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# **Recycling of bismuth oxides**

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ABSTRACT

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Introduction. The paper is devoted to the creation of an environmentally safe, technologically efficient and cost-effective high-performance integrated scheme for the recycling of lead-containing industrial products and waste, in particular, bismuth oxides and drosses formed during the melting of copper-electrolyte sludge, with the production of commodity monoelement products. To solve the problem, a combined technology is used, which is based on hydrometallurgical operations that allow separating chemical elements with similar properties with high extraction into finished products. The aim of the work is to study and develop fundamental approaches and rational integrated technologies for recycling bismuth drosses and oxides-industrial products of refining rough lead, using reducing melts of raw materials and bismuth-enriched sludge, electrolysis of bismuth lead to obtain rough bismuth containing  $\ge 90$  % Bi with its direct extraction of  $\ge 70$  %. Methods and approaches: melting at a temperature of 1,100...1,150 °C a charge of optimal composition containing bismuth oxides, sodium carbonate, silicon dioxide and carbon. Novelty: a decrease in the content of noble metals and accompanying chalcogenes in secondary coppercontaining raw materials with an increase in the amount of impurity elements. Results and discussion: joint melting (1,100...1,150 °C) of bismuth oxides, sodium carbonate, silicon dioxide and carbon, taken in the mass ratio 100 : (15-66) : (11-25) : (5-7), allows to transfer 89.0 - 93.6 % of bismuth and 99.5 - 99.7 % of lead from the initial oxides to bismuth lead containing ~7 % Bi and ~80 % Pb. The main phase of the Pb-Bi alloy is elemental lead. The increased flux consumption leads to an increase in the amount of recycled silicate slags that are poor in target metals, into which it passes,%: 1.4 Bi; 2 Pb; 47 Zn; 23 Sb; 33 Sn. Main slag phases are following: Na,CaSiO<sub>4</sub>, Na<sub>4</sub>Mg,Si<sub>3</sub>O<sub>10</sub>, MgO, Pb, ZnS, PbS. The practical relevance is determined by the optimal mode of reducing melting of bismuth oxides (100 %) to obtain lead bismuth, %: 66 Na<sub>2</sub>CO<sub>3</sub>, 25 SiO<sub>3</sub>, 5 C; the process temperature is 1,150 ° C. The presence of impurities makes it necessary to introduce reagent treatment of lead bismuth into the technological scheme for recycling bismuth oxides. Decontamination and alkaline softening will make it possible to obtain a Pb-Bi alloy suitable for pyroelectrometallurgical recycling.

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# Introduction

Reducing the amount of conditioned raw materials for non-ferrous metallurgy stimulates the development of cost-effective technologies for the extraction of non-ferrous and rare metals from intermediate products and industrial waste to obtain marketable products [1–5]. Non-ferrous Alloys Production Branch of JSC "Uralelektromed" applies Betterton-Kroll process at one of the rough lead pyrometallurgical refining stages. Betterton-Kroll process is used to remove bismuth from lead by calcium and

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magnesium addition to the molten bath [6-8]. The obtained bismuth drosses consisting of 3-5 % Bi and 80-85 % Pb are processed by smelting at 500-600 °C with the addition of NaNO<sub>2</sub> and NaOH. The result of the process is alkali flux (bismuth oxides of %: 1-5 Bi; 60-70 Pb) which is sent to the lead refining cycle, and Pb-Bi alloy (1-12 % Bi) of grades SSV-1, SSV-3, SSV-6, SSV-9, SSV-12, which is shipped to the customers. The turnover of bismuth oxides causes accumulation of valuable metals in the technological cycle. Whereas the demand for Pb-Bi alloy is limited, it is necessary to expand the range of commercial products as well as to increase the content of the target product and to enhance the added value of the product.

The production of rough bismuth during the processing of bismuth drosses and oxides is possible using pyro [9–11], hydro [12–14], pyroelectric [15–17] and hydroelectrometallurgical [18–20] methods. Electrometallurgical technologies implemented through two main production methods can be considered promising and can be applied for modernization of Non-ferrous Alloys Production branch.

