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Earth sciences

Depletion of converter slags to waste in the Vanyukov furnace during pyrometallurgical copper production at JSC Almalyk MMC

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<p>Received: November 6, 2023 Peer-reviewed: December 4, 2023 Accepted: January 4, 2024</p>	<p>ABSTRACT</p> <p>The article shows the possibility of involving man-made formations in the pyrometallurgical production of copper in the form of slag and clinker-zinc production for the purpose of comprehensive extraction of non-ferrous and precious metals from them at Almalyk MMC JSC. Clinker, a technogenic waste from zinc production, contains a significant amount of reducing elements in the form of metallic iron and carbon, as well as gold in the amount of 2.3 g/t and silver 250 g/t. In research, clinker works as a reducer of magnetite contained in the converter slag during its depletion and in the process of depletion (reduction) of the converter slag, noble metals are extracted into matte, and then into blister copper up to 95-98%. Converter slags from copper production of Almalyk MMC JSC contain 2.0-3.5% copper, and they, as a circulating product, are depleted in a reverberatory furnace with copper extraction of 75%. To increase the yield of copper from converter slag in Vanyukov furnaces, it is necessary to first deplete the converter slag in reduction processes and then transfer it for processing. It was found that using clinker, a technogenic waste from zinc production with a particle size of +5 - -10 mm, the recovery of converter slag in a converter from magnetite to wustite using the developed technology in 10-15 minutes exceeded more than 50.0% (the amount of magnetite decreased from 21.9 % to 9.8%). As a result of processing recovered converter slags in the Vanyukov furnace, it was possible to reduce the copper content in converter slags of copper production from 2.2-3.5% to 0.58-0.72% in waste slag. To increase the yield of copper from converter slag in the reverberatory and Vanyukov furnaces, it is necessary to first deplete the converter slag in reduction processes and then transfer it for processing.</p> <p>Keywords: copper, slag, converter slag, depletion, magnetite, extraction, clinker, concentrate.</p>
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Introduction

As is known, when choosing a method for processing copper sulfide concentrate, autogenous furnaces began to be chosen. The advantage of autogenous smelting processes is that it obtains sufficient heat for melting and physical and chemical processes, slag and matte formation in the furnace, due to the oxidation of metal sulfides, it is possible to work without the consumption of external fuel, all the necessary heat for metallurgical smelting is provided exclusively through exothermic reactions in such processes as: "Outokumpu", "JMCO", "Ausmelt", "Isasmelt", CFP, smelting in Vanyukov furnaces, and others. Analyzing various

pyrometallurgical methods for processing sulfide copper-nickel concentrates at enterprises in many foreign countries, today the most promising technology for their processing is smelting in a two-zone Vanyukov furnace to produce copper-rich matte. At the same time, these furnaces still have additional advantages such as high productivity and the production of process gases rich in SO₂ content for the production of sulfuric acid [[1], [2]].

At Almalyk MMC JSC in 2016. The Vanyukov autogenous furnace was built and put into production; a second larger furnace and a flash smelting furnace are being designed.

It should be noted that in the world's ore deposits, reserves of high-quality copper and iron

ores are significantly reduced, as well as the emerging danger to the environment during their processing, associated with the removal of a huge amount of metallurgical technogenic waste, in the form of slag and tailings of the processing plant. An analysis of the forecast for raw materials in the mining and metallurgical industry shows that the raw material reserves of quarries and stockpiled ores do not meet the needs of the processing plant as early as 2020; a dilemma arises: either reduce production or attract resources with reduced consumer characteristics. In this regard, the possibility opens up for their effective use as secondary sources of iron, copper and noble metals. In the slags of the copper industry, the elemental proportion of iron was about 35.4%, and from the literature it is known that an iron content of at least 25% is economically feasible [[3], [4], [5], [6], [7]].

