

**POSITIVE SYNERGISTIC EFFECT OF THE REUSE AND THE
TREATMENT OF HAZARDOUS WASTE ON
PYROMETALLURGICAL PROCESS OF LEAD RECOVERY FROM
WASTE LEAD-ACID BATTERIES**

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Abstract

Modification and optimization of the pyrometallurgical process of lead recovering from the waste lead-acid batteries have been studied in this paper. The aim of this research is to develop a cleaner production in the field of the secondary lead metallurgy. Lead smelting process with the addition of flux (sodium(I)-carbonate) and reducing agents (coke, iron) has been followed. The modified smelting process with the addition of hazardous waste (activated carbon) as alternative reducing agents has shown positive results on the quality of the secondary lead, the generated slag and the process gases. Filtration efficiency of the gases, the return of baghouse dust to the process and use of oxygen burners have positive effect on the environment protection and energy efficiency. Optimization of the recycling process has been based on the properties of the slag. Stabilization of slag is proposed in the furnace with addition of waste dust from the recycling of cathode ray tube (CRT) monitors. Phosphorus compounds from dust reduce leachability of toxic elements from the generated slag. Reduction the slag amount and its hazardous character through the elimination of migratory heavy metals and valorization of useful components have been proposed in the patented innovative device - cylindrical rotating washer/separator.

Keywords: secondary lead, pyrometallurgical process, cleaner production, hazardous waste, treatment

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Introduction

Metallurgical recycling of waste lead-acid batteries is being increasingly adopted process in the lead production with the very high rate of the lead recycling higher than 90 wt. % [1]. The process of recycling batteries has undergone considerable changes in order to balance the demand for lead production and solutions for common environmental lead processing problems. One of the major technology that is used for recycling lead-acid batteries is based on the Engitec technology [2,3]. The lead containing materials with desulfurized paste from crushed and separated batteries is smelted in a rotary furnace. Using the feed from the CX system the increase in furnace productivity is of about 25–30 wt. % [4].

The most critical operation of the recycling process is the smelting due to the waste produced by this process. The furnace gases are routed through a baghouse, where the particulates are collected in bag filters and these dusts are recycled to the furnaces. Gas emissions consist of the gaseous emissions from the plant [5]. Waste slag produced by this technology, where sodium(I)-carbonate is used as a fluxing agent for the reducing fusion, is the alkaline and highly soluble material, so called sodium lead slag [6]. It is an inevitable and the most abundant waste from the secondary lead smelting processes. Usually, 15-30 wt. % of the products of a batch rotary furnace are the slag, and in Europe 200.000 t/year of sodium lead slag is generated by the treatment of waste lead-acid batteries [7].

According to the European Waste Catalogue and Hazardous Waste List [8], the slag is hazardous waste which should be treated due to the higher than allowed concentrations of toxic substances and possible cumulative effects of multiple pollutants such as lead, arsenic and antimony. Safe disposal or possible recycling of the waste has often been discussed [9-12]. The preferred technology to treat hazardous waste is the value recovery from the waste [13]. If this is not technically or economically feasible, solidification/stabilization (S/S) is the next option [14]. Due to the environmental and economical reasons, there has currently been a growing trend for the use of industrial wastes or by-products as supplementary materials or admixtures in the production of composite cements. Despite some attempts of using, e.g. as an admixture in cement for stabilization/solidification purposes [6,15] the fabrication was abandoned and the material was dumped in hazardous waste landfills [7].

The improvement of the recycling design, besides the reducing emissions and waste production, added a number of benefits in the economics of smelting unit such as reducing the need of chemical reagents and energy consumption. The possibility of lead recovery from the waste lead-acid batteries in optimized and modified recycling process has been studied in this paper. Namely, the addition of hazardous wastes, activated carbon as alternative reducing agents and waste dust from the recycling of cathode ray tube (CRT) monitors as the slag stabilization agent, have been evaluated. In order to develop the cleaner production in the secondary metallurgy of lead, the minimization of the waste production, reduction of hazardous character of the waste through the elimination of migratory heavy metals and the valorization of useful components are examined.

