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Metallurgy

Technology for extraction of Pb, Cu, Zn from a feed based on lead cake from leached dust generated by reduction-oxidation blowing of melt

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ABSTRACT

The paper presents the theoretical basis and results of processing a mixture of complex types and compositions, based on lead cake, obtained after the preliminary removal of arsenic from dust and its subsequent leaching with sulfuric acid. The main goal of the technology is to involve the processing of substandard intermediate products of lead production together with lead cake and the selective extraction of non-ferrous metals into commercial products: copper into matte; lead - into rough lead: zinc - into slag. Choice of the composition of the feed charge was carried out taking into account the volumes obtained in production and is represented by the following structure, %: lead cake - 50; copper-lead matte – 40; quartz flux – 10. It has been established that the best results, ensuring high complex extraction of copper, lead, zinc and arsenic into the targeted smelting products, are achieved with a consumption of natural gas 1.4 times higher than its consumption from the stoichiometric required quantity (SRQ) for the reduction of lead compounds to metal lead. The optimal time for blowing the melt with natural gas is 15 minutes. The optimal oxygen consumption when blowing the intermediate matte obtained after the first stage was 1.1 times higher than its stoichiometric required amount (SRQ) for the oxidation of zinc and iron sulfide with their further transfer in the form of oxides to slag. The duration of matte blowing is 10 minutes. With the optimal established parameters, high technological indicators of the technology were achieved: extraction of lead into rough lead - 98.6%; copper in matte – 98.5%; zinc in slag – 94.1%.

Keywords: lead cake, feed charge, intermediate products, reduction blowing, oxidation blowing, copper, lead, zinc, extraction.

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Introduction

The dominant linear model in the production of non-ferrous metals from primary low-quality sulfide raw materials, although it no longer meets modern requirements in terms of environmental safety, nevertheless continues to function at its usual pace. Today it is no longer a secret to anyone that the pyrometallurgical production of copper, lead and copper, using technologies of the last century, is accompanied not only by low technological indicators but also by increasing volumes of substandard intermediate products and technogenic waste produced along the way. Finding rational, efficient technologies for their processing has no particular interest to manufacturers of basic products. The difficulty of processing this kind of raw material lies in the increased content of toxic arsenic in them, the presence of which determines the critical level of their impact on the environment and inhibits their further processing [[1], [2], [3], [4]].

Currently, the growth of substandard intermediate products is the main problem for non-ferrous metallurgy enterprises. Attempts to process them using existing technologies led to a decrease in technological, economic and environmental indicators of production. As a result, the compositions of technogenic waste of industry have become greatly complicated, which has led to their significant accumulation, with all the ensuing negative social, economic and environmental consequences. The current situation at non-ferrous metallurgy enterprises requires a radical approach to solving these problems.

From this perspective, the circular economy model has a great interest, widely spread in the world economy, within the framework of the Zero concept of waste [5]. This approach is not new. In the practice of the economy of the Soviet Union, special attention was previously paid to the development of so-called “waste-free technologies”, which essentially solved the same problems as the circular economy model proposed in the West, where solving the problems of integrated use of raw materials and preserving a clean environment was at the forefront [6]. In our opinion, regardless of the nature of the use of these solutions to maintain resource efficiency and environmental safety, whether in the West or in the economy of the post-Soviet countries, these tasks today should determine the main trend in the development of the economy, regardless of its affiliation.

Materials characterized by a complex chemical composition include fine dust from copper and lead production. Their peculiarity is their multicomponent nature, %: 35-50 Pb; 5-7 Cu; 6-9 Zn; 4-6 Fe; 5-13 As; others. Minor deviations in the furnace operating conditions, the chemical composition of the concentrate and other factors from the specified parameters can significantly change the quantitative ratio of metals in the dust towards a deterioration in its composition [[7], [8], [9], [10], [11], [12]].

The value of dust is enhanced by the fact that, along with their high content of heavy non-ferrous metals and arsenic, they concentrate a significant amount of dual-use metals (Re, Os, Se, Sc, etc.), and could be used well as an additional source for their extraction. However, the high content of arsenic in dust (5-13%) hinders the development of new highly efficient technologies. A very simple solution for enterprises was to sell them to third parties, which, using not entirely rational technologies, in the pursuit of profit, extracting one or two main base metals, do not ensure the comprehensive extraction of metals that are strategic for the economy of Kazakhstan with high added value. This approach, where dust is one of the key sources for the production of Re, Sc, Os and other metals, does not seem entirely rational.

The material composition of dust depends mainly on the composition of the feedstock and technological smelting conditions. The unique polymetallic nature of the ores and concentrates of Kazakhstan, and the multi-component substandard intermediate products and technogenic wastes obtained during their processing, containing a wide range of valuable metals, inherently require the development of new, separate technology for their processing to ensure the complexity of the extraction of valuable metals.

There are several works in the scientific literature devoted to dust processing, each of which is distinguished by its originality in solving the problem of arsenic removal [[13], [14], [15], [16], [17], [18]].

When organizing a technology for processing dust using a hydrometallurgical method, it seems that the most acceptable way to remove arsenic from dust is at the initial stage of the technology. This will improve the technological performance of the processes that form the basis of the overall technology and reduce the consumption of reagents spent on the removal and disposal of arsenic. At the same time, high greening of the technology is ensured due to a significant reduction in the ecological influence on the environment and human health caused by arsenic.

The purpose of this article is the extraction of lead, copper and zinc from a feed composed of lead cake from the leaching of dust obtained after preliminary removal of arsenic by reduction roasting with natural gas.

