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Improving the quality of converting products by the joint smelting of high-sulfur copper concentrate with copper-lead matte

Argyn A.A., *Zoldasbay E.E., Dosmukhamedov N.K.

Satbayev University, Almaty, Kazakhstan

** Corresponding author email: zhte@mail.ru*

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ABSTRACT

The paper presents the results of studies on the processing of copper-lead mattes with high-sulfur copper concentrate in a converter. The effect of high-sulfur copper concentrate on the quality of converting products is shown. Based on the obtained results, a comparative analysis of the technological indicators of the 1st period of converting copper-lead mattes according to the existing technology and in the joint processing of copper-lead mattes with copper concentrate was carried out. It has been established that when the high-sulfur copper concentrate is used as a sulfidizing agent, excess sulfur released as a result of the dissociation of higher sulfides is completely absorbed by the slag melt. It is shown that elemental sulfur, interacting with oxides of non-ferrous metals and impurities, has a significant effect on the equilibrium distribution of metals between the converting products and their extraction into targeted products. The influence of sulfur on the destruction of magnetite in the process of converting was also established. New data on the distribution of non-ferrous and associated metal impurities (As, Sb, etc.) were obtained during the conversion of copper-lead mattes with high-sulfur copper concentrate. High values were established for the extraction of non-ferrous metals and impurities into targeted products: copper into matte - up to 98%, lead, zinc, arsenic, and antimony into dust - 87%, 91%, 84%, and 38%, respectively. The possibility of a significant improvement in technical and economic indicators, the quality of converting products, and environmental protection during the joint smelting of high-sulfur copper concentrate with a copper-lead matte are shown. The developed technology for converting copper-lead mattes, with high-sulfur copper concentrate, is easily integrated into the plant structure of Kazzinc LLP without any special material costs.

Keywords: copper-lead matte, sulfide copper concentrate, converting, converter slag, white matte, sulfiding, distribution.

Information about authors:

Argyn Aidar Abdilmalikuly	*Ph.D., Satbayev University, 050013, Almaty, 22 Satbayev St., Kazakhstan. E-mail: aidarargyn@gmail.com*
Zoldasbay Erzhan Esenbaiuly	*Ph.D., Satbayev University, 050013, Almaty, 22 Satbayev St., Kazakhstan. E-mail: zhte@mail.ru*
Dosmukhamedov Nurlan Kalievich	*Candidate of Technical Sciences, Professor, Satbayev University, 050013, Almaty, 22 Satbayev St., Kazakhstan. E-mail: nurdos@bk.ru*

Introduction

In the scientific literature ,there is a sufficient number of works devoted to the improvement of the converting process, including the solution to the issue of converter slag processing [[1], [2]]. The results of extensive studies on the processing of copper concentrates in converters [[3], [4], [5], [6], [7], [8], [9], [10], [11]] have opened up wide opportunities for using the converter as a smelting unit for solid materials. This especially refers to the first period of converting copper matte, which ultimately leads to a significant reduction in total costs and an increase in the complexity of the use of raw materials. However, their introduction into production remains without due attention. Most plants continue to use well-established standard methods for processing them according to existing schemes.

The existing positive practical experience of direct processing of copper concentrates in converters shows that there are some ways that can be found to improve the quality of the resulting smelting products in the course of the converting technology itself. Moreover, such an approach, in our opinion, seems to be one of the most promising areas for improving the processing of copper-containing raw materials, both from a technological and economic point of view and from an environmental point of view. This is due to the fact that the involvement in the processing of primary raw materials with a complex chemical and mineralogical composition, the technological indicators of existing processes, and the quality of the obtained products of melts undergo significant changes in the direction of deterioration. Regarding the converting process, there is a strong complication of the compositions of converter slags, and a decrease in the quality of the converting products, which indicates the need to find rational methods for converting.

The direct transfer of the experience of foreign plants, both in terms of the design of aggregates and process modes, in relation to sulphide concentrates of Kazakhstan is complicated, due to their polymetallic nature, low copper content, and higher contents of impurities - Pb, As, Sb. Nevertheless, the search and development of technologies for the complex processing of difficult-to-recycle polymetallic copper-zinc, copper-lead-zinc concentrates in converters could be a significant reserve for metallurgical enterprises in terms of additional extraction of Cu, Au, Ag, and related - Zn, Pb, etc. metals into targeted commercial products.