The first variant of the implementation is the hydroelectrometallurgical method, which includes:

- reduction smelting of oxides with the addition of sodium carbonate, quartz and coke to produce slag which can be recycled in the copper smelting process, dust returned to smelting, and bismuth lead, cast into anodes, followed by electrolysis in a silicofluoride solution to obtain recycled cathode lead and anode sludge subjected to washing and drying;

- melting of sludge mixed with coal and sodium carbonate to obtain recycled slag and ingots of commercial rough bismuth;

- melting of recycled slag in a mixture with coal and sodium carbonate to obtain recyclable waste slag and ingots of commercial rough bismuth [21].

The second variant of the implementation is the pyroelectrometallurgical method, which includes:

- reduction smelting of oxides to produce slag, dust and ingots of bismuth lead;

- electrolysis of the latter in a chloride melt to produce cathode lead and ingots of enriched bismuth lead:

- secondary electrolytic processing of ingots in a chloride melt to produce cathode lead and ingots of commercial rough bismuth [22].

Bismuth from its oxygen compounds is obtained by reduction smelting in a molten sodium hydroxide in the presence of elemental sulfur. reduction smelting is carried out in the presence of coal at a ratio of

bismuth : alkali : coal : sulfur equal to 1 : (0.8 - 1.8) : (0.04 - 0.16) : (0.02 - 0.08) [23].

Low temperature reduction smelting includes mixing of bismuth-bearing material and starch followed by melting to obtain rough bismuth. Starch as a reducing agent makes it possible to lower the reduction temperature to 800 - 850 °C and to increase the direct extraction of bismuth to ~ 95 % [24]. Both approaches have a great interest for processing of oxidized drosses.

The aim of this study is to study and develop fundamental methods and cost-effective integrated technologies of bismuth drosses and oxides processing, which are obtained at rough lead refining. Bismuth drosses and oxides are processed applying reduction smelting of raw material and bismuth-enriched slime, and electrolysis of lead bismuth resulting in production of rough bithmuth containing  $\geq$  90 % Bi. The direct recovery of bismuth from processed products amounts to  $\geq 70$  %.

The objectives of this study are as follows: assessment of the material composition of the original oxides and the products obtained; experimental simulation of the basic operations, namely oxides smelting with the addition of sodium carbonate, silicon dioxide and a carbon-bearing reducing agent; justification of the main redevelopments of the proposed technological scheme.

# Methodology

In order to produce lead bismuth the charge containing bismuth oxides, sodium carbonate, silicon dioxide and carbon was melted at 1,100-1,150 °C (Table 1). The charge components were mixed and placed in an alundum crucible, which was installed into an electric resistance furnace with graphite heating elements, and covered with a graphite crucible. The furnace was heated to a preset temperature.



After the charge melting and isothermal holding for 20 min; the crucible with the melt was removed from the furnace, covered with a graphite crucible and cooled in the air. Then, the product was weighted and assayed.

It was expected that remelting of oxides would lead to separation of the melt into metallic and oxide phases, but the phase separation was not achieved (Experiment 1, Table 1). No separation was observed even when a carbon-bearing reducing agent was added to the charge (Experiment 2, Table 1). This agent was present in excess of stoichiometric quantity required for the reduction of lead and bismuth from oxides, due to the presence in the oxides of significant amounts of high melting point compounds ( $Zn_xPb_{1-x}O$ , CaPbO<sub>3-x</sub>, etc.). Therefore, further smelting was carried out with addition of fluxes to the charge to form a high melting point slag. Na<sub>2</sub>CO<sub>3</sub> consumption was calculated based on the achieved ratio of the total mass of lead and bismuth to the mass of NaOH in the charge from 1 to 10, and SiO<sub>2</sub> consumption based on produced slag containing 38–50 % of SiO<sub>2</sub>. (Experiments 3 and 4, Table 1).