A distinctive feature of the research is the development of a new technology for the complex extraction of lead, copper and zinc into targeted products from a charge composed of various substandard materials based on arsenic-free lead cake by sequentially blowing the melt with natural gas, then with oxygen. The minimum arsenic content in lead cake eliminates the need for complex, time-consuming sequential blowing of the melt to sublimate arsenic. This ensures maximum sublimation of arsenic into dust in the form of As2O3, complete oxidation of zinc and iron sulfides with subsequent conversion of their oxides into slag and the formation of matte with a high copper content (more than 50% Cu), which is easily reduced to blister copper.

Materials and research methods

Cake with the addition of converter slag, copper-lead matte and copper slips from lead production was used as the core of the complex feed charge. To calculate the rational composition of the charge, the results of comprehensive studies of the material composition of the feed materials and the forms of metals in them were used, obtained using an inductively coupled plasma mass spectrometer Agilent 7700 Series ICP-MS (USA), electron probe microanalyzer Superprobe 733 from JEOL (Japan) [[2], [8], [19]].

Mineralogical studies aimed at studying the surface structure of solid samples were carried out using a microscope Neofot (Carl Zeiss AG, Germany). Micro- and morphological analysis of the surface of individual samples was carried out using a JEOL scanning electron microscope EDS System (USA).

The compositions of the initial products forming the feed charge are given in Table 1.

The main methodological principle of the technology is a thermodynamic approach to describe the reduction-oxidation smelting of a balanced charge: lead cake and substandard sulfide intermediates (Table 1). The key core of the methodology is Big Data technology, which includes an iterative approach to calculating the quantitative ratios of the forming liquid phases: slag, matte and rough lead, depending on the composition and amount of source materials. The composition of the charge from various materials was carried out according to the sulfur content in the initial products, taking into account the production of matte with a high copper content. To obtain slag of optimal composition, ensuring minimal solubility of lead and copper in it, the required calculated amount of quartz flux was added to the charge [20].

Theoretical basis of technology

The interaction of charge components with natural gas and oxygen is based on a thermodynamic approach, including the establishment of quantitative ratios of the initial and resulting smelting products, the formation of liquid phases, etc.

By sequentially blowing the melt with natural gas to produce an intermediate matte, and then blowing it with oxygen, favourable conditions are created for the occurrence of basic physical and chemical processes: the enlargement of small particles of lead dissolved in the form of metal with the precipitation of lead in the form of rough lead; reduction of lead sulfide to metallic lead; destruction of intermetallic compounds of copper and iron (Me_xAs_y, Me_xSb_y) with maximum sublimation of arsenic and antimony into dust; oxidation of iron and zinc sulfides in the matte to their oxides, converting the latter into slag. The presence of residual lead sulfide in the melt inhibits the reduction of copper sulfide and other metals. This ensures the high quality of the resulting rough lead in terms of impurity content.

Considering that the main matrix of the charge is lead cake, consisting of lead, zinc and copper sulfates when developing the technology, we proceeded from the condition of ensuring their complete recovery by blowing the melt with natural gas at high temperatures (1200 °C).

During reductive blowing of the melt with natural gas, favourable conditions are created for the reduction of sulfates according to the reaction:

$$MeSO_4 + CH_4 = MeO + CO_2\uparrow + SO_2\uparrow + H_2O\uparrow, \quad Me - Pb, Cu, Zn \tag{1}$$

The resulting metal oxides interact with the components of sulfide materials (copper-lead matte, copper slips) according to reactions (2), and (3) to form liquid phases of rough lead and matte:

$$2PbO + PbS = 3Pb + SO_2\uparrow, \tag{2}$$

$$Cu_2O + FeS = Cu_2S + FeO, \tag{3}$$

Iron and zinc oxides interact with the flux and form a slag phase.

Metallic lead formed by reaction (2) will settle in the bottom phase. The main contribution to the

Table 1 - Chemical composition of initial products

Product Name	Cu	Pb	Zn	As	Sb	Fe	S	O	SiO_2	Others
Lead cake	0.41	87.53	0.11	0.05		0.58	0.78	8.24		2.3
Copper-lead matte	20.85	19.5	11.4	1.1	0.56	16.7	11.1	3.81		14.98
Converter slag	3.83	33.5	4.54	2.3	0.94	15.0		10.3	21.66	7.93
Copper slips	29.0	36.0	4.00	3.87	1.4		8.77			16.96

formation of metallic lead and the formation of the bottom phase will be made by reaction (2), the high rates of which are ensured by intense bubbling of the melt. Due to the absence of arsenic in lead cake, the need for long-term blowing of the melt with natural gas and oxygen is eliminated, which significantly increases the productivity of the technology as a whole.

Experimental part

For laboratory studies, the composition of the charge based on lead cake was calculated and prepared, %: lead cake – 50; copper-lead matte – 40; quartz flux – 10.

The choice and justification of the composition of the charge were carried out based on solving the problem of maximum involvement in the processing of substandard materials from lead production, taking into account the volumes obtained in production and the organization of their independent, separate smelting for high complex selective extraction of copper, lead and zinc from them.

The average composition of the charge was calculated taking into account the rational compositions of each product and the form of metals in them, is given in Table 2.

Experiments of reduction-oxidation melting of the charge were carried out at different flow rates of natural gas, oxygen and melt blowing time.

Installation diagram and experimental procedure. The experiments were carried out on a laboratory setup, the diagram of which is shown in Fig. 1.