Experimental Procedure

Lead smelting process

The recycling of waste lead-acid batteries, based on pyrometallurgical processes in furnaces has been examined. After the electrolyte removal, the batteries are broken, crushed and automatically separated into various components: plastic materials, metal grids, poles and pastes. The plastic materials (about 5 wt. % in battery) are separated and the metallic components (55 wt. % in battery) are classified for the smelting. The paste (mixture of lead oxides and sulfates), is desulfurized to remove most of the sulfur content.

Short rotary furnace (volume 3 m³), was fed with raw materials (the metallic components and desulfurized lead paste), flux (sodium(I)-carbonate) and reducing agents (coke, iron). The pyrometallurgical process has been followed; lead smelting from grids started at 330°C, while reduction process of lead started at 600°C. Optimal temperature of process was 950 – 1000°C. The energy is provided by oxygen/gas burners, which are cooled with water in a closed system.

The average moisture, lead and sulfur content in raw materials (metallic components and paste) that are fed into the furnace has been analyzed. Moisture meters are used to measure the percentages of water in raw materials. Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES Varian Vista 715 ES) was used for the determination of lead and sulfur in samples.

Modified lead smelting process

The process has been examined with the addition of hazardous waste as alternative reducing agents. Namely, the primary reducing agent (coke powder) was partially substituted with the alternative (activated carbon). Furnace was fed with raw materials (the metallic components and desulfurized lead paste) with flux (sodium(I)-carbonate) and reducing agents (coke powder and activated carbon).

Activated carbon was characterized taking into account the following parameters: share of moisture, ash, volatile matter, sulfur, metallic oxides, bulk density and calorific value).

Waste from lead smelting process

The recovering process of lead from the secondary raw materials is followed by generation of waste process gases and residues (baghouse dust and slag) which are analyzed.

The process gases treatment

The gases from rotary furnace are routed through baghouse, where particulates are collected in bag filters. After purification, gases are emitted in the atmosphere and baghouse dust is recycled in the furnaces. Temperature and quality of process gases are primary parameters in process control. Hot gases from furnace have been mixed with the cold gases from the ventilation system and treated in baghouse. The dust concentrations of particulates 0.3 µm in fume filters of baghouse have been measured continually at gases temperature 70–100°C by dust monitor S304 in the range of 0.1 mg/Nm³ to 1 kg/Nm³. If gas temperature has been higher than 100°C, fresh air has been brought. Burners are closed if gas temperature was higher than 120°C.

Waste sodium lead slag treatment

Slag generated from the furnace was collected and homogenized. The characteristics of the slag were evaluated on the basis of chemical composition and grain size distribution. Chemical composition of the slag was determined by ICP-OES Varian Vista 715 ES. The grain size distribution of the slag was determined using the sieving procedures.

Water washing (leaching) of waste sodium lead slag, is carried out in patented innovative device - cylindrical rotating washer/separator. The peculiarity of this device is in the continuous separation of soluble content, which contains certain amount of sodium, of fraction less than 1 mm (gauge, sulfate-oxide fraction) and fraction larger than 1 mm rich in useful metal-sulfide, solid, non-soluble fraction. Treatment of slag in this device has been tested at 30°C, with the stirring rate of 20 rpm and solid to liquid ratio 1:10.

The slag after the treatment was characterized by optical microscope (Jenapol U-Carl Zeiss polarizing microscope). Chemical analysis of the solutions samples after leaching (leachates) was carried out using ICP-OES Varian Vista 715 ES. Values of pH and Eh (electrochemical potential) have been recorded by pH meter INO-LAB pH - 720 and measured values have been shown as Eh-pH diagrams, obtained by using HSC Chemistry software [16].

Results and discussion

Lead smelting process

The results and the discussion are based on the monitoring and analyzing of the pyrometallurgical process and on the recognition of process control possibilities in order to achieve cleaner production of lead from waste lead-acid batteries.

The composition of raw materials and the charge, the average consumption of gas/oxygen, the amount of raw lead, process gases and generated slag at the end of the process, are shown in Tables 1 and 2.