It should be noted that in the known technologies of direct processing of copper concentrates in converters, the main goal was to use the converter exclusively as a smelting unit and obtain an additional amount of copper by smelting the concentrate. Despite the positive results achieved, the developed technologies also had a number of serious drawbacks in terms of loading a finely dispersed concentrate into the converter. In particular, the loading of the concentrate into the converter required careful special preparation (drying, grinding, using a complex loading installation). When loading the concentrate into the converter, it was not possible to ensure a low quantity of dust losses [12]. The method of loading finely dispersed materials into the converter, developed by the authors of [13], seems to be highly effective, which ensures the loading of the material into the converter with a minimum (no more than 0.5% of the weight of the loaded material) of its dust removal as a loss. The solution to the issue of loading finely dispersed material into the converter, which is important for practice, allowed the authors to simplify the technology of direct processing of concentrates in converters and improve the technological parameters of the converting process.

Due to the minimum dust losses, the injection unit developed in [13] was used to load high-sulfur copper concentrate into the converter.

It seems promising to simultaneously use high-sulfur copper concentrate not only as an additional source of copper production but also as a sulfidizing agent, which improves the quality of the resulting converting products. Detailed studies of industrial tests for the processing of copper and copper-zinc high-sulfur concentrates with copper mattes showed the fundamental possibility of improving not only the technological indicators of converting but also a significant increase in the quality of the obtained products [14].

The application of the developed technologies has particular relevance for the conditions of converting copper-lead mattes of Kazzinc LLP, where mattes are characterized by an increased content of harmful metal impurities: up to 25% lead, up to 4% arsenic, and up to 1.0% antimony. As a result of converting such mattes, poor-quality blister copper (96-98% Cu) is obtained. At the same time, recycled converter slags contain up to 35% lead, ~3% copper, and up to 1.5% total arsenic and antimony. Despite these shortcomings and low technological indicators of the process, due to the lack of an alternative method for processing copper-lead mattes, converting remains the main stage in the production of blister copper in the general technological flowsheet of lead production.

The purpose of this work is to study the behavior of non-ferrous and associated metals during the joint processing of high-sulfur copper concentrate with copper-lead matte in converters and to evaluate the effect of the concentrate on improving the quality of converter slag.

Experimental methodology

The solution of the set tasks was carried out on the basis of mathematical models [[15], [16], [17], [18], [19]], which describe with sufficient accuracy the calculation of the equilibrium yield of smelting products and the composition of chemically reacting systems. The methodology for determining the optimal technological parameters for converting copper-lead mattes is based on the analysis of the obtained results and plant practice data. An industrial array was accepted for analysis, including the number of material flows and the composition of the obtained products - mattes, slags, dust, and blister copper, the results of the forms of metals in the converting products, and the thermodynamic analysis of the behavior of non-ferrous and related metals.

The primary analysis of plant practice data was reduced to clarifying the factors influencing the distribution of metals between converting products.

The second stage included the determination of the optimal technological regimes and process parameters (matte composition, blast consumption, quartz consumption, blowing time) that affect the technological parameters of the process.

Technological indicators of converting were established using a specially developed program, which is based on an iterative algorithm for modeling the converting process. The developed program describes with sufficiently high accuracy the existing process of converting copper-lead mattes and makes it possible to predict the optimal parameters and technological modes of the process for the condition of joint melting of matte with high-sulfur copper concentrate.

The total array of data subjected to mathematical processing amounted to 65 observations. The results of metallurgical calculations of the process of converting copper-lead mattes, obtained for the given input parameters of plant practice, showed a good agreement in terms of the quantity and composition of the obtained products, and the distribution of metals between the converting products. This testifies to the high reliability of the research results obtained in the work, as well as the developed program, which establishes, on its basis, the physicochemical processes that occur during the converting of copper-lead mattes with high-sulfur concentrate, and outlines ways to improve the technological parameters of the process.

Results and discussion

As a sulfidizing agent, a high-sulfur copper concentrate of the Zyryanovsky deposit was used, composition %: 24.51 Cu; 2.5 Pb; 3.4 Zn; 28.6 Fe; 0.1 As; 0.2 Sb; 35 S; 3.6 SiO_2. 30% of the weight of the resulting converter slag was taken as the optimal concentrate consumption [20]. The concentrate was loaded 10 min before the converter slag was discharged.

