/implications: Effectiveness of amine method was confirmed in the pilot-scale tests, but it's difficult to say what will be the results of desulphurization by this method in industrial scale.
Originality/value: The value of this paper lies in demonstrating the possibilities of application of the new amine method of battery paste desulphurization, compared to for commonly used methods.
Keywords: Industrial application of cleaner production methods; Desulphurization process; Battery scarp; Recycling

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1. Introduction

Lead-acid batteries belong to a group of products which after use are a hazardous waste, however they become a valuable resource. Recovery of lead from lead-acid batteries is the type of business that combines environmental protection with economic profit. In addition, recovering and re-processing the lead contained in batteries limits the consumption of raw materials. The largest component (mass participation) of the lead-acid battery is metallic fraction the so-called lead paste (60-75%) obtained during the processing of battery scrap. The rest are electrolyte and various types of plastics. Leaded paste is primarily a mixture of $PbSO_4$, PbO_2, Pb_2O (SO_4), Pb_2O_3 and metallic Pb. $PbSO_4$ is the main lead carrier in the battery paste (40%). It is formed during the battery operation as a result of the reaction of metallic Pb and PbO_2 with the electrolyte (aqueous solution of sulphuric acid IV) [1,2].

2. Effect of battery paste 'quality' on environmental and technological aspects of secondary lead smelting

Raw lead is obtained by melting the metallic fraction and by a reduction of lead compounds (mainly $PbSO_4$, PbO). Pyrometallurgical lead smelting is carried out in rotary tilting furnace or Dörschl rotary rocking furnace. The reduction of lead compounds is obtained with the aid of added coke breeze and carbon monoxide which is nascent during Boudouard Reaction. Except coke breeze, technological additives such as iron scrap and soda ash are added to the charge. Iron scrap causes lead to precipitate from lead sulphide (PbS), as well as it is a slag - forming component. Whereas soda ash is added in order to fix sulphur and fluxing slag. As a result of melting of battery paste containing sulfur compounds, some of the sulfur passes into the slag in the form of sulfides, and the remaining large part is oxidized to form sulfur dioxide, threatening the atmosphere. The increasing requirements for the reduction of SO_2 emissions into the atmosphere and the Basel Convention provisions force a secondary lead producers to take steps to reduce emissions and render gases harmless. One of the possibilities to have an effect on SO_2 reduction is desulphurization of battery paste to a possibly low level before melting it. Efficiency of desulphurization of battery paste is determined by technological parameters of the process and lead paste "quality" itself. The technological parameters include reactant concentrations and phase ratios used in the paste leaching operation. By "quality" we mean mineralogical and chemical composition of the battery paste. The average chemical composition of sulphated lead acid battery paste is shown in Figure 1 [1,3,4].