The dumps of the Almalıyк MMC JSC plant have accumulated more than 1 billion 500 million tons of technogenic waste from the processing plant, 8.5 million tons of dump slag, and they contain more than 1.4 million tons of copper. In zinc production, clinker is a technogenic waste from Waeltzing zinc cakes; today more than 450 thousand tons of it have accumulated in dumps; it contains gold in the amount of 2.7-3.5 g/t and silver 160-250 g/t [[8], [9], [10]].

However, converter slags containing copper obtained by converting copper matte in the Vanyukov furnace itself are not processed; the technology does not allow it due to the oxidizing atmosphere in the reaction zone of the furnace; they are shipped to the enrichment plant, to the head of the enrichment process, and together with the ore undergo re-enrichment (crushing, grinding, flotation) to obtain copper sulfide concentrate. Of the total volume of converter slag produced during copper production at Almalıyк MMC JSC, 30% is processed in reverberatory furnaces, and 70% is transferred to the plant's processing plant.

In order to reduce (dissolved, mechanical) losses of metals, in the production of copper by pyrometallurgical means in autogenous and classical furnaces, they adhere to the main task - the need for the copper content in the slag to be minimal, however, in the slag the high concentration of iron oxides, especially in the form of magnetite, on the contrary, sharply increases his. This occurs due to the fact that, being in excess, magnetite is able to separate from the dissolved state into the solid state and form an additional heterogeneous phase. In turn, the solid phase of magnetite during melting in

a reverberatory furnace forms a magnetite deposit in the bottom part (bottom) of the furnace, and when melting in the Vanyukova furnace, it bubbles (circulates) in the volume of the furnace in the form of a suspension-dirt, disrupting the production technology [[11], [12], [13], [14]].

Scientific research is being conducted around the world to reduce the excess magnetite content in iron silicate slags of copper production, its reduction to wustite in processes during pyrometallurgical copper production, using carbon (coke), natural gas or man-made waste containing reducing elements.

It has been substantiated that the recovered converter slag to a residual magnetite content of 18-28% to 8-10% can be loaded in liquid and solid form into melting furnaces without a negative impact on the smelting process and without fear of magnetite release into the solid phase [[15], [16]].

The concentration of magnetite-oxide of ferric iron in slag can be quite high and range from 5% to 24%. An increased content of magnetite during the smelting process can lead to disruption of the smelting technology, which in turn leads to an increase in copper losses with waste slag. In the pyrometallurgical production of copper, one of the important points when melting sulfide copper concentrates in smelting furnaces is the reduced content of magnetite in the waste slag. For example, in a reverberatory furnace, magnetite in an amount of 2-9% can be supplied with the concentrate [[17], [18], [19], [20]].

Magnetite content of 2-9% may be present in concentrates as shown in Fig. 1 - Fig. 4 thin sections of ore from the Kalmakir mine of the Almalıyк MMC made at the State Enterprise IMR.

The reduction of iron oxide from the ferric state is possible when it is reduced to ferrous oxide. The converter slag magnetite reducer can be not only coke, natural gas, metallic iron, but also technogenic raw materials that contain these elements. Such technogenic raw materials, which contain carbon and iron, can be clinker, as well as noble metals Au and Ag.

Selection and justification of research objects.

The main objects of research were industrial converter slags of Almalıyк MMC JSC, the chemical composition of which is given in Table 1. Both stale, accumulated and freshly formed converter slags were subjected to chemical analysis.

To conduct laboratory studies and clarify the main reactions occurring during the reduction process during conversion, the clinker composition was used, which is given in table. 2.

