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«НАУКА И ПРОСВЕЩЕНИЕ»



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THE ANALYSIS OF PHYSICOCHEMICAL PROPERTIES OF METALLURGICAL MOLTEN SLAGS

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Abstract. Physicochemical properties of metallurgical slags wasted from copper production have been shown in this article. There are many information has been given about theoretical bases of processes which occurring during the smelting of copper-saved raw materials. And so main technological parameters of taking of copper-saved molten phase have been found which forms after smelting process.

Keywords: copper slag, molten phase, physicochemical properties, smelting.

АНАЛИЗ ФИЗИКО-ХИМИЧЕСКИХ СВОЙСТВ МЕТАЛЛУРГИЧЕСКИХ ШЛАКОВ

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Аннотация: В статье рассмотрено физико-химические свойства металлургических шлаков медного производства. Дано полезные информации о теоретических основах процессов, которые происходящие при плавление сырьевых материалов. А также, определены основные технологические параметры получения расплава, образующейся при процесс плавление медных концентратов.

Ключевые слова: медный шлак, расплав, физико-химические свойства, плавление.

Introduction. Pyrometallurgy is a branch of extractive metallurgy. It consists of the thermal treatment of minerals and metallurgical ores and concentrates to bring about physical and chemical transformation in the materials to enable recovery of valuable metals.

Most pyrometallurgical processes require energy input to sustain the temperature at which the process takes place. The energy is usually provided in the form of fossil fuel combustion, exothermic reaction of the material or from electrical heat. When enough material is present in the feed to sustain the process temperature solely by exothermic reaction (i.e. without the addition of fuel or electrical heat), the processes is said to be "autogenous". Pyrometallurgical processes are generally grouped into one or more of the following catego-

ries: calcining: roasting: smelting: refining. In metallurgy of copper for thermal treatment of copper sulfide concentrates often it uses smelting process. Smelting involves thermal reactions in which at least one product is a molten phase. As a result of interactions between substances the molten phase divides to two molten layers: in down – matte and in up-layer – slag. Other materials may need to be added as flux, aiding the melting of the oxide ores and assisting in the formation of slag, as the flux reacts with impurities, such as silicon compounds [1, p 15].

Materials and methods. Pyrometallurgy is the dominant technology for current copper extraction, by which almost 80 % of total copper in the world has been generated. Pyrometallurgical production of molten copper generates two slags, smelting and converting. Approximately 2,0 – 3,0 tons of copper slag are generated per ton of copper production, depending on the properties of copper concentrates and operating conditions in the pyrometallurgical process. Generally, copper slag contains about 35 – 45 wt. % copper, indicating that it is a valuable secondary resource for recycling and utilization. Chemical content of some slags has been shown in table 1.

Table 1

Chemical content of converting slags.

№	Content, %							
	Cu	Fe (total)	SiO ₂	Al ₂ O ₃	CdO	Fe ₃ O ₄	S	MgO
1	2,4	45,3	20,2	1,6	1,7	27,3	1,3	0,4
2	2,51	48,8	22,4	1,8	1,44	19,1	-	-
3	3,05	48,7	21,2	3,1	0,56	22,02	-	0,56
4	3,3	49,5	24,0	-	2,5	-	2,1	-
5	3,56	46,5	19,0	3,26	1,57	-	2,0	-

The copper slag used in the experiments is a byproduct generated during the converting of molten copper matte in Bessemer converter of Almalyk Mining and Metallurgical Complex (Almalyk, Uzbekistan). The X-ray diffraction (XRD) spectrum of an average sample is shown in Figure 1, indicating that the main crystal phases in the slag are fayalite (Fe₂SiO₄) and magnetite (Fe₃O₄) [2, p 5].