It was not possible to organize continuous production of rough lead in laboratory conditions with sequential blowing of the melt with natural gas and oxygen, so the experiments were carried out in two stages.

Experimental methodology. All experiments were carried out at a constant temperature of 1200 °C. Initial sample – 200 g.

After thorough mixing, the initial mixture was loaded into an alundum crucible (9), which was placed in a quartz reactor (7) located in a tubular furnace (8). The reactor was plugged with a plug (6), cooled with water and equipped with two holes for the input and output of gases. The exhaust gases from the furnace entered the Drexel vessel with water (10). The temperature in the furnace was set and controlled by an automatic control and measuring unit (11). After the complete melting of the charge, the melt was blown through the tube (5), first with natural gas, then with oxygen, which was supplied from cylinders (1), and (2), respectively. The sequential supply of gases was carried out by a 2-way valve (4). The gas flow was regulated by rotameters (3).

Table 2 - Rational composition of the average charge

Compounds	Cu	Pb	Zn	Fe	S	As	Sb	SiO_2	O_2	Others	**Total:**
Cu_2S	2.54				0.64						**3.18**
$CuSO_4$	0.21				0.10				0.21		**0.51**
Cu	5.80										**5.80**
PbS		2.59			0.40						**2.99**
$PbSO_4$		0.60			0.09				0.19		**0.88**
PbO		43.23							3.34		**46.57**
Pb		5.21									**5.21**
ZnS			4.56		2.24						**6.80**
$ZnSO_4$			0.06		0.03				0.05		**0.14**
As_2O_5						0.03			0.01		**0.04**
FeS				2.03	1.16						**3.19**
$FeSO_4$				0.29		0.17			0.33		**0.79**
Fe_3O_4				4.00					1.52		**5.52**
Fe_3As_2				0.49		0.44					**0.93**
Fe_3Sb_2				0.16			0.22				**0.38**
SiO_2								7.48			**7.48**
Others										9.60	**9.60**
Total:	**8.55**	**51.63**	**4.61**	**6.97**	**4.66**	**0.63**	**0.22**	**7.48**	**5.65**	**9.60**	**100.0**

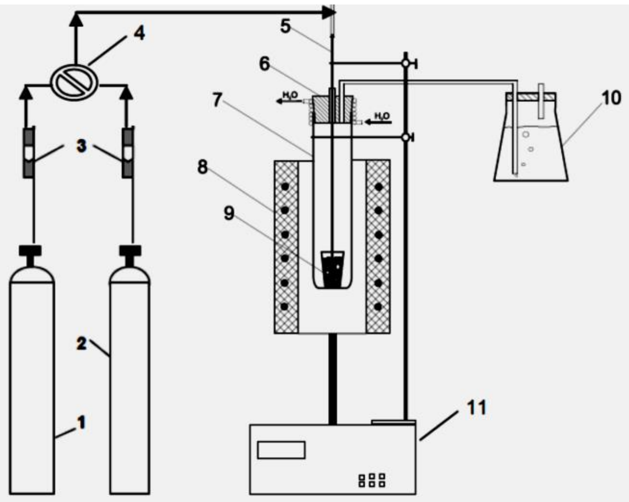

Figure 1 – Installation diagram for studying the distribution of Cu, Pb, Zn, and As during reduction-oxidation melting of the charge: 1 – natural gas cylinder; 2 – oxygen cylinder; 3 – rotameters RM-GS 004 KL4; 4 – 2-way valve; 5 – alundum tube for blowing the melt; 6 – plug with water cooling; 7 – quartz reactor; 8 – electric furnace Nabertherm 50/250/12 with temperature controller B 410; 9 – crucible with a sample; 10 – Drexel vessel ; 11 – control and measuring unit.

In the experiments, the influence of the consumption of natural gas, oxygen and the duration of blowing on the technological parameters of the smelting charge was determined. Natural gas consumption varied from 1 to 1.7, in fractions of the stoichiometric required amount (SRQ) for the complete reduction of lead from its sulfates and oxides. Melt blowing time – 5, 10, 15, 20 minutes.

At the first stage, upon reaching the required temperature, the melt was kept for 5 minutes to obtain a homogeneous melt, then the blowing tube was inserted and the melt was purged with natural gas for a specified time. Upon completion of the purging, the tube was removed from the melt, and the furnace was cooled in a stream of natural gas. After the furnace cooled, the crucible with the sample was removed from the quartz reactor, the smelting products were broken and separated: rough lead, matte and slag.

In the second stage, the intermediate matte obtained in the first stage was purged with oxygen. The procedure for conducting the experiments was the same as in the case of blowing the melt with natural gas. The experimental temperature of 1200 °C ensured the production of liquid slag with a minimum content of lead, copper and high, up to 16%, zinc. During the experiments, the optimal oxygen consumption was determined to ensure high extraction of lead, copper, zinc and arsenic into the targeted products.

The dust yield was calculated based on the difference between the amount of the initial sample and the sum of the amount of obtained smelting products.

Each experiment was repeated three times. The smelting products obtained after the experiments were subjected to comprehensive studies. The established results for the metal content in each product showed good agreement (error +/-0.81% abs.). Based on the results of averaged data on the yield of smelting products and the content of elements in each obtained product, the material balances of the reduction and oxidation stages of the melting of the charge, and then, the final material balance of the smelting of the charge under the conditions of reduction-oxidation blowing were calculated.

Laboratory experiments of reduction-oxidation smelting of the charge. The first stage of research included determining the optimal technological parameters for the reduction-oxidation melting of the charge.