Table 1

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Experiment	Oxides, g	Na <sub>2</sub> CO <sub>3</sub> , g	SiO <sub>2</sub> , g	Graphite, g
1	100	_	_	—
2	100	_	_	5
3	100	15	11	7
4	100	66	25	5

Composition of the charge for the production of bismuth lead

The samples of treated bismuth oxides produced in the refining cycle of rough lead at Non-ferrous Alloys Production Branch of JSC "Uralelektromed", and smelting products of the initial charge (Pb-Bi alloy, slag, dust) were analyzed by various physical and chemical methods. Size distribution was determined by screen analysis using a standard set of screens; bulk density – by weighing in a flask of known volume; true density – using a measuring flask; moisture – by drying. To study the elemental composition, the oxide sample was ground in a laboratory grinder to a particle size of less than 0.1 mm. The chemical composition of the analyzed materials was determined by atomic emission spectrometry with inductively coupled plasma (Optima 4300 DV) and X-ray fluorescence spectrometry (S4 Explorer). The phase composition was estimated by X-ray diffraction analysis on an automated diffractometer DRON-2 in Cu K $\alpha$ -radiation, the subsequent phase identification was carried out using the ICDD 2013 database. A JSM-59000LV scanning electron microscope with an OXFORD INCA Energy 200 energy dispersive X-ray spectrometer was used to determine the elemental composition of phases.

# **Results and their discussion**

The results obtained (Table 2) confirm that the addition of fluxes and reducing agent to the charge leads to generation of three phases: metallic, accumulating bismuth and lead; slag, which receives the major amount of oxides; and dust and gas, concentrating elements and compounds with high elasticity of vapor. In experiments 3 and 4 (Table 2) the following products are reduced from initial oxides, %: 89.0–93.6 Bi; 99.5–99.7 Pb; 0.2–0.4 Zn; ~30 Sb; 7.2 Sn with a transition to lead bismuth of the following composition, %: 7.06–7.32 Bi; 80.6–81.6 Pb.

According to X-ray phase analysis, the main phases of the *Pb-Bi* alloy (experiments 3 and 4) are elemental lead and galena *PbS* (Fig. 1).

An increase in flux consumption (Experience 4, Table 1, 2) leads to an increase in mass of released slag from 44.8 to 93.1 % of the amount of oxides. Silicate slags poor in target metals were obtained, %: 0.06–0.08 Bi; 1.23–1.81 Pb; 3.3–6.7 Zn; 0.6–1.2 Sb; 0.7–1.6 As; 0.5–1.2 Sn; 17.9–21.6 SiO<sub>2</sub>; 22.5–36.7 Na<sub>2</sub>O;



Table 2

Product,	Experiment No. 3: Content ( $\beta$ ), % / Distribution ( $\epsilon$ ) of the component, %						
Q-ty, g	Bi Pb Zn Sb		Sb	As	Sn		
Alloy 67.3	7.06/89.0	81.64/99.0	0.03/0.4	1.15/32.2	_	0.17/7.2	
Slag 44.8	0.06/0.5	1.81/1.0	6.72/46.9	1.24/23.1	1.55/39.9	1.17/33.6	
Dust 20.8	2.69/10.5	—	16.29/52.8	5.16/44.7	5.03/60.1	4.43/59.1	
Product,	Experiment No 4: Content ( $\beta$ ), % / Distribution ( $\epsilon$ ) of the component, %						
Q-ty, g	Bi	Pb	Zn	Sb	As	Sn	
Alloy 68.3	7.32/93.6	80.55/99.7	0.02/0.2	1.07/30.4	_	_	
Slag 91.3	0.08/1.4	1.23/2.0	3.31/47.0	0.61/23.1	0.65/34.1	0.46/27.2	
Dust 36.4	0.73/5.0	_	3.39/52.7	3.07/46.5	3.15/65.9	3.12/72.8	

#### Bismuth oxide melting products at a temperature of 1,150 °C



*Fig. 1.* Diffractograms of bismuth lead: a -experiment 4; b -experiment 3; 1 -Pb, 2 -PbS

3.9–7.4 MgO; 2.5–6.3 CaO, which receive, %: 0.5–1.4 Bi; 1.5–2.0 Pb; ~47 Zn; 23 Sb; 34.1–39.9 As; 27.8–34.4 Sn. The phase composition of the slag (Experiments 3 and 4) is shown in Fig. 2.