In the process of research, two modes of the process of converting copper-lead mattes were studied: the first is converting according to the existing technology and the second is the converting of copper-lead mattes with high-sulfur copper concentrate.

To evaluate the behavior of Cu, Pb, Zn, As, and Sb during the converting process, the following plant data were analyzed: the temperatures of converter slags at each unloading from the converter, one-time measurements of the melt temperature during each loading of a new portion of the matte and its blowing.

A comparative analysis of technological indicators of 2 converting modes is given in Table 1.

Table 1 - Results of technological indicators of converting copper-lead mattes: 1 – the mode according to the existing technology; 2 - converting copper-lead mattes with high sulfur copper concentrate

1st mode - existing technology

# of discharge	Products	Chemical compositions of products, %								Air, m^3	Flux (SiO_2 85%), t	Blowing time, min
		Cu	Pb	Zn	As	Sb	Fe	S	SiO_2			
Initial products	Initial matte	35.50	26.00	1.42	2.81	0.71	15.15	15.09	-	-	-	-
	Converter slag	3.83	33.5	4.54	2.8	0.95	12.7	-	15.7			
Discharge #1	Matte	49.59	22.94	0.61	3.34	0.97	6.71	13.40	-	6946.66	1.58	60
	Slag	4.07	26.74	2.34	1.04	0.13	26.74		28.36			
	Dust	0.83	56.35	4.22	6.13	0.03	0.98	6.36	1.20			
Discharge #2	Matte	54.37	22.09	0.16	3.61	1.03	3.99	12.74	-	3327.21	0.76	30
	Slag	3.91	23.17	2.72	0.77	0.16	27.10	-	23.70			
	Dust	0.63	48.99	8.58	4.30	0.47	1.52	2.50	1.90			
Discharge #3	Matte	55.71	21.04	0.18	3.70	1.04	3.43	13.11		1390.69	0.45	12
	Slag	4.34	24.59	1.51	0.78	0.16	22.88		25.11			
	Dust	0.41	53.79	3.31	1.76	0.53	0.96	2.23	1.37			
Discharge #4	White matte	56.82	20.46	0.22	3.62	1.05	2.95	13.59		718.41	0.25	10
	Slag	11.94	18.42	1.27	0.77	0.10	23.40		23.64			
	Dust	1.07	25.24	0.02	4.37	0.67	1.52	2.26	0.82			

2nd mode - new technology: converting copper-lead mattes with high-sulfur copper concentrate

# of discharge	Products	Chemical compositions of products, %								Air, m^3	Flux (SiO_2 85%), t	Blowing time, min
		Cu	Pb	Zn	As	Sb	Fe	S	SiO_2			
Initial products	Initial matte	35.50	26.00	1.42	2.81	0.71	15.15	15.09	-	-	-	-
	Converter slag	3.83	33.5	4.54	2.8	0.95	12.7	-	15.7			
	Copper concentrate	24.51	2.5	3.4	0.1	0.2	28.6	35	3.6			
Discharge #1	Matte	52.43	19.23	0.50	2.31	0.78	7.49	14.00		5262.62	1.03	50
	Slag	1.09	1.26	0.21	0.07	0.10	48.13		26.88			
	Dust	0.59	63.02	9.03	5.76	0.70	1.30	5.85	0.46			
Discharge #2	Matte	58.78	15.37	0.30	1.53	0.76	5.28	15.05		2234.16	0.44	25
	Slag	0.58	1.08	0.33	0.06	0.07	47.37		28.07			
	Dust	0.62	55.82	9.69	8.12	0.73	2.90	8.82	1.14			
Discharge #3	Matte	64.86	8.28	0.28	0.74	0.70	5.10	17.33		818.56	0.16	17
	Slag	1.47	0.67	0.35	0.05	0.06	47.16		26.06			
	Dust	1.22	64.71	7.31	6.94	0.87	2.84	8.82	1.01			
Discharge #4	White matte	70.57	4.01	0.22	0.56	0.65	3.54	18.16		879.69	0.17	19
	Slag	0.39	0.15	0.23	0.03	0.04	48.06		27.32			
	Dust	0.79	58.82	10.80	2.80	1.03	3.86	11.31	1.81			

It has been established that under the conditions of the existing practice of converting, there is a large overconsumption of quartz (more than 1.5 times), from its optimal consumption (Table 1). An excess of quartz requires additional heat consumption for its melting and further transfer to slag, which is covered by an increase in blast consumption. This significantly reduces the quality (compositions) of the resulting products (Table 1), which leads to a negative redistribution of non-ferrous and related metals among the conversion products.