The results of the experiments are presented in Fig. 2, 3, and 4 in the form of the dependence of the influence of natural gas consumption and blowing time on the extraction of copper, lead, zinc and arsenic.

The best results, ensuring high complex extraction of copper, lead, zinc and arsenic into the targeted smelting products, are achieved at a natural gas consumption 1.4 times higher than its consumption from the stoichiometric required quantity (SRQ) for the reduction of lead compounds to metallic lead. The optimal time for purging the melt with natural gas is 15 minutes.

The optimal oxygen consumption when blowing the intermediate matte obtained after the first stage was 1.1 times higher than its stoichiometric required amount (SRQ) for the oxidation of zinc and iron sulfide with their further transfer in the form of oxides to slag. The duration of matte purging is 10 minutes.

The results of the material balances of the reduction-oxidation melts of the charge, calculated based on the results of experiments performed at optimal parameters of blowing with natural gas and oxygen, are shown in Tables 3 and 4.

The final material balance of the charge processing technology is presented in Table 5.

During reduction smelting of the charge with natural gas, the yield of products was, % (of the total charge): rough lead - 44.23; matte – 20.7; slag – 26.78; dust, gases – 2.1. Optimal slag composition, wt.%: 17 Fe; 27.41 SiO_2; 5.75 CaO, ensures minimal solubility of copper and lead in it, which significantly increases their extraction into matte and rough lead, respectively.

Mineralogical studies of the forms of copper and lead in the resulting slags showed their insignificant presence in the form of small inclusions of dissolved oxides. The established low copper contents in the slag (0.16%) and rough lead (0.12%) ensured the production of high quality rough lead - with a lead content of 99.52%. The recovery of lead into rough lead was 98.1%. At the same time, a high extraction of copper into matte was achieved – 98.5%. Despite the high performance, the resulting matte is characterized by a high content of zinc ~22% and iron – up to 11%. Studies of their forms in matte showed their presence in the form of sulfides. Although the resulting matte in terms of copper content in it (40.3% Cu) corresponds to the composition of factory mattes, the presence of zinc and iron sulfides in it deteriorates its quality. It should be expected that with further conversion of such mattes to blister copper, the costs of the process will increase significantly.

The obtained results indicate that it is not possible to obtain high-quality copper matte in one step of blowing the melt with natural gas. The fact is fully consistent with the thermodynamic laws of the physical and chemical processes mentioned above: when blowing the melt with natural gas, the thermodynamic probability of the reduction of lead compounds (sulfates, sulfides, oxides) with natural gas with the formation of rough lead is significantly higher than the reduction of zinc and iron sulfides. While lead compounds (sulfates, oxides, sulfides) are present in the melt, zinc and iron sulfides are not reduced by natural gas. As a result, those metals are concentrated in the obtained matte, which is fully confirmed by the results of the experiments (Table 3).

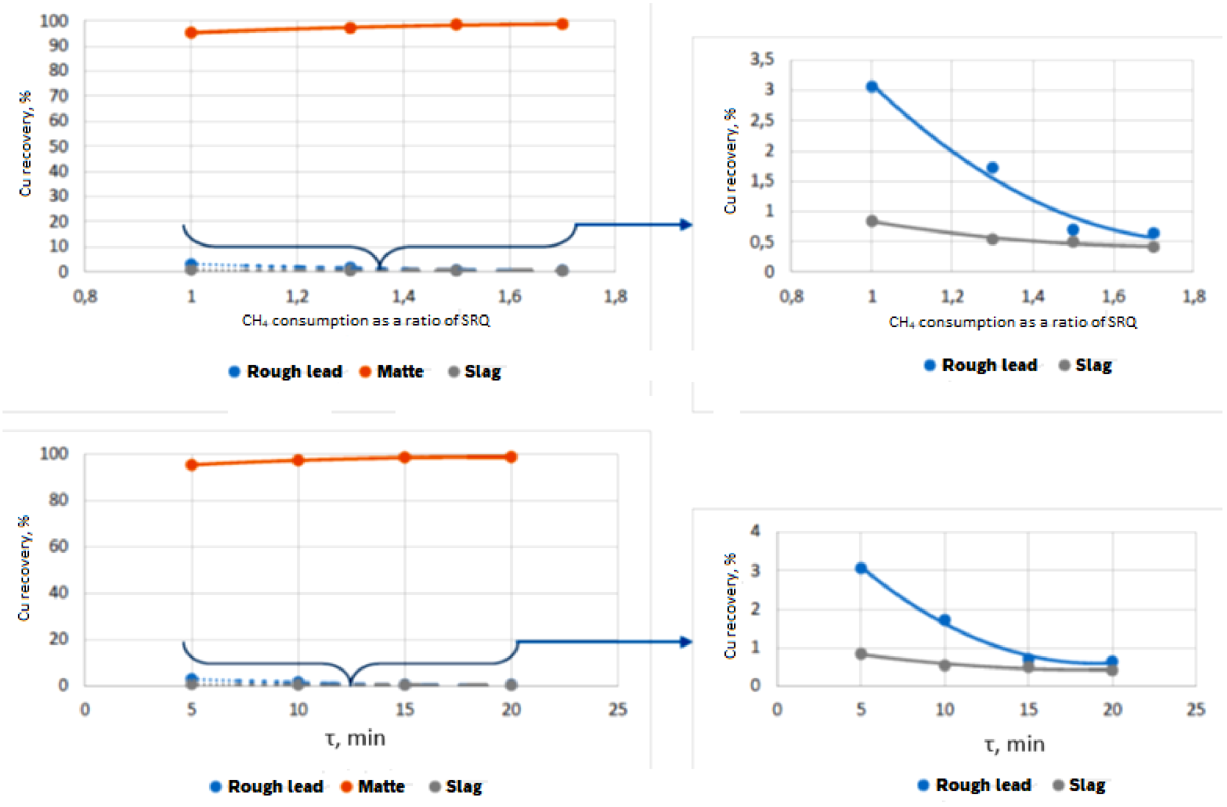

Figure 2 – Impact of natural gas consumption CH_4 (ratio of SRQ) and blowing time (τ, min) to extract copper into smelting products

