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DOI: 10.31643/2022/6445.36

Analysis of Existing Technologies for Depletion of Dump Slags of Autogenous Melting

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Received: *March 25, 2022*
Peer-reviewed: *April 09, 2022*
Accepted: *April 28, 2022*

ABSTRACT

Pyro-metallurgy of copper production is characterized by the output of copper slag, which is regarded as a kind of solid waste. Moreover, this slag is identified as hazardous because it contains impurities, like Pb, As, and Cu. Obtaining dump slags in autogenous processes does not always meet the requirements of effective technologies, most often slags contain more than 1.0% of copper and need to be depleted. This work is presented a brief analysis of existing technologies used for copper slag depletion. The analysis of the existing technologies for the depletion of autogenous smelting dump slags showed that the most promising option seems to be the depletion of copper slags in one PV unit since by improving the process itself, by changing the unit design, it is possible to achieve technologically complete production of matte and dump slag with low copper content. There were proposed two technologies of improvement: electro-heating of slag siphon using the graphite electrodes and depletion process in two-zone PV furnace.

Keywords: Copper slag, reduction treatment, depletion, slag siphon, two-zone Vanyukov furnace.

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Introduction

Comparative analysis of technical indicators of autogenous processes indicates that slags require several measures to deplete them. For example, in the Norand process, the copper content in slags can reach 15%, KFP - 1.2%, KVP - 1-1.5%, Ausmelt - 0.8-1.0%, Mitsubishi - 0.5%, PV - 0.5-0.6%. The best indicators for dump slags are possible in the Mitsubishi and PV processes, however, a significant deterioration in the composition of concentrates in recent years leads to a violation of the technology and the production of copper-rich slags [[1], [2], [3], [4], [5], [6], [7]]. Slag depletion technologies have two main directions: the improvement of matte smelting itself with the production of dump slags and the use of separate units that allow slag depletion (for example, an electric furnace with several high-power units). The first option is expedient, promising, and economically viable. Improvement of the melting process on matte and the design of the furnace will make it possible to achieve the most significant results in slag depletion [[8], [9]].

Carrying out autogenous smelting of copper raw materials is closely related to the solution of slag depletion issues, which involves the implementation of the following conditions: obtaining a minimum amount of slag with low copper content, while the maximum should be fluidity, slag surface tension, minimum slag density, optimal silicon dioxide content, optimal temperature conditions for the separation of matte and slag [[10], [11], [12]]. Temperature conditions, maintenance of thermal balance due to oxidation of iron sulfides, control of moisture, and silicon oxide in concentrates are of exceptional importance for autogenous smelting. In a certain situation, to maintain the heat balance of the furnace, it is possible, and sometimes necessary, to use additional fuel, for example, natural gas, fuel oil, or coal [[13], [14]].

To compensate for the unsatisfactory heat balance, the insufficient temperature of the melt at the outlet of the furnace, and additional precipitation of the matte phase from the slag melt, it is very important to improve the operation of slag electric mixers on PV furnaces. Analysis of the influence of various factors on the PV process showed that all of them are of decisive importance for the efficient course of the smelting process, the main of which are indicators for the composition of dump slags, which determine the technical and economic characteristics of the entire technology [[14], [15]].

Method

The samples of the slags were obtained from the Vanyukov furnace in Balkhash Copper-Smelting Plant. These samples were analyzed by chemical and X-ray fluorescence analysis. X-ray fluorescence multi-element automated analysis was carried out on a wave-dispersive combined spectrometer Axios.

To simulate the oxidation zone of a two-zone PV furnace the slag was heated to a temperature of 1300 °C in the presence of a reducing agent, then the melt was kept for 1 hour. The consumption of coal was calculated as 2.5 g per 100 g of slag.