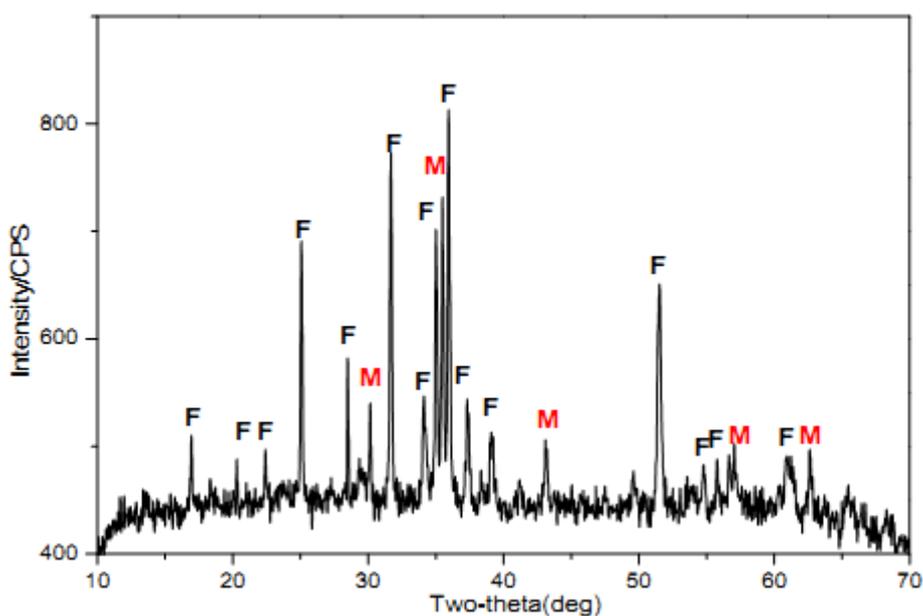


Fig.1. X-ray diffraction patterns of copper slag (F – fayalite, M – magnetite)

Results and Discussion. It is the most important in metallurgical processes what studying of physico-chemical properties and thermal behavior of molten slags. Because it bonds to recovering of metal and coefficient of productivity of copper smelting plants. Taking knowledge about physical and chemical properties of molten slags helps to controlling of processes, improving recovery of copper and other valuable metals from secondary technogenic materials. Physicochemical properties of slag are include: crystalline structure, diffusion, density, specific gravity, ductility, viscosity, melting and boiling points, adsorbing and chemisorbing of materials, activity, acidity, basicity, specific surface of contacting borders and concentrates of components [3, p 127].

We can find effects of this parameters to recovering metal index with making thermodynamic phase analysis. The X-ray diffraction phase analysis of the residue obtained during smelting at 1200 – 1350 °C showed that fayalite and magnetite were present as major phases in the slag (Figure 2).