An important change in technological parameters is observed in the conditions of converting copper-lead mattes with high-sulfur copper concentrate.

When loading sulfide copper concentrate into the converter, it is necessary to take into account the additional amount of iron introduced with the concentrate in order to make a calculated correction to the flow rate of the loaded quartz flux. On the basis of statistical and information processing and multivariate analysis of the results of studies on the depletion of converter slags with concentrate and industrial data on the composition of the conversion products (matte, slag), an equation was constructed that allows determining the required flux consumption (Gf). Equation depends on the composition of the matte, slag, and consumption of the concentrate loaded into the converter. As a result of mathematical processing, the following equation was obtained:

$$G_f = -2{,}411 - 0{,}2719[Cu] + 0{,}481[Fe] + 0{,}1661[G_c] + 0{,}7453(SiO2) + 0{,}0869(Fe),\ r = 0{,}87 \qquad (1)$$

where:
[Cu], [Fe] – the content of copper, iron in the original matte, % (wt.);
(SiO2), (Fe) – the content of silica, iron in the converter slag, % (wt.);
[G_c] – concentrate consumption, % of matte weight.

From the analysis of equation (1) it follows that the flux consumption is largely correlated with the iron content in the matte and the SiO2 content in the converter slag. Concentrate consumption has a less significant effect on flux consumption.

The total consumption of quartz flux according to the existing technology is 3.04 tons per ton of matte and is 1.6 times higher than its consumption (1.87 tons per ton of matte). When converting mattes with high-sulfur copper concentrate, the total consumption of quartz flux increases slightly from its optimal level - 1.97 tons per ton of matte.