Results and discussion

Analysis of existing technologies for copper slag depletion

Depletion of slags when using a technology separate from smelting is possible using various processes such as pyro, hydro, and a combination of pyro-hydrometallurgical methods for metal recovery from copper slag [16]. One of the most promising is the reduction methods using electrothermal furnaces with various methods of supplying the reducing agent. Solid (coke, coal) and gaseous (coal-air mixture, natural and generator gas) substances are used as reducing agents. In world practice, separate or combined with a melting unit electrothermal furnaces, furnaces with a reducing bubbling using coal, natural, or generator gas are most often used [17]. There are known examples of slag depletion in the presence of pyrite, pyrrhotite, calcium sulfide, and cast iron [18]. It is possible to use turbulent mixing of a superheated slag melt for purification from copper with the introduction of CaC_2 into the process as a reducing agent [19]. The effect of an electric field on a slag melt was studied in [20]. It was found that there is a 3-fold increase in the deposition rate of copper drops with a diameter of 5 mm. It is noted that with an increase in the size of the metalized droplet or with an increase in the Cu_2O content in the slag, the effect of the electric field decreases.

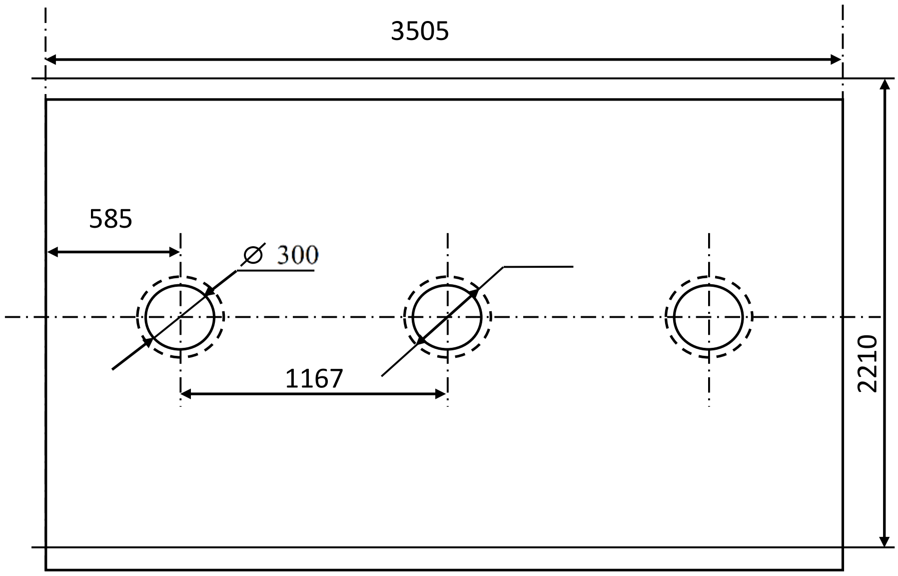
Methods of depletion of slags from copper production using sulfide reagents are seldom used due to environmental pollution with sulfur dioxide and to reduce the number of waste slags. Environmentally friendly methods are hydrometallurgical, in particular, the most common

and industrially implemented is flotation, which includes the preparation of slag by crushing and grinding in several stages, flotation together with ore material (or separate for slag) to obtain sulfide copper concentrate suitable for smelting on matte [21]. This method assumes the availability of the necessary flotation capacity at the concentrator. The disadvantages of such technologies are the relatively low extraction of copper into concentrate and the low quality of these concentrates themselves. Moreover, copper slag wastes after floatation treatment, still contain heavy metals with hazardous properties posing environmental risks, so they needed further utilization [22].

A method has been developed for the depletion of copper slag by leaching using various solvents such as sulfuric acid, hydrochloric acid, ammonia, cyanide, etc. [[23], [24], [25], [26]]. An intensification of the process of leaching of copper slags with the addition of hydrogen peroxide under pressure, as well as with the use of chlorine, has been proposed [[27], [28]]. Improvement of matte smelting itself with the production of dump is more expedient, promising, and economically viable and an additional increase in the slag settling zone, in which depletion occurs with the introduction of a reducing agent, is the most promising direction.