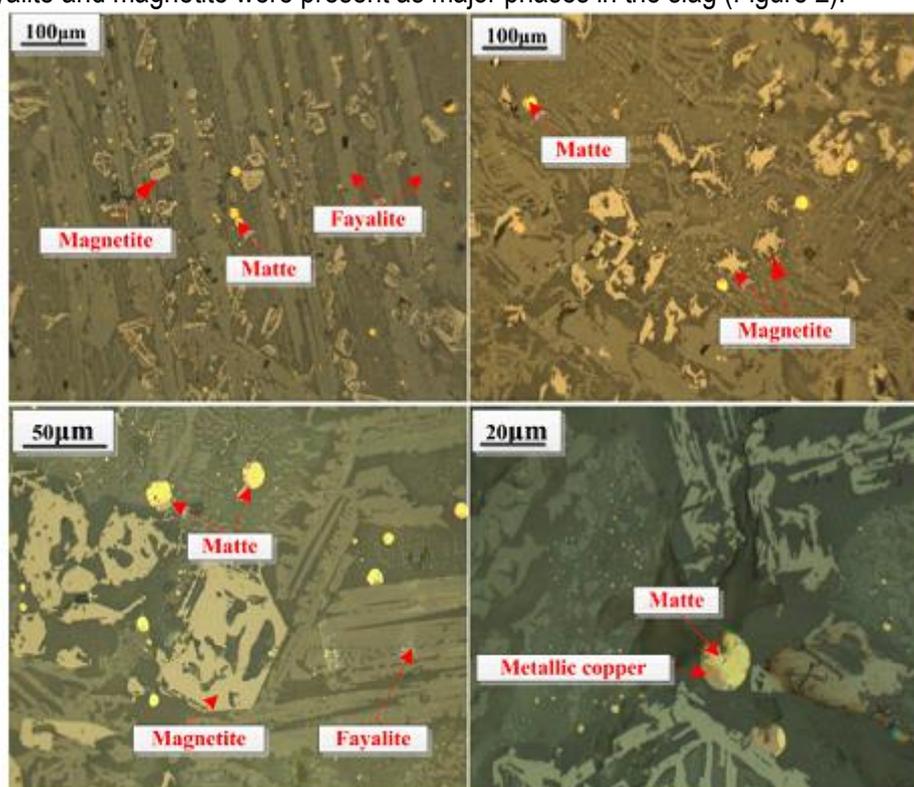


Fig.2. Microstructure of copper slag

It is also consists of: $\text{Cu}^{1+}\text{Fe}^{3+}\text{O}_2$ – delafossit, Cu_2O – cuprite, CuFe_5O_8 – shpinels, glassy phase which considered from oxides $\text{CaO} \cdot \text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 \cdot \text{Cu}_2\text{O}$, $\text{CaO} \cdot \text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{Cu}_2\text{O}$, $\text{CaO} \cdot \text{SiO}_2 \cdot \text{Al}_2\text{O}_3$.

Conclusions:

(1) Iron element in the copper slag mainly existed in the form of fayalite and magnetite, and the copper is present in sulfide form with fine size as well as being closely embedded in the fayalite matrix, revealing that traditional physical beneficiation process may result in poor valuable metal recovery.

(2) XRD analysis showed that the reconstruction of mineral phases for copper slag is effective because more fayalite was transformed to magnetite, which is beneficial to magnetic separation. Optical microscopy and ESEM-EDS analysis of modified slag indicated that valuable mineral (matte and magnetite) particles in the slag aggregate together and grow obviously, and the size is mostly over 50 µm, which is extremely favorable to the beneficiation of copper and iron.

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THE ANALYSIS OF THE ARCH OF SERVICE OF AUTOGENOUS SMELTING FURNACES DURING PROCESSING OF COPPER SULFIDE CONCENTRATES

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Abstract. In article questions of increase of an overall performance of the furnace of oxygen-torch fusion of sulphidic copper concentrates by the analysis of service of the arch, influence on its firmness of various technology factors and increase on this basis of campaign of the unit between major repairs are considered.

Keywords: oxygen-torch furnace, sulphidic concentrate, autogenous process, extraction.

АНАЛИЗ СЛУЖБЫ СВОДА АВТОГЕННЫХ ПЛАВИЛЬНЫХ ПЕЧЕЙ ПРИ ПЕРЕРАБОТКЕ СУЛЬФИДНЫХ МЕДНЫХ КОНЦЕНТРАТОВ

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Аннотация: В статье рассматриваются вопросы повышения эффективности работы печи кислородно-факельной плавки сульфидных медных концентратов путём анализа службы свода, влияния на её стойкость различных технологических факторов и повышения на этой основе кампании агрегата между капитальными ремонтами

Ключевые слова: кислородно-факельная печь, сульфидный концентрат, автогенный процесс, извлечение.

Introduction. One of the major ways of scientific and technical progress in the nonferrous metallurgy which development is provided in the basic directions of social and economic development of Uzbekistan in the XXI century, is wide introduction in practice power- and resource saving technologies and the equipment. World experience of development of metallurgical manufacture shows that in a current of last several decades technol-

ogy of processing of copper raw materials improve mainly on the basis of autogenous processes [1, p 83].