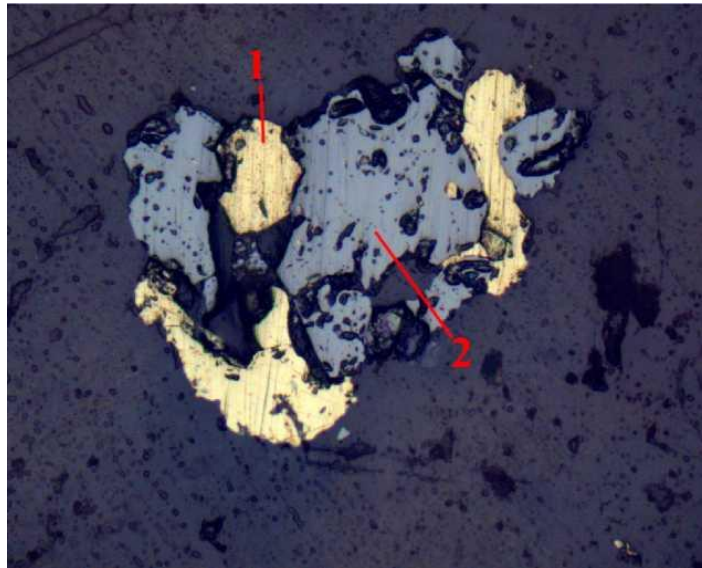


Fig. 1 - Fragments of samples containing 1-chalcopyrite, 2-magnetite (magnification x200)

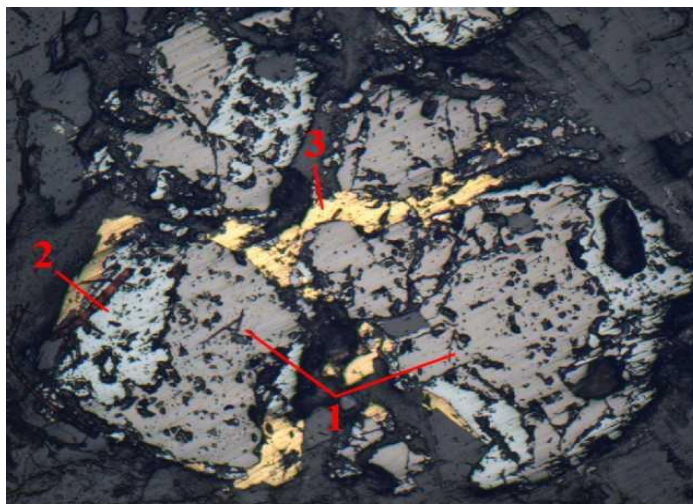


Fig. 2 - Fragments of samples containing 1-hematite, 2-magnetite, 3-chalcopyrite (magnification x200)

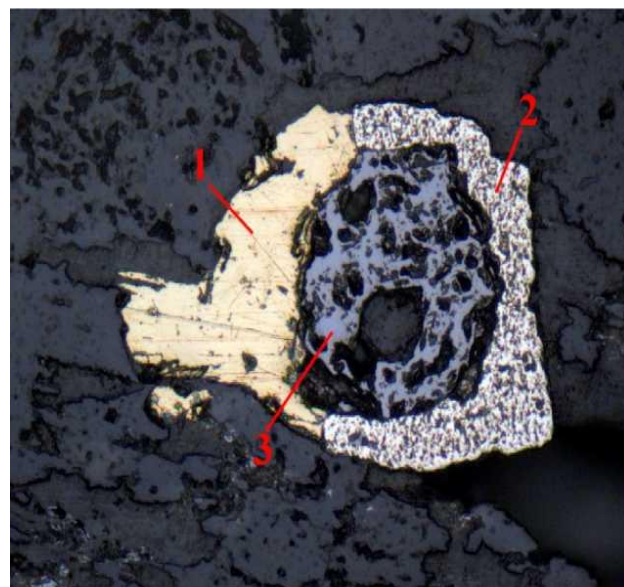


Fig.3 - Fragments of samples containing 1-chalcopyrite, 2-pyrite, 3-magnetite (magnification x200)