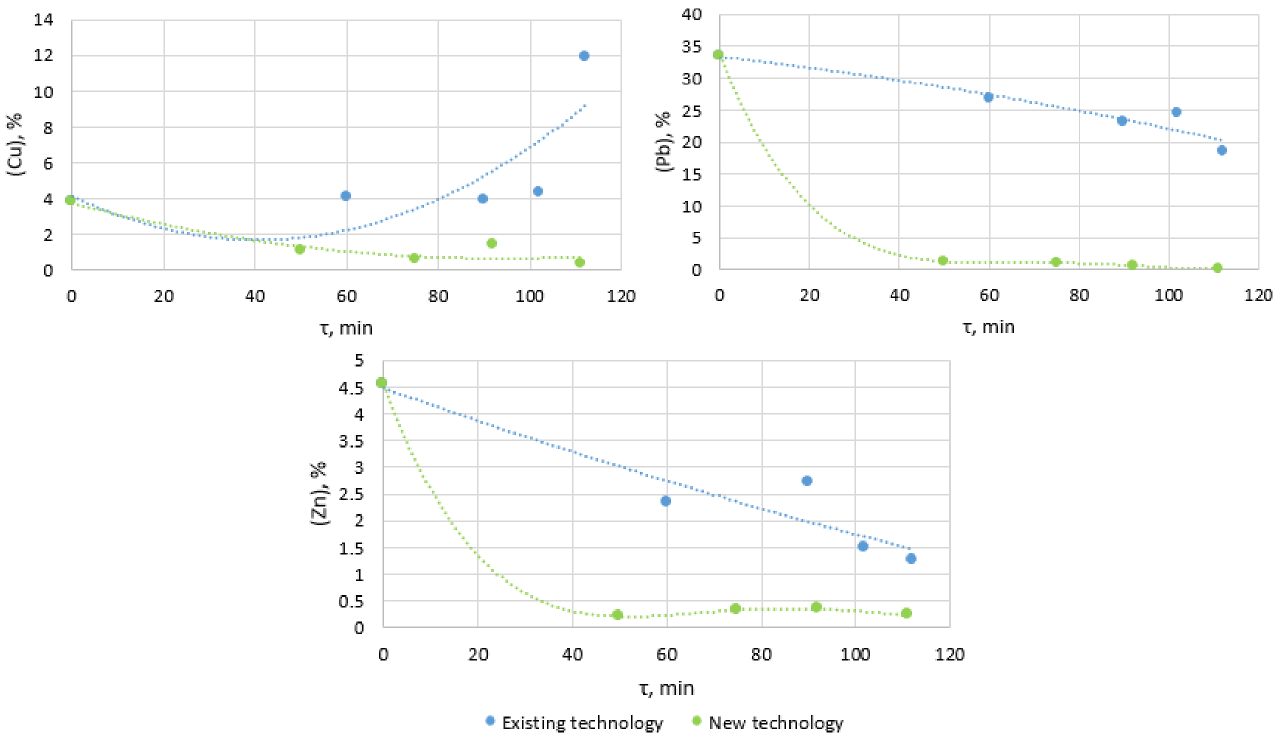


Figure 1 - Dynamics of changes in the content of Cu, Pb, and Zn in the converter slag on the duration of the process

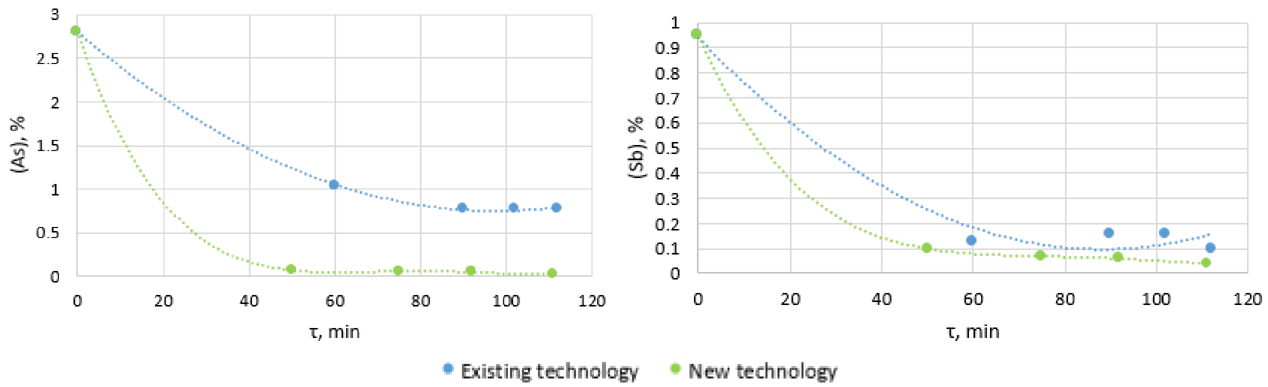


Figure 2 - Dynamics of changes in the content of As and Sb in the converter slag on the duration of the process

The results of a comparative analysis of the dynamics of changes in the content of Cu, Pb, Zn, As, and Sb in converter slags depending on the duration of the process according to the existing technology and during direct smelting of high-sulfur copper concentrate with a matte are shown in Figs. 1 and 2.

For the existing technology, with the exception of copper, the content of impurity metals - Pb, Zn, As, and Sb, in the 1st converting period, depending on the duration of the process, decreases. The increase in copper content seems quite natural. The accumulation of sulfide mass in the converter with an increase in the duration of the 1st period provides for an increase in the copper content in it; therefore, according to the general dependence ***(Cu) – ƒ [Cu]*** established for oxidative processes [21], the copper content in matte will grow.

The observed decrease in the content of Pb, Zn, As and Sb in the converter slag is consistent with the theory of the converting process. In this case, the completeness of their sublimation into dust depends on the consumption of quartz. Figures 1, 2, and Table 1 show that the contents of Cu, Pb, Zn, As, and Sb in converter slags remain quite high. This has a significant impact on the overall throughput of the process and the quality of the blister copper.

During converting copper-lead mattes with high-sulfur copper concentrate, a sharp decrease in metal impurities in converter slags is observed depending on the blowing time: Pb - 6.5 times, Zn - 6 times, As - 7.5 times. For antimony, although a decrease in

Table 2 - Comparative analysis of the compositions of the products of converting copper-lead mattes of the 1st period

Products	Chemical composition, wt. %							
	Cu	Pb	Zn	Fe	As	Sb	S	SiO_2
White matte	56.39 70.55	20.98 4.03	0.20 0.22	3.54 2.91	3.59 0.56	1.04 0.65	13.55 18.16	-
Converter slag	7.94 1.19	22.25 0.72	2.07 0.23	24.71 47.85	2.40 0.27	0.61 0.2	-	22.28 26.8
Converter dust	1.13 0.81	55.73 58.89	0.85 8.7	2.62 0.36	5.25 5.33	0.80 1.34	5.92 9.98	1.11 0.32

The numerator is existing technology. **The denominator** is a new technology.

slags is observed (~ 2 times), it is not significant, which is associated with the complex form of its presence in slags. The copper content in converter slags decreases by about 3 times, which is explained by a sharp decrease in the magnetite content in slags. As shown by the results of mineralogical studies of converter slag samples, the magnetite content in them is reduced from 18% according to the existing technology to ~3%.