One of the basic requirements to modern technology is high degree of integrated approach of use of raw materials. This concept should join as much as possible high extraction of all valuable components of ore, and also use of a silicate part of ore weight. Besides, when to processing subject sulphidic ores and concentrates, it is necessary to mean that they possess enough high warmth of combustion and consequently should be considered not only as a source of valuable components but also as power fuel, i.e. should join in concept of integrated approach of use of raw materials and use of its internal power resources.

Materials and Methods. Autogenous processes are carried out completely at the expense of internal power resources without expenses of extraneous sources of thermal energy. At processing of sulphidic raw materials pyrometallurgical autogenous process it is reached at the expense of warmth exothermic reactions of burning of sulphides processed raw materials and reactions of slag-forming.

One of the basic indicators of perfection of furnaces of oxygen-torch fusion is duration of campaign between major repairs.

Furnace major repairs are connected with almost regeneration of a laying and replacement of some equipment, in its carrying out major repairs of a copper-utilization, pipes-dryers and system of powder taking are carried out. Practice has shown that term of a stop of the furnace on major repairs is defined by a copper-utilizator condition, the furnace by manufacture of operating repairs can be deduced on major repairs in 2-3 years.

Duration of major repairs of the furnace depends on amount of works and is equal 1-1,5 months. Furnace and complex repair as a whole - the big laborious work, on the daily volume dismantling and installation works surpassing volumes of building of the new furnace and a complex.

Results and Discussion. On the basis of the long analysis behind a condition of the arch of the furnace it has been established that on change of its thickness during operation certain influence is rendered by following technological parametres: the maintenance in copper concentrate, silicon dioxide and sulphur; the copper maintenance in matte; the maintenance silicon dioxide and copper in slag. Regular supervision over a condition of the arch of the furnace in its long operation have allowed to save up necessary data on degree of influence of these parametres on furnace wall materials.

The analysis is spent taking into account that OTF is the difficult multifactorial process having likelihood character. Hence, it is possible to apply methods of the theory of probability and calculus of variations to its studying.

Symbols of entrance indicators, and also limits of a variation of the technological parametres influencing a condition of the arch, are accepted the following (are taken from practice):

- X1 - The copper maintenance in slag (limits of its change from 0,58 to 0,9 %);
- X2 - The copper maintenance in concentrate (14,1 - 19,0 %);
- X3 - The copper maintenance in matte (33,0 - 42,0 %);
- X4 - The maintenance silicon dioxide in concentrate (9,6 - 16,0 %);
- X5 - The maintenance silicon dioxide in slag (33,6 - 38,0 %);
- X6 - The sulphur maintenance in concentrate (25,0 - 31,0 %).

Target indicator (parametre) of considered system is Y1 - the average thickness of the arch received as a result of repeated measurements of a thickness of the arch through certain time intervals. The limit of change Y1 for the analyzed period has made 0,3-0,85.

By static processing of the received information with use of modern computer technologies the basic interrelations between entrance and target parametres have been revealed. The mathematical description of factors, a dispersion, a root-mean-square deviation, an average error and correlation factors (table 1 have been thus defined.)

The data presented to tab.1 shows that such technological parametres as the copper maintenance ($r_2 = 0,24$) and sulfurs ($r_6 = 0,38$) in concentrate, in considered limits of a variation poorly influence reduction of a thickness of the arch. Other parametres, namely the copper maintenance in slag ($r_1 = 0,52$) and matte ($r_3 = 0,51$), the maintenance silicon dioxide in concentrate ($r_4 = 0,44$) and slag ($r_5 = 0,54$) make considerable impact on target parametre. Therefore at management of technological process it is necessary to watch carefully changes of these indicators and not to suppose their big change.