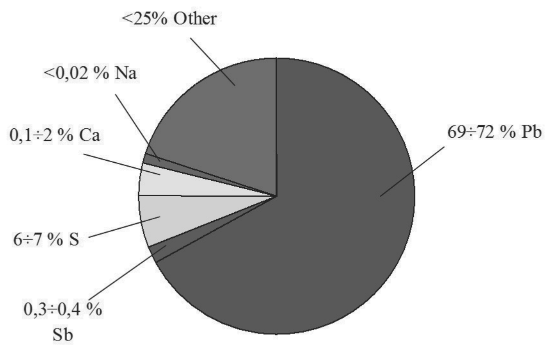

Fig. 1. Average chemical composition of lead-acid battery paste

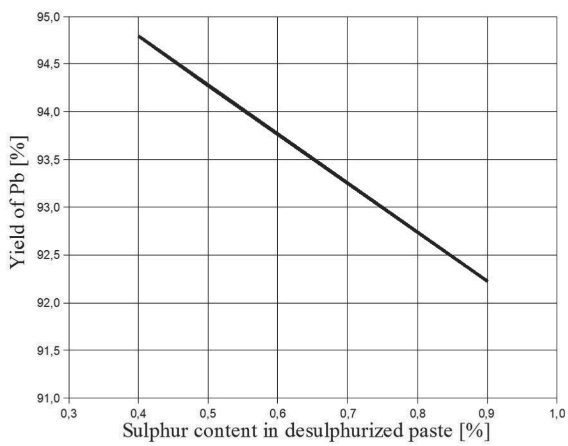

Fig. 2. Dependence between sulphur content and yield of lead

The sulfur contained in the paste affects not only the quantity of generated technological gases, but also the individual process parameters: the yield of lead, technological additives consumption, the amount of formed slag and natural gas consumption. The study, carried out by the Institute for Nonferrous Metals, show that the yield of lead from the smelting process of desulphurized paste is greater than from the sulphurized paste. This dependence is shown in Figure 2 [5].

Moreover a dependence between the amount of sulphur in the battery paste and the amount of formed slag was specified. This dependence is shown in the graph presented in Figure 3 below.

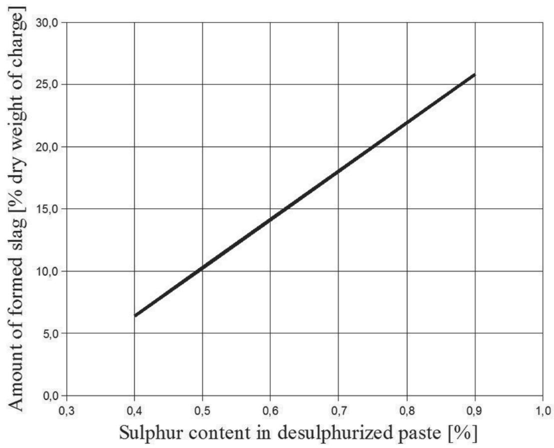

Fig. 3. Dependence between sulfur content and nascent slag

The second most important element contained in the battery paste, after the sulphur is lime. However, there is a close dependence between lime content and moisture, which affects the technological process of lead smelting. The moisture content increases proportionally with the lime concentration in the paste. The research results show that the best technological rates of lead smelting are obtained when smelting battery paste with low sulfur content (<1%) and lime content (<0.5%) [6,7].

3. Technologies for desulphurization of battery paste

Worldwide there are various technologies to remove sulfur contained in the battery paste. The most important technology for desulphurization of battery paste is technology using solutions of caustic soda NaOH or soda ash Na_2CO_3. Except above mentioned methods, there are number of technologies using different chemical compounds to desulphurize battery paste. Even though they are not as highly developed as processes using soda solution, they still can be an effective alternative. Battery paste can be desulphurized using the following compounds [4, 8-13]:

- ammonium carbonate, ammonium bicarbonate and ammonia with carbon dioxide,
- hydroxide, carbonate or potassium bicarbonate,
- sodium carbonate and sodium bicarbonate,
- sodium chloride solution containing dilute hydrochloric acid,

- solutions of amines,
- solutions of citric acid and sodium citrate.

3.1. Desulphurization of battery paste in Poland

In Poland, two plants deal with recycling of used batteries: "Orzeł Biały" S.A. and "Baterpol" Sp. z o.o. These companies use different technologies for the recovery of lead. "Baterpol" uses desulphurization of battery pastes by "soda method" according to CX technology by "Engitec Technologies SpA". This method bases on the conversion of lead sulfate into lead carbonate under influence of soda ash solution. The products of this process are lead paste with reduced sulfur content and the sodium sulfate solution. The obtained paste is a finished product ready for further metallurgy processing in the furnace. Sodium sulfate solution is purified and filtered and then it is sent to the line of evaporation and crystallization. Anhydrous Na_2SO_4 is used as an semi-finished product in the household chemistry, the glass industry, textile and tanning. Currently "Orzeł Biały" as distinc from a competitive company, "Baterpol", does not apply a operation desulphurization of battery paste. However, in order to meet environmental standards and some economic aspects, the company analyzes the possibility of implementation of a new battery paste desulphurization technology using amine solution.