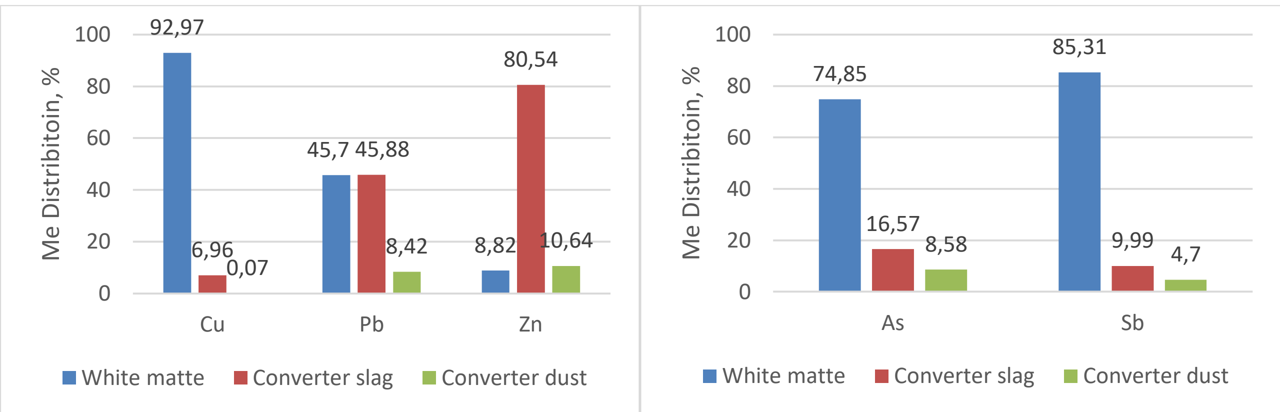
The obtained results fully confirm the conclusions made on the basis of thermodynamic calculations [20] that under the conditions of matte converting, together with copper concentrate, a sufficiently deep "washing" of the slag melt with drops of copper concentrate sulfides occurs with further coalescing of finely dispersed matte droplets and their precipitation into the bottom phase. The active behavior of the sublimation of impurities - Pb, Zn, As, and Sb into dust is ensured due to the high rates of the interaction of their oxides with the dissociation products of higher sulfides and complete sulfidation of the converter slag due to elemental sulfur and iron sulfide introduced with the concentrate.

The results shown in Figures 1 and 2 show that direct processing of the concentrate in converters significantly increases the quality of the obtained converter slag. At the same time, the possibility of reducing the total duration of the 1st conversion period, in comparison with the existing technology, by about 20 minutes is visible.

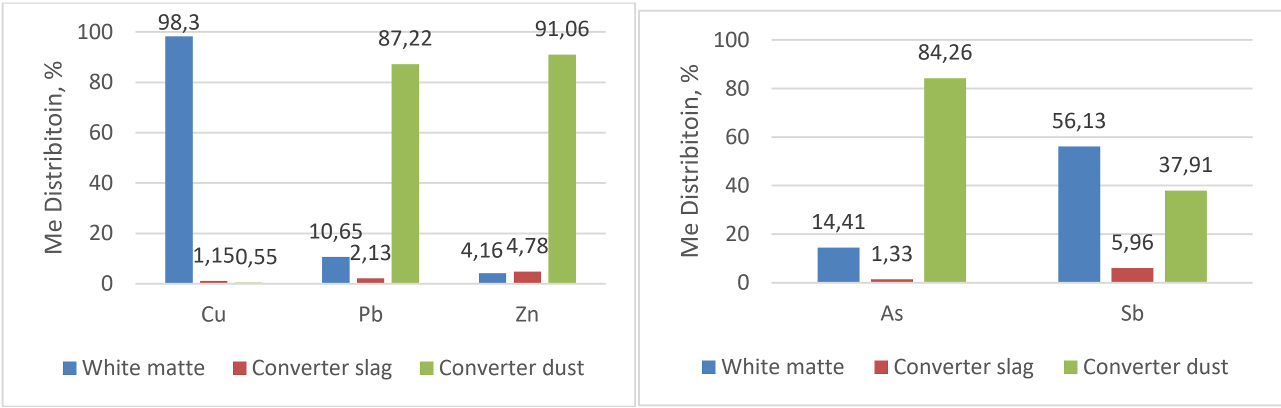
A comparative analysis of the results on the composition of products obtained under the conditions of the 1st period of converting copper-lead mattes according to the existing technology and during the joint processing of high-sulfur copper concentrate together with the matte is shown in Table 2.