The amount of fluxes ( $Na_2CO_3$ ,  $SiO_2$ ) and reducing agent (graphite) taken in mass ratios (Table 3) was varied to streamline the reduction smelting operations of bismuth oxides.

The amount of fluxes was taken on the basis of preliminary calculation of compositions slags in the binary system of  $Na_2O-SiO_2$ , which allows predicting the melting temperature of the latter. The calculation was carried out in two alternatives based on possible yield of both meta- and ortho-silicates of sodium,



Fig. 2. Diffractograms of slags in the production of bismuth lead: a -experiment 4; b -experiment 3; 1 -Na<sub>2</sub>CaSiO<sub>4</sub>,  $2 - Na_4Mg_2Si_3O_{10}, 3 - MgO, 4 - Pb, 5 - Zn\bar{S}, 6 - PbS$ 

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	Composition of the	charge for reduction si	neiting of Distitutit oxid	165
Experiment	Oxides, g	Na <sub>2</sub> CO <sub>3</sub> , g	SiO <sub>2</sub> , g	Graphite, g
5	100	15	11	7
6	100	15	26	5
7	100	22	13	3
8	100	33	12,5	5
9	100	66	25	5

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whereby the proportion of SiO<sub>2</sub> was maintained at 45–75 % wt. %, according to the liquidus temperature of 800–1100 °C.

The criterion which determined optimum conditions for the main operations of reduction smelting of bismuth oxides is the recovery ratio of the target metals in the metallic phase (Tables 4 and 5).

Flux consumption is fundamental for smelt process performance. For experiments 5 and 7 the calculated composition of slags, %: 42.4–78.2 Na<sub>2</sub>O; 21.8–57.6 SiO<sub>2</sub>, based on the diagram of the binary system state, should promote the phase separation, which in practice was not confirmed, demonstrating the absence of complete melting of the material. Additional information can be received by switching to the ternary system Na<sub>2</sub>O-SiO<sub>2</sub>-CaO, where imaging points of the assumed slag compositions, %: 67.8–70.2/33.8– 36.3 Na<sub>2</sub>O; 19.6–22.4/41.9–46.0 SiO<sub>2</sub>; 9.9–10.2/20.2–21.8 CaO fall into areas with liquidus temperatures of 1200–1500 °C, significantly higher than the target temperature.



Table 4

Optimization of the charge composition								
Product,	Experiment No 6: Content ( $\beta$ ), % / Distribution ( $\epsilon$ ) of the component, %							
Q-ty, g	Q-ty, g Bi		Zn	Sb	As	Sn		
Alloy 67.3	7.06/89.0	81.64/99.0	0.03/0.4	1.15/32.2	_	0.17/7.2		
Slag 44.8	0.06/0.5	1.81/1.0	6.72/46.9	1.24/23.1	1.55/39.9	1.17/33.6		
Dust 20.8	2.69/10.5	_	16.29/52.8	5.16/44.7	5.03/60.1	4.43/59.1		
Product,	Expe	eriment No 8: Co	ontent ( $\beta$ ), % / D	Distribution ( $\epsilon$ ) of	of the componen	t, %		
Q-ty, g	Bi	Pb	Zn	Sb	As	Sn		
Alloy 68.3	7.32/93.6	80.55/99.7	0.02/0.2	1.07/30.4	—	—		
Slag 91.3	0.08/1.4	1.23/2.0	3.31/47.0	0.61/23.1	0.65/34.1	0.46/27.2		
Dust 36.4	0.73/5.0	_	3.39/52.7	3.07/46.5	3.15/65.9	3.12/72.8		
Product,	Experiment No 9: Content ( $\beta$ ), % / Distribution ( $\epsilon$ ) of the component, %							
Q-ty, g	Bi	Pb	Zn	Sb	As	Sn		
Alloy 68.3	7.32/93.6	80.55/99.7	0.02/0.2	1.07/30.4	_	—		
Slag 91.3	0.08/1.4	1.23/2.0	3.31/47.0	0.61/23.1	0.65/34.1	0.46/27.2		
Dust 36.4	0.73/5.0	_	3.39/52.7	3.07/46.5	3.15/65.9	3.12/72.8		
		Operating	time of bismuth	n lead				
Product,	Expe	eriment No 9: Co	ontent ( $\beta$ ), % / D	Distribution ( $\epsilon$ ) of	of the componen	t, %		
Q-ty, g	Bi	Pb	Zn	Sb	As	Sn		
Alloy 67.5–74	4.32-8/	52.3-86.7/	0.03-0.34/	2.5-2.9/	0.28-0.76/	0.7-0.93/		
	59.9–96	70.1–97	0.4–3.7	71.3-84.8	11.2–29.6	30.4-44.3		
Slag 73–91	0.03-1.2/	0.3–15.3/	0.08–13.3/	0.23–1.47/	0.67-6.68/	0.76-5.42/		
	0.5-20.4	0.4–25.3	3.6-78.2	7.1–55.7	28.4-48.3	41-54.9		
Dust 36–55.5		_			_	_		