"Amine" technology was developed by the Institute of Nonferrous Metals. The assumptions of this method is to obtain desulphurized paste ($PbCO_3$; PbO) while the sulfur is fixed to the form of gypsum ($CaSO_4$ * $2H_2O$). "Amine" technology has been tested so far only in laboratory scale, laboratory production scale and the pilot scale in the pilot plant that was built at the "Orzeł Biały" plant. Experimental installation of desulphurization of battery paste by amine method has been designed and manufactured by the ”Bipromet SA” company based on the submitted by the Institute of Nonferrous Metals description of the technology [3, 4].

4. Desulfurization of battery paste by sodium method

The sodium method is commonly known and used method in the world for desulfurization of battery paste to less than 1%. The method converts sulfur contained in the paste into the sodium sulphate using carbonate sodium. As a result of the process suspension of desulphurization paste and solution of sodium sulphate are obtained. Paste desulphurization process line is equipped with process gas extraction and dedusting installation.

As a result of this process in the desulphurization reactor the following chemical reactions occur:

$$PbSO_{4(s)} + Na_2CO_{3(aq)} = PbCO_{3(s)} + Na_2SO_{4(aq)} + Q \qquad (1)$$

To achieve high efficiency of the desulphurization process, the reaction must be carried out using an excess of carbonate. Then excess of sodium carbonate is introduced into the reactor and is neutralized according to the following reaction:

$$H_2SO_{4(aq)} + Na_2CO_{3(aq)} = Na_2SO_{4(aq)} + H_2CO_{3(aq)} + Q \qquad (2)$$

The next step in the process is the transportation of the products of chemical reactions, that occur during mixing a paste with sodium carbonate and electrolyte, to the filter press. Separation of lead carbonate from the solution of sodium sulphate is carried out on the filter press. In the next step, washing $PbCO_3$ by condensation in special neutralization reactors is carried out. After that re-separation of lead carbonate from the solution of Na_2SO_4 takes place on filter press. Contaminated sodium sulfate is than treated with lye and sodium sulphide. The main products of the process are paste with reduced sulfur content and solution of sodium sulphate. The purified solution of Na_2SO_4 is than directed in to the process of crystallization and drying [3,4].

The main technological desulphurization nodes in sodium method are:

- paste leaching node,
- desulphurized paste filtering node,
- sodium sulphate cleaning and storage node,
- sodium sulphate crystallization node,
- crystalline sodium sulfate drying and storage node.

5. Desulphurization of battery paste by amine method

Battery paste desulphurization process consists of the reaction of lead sulfate with an aqueous solution of amine. Under the influence of leaching the lead sulfate by the solution of amine, the lead sulfate is converted into the amine-$PbSO_4$ complex. Next follows the separation of lead to the form of lead carbonate $PbCO_3$. This is done by the saturation of the complex by the transmitted from the solution of amine CO_3 ions. The resulting suspension of lead carbonate is filtered in a filter press. The filtrate is directed to the process of acidification by sulfuric acid, resulting in absorbed carbon dioxide excess removal and precipitation of the residual lead sulphate. The residual lead sulphate is directed to the filtration process and then returned to the leaching process. In the next technological operation the removal of sulphate from an aqueous solution of amine, under the influence of $Ca(OH)_2$ hydrated lime suspension, occurs. As a result sulfur is converted into the form of gypsum. In this operation the amine solution is contaminated with redundant calcium ions which affects negatively the desulphurization process.

Therefore, the amine solution is saturated by carbon dioxide gas (amine regeneration), in order to precipitate calcium to the form of carbonate. As a result of this operation the amine initial form is restored so it can be used again in the desulphurization process.