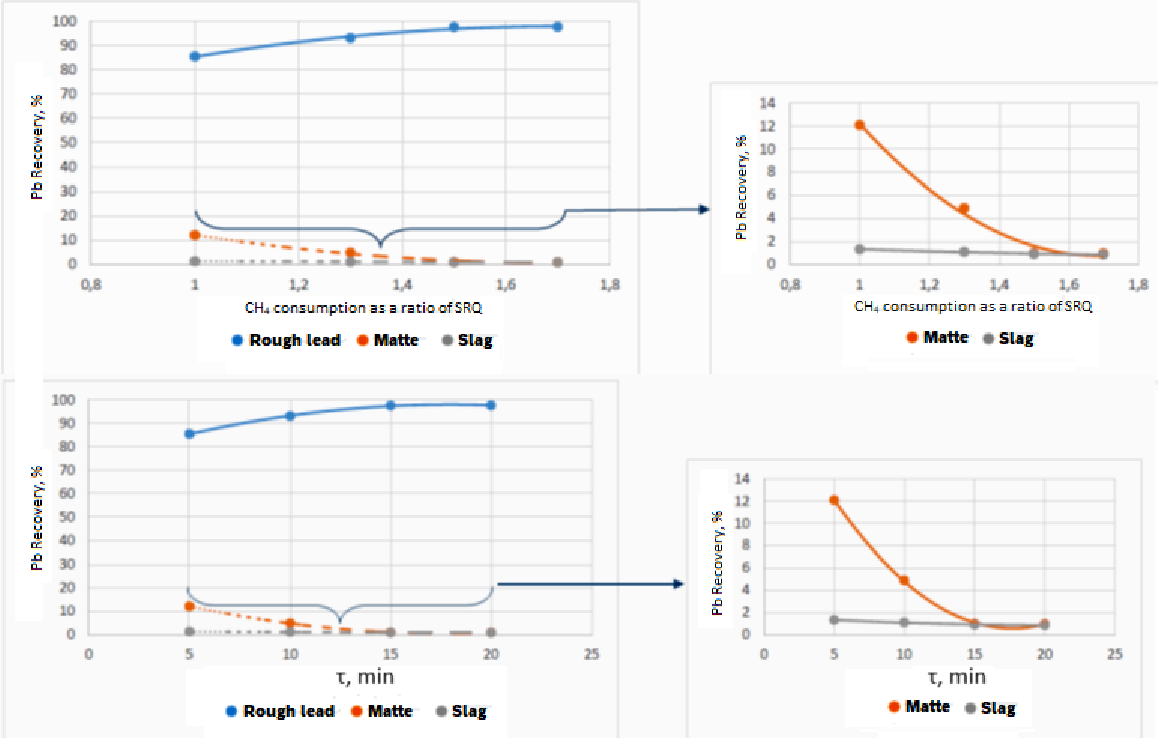

Figure 3 – Impact of natural gas consumption CH4 (ratio of SRQ) and blowing time (τ, min) to extract lead into smelting products

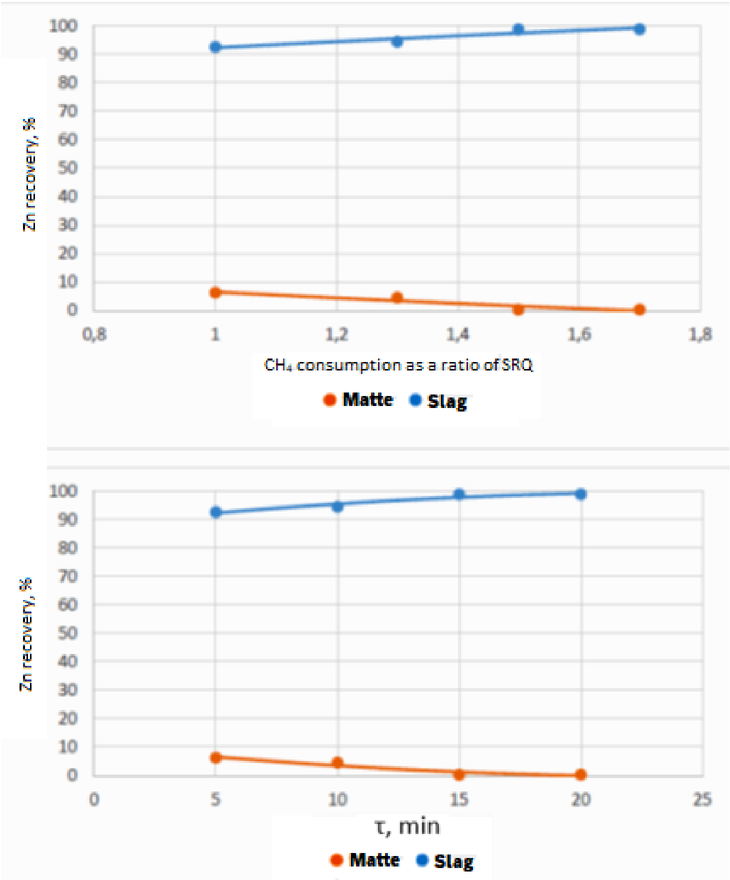

Figure 4 – Impact of natural gas consumption CH4 (ratio of SRQ) and blowing time (τ, min) to extract zinc into smelting products