### Results of melting of bismuth oxides at a temperature of 1150 °C

Table 5

Composition of slags in the Na<sub>2</sub>O-SiO<sub>2</sub> binary system

Content in the charge, mass.%				Content in the slag, mass.%			
				Estimated value		Actual value	
Oxides	ides Na <sub>2</sub> CO <sub>3</sub> SiO <sub>2</sub> C		Na <sub>2</sub> O	SiO <sub>2</sub>	Na <sub>2</sub> O	SiO <sub>2</sub>	
100	15	11	7	46.5-78.2	21.8-53.5	_	_
	22	13	3	42.4-75.2	24.8-57.6		
	15	26	5	26.9–78.2	21.8-73.2	25	75
	33	12.5		43.3-75.9	24.1-56.7	65.6	34.4
	66	25		27.6-61.2	38.8-72.4	44.7-60.8	39.2–55.3

Similar considerations can be applied to the composition of slag in systems Na<sub>2</sub>O-SiO<sub>2</sub>-MgO and Na<sub>2</sub>O-SiO<sub>2</sub>-FeO. Consideration of multicomponent phase diagrams leads to similar results.

Increasing SiO<sub>2</sub> consumption to 26 % of the oxides while maintaining the proportion of Na<sub>2</sub>CO<sub>3</sub> at 15 % (Experience No. 7) leads to separation of the metallic and slag phases. In the resulting bismuth lead (60 % of oxides), containing 8.2 % Bi and 93.4 % Pb, 90–92 % of these metals are extracted. The slag (62 % of oxides) with a low bismuth content (0.11 % wt.) is characterized by a large proportion of lead (up to 23.4 % wt.).



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The third melting product (24.1 % of oxides) is a dust-gas mixture. In general, with acceptable melting rates, such a ratio of fluxes transfers the imaging point of the slag composition (%: 23.1 Na<sub>2</sub>O, 63.0 SiO<sub>2</sub>, 13.9 CaO) to the region where the liquidus temperature reaches 1,200 °C, as a result of which minor deviations from the specified flow rates for the dosage of fluxes, possible in the practical implementation of the process, will lead to disruption of its course.

An increase in the consumption of Na<sub>2</sub>CO<sub>3</sub> to 33 % of the amount of oxides led to similar results when the share of SiO<sub>2</sub> was fixed at the level of 12.5 %. In this embodiment, the 55 % yield of the metal alloy of the following composition, %: 7.3 Bi; 80.2 Pb, had low extraction of bismuth (75 %) and lead (80 %). Slag yield amounted to 71 %, and contained, %: 0.8 Bi, 12.9 Pb, the imaging point of which on the Na<sub>2</sub>O-SiO<sub>2</sub>-CaO diagram, %: 68.4 Na<sub>2</sub>O, 21.7 SiO<sub>2</sub>, 9.9 CaO, was closely adjacent to the area in which no delamination had been observed earlier, and therefore to implement the process in practice, a high accuracy of dosage of fluxes is required. The output of dust and gas during smelting was 24.1 % of the oxide content. A change in the composition of the charge towards a simultaneous increase in the ratio of Na<sub>2</sub>CO<sub>3</sub> (66 %) and SiO<sub>2</sub> (25 %) also leads to the delamination of condensed phases. Lead-bismuth alloy with the yield of 62 % consists of 7.7 % Bi and 84.2 % Pb, while the target metals are quantitatively recovered in the alloy containing 89 % Bi and 94 % Pb.