Battery paste desulphurization process is described by the following reactions [3, 4, 14]:

$$\text{aqueous solution of amine}/CO_3^{2-} + PbSO_4 \text{ (contained in paste)} \rightarrow [\text{amine-}PbSO_4] + PbCO_3\downarrow \qquad (3)$$

$$[\text{amine-}PbSO_4] + CO_2 \rightarrow PbCO_3\downarrow + [\text{amine-}SO_4^{2-}\text{-}CO_3^{2-}\text{-}Pb_2^{+}] \qquad (4)$$

$$[\text{amine-SO4}^{2-}\text{-}CO_3^{2-}\text{-}Pb_2\text{+}] + H_2SO_4 \rightarrow PbSO_4\downarrow + CO_2\uparrow + [\text{amine-}SO_4^{2-}] \qquad (5)$$

$$[amine\text{-}SO_4^{2-}] + Ca(OH)_2 \rightarrow CaSO_4 \cdot 2H_2O\downarrow + [amine\text{-}Ca^{2+}] \quad (6)$$

$$[amine\text{-}Ca^{2+}] + CO_2 \rightarrow CaCO_3\downarrow + \text{aqueous solution of amine}/CO_3^{2-} \quad (7)$$

The product of the process is desulphurized paste ($PbCO_3$) and gypsum ($CaSO_4$*$2H_2O$). In the technological cycle, solution of amine enables transition of the sulfur from the lead sulfate to form of gypsum.

Technology of battery paste desulphurization by solution of amine was divided into the following nodes:

- leaching node,
- acidification node,
- crystallization of gypsum node,
- amine regeneration node,
- lime milk preparation node.

6. Comparison of technological and ecological effects of both processes for desulphurization of battery paste

In the analysed desulphurization technologies (desulphurization of battery paste by sodium method and by amine method) the basic feed material in a batch process is sulphurized battery paste. The main and most important chemical element in the paste is lead. Depending on the used battery scrap processing technology, both the lead and the sulfur content may occur at different levels.

The comparative analysis of two different battery paste desulphurization technologies included assessment of:

- sulfur removal efficiency - directly linked to the emission of SO_2 into the atmosphere,
- influence of the lead paste "quality" on metallurgical melting individual indicators.

The comparative basis for the existing sodium technology and amine technology are industrial tests of desulphurization paste melting in the BJ Industries rotary-tilting furnace. The results of melting desulphurization paste using sodium and amine method were compared with “low quality" melting sulphated paste [3,4].

6.1. Technological effects

The best technological effects resulting from the desulphurization paste melting compared to the sulfured paste in two methods are:

- reduction of the technological additives consumption,
- increase of the raw lead production efficiency,
- reduction of the lead loss in the slag,
- increase of the paste charge into the furnace.

As a result of two desulphurization battery pastes technologies comparison, it can be concluded that amine method is characterized by better technological effects (Figure 4).

The calcium content in the paste is directly proportional to the consumption of soda. Therefore, the increased soda consumption in the case of desulphurization paste melting by amine method, resulted from the higher content of calcium in the paste before desulphurization process. Amine desulphurization method is characterized by smaller losses of lead in the slag compared with the sodium method. It also influences directly increased efficiency and productivity of lead. A comparative analysis of the technological parameters is presented in following graphs (Figures 5, 6) [3,6,7].

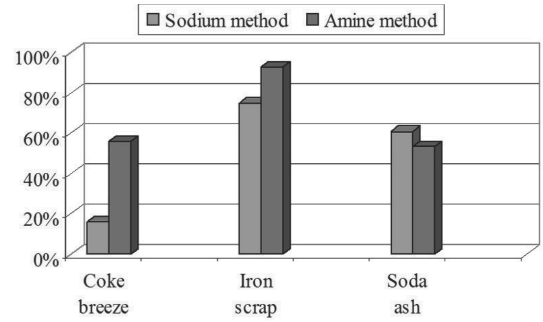

Fig. 4. Reduction of technological additives consumption (sulphurized paste =100%)