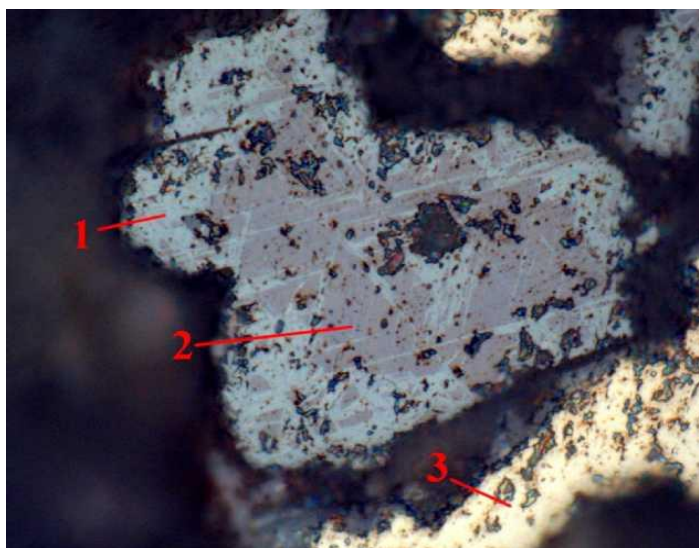


Fig.4 - Fragments of samples containing 1-hematite, 2-magnetite, 3-chalcopyrite (magnification x100)

Table 1 - Chemical composition of Almalyk MMC converter slags

No. slag	Content, wt. %								
	Cu	Zn	Pb	Fe	Fe ₃ O ₄	SiO ₂	CaO	Al ₂ O ₃	S
1	2.94	1.95	1.3	47.0	20.7	22.5	1.95	3.20	1.0
2	3.57	1.75	1.1	46.9	21.1	19.1	1.57	3.11	0.90

Table 2 - Chemical composition of clinker from the zinc plant of Almalyk MMC

No. samples	Clinker content , wt. %								
	Cu	Pb	Zu	SiO ₂	S	C	Fe	Au	Ag
1	2.72	1.32	2.05	19.00	-	25.20	22.00	2.35 g/t	185 g/t

The process of recovering magnetite from converter slag composition: Cu-2.94; Zn-1.95; Pb-1.3; Fe-47.0; Fe₃O₄-20.7; SiO₂-22.5; CaO-1.95; Al₂O₃-3.20; S-1.0 clinker occurs in solid and liquid phases, since the process takes place at a temperature of 1250 °C, and the melting point of iron is 1539 °C, carbon 3527 °C.

With such a content of magnetite in the converter slag, it becomes possible to mix it with concentrate and load it even into the Vanyukov autogenous furnace. In order to deplete converter slag as a recyclable product, tests were carried out on its preliminary recovery in the Vanyukov furnace. As a reducing agent for magnetite - ferric iron of the

iron silicate melt of copper production, clinker was used - a technogenic solid residue from the Waeltz process of zinc cakes from zinc production, containing more than 50% of reducing elements in the form of metallic iron and carbon.

Discussion of the research results

It was settled (fig.5) that using clinker size + 5 - 10 mm when reducing converter slag in a converter from magnetite to wustite using technology (Fig. 6), more than 50.0% was restored in 10-15 minutes (the amount of magnetite decreased from 21.9% to 9.8%).

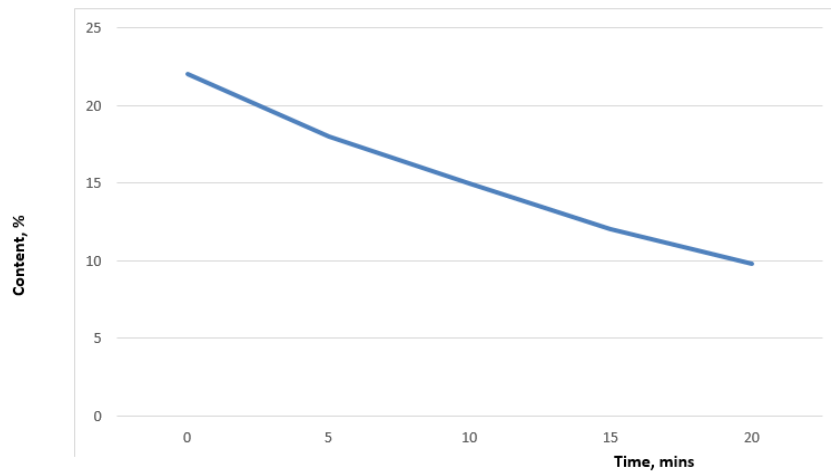


Fig. 5 - Dependence of magnetite reduction in the composition of converter slag from time to time.