Table 1. Average composition of raw materials fed into the furnace

Parameter	Desulfurized paste, wt. %	Metal, wt. %	Grids, wt. %
Lead	74.0	98.0	77.2
Sulfur	0.8	0.01	7.8
Moisture	11.0	-	9.5

The highest percentage of lead was in the form of metal and sulfur in grids. Significantly smaller content of sulfur in paste is consequence of its desulfurization. The removal of sulfur from lead paste prior to smelting is desirable process and is in accordance with industrial and ecological reasons. Positive effects of lead melting process from desulfurized paste are as follows: lead smelts at lower temperature, lower content of flux is necessary in the raw material mixture, the content of by-products (soda, slag, powder components) is smaller, the share of sulfur(IV)-oxides is lower in process gases, the consumption of chemical reagents in purification process is smaller, the degree of lead extraction is higher.

'Grids and poles', from batteries have high antimony content [5]. Its separation from the desulfurized paste with low antimony content, in smelting process, is desirable. In this way, the content of very toxic antimony was reduced in the generated waste.

Table 2. Average composition of the furnace charge at the beginning and at the end of the lead smelting process

Input, wt. %		Output, wt. %	
Metal	52.0	Raw lead	72.2
Desulfurized paste	41.0	Slag,	9.5
Coke	3.0	Process gases (SO ₂ , CO, CO ₂)	18.3
Iron	2.0		
Sodium(I)-carbonate	2.0		
Average consumption, m ³			
Natural gas			830
Oxygen			2173

Metal component and desulfurized paste, as the largest share in the charge, are fed into the short rotary furnace.

The use of the oxygen/gas burners is recommended to reduce the total amount of the process gases. Furthermore, the consumption of natural gas and oxygen in investigated process has been 600 kWh per 1 t of lead and 140 kg per 1 t of lead, respectively. Energy efficiency of the process is achieved by using the oxygen burners in combination with heat recuperation energy saving (up to 30 %).

The use of short rotary furnace and oxygen burners is one of the best available techniques in the secondary metallurgy of lead (BAT) [17].

Modified lead smelting process

The possibility of a partially replacement of the primary reducing agent (coke), with the alternative reducing agent, hazardous waste (activated carbon), from the water treatment plants, has been investigated. A detailed characterization of waste activated carbon was the initial phase of this part of investigation (see Table 3). The results of chemical analysis of activated carbon in an accredited laboratory have confirmed that it is hazardous waste [18].

Table 3. Characteristics of waste activated carbon

Moisure, wt. %	3.12
Ash, wt. %	6.04
Volalite matter, wt. %	7.22
Bulk density, kg/m ³	468
Calorific value, kJ/kg	28486
Sulfur, wt. %	0.35

Laboratory investigation of process with partial replacement of primary reducing agent with the waste activated carbon has shown positive results in terms of the quality of lead, compositions of the generated slag and the process gases. Composition of the charge has been proposed with the raw materials and energy quantities, based on the

production capacity of 1t of lead, and are shown in Table 4. Therefore, the technological process and the measures prescribed for the process when alternative reducing agents are used enable the significant economic and energy savings.

It may be concluded that waste activated carbon can be utilized as a secondary raw material, i.e. reducing agent in lead metallurgy. However, its application must be cautious accompanied with prescribed measures due to its hazardous properties [18]. Waste activated carbon can be used as an addition to solid granulated coke in the reduction smelting process of lead, without changes in the technological recycling process of waste lead acid batteries and with significant energy saving. Additionally, the emissions of sulfur oxides have been significantly reduced due to the substitution of coke which always contains sulfur.

Table 4. Proposed weight quantities of raw materials and energy

Raw materials, wt. %		Energy	
Waste lead-acid batteries	86.0	Electrical energy, kWh	315
Sodium(I)-carbonate	5.5	Mazut (fuel oil), kg	150
Coke	3.5	Liquid oxygen, Nm ³ /t	0.02
Iron	2.5	Water, m ³	0.40
Waste activated carbon	1.5	Compressed air, Nm ³	120

Waste from lead smelting process

The recovery of lead from waste lead-acid batteries in pyrometallurgical process has been followed by the emission of process gases and generation of slag that might cause environmental pollutions. Due to this, the controlled execution of process and the adequate waste treatment is the basis of the environmental protection.

The process gases treatment

Efficient filtration which eliminates powder component emission and use of oxygen burners which reduces gas pollutions emission have positive effect on the environmental protection during the industrial process of lead recovery from waste lead-acid batteries. Process gases from furnace have 18.3 wt. % in overall material balance at the exit from the furnace (see Table 2). The composition of process gases and dust after filtration is shown in Table 5.