Improvement of slag siphon

The slag siphon structurally is a continuation of the melting zone of the PV, adjacent to the outer part of the slag partition, and in solving the problem of depletion of the slag PV and obtaining the waste slag is of great importance. Improving the operation of the PV slag siphon is expected to take several



Picture 1 – Layout of electrodes in a slag siphon

measures that will affect the processing of copper sulfide concentrates, improve the technical and economic indicators of the process, increase copper recovery, significantly reduce its losses with slag, and eliminate disturbances in the normal operation of PV furnaces. The stable operation of the slag siphon of the PV furnace is often disturbed by deposition processes, which is also facilitated by changes in the composition of the charge, for example, an increase in the content of zinc in concentrates. The continuous discharge of slag from the PV furnace into the electric mixer prevents the formation of build-ups, which are the result of the absence of horizontal movement of the melt and local peroxidation of the melt in the bubbling zones. In the slag siphon, it is necessary to create a regime of free movement of the melt, the possibility of sedimentation of copper sulfide particles, which is possible at a certain temperature regime, the creation of a reducing atmosphere, and the optimal composition of the slag.

A variant is proposed using three graphite electrodes with a diameter of 300 mm and a transformer similar to that used for a slag mixer. The use of electric heating of the slag siphon will allow, when the temperature of the melt in the slag siphon reaches at least 1300 °C, to ensure sufficiently complete separation of slag and matte. The electrodes in the siphon will operate at a relatively constant level of the slag melt with a uniform flow of slag through the slag siphon, which will provide optimal conditions for additional heating of the slag and the most complete separation of the matte phase from the slag and prevention of build-up in the siphon (Picture 1).

Additional heating of the slag in the slag siphon will reduce the power consumption in the slag mixer to maintain the melt temperature at least 1300 °C. The use of graphite electrodes with a diameter of 300 mm will allow for maintaining the existing width of the slag siphon.

Depletion in a 2-zone furnace

This process would be possible by dividing the reaction zone of the furnace into two zones oxidizing and reducing using a water-cooled partition. Slag samples were obtained from the Vanyukov furnace and their content is shown in Table 1.

Activated carbon was used as a reducing agent with the following content wt. %: 74.3 C, 0.16 S, 0.025 P, 1.12 Fe, 0.93 SiO_2, 1.56 Al_2O_3; melting temperature was – 1300 ^{0}C. The reduction treatment was carried out on a laboratory scale.

The slag was heated to a temperature of 1300 °C in the presence of a reducing agent, then the melt

Table 1 - Content of main components in slag before/after reduction treatment

№ of test	Slag content, %					
	Before treatment			After treatment		
	Cu	SiO_2	Fe_3O_4	Cu	SiO_2	Fe_3O_4
11	0.93	32.05	7.80	0.43	33.1	2.5
12	0.97	31.90	7.90	0.47	32.9	2.6
13	1.033	31.30	7.95	0.50	32.9	2.6

was kept for 1 hour. The consumption of coal was calculated as 2.5 g per 100 g of slag. At the end of the reduction process - slag and the bottom phase were obtained. The bottom phase had a similar composition to the matte obtained during smelting in a PV furnace.

Table 1 also shows the results of reduction processing, and it's seen that during the melting process the destruction of magnetite took place, its content had dropped by 5.3-6.5 % from 7.8 -7.95% to 2.5-2.6%, and this consequently had a positive effect on prevention of copper losses with slags. The presented results of analysis of slag samples after interaction with activated carbon indicate a decrease in copper content in the range of 0.43-0.50%, in comparison with its content in slags before reduction treatment in the range of 0.93-1.03%. Such a decrease in the copper content is associated with the process of destruction of magnetite, and the transition of iron oxides to fayalite.