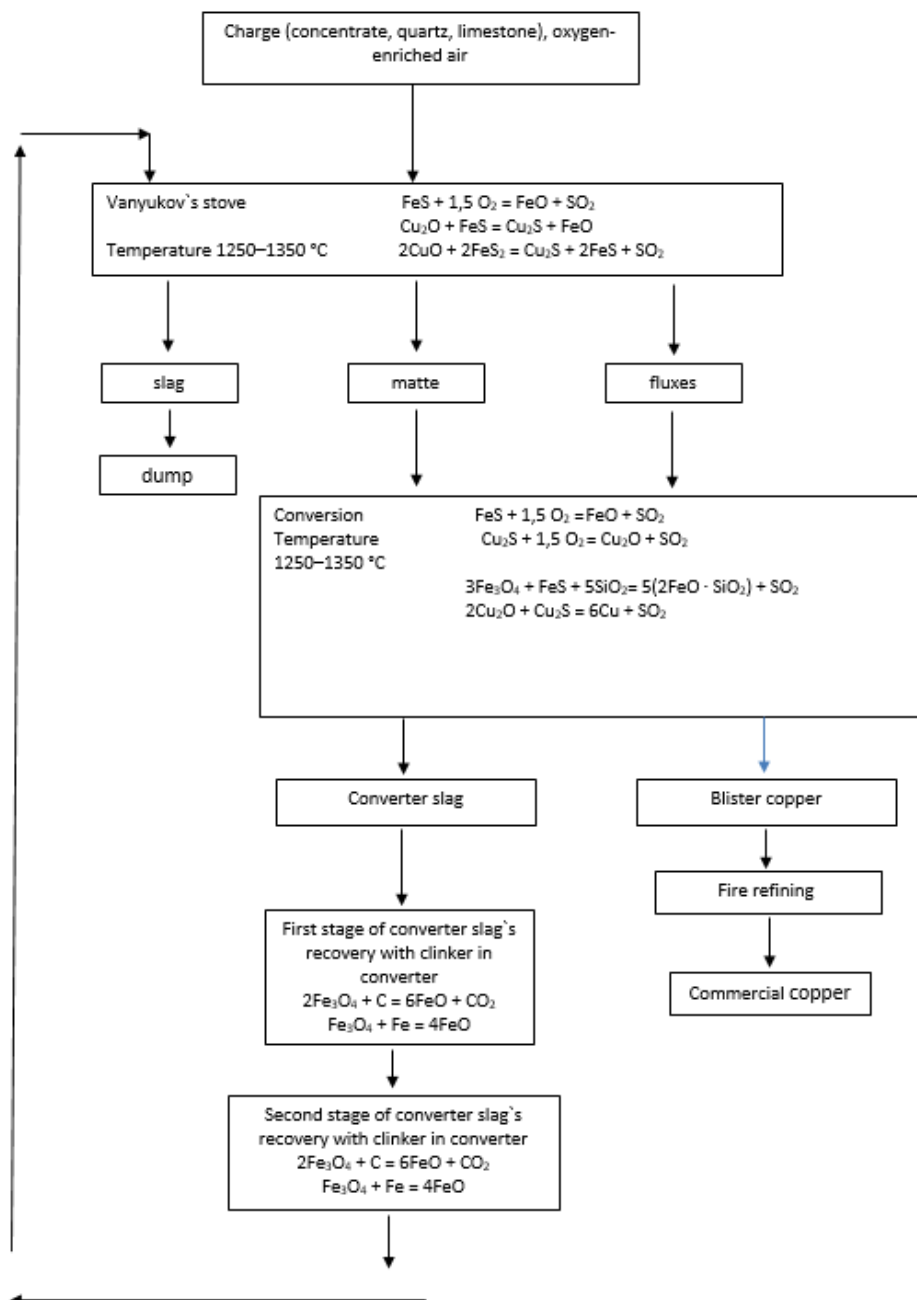


Fig.6 - Technology for processing recovered converter slag in the Vanyukov furnace

Table 3 - Operation of the Vanyukov furnace in normal mode when smelting copper sulfide concentrate without the addition of converter slag concentrate as part of the charge.