Table 3 - Material balance for reduction smelting of the charge with natural gas at optimal parameters: consumption of CH_4 is 1.4 times higher than its consumption from the SRQ for the reduction of lead compounds; blowing time – 15 minutes; T = 1200 °C

Name of the products	**Qty**		**Cu**			**Pb**			**Zn**			**Fe**			**As**		
	g.	**%**	**I**	**II**	**III**	**I**	**II**	**III**	**I**	**II**	**III**	**I**	**II**	**III**	**I**	**II**	**III**
Inlet:																	
Charge (feed)	200.00	99.10	17.09	8.54	100.0	103.25	51,63	100.0	9.23	4.61	100.0	13.94	6.97	100.0	0.93	0.93	100.0
Natural gas	1.82	0.90															
Total:	**201.82**	**100.0**	**17.09**		**100.0**	**103.25**		**100.0**	**9.23**		**100.0**	**13.94**		**100.0**	**0.93**		**100.0**
Outlet:																	
Rough lead	101.78	44.23	0.12	0.12	0.70	101.29	99.52	98.10									
Matte	41.80	20.71	16.86	40,34	98.89	0.72	1.73	0.70	9,12	21.81	98.77	4.64	11,11	33.3	0.03	0.07	3.0
Slag	54.01	26.76	0.05	0.03	0.11	0.83	1.53	0.80	0.02	0.04	0.23	9.19	17.01	65.9	0.02	0.03	2.0
Dust, gases	4.23	2.10	0.05	1.21	0.30	0.41	9.77	0.40	0.092	2.18	1.0	0.11	2.64	0.8	0.88	20.89	95.0
Total:	**201.82**	**100.0**	**17.09**		**100.0**	**103.25**		**100.0**	**9.23**		**100.0**	**13.94**		**100.0**	**0.93**		**100.0**

Sb			**S**			**O**			**SiO_2**			**CaO**			**CH_4**			**Others**			**Total:**
I	**II**	**III**	**I**	**II**	**III**	**I**	**II**	**III**	**I**	**II**	**III**	**I**	**II**	**III**	**I**	**II**	**III**	**I**	**II**	**III**	
Inlet:																					
0.5	0.5	100	9.7	9.7	100	11.3	11.3	100	14.9	14.9	100	3.1	3.1	100				16.1	8.02	100	200.0
															1.8	100	100				1.8
0.5		**100**	**9.7**		**100**	**11.3**		**100**	**14.9**		**100**	**3.1**		**100**	**1.8**		**100**	**16.1**		**100**	**201.8**
Outlet:																					
0.03	0.03	6.0																0.2	0.33	2.1	101.8
0.00	0.01	1.0	9.7	23	100													0.8	1.84	4.8	41.8
0.01	0.02	3.0				11.2	20.7	99.0	14.8	27.4	99.0	3.1	5.8	99.0				14.8	27.4	92.1	54.0
0.40	9.54	90				0.11	2.7	1.0	0.1	3.54	1.0		0.7	1.0	1.8	43.0	1000	0.2	3.80	1.0	4.2
0.45		**100**	**9.7**		**100**	**11.3**		**100**	**14.9**		**100**	**3.1**		**100**	**1.8**		**100**	**16.1**		**100**	**201.8**

I – quantity, g; **II –** content, %; **III –** extraction, %.

Table 4 - Material balance of oxidative smelting of intermediate matte with oxygen at optimal parameters: oxygen consumption - 1.1 times higher than its consumption from SRQ for the oxidation of FeS and ZnS ; purge time – 10 minutes; T = 1200 °C

Name of the products	**Qty**		**Cu**			**Pb**			**Zn**			**Fe**			**As**		
	G	**%**	**I**	**II**	**III**	**I**	**II**	**III**	**I**	**II**	**III**	**I**	**II**	**III**	**I**	**II**	**III**
Inlet:																	
Matte	41.80	59.64	16.86	40.34	100.0	0.72	1.73	100.0	9.11	21.81	100.0	4.64	11.11	100.0	0.028	0.07	100.0
Air	28.29	40.36															
Total:	**70.09**	**100.0**	**16.86**		**100.0**	**0.72**		**100.0**	**9.11**		**100.0**	**4.64**		**100.0**	**0.028**		**100.0**
Outlet:																	
Matte	29.96	42.74	16.83	56.18	99.80	0.22	0.72	30.0	0.45	1.52	5.0	4.50	15.03	97.0	0.028	0.09	100.0
Slag	8.83	12.60	0.03	0.38	0.20				8.66	98.04	95.0	0.14	1.58	3.0			
Dust, gases	31.30	44.65				0.50	1.62	70.0									
Total:	**70.09**	**100.0**	**16.86**		**100.0**	**0.72**		**100.0**	**9.11**		**100.0**	**4.64**		**100.0**	**0.028**		**100.0**

Sb			S			O			N₂			Others			Total:
I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	
0.004	0.01	100.0	9.66	23,10	100.0							0.77	1.84	100.0	41.80
						5.94	21.0	100.0	22,35	79,0	100.0				28.29
0.004		**100.0**	**9.66**		**100.0**	**5.94**		**100.0**	**22,35**		**100.0**	**0.77**		**100.0**	**70.09**
0.004	0.01	100.0	7.24	24.17	75.0							0.68	2.26	88.0	29.96
															8.83
			2.41	7.71	25.0	5.94	18.98	100.0	22.35	71.40	100.0	0.09	0.30	12.0	31.30
0.004		**100.0**	**9.66**		**100.0**	**5.94**		**100.0**	**22.35**		**100.0**	**0.77**		**100.0**	**70.09**

I – quantity, g; **II –** content, %; **III –** extraction, %.