It is easy to see a significant improvement in the quality of the resulting converter slag. The copper content in them is reduced by more than 6 times. A sharp decrease in lead from 22% to 0.72% was achieved, which indicates its high sublimation into dust. The content of zinc and arsenic in the slag is reduced by 10 times, and the content of antimony in them is 3 times less.

As evidenced by the data of a comparative analysis of the distribution of metals between the products of the 1st conversion period (Fig. 3), when the copper concentrate is added, high rates of distribution of metals into the targeted products are achieved. It can be argued that direct processing of high-sulfur copper concentrate with matte in a converter under conditions of vigorous bubbling of the melt achieves complete assimilation of sulfur by the melt and a significant increase in the quality of the products obtained compared to the existing technology.



A)



B)

Figure 3 - Distribution of non-ferrous metals and impurities between converting products: according to the existing technology (A); new technology (B).

Conclusions

Based on the study of the behavior of non-ferrous and related metals (Pb, Zn, As, Sb), the principal possibility of improving the quality of converting products during direct processing of high-sulfur copper concentrate with copper-lead matte in converters are shown.

A comparative assessment of the technological parameters of the existing technology for converting copper-lead mattes and the new technology for converting copper-lead mattes with high-sulfur copper concentrate was carried out. It has been established that during the direct processing of copper concentrate in the converter, a high recovery of copper into blister copper (up to 98.3%) is achieved by reducing its losses with converter slag.

The use of concentrate as a sulfiding agent provides high values for the distribution of impurity metals - Pb, Zn, As, and Sb into dust: 87.22; 91.06; 84.26, and 37.91%, respectively. This leads to their removal from the "smelting-converting" process chain and significantly improves the quality of the obtained products.

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

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Жоғары күкіртті мыс концентратын мыс-қорғасын штейнімен бірге балқыту арқылы конвертерлеу өнімдерінің сапасын арттыру

Арғын А.Ә., Жолдасбай Е.Е., Досмұхамедов Н.Қ.

Сәтбаев университеті, Алматы, Қазақстан

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ТҮЙІНДЕМЕ
Жұмыста конвертерде жоғары күкіртті мыс концентратымен бірге мыс-қорғасын штейндерін қайта өңдеу бойынша зерттеулердің нәтижелері келтірілген. Жоғары күкіртті мыс концентратының конвертер өнімдерінің сапасына әсері көрсетілген. Алынған нәтижелер негізінде мыс-қорғасын штейндерін қолданыстағы технология бойынша және мыс-қорғасын штейндерін мыс концентратымен бірлеге өңдеу кезінде конвертерлеудің 1-ші кезеңінің технологиялық көрсеткіштеріне салыстырмалы талдау жүргізілді. Жоғары күкіртті мыс концентратын сульфидизатор ретінде пайдаланған кезде жоғары сульфидтердің диссоциациялануы нәтижесінде бөлінетін артық күкірт шлак балқымасына толық сіңетіні анықталды. Түсті металл оксидтерімен және қоспалармен әрекеттесетін күкірт металдардың конвертер өнімдері арасында тепе-тең бөлініп таралуына және олардың мақсатты өнімдерге бөлініп алуына айтарлықтай әсер ететіні көрсетілген. Сондай-ақ, күкірттің конвертерлеу процесінде магнетиттің бүлінуіне әсері анықталды. Мыс-қорғасын штейндерін жоғары