The slag yield expectedly rises (up to 103 % of the oxides amount). The content of bismuth and lead in the slag is low (%): 0.66 Bi; 11 Pb. It corresponds to the position of the imaging point on the diagram Na<sub>2</sub>O-SiO<sub>2</sub>-CaO, %: 23.7 Na<sub>2</sub>O, 62.1 SiO<sub>2</sub>, 14.2 CaO for the area with the liquidus temperature of 1,100–1,150 °C. It was observed that the yield of the gas and dust mixture had increased up to 30.9 %. The reducing agent consumption of ~5 % is in line with the data on similar material treatment practice. The indicated consumption rate takes into account the surplus of reducing agent compared to the stoichiometrically necessary quantity for lead and bismuth recovery from oxides, and the change in the amount of the reducing agent does not significantly influence the melting results.

Thus, the reduction smelting mode of bismuth oxides, %: 66 Na<sub>2</sub>CO<sub>3</sub>; 25 SiO<sub>2</sub>; 5–7 C, at the temperature of 1,150 °C, set during experiment 9 are optimum. Combined melting of bismuth oxides, Na<sub>2</sub>CO<sub>3</sub>, SiO<sub>2</sub>, and carbon at the ratio of 100 : 15 : 26 : 5 and 100 : (33–66) : (13–26) : (5–7) allows splitting off the bismuth lead alloy with the yield of 61.8–74.0 % of the oxide content. The obtained bismuth lead alloy has the following composition (%): 7.1–8.0 Bi; 81.3–86.1 Pb; 0.08 Zn; 2.54 Sb; 0.76 As; 0.70 Sn; 0.99 Cu; 0.03 Ag. The ratio of metal recovery into alloy is the following (%): 95.6 Bi; 94.6 Pb; 0.8 Zn; ~71.3 Sb; 30.4 Sn; 67.5 Cu. According to the X-ray phase analysis findings the major phase of lead-bismuth alloy is elemental lead.

Silicate slag with the yield of 73–103 % of the oxides was produced. Its composition was as follows, %: 0.03–1.20 Bi; 0.3–15.4 Pb; 5.9 Zn; 0.25 Sb; 0.99 As; 0.76 Sn; 0.02 Cu; 0.001 Ag; 24.0 SiO<sub>2</sub>; 55.6 Na<sub>2</sub>O; 7.7 MgO; 6.9 CaO; 0.5 FeO. The following elements go into the silicate slag, %: 6.6 Bi; 7.7 Pb; 78.2 Zn; 8.7 Sb; 41 Sn; 4.8 Cu. Phase composition of the slag includes Na<sub>2</sub>CaSiO<sub>4</sub>, Na<sub>4</sub>Mg<sub>2</sub>Si<sub>3</sub>O<sub>10</sub>, MgO, Pb. The third product of the melting is dust and gas mixture (40 - 43 %), where some of the charge target components are concentrated, %: 21.0 Zn; 20.0 Sb; 22.1 As; 28.6 Sn; 27.7 Cu. Thus, the reduction smelting mode of bismuth oxides (100 %), recommended for further studies and calculations, was set: 66 Na<sub>2</sub>CO<sub>3</sub>; 25 SiO<sub>2</sub>; 5–7 C; process temperature is 1,150 °C.

The content of impurities in the obtained alloy is significantly higher than accepted in the practice of similar production processes. It might cause serious difficulties in the direct pyro-electrometallurgical processing of lead bismuth. This is confirmed by the results of a laboratory experiment on the electrolytic refining of bismuth dross, %: 0.1–1.2 Bi; 0.6–12.0 Zn; 0.3 Sb; the rest percentage is Pb, obtained by Polymetal Production branch of JSC "Uralelektromed". The electrolyte was a melt of an equimolar eutectic mixture of PbCl<sub>2</sub> and KCl, the process temperature was 823 K (550 °C). It was identified that besides bismuth (6.4–30 % Bi), significant amount of electrically positive antimony (16.5 % Sb) accumulates in anode product, which does not allow to obtain rough bismuth. Thus, it is required to include reagent treatment of the alloy (decoppering, alkaline softening), similar to refining of rough Pb, at minimum bismuth loss with Cu slurry and alkaline fusions. The reagent treated alloy can pass to pyrometallurgical stage.