Date Name of material slag hole.	Cu	SiO ₂	Fe	CaO
01.12.2022	0.64	28.84	50.11	2.80
02.12. 2022	0.73	26.40	49.27	2.63
03.12.2022	0.65	28.52	51.63	2.91
04.12.2022	0.54	29.92	51.08	2.80
05.12.2022	0.62	29.16	50.11	2.86
06.12.2022	0.56	32.52	46.64	2.57
07.12.2022	0.63	29.74	48.44	3.64
08.12.2022	0.60	28.86	52.60	2.46
09.12.2022	0.55	31.00	48.58	2.69

Table 4 - Copper content in the dump slag of the PZHV, for 10 days from 10 – 19 December 2022 when processing recovered converter slag.

Date Name of material slag hole.	Cu	SiO ₂	Fe	CaO
12/10/2022	0.65	34.20	51.83	2.58
11.12. 2022	0.58	29.08	49.86	2.74
12/12/2022	0.59	27.56	50.27	2.35
12/13/2022	0.65	29.30	52.66	2.35
12/14/2022	0.69	30.24	52.35	2.69
12/15/2022	0.59	29.80	51.86	2.40
12/16/2022	0.61	29.40	50.58	2.24
12/17/2022	0.59	29.20	51.97	2.80
12/18/2022	0.68	29.12	52.05	2.40
12/19/2022	0.72	29.70	51.72	2.55

The amount of copper sulfide (semi-sulfide copper) has significantly decreased from its initial content from 3.6% to 1.96

In December 2022 The second stage of industrial testing of the processing of recovered converter slag from copper production in the liquid bath furnace (LBA) - the Vanyukov furnace - was continued in the conditions of Almayk MMC JSC. Table 3 shows the operation of the Vanyukov furnace in normal mode from 12/01/2022 to 12/09/2022, with copper content (standard for PV) in the matte: 45 - 50%.

Heat compensation from loading cold solid converter slags (metal oxides) from the dump occurs by loading clinker due to the exothermic reaction of oxidation of carbon and iron present in the clinker – a technogenic waste from the Almayk MMC JSC ACP plant.

In table 4 shows the copper content in the waste slag during the processing of recovered converter slag.

The data in Tables 4 show that the copper content in the dump slag when operating in the

PZhV mode for 10 days from 12/10/2022 to 12/19/2022 with the loading of recovered converter slag is 0.58% - 0.72%. They do not exceed the data on the copper content in the waste slag of the PZhV furnace (Vanyukov furnace) without loading converter slag.

Conclusions

It was established and recommended that the use of clinker - technogenic waste from zinc production with a particle size of +5 - -10 mm when restoring converter slag in a converter from magnetite to wustite using the developed technology in 10-15 minutes decreased from 21.9% to 9.8%, with this contents can be loaded into the Vanyukov oven.

In the process of smelting sulfide copper concentrate and solid recovered converter slag from copper production in the Vanyukov furnace, no changes in technology indicators were observed.

The lack of heat during the smelting process in the Vanyukov furnace when loading reduced

converter slag in a cold state is compensated by additional clinker blending of technogenic waste raw materials from the zinc plant AGMK, which is a coolant (an exothermic oxidation reaction of metallic iron and clinker carbon), as well as additional raw materials of noble metals.

A two-stage technology for processing technogenic raw materials in the form of converter slag has been developed in copper production, in the first stage by restoring it in a converter, and in the second stage, after its recovery, it is mixed when melting sulfide copper concentrates in a single-zone Vanyukov furnace. Clinker-zinc production is used as a reducing agent; the iron and carbon contained in it reduce the excess part of magnetite, and 95% of noble metals are extracted from it. As a result, it was possible to deplete the converter slags of copper production in copper from 2.2-3.5% to a waste level of 0.58 - 0.72%, which is the goal of this technology.