Measured values of sulfur(IV)-oxide emissions in the air with dust and metals were in accordance with the values from BAT [17]. Production of sulfur(IV)-oxide from smelting processes (capacity 35000-40000 t of lead per year) with desulfurized paste is estimated at 1070-2000 g of sulfur(IV)-oxide per 1 t of metal. Mass of metals from the same process is estimated at 5-25 g of lead per 1 t of metal.

Energy saving (up to 30 %) was the consequence of oxygen burners used in combination with the heat recuperation, resulting in significant reduction of gas volume on the exit and total amount of nitrogen-oxide emissions.

Content of powder components in process gases after purification in baghouse was smaller than 1 mg/Nm³ due to filter efficiency higher than 99 %. Being recycled in the furnaces baghouse dust is collected and transported in bag filters. The return of baghouse dust to the process is in accordance with BAT [17].

Table 5. Composition of process gases and dust after filtration

		Total gases from process		Total gases after filtration		
		Average flow 1680 Nm ³ /h, Temperature 700° C		Average flow 35 000 Nm ³ /h, Temperature 72°C		
		mg/Nm ³	g/h	mg/Nm ³	g/h	
Dust	Total	25600	43008	1.00	35.00	
	Pb	7600	12768	0.50	17.50	
	Zn	50	84	0.01	0.35	
	Sb	2000	3360	0.10	3.50	
	Fe	100	168	0.01	0.35	
	Na	450	756	0.10	3.50	
		vol. %	Nm ³ /h	vol. %	Nm ³ /h	
		O ₂	11.6	195	20.50	7192
		N ₂	43.5	731	77.30	27054
		CO ₂	15.1	254	0.70	250
		CO	1.7	29	0.10	29
		mg/Nm ³	g/h	mg/Nm ³	g/h	
Gases	SO _x	5000	8400	24.00	840	
	NO _x	500	840	30.80	1078	
	HCl	5.00	8.00	0.24	8.00	

Waste sodium lead slag treatment

Waste sodium lead slag, was generated in short rotary furnace, with 9.5 wt. % in overall material balance at the exit from the furnace (see Table 2). Considering the composition of the slag and its properties, the efficiency of the lead reduction process in the furnace and unwanted effects of hazardous wastes from this process on the environment have been monitored.

Real sample of industrial soda slag, generated in lead reduction smelting process was characterized. The average weight percent of the main elements in the slag samples are: 22.5 wt. % iron, 22.5 wt. % sodium, 7.35 wt. % lead, 5.03 wt. % sulfur, 9.50 wt. % carbon, 0.10 wt. % arsenic, 0.50 wt. % antimony, 1.50 wt. % silicon. Iron and sodium were detected as the main elements in the slag, with significant carbon content. The averages of lead content were 7.35 wt. % as useful components of charge (for example 5-10 wt. % of lead), which content depends on the efficiency of smelting process and may be partly valorized. High concentrations of the selected elements in the slag generated in pyrometallurgical process of waste lead-acid batteries are indicated as an uncompleted lead reduction process and the retention of lead in the slag. In accordance with that, the process optimization is required.

Granulometric analysis of waste slag contains about 33.5 wt. % of fraction smaller than 1 mm and 66.5 wt. % of fraction greater than 1 mm. One of its properties is that this type of slag decomposes in contact with the air forming powder. Bulk density of the slag was 1249 kg/m³.

Knezevic *et al.* [6] and Djokic *et al.* [19] showed detailed properties of this kind

of slag and concluded that it contains toxic substances (arsenic and antimony) and soluble alkalis. They also found that it cannot be disposed of in a landfill without the pretreatment and the formation of a stable form. Dissolving of the slag components causes migration of ions into water inducing a significant pollution of environment.

Optimization of the recycling process of waste lead-acid batteries was discussed from the viewpoint of the qualitative and quantitative properties of the generated slag, with the aim of the process execution in a way that generates a minimal amount of stable slag. Additionally, the proper waste management for this kind of waste involves treatment and the formation of its stable form in order to prevent the potential negative consequences for disposal of slag in the environment.