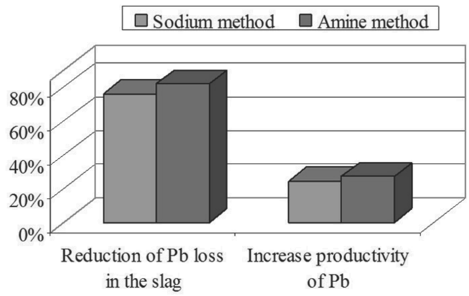

Fig. 5. Comparative analysis of the technological parameters

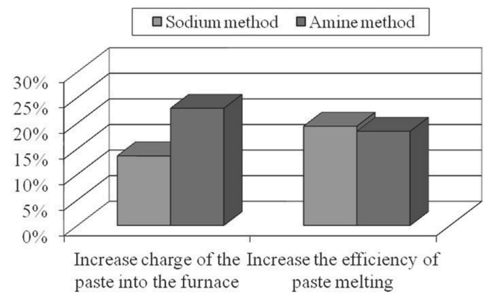

Fig. 6. Increase in the efficiency of technological parameters (sulphurized paste = 0%)

6.2. Ecological effects

Both battery paste desulphurization technologies are the emission sources of various environmental pollutants. Both amine and sodium method emit sulfuric acid vapour and carbon dioxide. While in case of the possible operation of the new amine technology, it will be also a source of vapour amine emissions amines and hydrated lime dust.

In the event of desulphurization paste melting by amine or sodium method the main pollutants emitted into the atmosphere are: sulfur dioxide, carbon monoxide and nitrogen oxides. One of the most dangerous pollutants produced during desulphurization process is sulfur dioxide. In the case of the sodium method a higher SO_2 emissions (to air) take place, which is a consequence of a greater quantity of sulfur contained in the paste (Tab. 1).

However, both methods of removing sulfur from the lead paste are characterized by a slight influence on the environment [3,6,7].

Table 1.
The chemical composition of paste desulphurization by two methods

Desulfurization method	Chemical composition, %				
	Pb	Sb	S	Ca	Na
„Sodium" method	73.10	0.25	1.57	0.15	1.71
„Amine" method	75.60	0.24	0.50	0.35	0.02

Apart from the type of used desulphurization method, a significant reduction in the amount of waste in the form of slag occurs (Fig. 7). Comparing the amount of slag generated in both desulphurization technologies the amine method is more advantageous. Generated slag contains small amounts of lead and sulfur and is ecologically safe. As opposed to sodium method the slag does not have a tendency to leach in the water.

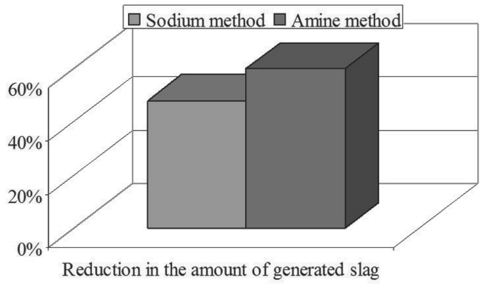

Fig. 7. Reduction in the amount of generated slag (sulphurized paste = 100%)

The consequence of higher amounts of slag formed during the desulphurization paste melting by sodium method are higher losses of lead accumulating in the slag. Furthermore, the amount of sulfur passing into the slag, applying the sodium method is also higher.

7. Summary and conclusions

The subject of this analysis is the comparison of the technological parameters of two desulphurization methods. The analysis included the efficiency and environmental impact assessment. The analysis enabled also evaluation of the sulphur removal technology effectiveness.

Summarizing:

- Both paste desulphurization systems are waste-free,
- Desulphurization of battery paste using amine method allows to obtain better results in the lead technological melting,
- Both methods of battery paste desulphurization allow to reduce sulfur to less than 1%,
- Nevertheless the level to which the sulphur is removed from the lead paste, primarily depends on technological and economic factors of the whole process of desulphurization,
- The higher sulphur content (1.57%) in sodium method is more economical in aspect of the whole process of desulphurization,
- Both methods of removing sulphur from lead paste are characterized by negligible influence on the environment,
- Both methods of paste desulphurization lead to the formation of commercial products.

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