## Conclusions

1. Combined melting of (1,100-1,150 °C) bismuth oxides, sodium carbonate, silicon dioxide and carbon, taken in mass ratios of 100: (15-66) : (11-25) : (5-7), allows to convert 89.0-93.6 % of bismuth and 99.5–99.7 % of lead from original oxides in to lead bismuth, containing 7.06–7.32 % Bi and 80.6–81.6 % Pb. The main phase of lead bismuth alloy is elemental lead. The obtained alloy can be further processed using conventional technologies for separation of bismuth and lead.

2. Increased consumption of flux results in enhanced yield of recyclable silicate slag with low content of target metals, %: 0.06–0.08 Bi; 1.23–1.81 Pb; 3.3–6.7 Zn; 0.6–1.2 Sb; 0.7–1.6 As; 0.5–1.2 Sn; 17.9–21.6 SiO<sub>2</sub>; 22.5–36.7 Na<sub>2</sub>O; 3.9–7.4 MgO; 2.5–6.3 CaO, in which %: 1.4 Bi; 2 Pb; 47 Zn; 23 Sb; 33 Sn are converted. The main slag phases are Na<sub>2</sub>CaSiO<sub>4</sub>, Na<sub>4</sub>Mg<sub>2</sub>Si<sub>3</sub>O<sub>10</sub>, MgO, Pb, ZnS, PbS.

3. Combined melting (1,150 °C) of bismuth oxides, sodium carbonate, silicon dioxide and carbon, taken in mass ratios of 100:15:26:5 and 100:(33-66):(13-26):(5-7) makes it possible to release lead bismuth (the output is 61.8–74.0 % of the content of oxides) with the following composition, %: 7.1–8 Bi, 81.3–86.1 Pb, 0.08 Zn, 2.54 Sb, 0.76 As, 0.7 Sn, 0.99 Cu, 0.03 Ag. Rates of metals extraction to alloy are 95.6 % for Bi, 94.6 % for Pb, 0.8 % for Zn, 71.3 % for Sb, 30.4 % for Sn, 67.5 % for Cu. The main phase of the alloy is elemental lead.

4. Increased flux consumption (66 % Na<sub>2</sub>CO<sub>3</sub>, 25 % SiO<sub>2</sub> of Bi-oxides) makes it possible to obtain easily fusible recyclable silicate slag (the output is 73 - 103 % of Bi-oxides) with the following composition, %: 0.03-1.20 Bi, 0.3-15.4 Pb, 5.9 Zn, 0.25 Sb, 0.99 As, 0.76 Sn, 0.02 Cu, 24.0 SiO<sub>2</sub>, 55.6 Na<sub>2</sub>O, 7.7 MgO, 6.9 CaO, 0.5 FeO. The following elements are recovered to slag, %: 6.6 Bi, 7.7 Pb, 78.2 Zn, 8.7 Sb, 41.0 Sn, 4.8 Cu. Na<sub>2</sub>CaSiO<sub>4</sub>, Na<sub>4</sub>Mg<sub>2</sub>Si<sub>3</sub>O<sub>10</sub>, MgO, Pb are the main phases.

5. The optimal mode of reduction smelting is determined for bismuth oxides (100 %) to obtain lead bismuth with %: 66 Na<sub>2</sub>CO<sub>3</sub>, 25 SiO<sub>2</sub>, 5-7 C. The process temperature is 1,150 °C. The presence of impurities makes it necessary to introduce reagent treatment of lead bismuth into the technological scheme for processing of bismuth oxides. Decoppering and alkaline softening will make it possible to obtain a Pb-Bi alloy suitable for pyroelectrometallurgical processing.

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## **Conflicts of Interest**

The authors declare no conflict of interest.

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