In order to reduce the toxic elements leachability from slag (lead, arsenic, antimony), stabilization of slag in furnace with addition of adequate agents containing phosphate group was proposed. In the presence of melted metal and slag low water-solubility compounds were generated in contact of lead with the stabilization/agglomeration agents. Addition of 20 wt. % three-superphosphate relative to the amount of the charge has significant effect on the reduction of leaching degree of lead from slag. The stabilization of the secondary lead slag in the furnace is proposed with the possibility of re-using of fine fraction (dust) from the recycling of CRT monitors which is a mixture of metal oxides (lead, barium, strontium) and phosphorus compounds.

Simulation of slag composition and reduced production of slag can be achieved by determining the charge composition and share control of certain elements in the charge (Fe:Na, Fe:S, amount of added reducing agent) [5].

New technological procedure for treatment of waste sodium lead slag is based on continuous washing (leaching) of slag with water in innovative patent device - cylindrical rotating washer/separator. In this way, water soluble components of slag are removed, amount of slag is reduced and slag is converted into a stable form of waste. Furthermore, useful components of slag are valorized (see Figure 1).

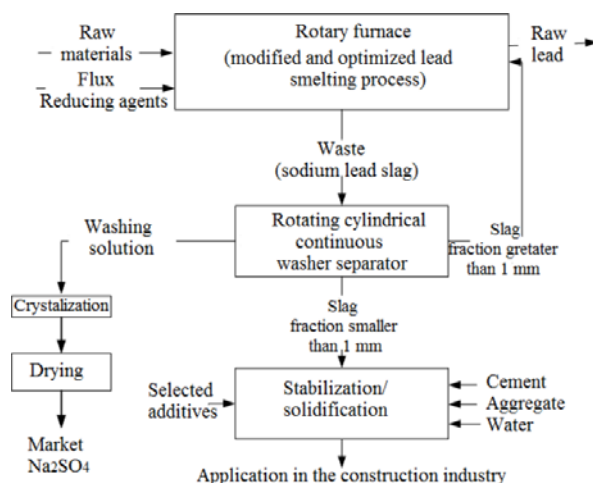


Figure 1. Process flow-sheet for managing of recycling process of waste lead-acid batteries

The essence of the proposed waste sodium lead slag treatment is the continuous separation the soluble content (the gauge, oxide-sulfate) and useful components (metal-sulfide), solid and insoluble fraction of slag. By the proposed treatment it is necessary to have fraction larger than 1mm, which contains useful components (metal-sulfide, solid, non-soluble fraction). This fraction is returned to smelting process in order to re-use the mentioned components. The proportion of these useful components as compared to the total weight of treated slag is approximately 25.4 wt. %. The second product of proposed treatment method is fraction smaller than 1 mm (gauge, sulfide-oxide fraction) adequate for further treatment by solidification/stabilization process in concrete cement matrix for the application in civil engineering. The proportion of this fraction as compared to the total weight of treated slag is amounted to 56.8 wt. %. The amount of slag after leaching has been reduced up to 17.8 wt. %.

Optical analysis of slag samples, after removing its water soluble components (see Figure 2) indicates that the main constituents of the slag after leaching in water solution are iron, lead and residual coke. Iron is present in oxide form (magnetite - Fe_3O_4 , wustite - FeO) and in the sulfide form (pyrite - FeS). Lead is present in the form of metallic lead, as well as in the sulfate form as anglesite (PbSO_4) and sulfide form as galena (PbS).