Conclusion

All the proposed solutions for slag depletion, for the implementation of which industrial installations of operating units are required, occupying vast territories, consuming significant material and energy resources, are economically and ecologically unprofitable. The most promising option seems to be the option of depletion of copper slag in one PV unit since by improving the process itself, by changing the unit design, it is possible to achieve a technologically complete production of matte and dump slag with low copper content. The use of graphite electrodes for additional heating of the slag in the slag siphon will reduce the power consumption in the electrical mixer and at the same time will allow maintaining the existing width of the slag siphon. On the other hand, in comparison with similar developments, the proposed technology for melting copper sulfide concentrates in a two-zone PV furnace will make it possible to obtain slags with a copper content of 0.7% or less, with minimal costs for equipment reconstruction.

Conflict of interests

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

Acknowledgments

This research was funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan (Grant No. AP08855511).

Cite this article as: Kenzhaliyev BK, Kvyatkovskiy SA, Dyussebekova MA, Semenova AS, Nurhadiyanto D. Analysis of Existing Technologies for Depletion of Dump Slags of Autogenous Melting. Kompleksnoe Ispol'zovanie Mineral'nogo Syr'a = Complex Use of Mineral Resources 2022;323(4):23-29. https://doi.org/10.31643/2022/6445.36

Автогенді балқыту қалдықтарын қожды сарқудың қолданыстағы технологияларын талдау

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Мақала келді: *25 наурыз 2022*
Сараптамадан өтті: *09 сәуір 2022*
Қабылданды: *28 сәуір 2022*

ТҮЙІНДЕМЕ
Мыс өндірісінің пирометаллургиясы қатты қалдықтарға жататын мыс қождарының бөлінуімен сипатталады. Сонымен қатар, бұл қож қауіпті болып саналады, өйткені оның құрамында Pb, As және Cu сияқты қоспалар бар. Автогендік процестерде үйінді қождарын алу әрдайым тиімді технологиялардың талаптарына сәйкес келмейді, көбінесе қождар құрамында 1,0% - дан астам мыс бар және оларды жұтаңдату қажет. Бұл жұмыста мыс қождарын азайту үшін қолданылатын қолданыстағы технологияларға қысқаша талдау берілген. Автогенді балқытудың үйінді қождарын жұтаңдатудың қолданыстағы технологияларын талдау нәтижесінде ең перспективалы нұсқа ПВ-ның бір агрегатында мыс қождарын жұтаңдату екендігі анықталды, өйткені процестің өзін жақсарту, қондырғының дизайнын өзгерту арқылы технологиялық тұрғыдан аяқталған, штейн мен мыстың мөлшері аз болатын үйіндіні өндіруге қол жеткізуге болады. Жұмыста жетілдірілген екі технология ұсынылған, олар: қож сифонын графит электродтар арқылы электр тогымен жылыту және екі аймақтық ПВ пешінде жұтаңдату процесі.

Түйін сөздер: Мыс қожы, қалпына келтіру, сарқылу, қож сифоны, Ванюковтың екі аймақтық пеші.

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Анализ существующих технологий обеднения отвальных шлаков автогенной плавки

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Поступила: *25 марта 2022*
Рецензирование: *09 апреля 2022*
Принята в печать: *28 апреля 2022*

АННОТАЦИЯ
Пирометаллургия медного производства характеризуется выходом медных шлаков, которые относят к твердым отходам. Кроме того, этот шлак считается опасным, так как содержит такие примеси, как Pb, As и Cu. Получение отвальных шлаков в автогенных процессах не всегда соответствует требованиям эффективных технологий, чаще всего шлаки содержат более 1,0% меди и нуждаются в обеднении. В данной работе представлен краткий анализ существующих технологий, используемых для обеднения медных шлаков. Анализ существующих технологий обеднения отвальных шлаков автогенной плавки показал, что наиболее перспективным вариантом является обеднение медных шлаков в одном агрегате ПВ, так как путем совершенствования самого процесса, изменением конструкции агрегата можно добиться технологически завершенного производства штейна и отвального шлака с низким содержанием меди. Предложены две технологии совершенствования: электрообогрев шлакового сифона графитовыми электродами и процесс обеднения в двухзонной печи ПВ.

Ключевые слова: Медный шлак, восстановительная обработка, обеднение, шлаковый сифон, двухзонная печь Ванюкова.

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