Table 5 – Summary material balance of reduction-oxidation smelting of the charge

Name products	Qty		Cu			Pb			Zn			Fe			As			Sb		
	G	%	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III
Inlet:																				
In charge	200.0	86.9	17.1	8.5	100	103.3	51.6	100	9.2	4.61	100	13.9	6.97	100	0.9	0.9	100	0.5	0.5	100
Air	28.29	12.3																		
Natural gas	1.81	0.79																		
Total:	**230.1**	**100**	**17.1**		**100**	**103.3**		**100**	**9.2**		**100**	**13.9**		**100**	**0.9**		**100**	**0.5**		**100**
Outlet:																				
Rough lead	101.8	44.2	0.12	0.1	0.7	101.3	99.5	98										0.1	0.1	6.0
Matte	29.96	13.0	16.8	56	98.5	0.22	0.72	0.2	0.46	1.52	4.94	4.50	15.0	32.3	0.1	0.1	3.0	0.00	0.0	1.0
Slag	62.62	27.2	0.09	0.1	0.5	0.61	0.97	0.6	8.68	13.8	94.0	9.33	14.8	66.9			2.0	0.01	0.0	3.0
Dust, gases	35.74	15.5	0.05	0.1	0.3	1.14	3.18	1.1	0.09	0.26	1.0	0.11	0.31	0.8	0.8	2.5	97	0.40	1.1	94.0
Total:	**230.1**	**100**	**17.1**		**100**	**103.2**		**100**	**9.23**		**100**	**13.9**		**100**	**0.9**		**100**	**0.45**		**100**

S			O			N₂			SiO2			CaO			CH₄			Others			Total:
I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	I	II	III	
Inlet:																					
9.66	9.66	100.0	11.30	11.3	65.55				14.96	14.96	100.0	3.14	3.14	100.0				16.05	8.02	100.0	200.0
			5.94	21.0	34.45	22.35	79.0	100.0													28.29
															1.82	100.0	100.0				1.82
9.66		**100.0**	**17.24**		**100.0**	**22.35**		**100.0**	**14.96**		**100.0**	**3.14**		**100.0**	**1.82**		**100.0**	**16.05**		**100.0**	**230.11**
Outlet:																					
																		0.34	0.33	2.10	101.78
7.24	24.17	75.0																0.68	2.26	4.22	29.96
			11.19	17.87	64.9				14.81	23.65	99.0	3.11	4.96	99.0				14.78	23.60	92.10	62.62
2.41	6.75	25.0	6.05	16.93	35.1	22.35	62.52	100.0	0.15	0.42	1.0	0.03	0.09	1.0	1.82	5.09	100.0	0.25	0.71	1.58	35.74
9.66		**100.0**	**17.24**		**100.0**	**22.35**		**100.0**	**14.96**		**100.0**	**3.14**		**100.0**	**1.82**		**100.0**	**16.05**		**100.0**	**230.11**

I – quantity, g; **II –** content, %; **III –** extraction, %.

Commercial, copper-rich matte is obtained in the second stage - by blowing the intermediate matte with oxygen, where the main amount of zinc and iron sulfides are oxidized to their oxides and turned into slag. In this case, the copper content in the matte increases from 40% to ~57% and zinc-rich slag is formed (Table 3).

From the results of the final material balance (Table 4) it is clear that when melting a charge using reduction-oxidation blowing, the yield of products is, % (of the total charge): rough lead - 44.5; copper matte – 13.0; slag – 27.2; dust and gases – 15.3.

Results of laboratory studies on joint smelting of lead cake with various substandard lead production materials fully confirm the provisions established in the theoretical part of the technology.

Based on the conducted research, technological regimes and optimal parameters for the joint processing of lead cake and copper-lead matte by two-stage reduction-oxidation blowing of the melt were recommended for practical application: with natural gas, then with oxygen:

– melt blowing time:

- natural gas – 15 minutes;
- oxygen – 10 min.

– gas consumption:

- CH_4 – 1.4 times, its consumption from the stoichiometric required amount (SRQ) for the reduction of lead compounds;
- oxygen – 1.1 times, its consumption from the stoichiometric required amount (SRQ) for the oxidation of zinc and iron sulfide.

– temperature – 1200 °C.

With the established optimal parameters, high technological indicators were achieved (Table 4):

– composition of rough lead, wt.%: 99.53 Pb; 0.12 Cu; 0.03 Sb.

– matte composition, wt.%: 56.2 Cu; 0.72 Pb; 1.52 Zn; 15.03 Fe; 24.17 S; 0.09 As.

– slag composition, wt.%: 14.89 Fe; 23.65 SiO2; 13.86 Zn; 0.14 Cu; 0.97 Pb.

– extraction of metals into targeted products:

- lead into rough lead – 98.6%;
- copper in matte – 98.5%;
- zinc to slag – 94.1%;
- arsenic and antimony in dust - up to 97 and 94%, respectively.