Table 1

The mathematical description of factors

Index	Mathematical waiting	dispersion	root-mean-square deviation	average error	correlation factors
Y_1	0,32	249,001	0,014	0,003	-
X_1	0,732	0,068	0,261	0,067	$r_1 = 0,52$
X_2	16,14	1,03	1,016	0,262	$r_2 = 0,24$
X_3	37,2	8,06	2,85	0,734	$r_3 = 0,51$
X_4	13,8	3,52	1,88	0,484	$r_4 = 0,44$
X_5	36,33	1,68	1,29	0,334	$r_5 = 0,54$
X_6	29,2	0,526	0,725	0,187	$r_6 = 0,38$

On the basis of the received data we construct the analytical dependences characterising functions $\delta = f(X_1)$.

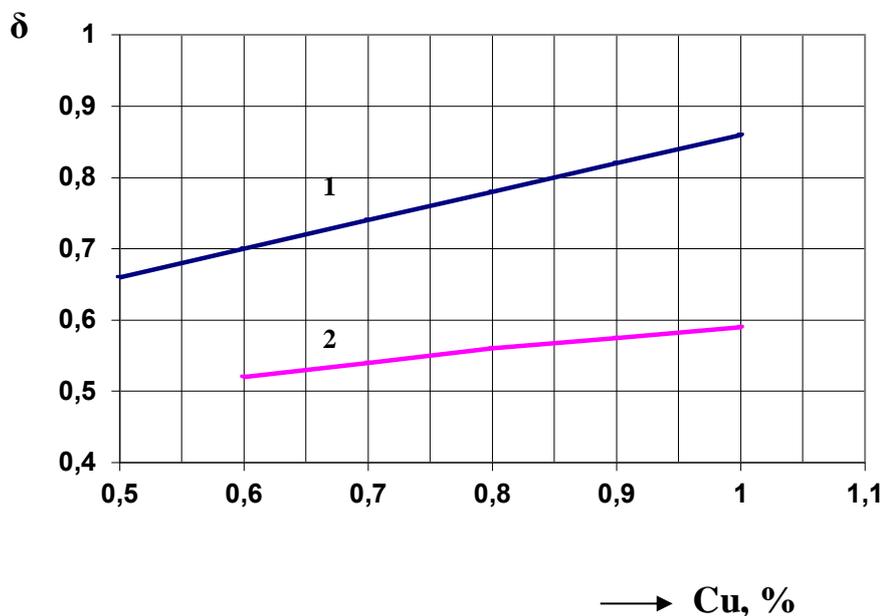


Fig.1. Model (1) and experimental (2) relationship of arch's thickness and amount of copper in the slag

Conclusion. On these equations regresses which can be used for the approached estimation of degree of influence of considered technology factors for an average thickness of the arch (fig.1) have been constructed. Comparison of lines of regresses with experimentally constructed dependences show that the developed nonlinear models inadequately reflect occurring processes in the furnace.

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USAGE OF REDUCING-SULFIDIZING AGENTS IN COPPER-BEARING SLAGS DEPLETION

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Abstract. The innovation method of decreasing of copper loss with slag has been shown in this article. For making research it has been used from reducing-sulfidizing complex, which consists of wastes of beneficiation sulphidic materials and calcium carbide. According to taken results implementing this research on an industrial scale it will increase the coefficient of productivity.

Keywords: copper slag, matte, slag processing, reducing agent, sulfidizing agent.

ИСПОЛЬЗОВАНИЕ ВОССТАНОВИТЕЛОВ И СУЛЬФИДИЗАТОРОВ В ОБЕДНЕНИЕ МЕДСОДЕРЖАЩИХ ШЛАКОВ

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Аннотация: В статье рассмотрен инновационный метод снижения потерь меди со шлаком. Для проведения этого исследования использованы восстановительно-сульфидирующих комплексы (ВСК), состоящие из отходов автомобильных шин. Полученные результаты показывает, что внедрение данной технологии в промышленность позволит повысить их производительность.