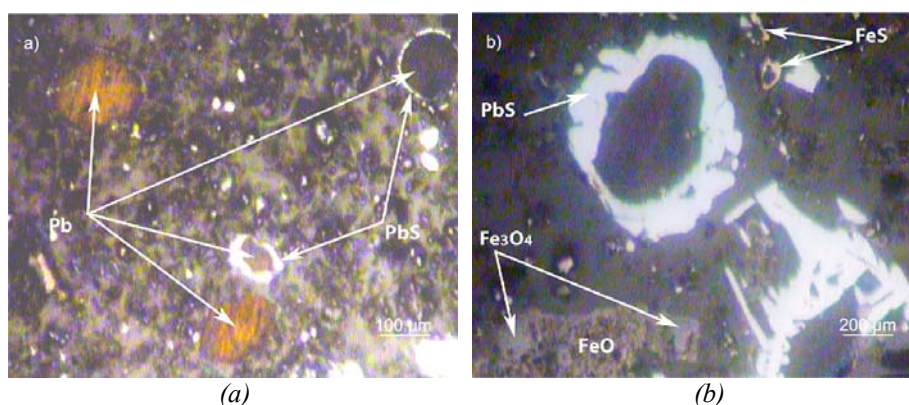


Figure 2. Optical microscopy of slag samples after treatment

Additional product obtained by proposed treatment method is washing solution, which contains certain amount of sodium (14600 mg/l). Concentrations of sulfur and arsenic in washing solutions after treatment of slag were 2350 mg/l and 35.0 mg/l, respectively. The highest leaching degree from slag has sodium (65 wt. %), while sulfur (39 wt. %) and arsenic (35 wt. %) have smaller values of leaching degree. Diagrams of Eh-pH for systems Na-S- H_2O and S-Na- H_2O at 25°C, presented in Figure 3 (a,b), show that alkaline medium (pH 11.40) and reduction potential -240.7 mV favors the formation of Na^+ and NaSO_4^- ions as dominant species in this system. According to presented results this solution can be joined with solution from lead paste desulfurization process, and may be used in commercial grade sodium-sulfate production.

Leaching mechanism and behavior of lead and arsenic from sodium lead slag previously stabilized/solidified in cement matrix using additives: magnesium-oxide,

calcium-oxide, barium-hydroxide and gypsum were also investigated. Results indicated dissolution of lead and arsenic from the outer layer of specimens, followed by depletion of possible mobile forms. The analysis of leachates from samples with various compositions showed that proper selection of additives may reduce leaching of lead and arsenic below the specified limits [20-22].

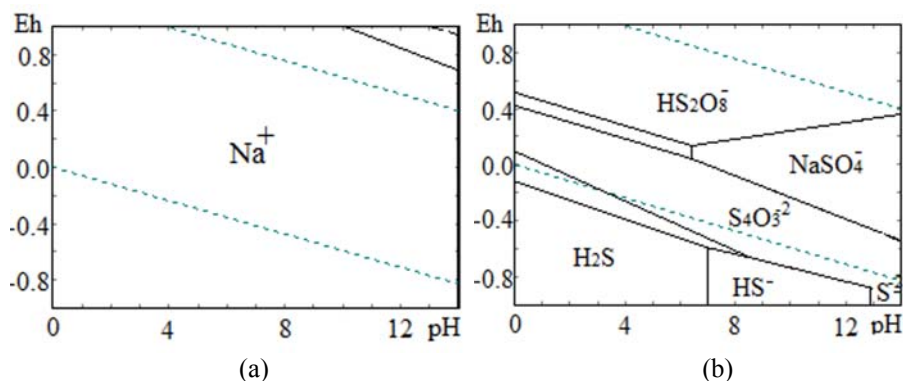


Figure 3. E-pH diagrams in systems Na-S-H₂O (a) and S-Na-H₂O (b) at 25°C

Conclusion

One of the conclusions of this study is that the use of hazardous wastes has positive synergistic effect on modification and optimization of pyrometallurgical process of lead recovery from waste lead acid batteries. Due to the technological process and the measures prescribed for the modified process, waste activated carbon, a reducing agent in lead metallurgy can be utilized as a secondary raw material, with the significant economic and energy savings. Additionally, the optimization of process is based on stabilization of the secondary lead slag in the furnace. Namely, the reduction of toxic elements leachability from slag, is proposed with the possibility of re-use of fine fraction (waste dust), which is a mixture of metal oxides and phosphorus compounds, from the recycling of CRT monitors. Energy efficiency of the process is achieved by using the oxygen burners in combination with heat recuperation energy saving (up to 30 %).

Treatment of wastes from pyrometallurgical process of lead recovery from batteries is based on efficient filtration of process gases, return of baghouse dust to the process and the use of oxygen burners which have positive effect on the environmental protection from this process. The treatment of waste sodium lead slag is proposed as a new technological procedure based on continuous removing of its water soluble components, reduction of its amount and conversion to stable form of waste. The essence of the proposed treatment is the re-use of useful components from slag based on re-smelting of metal-sulfide fraction larger than 1 mm, solidification/stabilization of gauge (sulfate-oxide fraction smaller than 1 mm) in concrete cement matrix and crystallization of sodium(I)-sulfate from washing solution, joined with solution from lead paste desulfurization process.

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