Conclusions

Based on the results of studies on the forms of metals in lead cake and substandard intermediate products of lead production, technological calculations were carried out for the layout of a charge of a new composition and laboratory experiments on its smelting under conditions of reduction-oxidation blowing. New data have been obtained on the complex selective extraction of Cu, Pb, Zn and As into the targeted smelting products.

Optimal conditions for melting the charge have been established: temperature – 1200 °C; blowing the melt with CH_4 – 15 min., oxygen – 10 min. High extraction of lead into rough lead was achieved – 98.6%; copper in matte – 98.5%; zinc to slag – 94.1%; arsenic and antimony into dust - up to 95 and 90%, respectively.

High-quality rough lead, matte and slag were obtained, which can easily be processed to produce commercial lead, copper and zinc using known technologies at minimal cost. The high copper content in the matte, more than 70%, will significantly reduce the costs of subsequent fire refining and electrolysis operations to obtain commercial copper cathodes.

Conflict of interest. On behalf of all authors, the corresponding author confirms that there is no conflict of interest.

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Шаңды шаймалаудан алынған қорғасын қоқымы негізіндегі шикіқұрамнан балқыманы тотықсыздандырып-тотықтырып үрлеу арқылы Pb, Cu, Zn бөліп алу технологиясы

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ТҮЙІНДЕМЕ

Жұмыста шаңнан мышьякты алдын ала алып тастап және оны күкірт қышқылымен шаймалағаннан кейін алынған қорғасын қоқымы негізіндегі шикіқұрамның түрі мен құрамы бойынша күрделі өңдеудің теориялық базасы мен нәтижелері келтірілген. Технологияның негізгі мақсаты – қорғасын қоқымымен бірге қорғасын өндірісінің кондициялық емес жартылай өнімдерін өңдеуге тарту және түсті металдарды тауарлық өнімдерге селективті бөліп алу: мысты – штейнге; қорғасынды – қара қорғасынға: мырышты – қожға. Шикіқұрамның құрамын таңдау олардың өндірісте шығатын көлемін ескере отырып жүзеге асырылды және мынадай құрылымда ұсынылды, %: қорғасын қоқымы – 50; мыс-қорғасынды штейн – 40; кварцты флюс – 10. Белгіленген балқыту өнімдеріне мыс, қорғасын, мырыш және мышьяк жоғары кешенді алынатын ең жақсы нәтижелерге қорғасын қосылыстарының металл қорғасынға дейін тотықсыздануын қамтамасыз ететін табиғи газды стехиометриялық қажетті мөлшерден (СНК) тұтынудан 1,4 есе жоғары тұтыну арқылы қол жеткізілетіні анықталды. Балқыманы табиғи газбен үрлеудің оңтайлы уақыты - 15 минут. Бірінші кезеңнен кейін алынған аралық штейнді үрлеу кезіндегі оттегінің оңтайлы шығыны мырыш пен темір сульфидінің тотығуы үшін оның стехиометриялық қажетті мөлшерінен (СНК) 1,1 есе жоғары болды, олар одан әрі оксидтер түрінде қожға көшеді. Штейнді үрлеу ұзақтығы – 10 минут. Белгіленген оңтайлы параметрлерде технологияның жоғары технологиялық көрсеткіштеріне қол жеткізілді: қорғасынның қара қорғасынға бөлінуі – 98,6%; мыстың штейнге – 98,5%; мырыштың қожға – 94,1%.

Түйін сөздер: қорғасын қоқымы, шикіқұрам, жартылай өнімдер, тотықсыздандырып үрлеу, тотықтырып үрлеу, мыс, қорғасын, мырыш, бөліп алу.

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Технология извлечения Pb, Cu, Zn из шихты на основе свинцового кека от выщелачивания пыли путем восстановительно-окислительной продувки расплава

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АННОТАЦИЯ

В работе представлены теоретическая база и результаты переработки сложного по типу и составу шихты, составленной на основе свинцового кека, полученного после предварительного удаления из пыли мышьяка и последующего ее выщелачивания серной кислотой. Основная цель технологии – вовлечение на переработку некондиционных полупродуктов свинцового производства совместно со свинцовым кеком и селективное извлечение цветных металлов в товарные продукты: меди – в штейн; свинца – в черновой свинец: цинка – в шлак. Выбор компоновки шихты осуществлен с учетом получаемых их объемов на производстве и представлена следующей структурой, %: свинцовый кек – 50;

медно-свинцовый штейн – 40; кварцевый флюс – 10. Установлено, что наилучшие результаты, обеспечивающие высокое комплексное извлечение меди, свинца, цинка и мышьяка в целевые продукты плавки достигаются при расходе природного газа в 1,4 раза превышающем его расход от стехиометрического необходимого его количества (СНК) для восстановления соединений свинца до металлического свинца. Оптимальное время продувки расплава природным газом – 15 минут. Оптимальный расход кислорода при продувке промежуточного штейна, полученного после первой стадии, в 1,1 раза превышал его стехиометрическое необходимое количество (СНК) для окисления сульфида цинка и железа с дальнейшим переводом их в виде оксидов в шлак. Продолжительность продувки штейна – 10 минут. При установленных оптимальных параметрах достигнуты высокие технологические показатели технологии: извлечение свинца в черновой свинец – 98,6%; меди в штейн – 98,5%; цинка в шлак – 94,1%.

Ключевые слова: свинцовый кек, шихта, полупродукты, восстановительная продувка, окислительная продувка, медь, свинец, цинк, извлечение.

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