Ключевые слова: медный шлак, штейн, переработка шлака, восстановитель, сульфидизатор

Introduction. The pyrometallurgical processing of copper concentrates generates large amounts of copper-containing slag. Management options for this slag include recycling, recovery of metal values, production of value added products and disposal. However, there are no universal methods to recover copper from copper-bearing slags as the chemical and phase composition of a slag depend on factors such as the type of ore mined and the type of pyrometallurgical process utilized.

The reverberatory furnace slag that has been dumped in the vicinity of the Copper Smelter Plant of Almalyk Mining and Metallurgical Complex (AMMC), Uzbekistan, is currently processed by flotation using an existing production line at the nearby Almalyk Copper Concentrator. However, the copper recovery obtained has been rather low (about 40%). Previous research indicated that such a low recovery was due to the presence of copper oxides in the slag, as well as to the fact that copper sulphides were predominantly found in par-

ticle size fractions below 38 μm . Accordingly, the objective of the present work was to investigate whether implementation of the pyrometallurgical processing of the slag or the slag flotation tailings could result in an increase in copper recovery [1, p 1207].

Materials and Methods. The slag type used in copper industry is normally a fayalitic based slag. After processing the slag in the submerged arc furnace the slag still contains valuable metals. A typical slag composition including the main metal contents is given in Table 1.

Table 1.

Typical slag composition

№	Cu	Fe (total)	SiO ₂	Al ₂ O ₃	CdO	Fe ₃ O ₄
1	1,60	44,2	26,0	1,7	1,6	16,5

The solidification of the slag in ladles follows a crushing and classification procedure. The product is called iron-silicate rocks. This material is used in the construction industry for hydraulic or road construction. It is comparable with magmatic rocks, such as basalt, diabas or gabbro. The electron probe micro analysis (EPMA) of a granulated slag sample visualizes the localization of copper and iron.

To investigate turbulent stirring conditions an inert gas injection by a lance was installed inside the crucible. The qualitative liquid slag movement by using purging gas and in an induction field (assumption: inductively coupling of the slag) is shown in Figure 1.