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

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«Алмалық ТМК» АҚ пирометаллургиялық мыс өндірісі кезінде Ванюков пешіндегі конверторлық шлактарды қалдықтарға шығару.

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ТҮЙІНДЕМЕ

Мақалада «Алмалық ТМК» АҚ-да техногендік түзілімдерді олардан түсті және асыл металдарды кешенді түрде алу мақсатында шлак және клинкер-мырыш түріндегі мыс пирометаллургиялық өндірісіне тарту мүмкіндігі көрсетілген. Мырыш өндірісінің техногендік қалдықтары болып табылатын клинкер құрамында металдық темір және көміртек түріндегі тотықсыздандырғыш элементтердің айтарлықтай мөлшері, сонымен қатар 2,3 г/т алтын және 250 г/т күміс бар. Ғылыми зерттеулерде клинкер конвертер қожында болатын магнетиттің жұтануы кезінде және конвертер қожының жұтануы (редукциясы) процесінде тотықсыздандырғыш ретінде жұмыс істейді, асыл металдар штейнге, содан кейін 95-98% дейін тазаланбаған мыс алынады. «Алмалық ТМК» АҚ мыс өндірісінің түрлендіргіш қождарында 2,0-3,5% мыс бар және олар айналым өнімі ретінде 75% мыс алынатын шағылыстырғыш пеште жұтандалады. Алайда, Ванюковтың автогендік пештерін енгізумен (оларда конвертер қождары өңделмейді) мыс өндіру үшін конвертер қождарының бір бөлігі, комбинаттың техногендік шикізатына айнала отырып, кен шикізатын байыту процесінде, конвертер қожынан тазаланбаған мысқа төмен өтпелі экстракциясы бар сульфидті мыс концентратын алу үшін байыту фабрикасына қайтарылады. Шағылыстырғыш және Ванюков пештеріндегі конверторлық шлактардан мыс шығымын арттыру үшін алдымен конвертер қожын тотықсыздандыру процестерінде жұтандатып, содан кейін өңдеуге беру керек.

Түйін сөздер: мыс, шлак, конвертерлік қож, жұтандату, магнетит, бөліп алу, клинкер, концентрат.

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Освобождение конвертерных шлаков в отходы в печи Ванюкова при пирометаллургическом производстве меди на АО «Алмалыкский ГМК»

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<p>Поступила: 6 ноября 2023 Рецензирование: 4 декабря 2023 Принята в печать: 4 января 2024</p>	<p>АННОТАЦИЯ</p> <p>В статье показана возможность вовлечения техногенных образований в пирометаллургическое производство меди в виде шлаков и клинкерно-цинкового производства с целью комплексного извлечения из них цветных и благородных металлов на АО «Алмалыкский ГМК». Клинкер – техногенный отход производства цинка – содержит значительное количество восстанавливающих элементов в виде металлического железа и углерода, а также золото в количестве 2,3 г/т и серебро 250 г/т. В исследованиях клинкер работает как восстановитель магнетита, содержащегося в конвертерном шлаке, при его обеднении и в процессе обеднения (восстановления) конвертерного шлака извлечение благородных металлов в штейн, а затем в черновую медь до 95-98 %. Конвертерные шлаки медного производства АО «Алмалыкский ГМК» содержат 2,0-3,5% меди и их, как оборотный продукт, обедняют в отражательной печи с извлечением меди 75%. Однако с внедрением автогенных печей Ванюкова (в них не перерабатываются конвертерные шлаки) для производства меди часть конвертерных шлаков, превращаясь в техногенное сырье комбината, возвращается на обогатительную фабрику в процессе обогащения рудного сырья, для получения сульфидного медного концентрата с низким сквозным извлечением из конвертерного шлака в черновую медь. Для увеличения выхода меди из конвертерного шлака в отражательных печах и печах Ванюкова необходимо сначала обеднить конвертерный шлак в восстановительных процессах, а затем передавать его на переработку.</p> <p>Ключевые слова: медь, шлак, конвертерный шлак, обеднение, магнетит, извлечение, клинкер, концентрат.</p>
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