күкіртті мыс концентратымен бірге конвертерлеу кезінде түсті және ілеспе қоспа-металдардың (As, Sb және т.б.) бөлініп таралуы бойынша жаңа деректер алынды. Түсті металдар мен қоспалардың мақсатты өнімдерге бөліп алу бойынша жоғары мәндер анықталды: мыстың штейнге өтуі –98% – ға дейін, қорғасын, мырыш, мышьяк және сурьманың шаңға өтуі тиісінше 87%, 91%, 84% және 38% болады. Мыс-қорғасын штейнімен бірге жоғары күкіртті мыс концентратын бірге балқыту кезінде техникалық-экономикалық көрсеткіштерді, конвертерлеу өнімдерінің сапасын және қоршаған ортаны қорғауды айтарлықтай жақсарту мүмкіндігі көрсетілген. Мыс-қорғасын штейндерін жоғары күкіртті мыс концентратымен бірге конвертрлеу технологиясы "Қазцинк" ЖШС зауыттық құрылымына материалдық шығындарсыз оңай интеграцияланады.

Түйін сөздер: мыс-қорғасын штейні, сульфидті мыс концентраты, конвертерлеу, конвертерлі шлак, ақ матт, сульфидтеу, бөлініп таралу.

Авторлар туралы ақпарат:

Арғын Айдар Әбділмәлікұлы — *PhD, Satbayev University, 050013, Алматы, Сатпаев көш. 22, Казақстан. E-mail: aidarargyn@gmail.com*

Жолдасбай Ержан Есенбайұлы — *PhD, Satbayev University, 050013, Алматы, Сатпаев көш. 22, Казақстан. E-mail: zhte@mail.ru*

Досмухамедов Нурлан Калиевич — *Т.ғ.к., профессор, Satbayev University, 050013, Алматы, Сатпаев көш. 22, Казақстан. E-mail: nurdos@bk.ru*

Повышение качества продуктов конвертирования путем совместной плавки высокосернистого медного концентрата с медно-свинцовым штейном

Аргын А.А., Жолдасбай Е.Е., Досмухамедов Н.К.

Satbayev University, Алматы, Казахстан

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АННОТАЦИЯ

В работе приведены результаты исследований по переработке медно-свинцовых штейнов совместно с высокосернистым медным концентратом в конвертере. Показано влияние высокосернистого медного концентрата на качество продуктов конвертирования. На основании полученных результатов проведен сравнительный анализ технологических показателей 1-го периода конвертирования медно-свинцовых штейнов по существующей технологии и при совместной переработке медно-свинцовых штейнов с медным концентратом. Установлено, что при использовании высокосернистого медного концентрата в качестве сульфидизатора, выделяемая в результате диссоциации высших сульфидов избыточная сера полностью усваивается шлаковым расплавом. Показано, что элементарная сера, вступая во взаимодействие с оксидами цветных металлов и примесей, оказывает существенное влияние на равновесное распределение металлов между продуктами конвертирования и их извлечению в целевые продукты. Установлена также влияние серы на разрушение магнетита в процессе конвертирования. Получены новые данные по распределению цветных и сопутствующих металлов-примесей (As, Sb и др.) при конвертировании медно-свинцовых штейнов совместно с высокосернистым медным концентратом. Установлены высокие значения по извлечению цветных металлов и примесей в целевые продукты: меди в штейн – до 98%, свинца, цинка, мышьяка и сурьмы в пыль – 87%, 91%, 84% и 38 %, соответственно. Показана возможность существенного улучшения технико-экономических показателей, качества продуктов конвертирования и охраны окружающей среды при совместной плавке высокосернистого медного концентрата совместно с медно-свинцовым штейном. Разработанная технология конвертирования медно-свинцовых штейнов совместно с высокосернистым медным концентратом легко интегрируется в заводскую структуру ТОО «Казцинк» без особых материальных затрат.

Ключевые слова: медно-свинцовый штейн, сульфидный медный концентрат, конвертирование, конвертерный шлак, белый матт, сульфидирование, распределение.

Информация об авторах:

Аргын Айдар Абдилмаликулы — *PhD. Satbayev University, 050013, Алматы, ул. Сатпаева 22, Казахстан. E-mail: aidarargyn@gmail.com*

Жолдасбай Ержан Есенбайулы — *PhD, Satbayev University, 050013, Алматы, ул. Сатпаева 22, Казахстан. E-mail: zhte@mail.ru*

Досмухамедов Нурлан Калиевич — *К.т.н., Профессор. Satbayev University, 050013, Алматы, ул. Сатпаева 22, Казахстан. E-mail: nurdos@bk.ru*

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