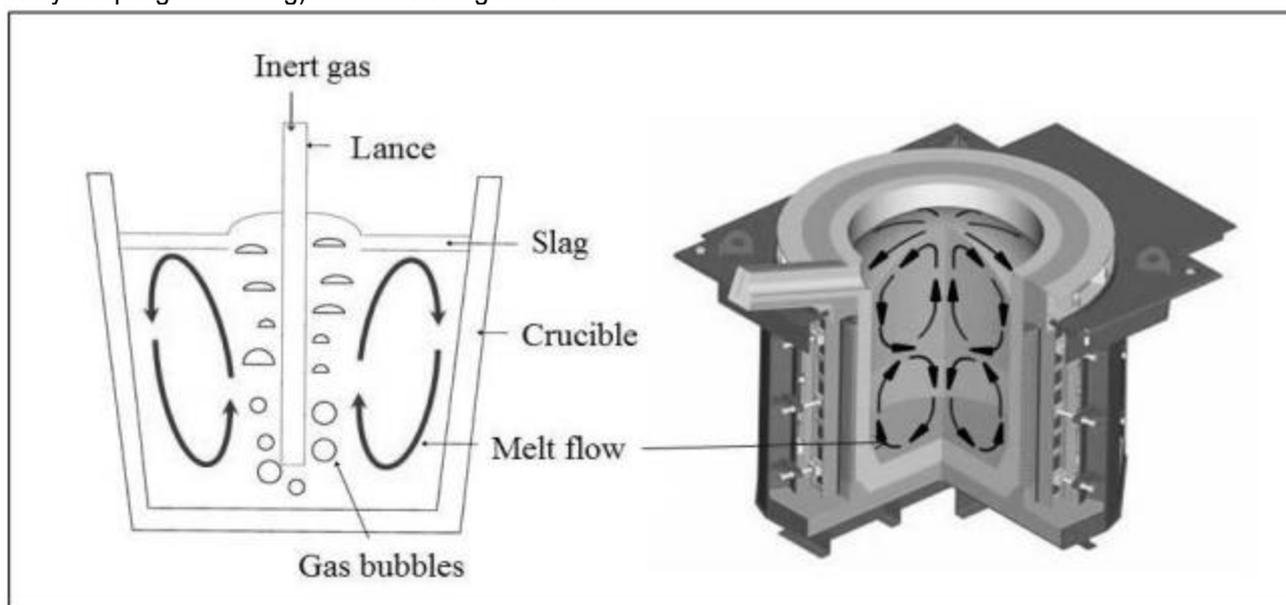


Fig.1. Slag stirring in lab-scale crucible induction furnace with and without injection lance

Results and Discussion. In order to get a stable arc, minimum feedstock for the trials is 2 kg. In three trials, 5 wt. % CaC₂ and 5 wt. % FeS₂ were mixed with the feedstock. In order to prevent further temperature increase, holding time is 20 min. Due to the furnace construction the melt must be cast after the end of holding time. It gets obvious that the trial conditions were not comparable to the general parameters.

Nevertheless, the results are published as a “benchmark” for ideal settling conditions. Background is the temperature dependence of the viscosity, which is described by the Arrhenius equation:

$$\ln \eta = A_{\eta} - \frac{E_{\eta}}{R \cdot T}$$

η = viscosity [$\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$], A_{η} = constant; E_{η} = activation energy, R = Gas constant [$\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$], T = Temperature [K].

The formula shows that a higher melt temperature leads to a viscosity decrease. A faster settling velocity of the metallic inclusions is the result. A visible separation of metal and slag phase is attained. The analysis

of the metal phases showed that especially in the trial using the reducing agent the removed copper from the slag is reduced, settled and coagulated on the furnace bottom. Due to the process temperatures, Fe and Cd are reduced and settled down to the regulus, too. The following table lists the degree of cleaning of copper, cadmium, cobalt and silver as average values from the top and middle layers. Zinc was not considered due to the volatile character of metallic Zn and ZnO at the operational temperature of 1300 °C.

Table 2

The degree of cleaning of copper and other valuable components

	Cu [wt. %]	Cd [wt. %]	Co [wt. %]	Ag [wt. %]
Me-content in slag feedstock	1,60	1,60	0,23	0,005
Degree of slag cleaning after the trials:				
Without additive	53 %	87 %	77,4 %	83,2 %
With adding 5 % of CaC ₂ and 5 % of FeS ₂	92,6 %	98,5 %	95 %	99,7 %

The results determine that the maximum decrease of the copper content (0,38 wt. %) is obtained by using CaC₂ and FeS₂. By using purging gas, no significant improvement of slag cleaning compare to the trials under marginal stirring conditions is conducted. The degree of lead cleaning is improved by using purging gas and/or CaC₂ and FeS₂. A significant increase of the heavy metals in the bottom part of the crucible was observed, especially in the trials without using purging gas. In trials by using the reducing-sulfidizing agent CaC₂ and FeS₂ a coagulated metal phase was created. Possible explanation is the higher density of the reduced copper particles compared to the copper matte leading to a faster settling velocity of the copper inclusions. These phases contain mainly iron, copper and a few percentage of molybdenum.

Conclusion. Preliminary lab-scale results show that an intensive pyrometallurgical slag treatment leads to a further cleaning rate of the heavy metals in copper slags resulting from SAF. By marginal stirring a cleaning rate of 21 % Cu compared to the feedstock was achieved, under turbulent stirring conditions a cleaning of 25 % Cu and without stirring a cleaning rate of 53 % Cu was obtained. By overheating the slag, the maximum cleaning rate of 57 % was reached. Turbulent stirring conditions improve the cleaning rate of lead due to partial evaporation. By using CaC₂ and FeS₂ as reducing-sulfidizing agent under similar stirring conditions a maximal cleaning rate of copper and cadmium was achieved. The bath movement improves the reduction character. By using different additives a further reduction is achieved. Future investigations to analysis the copper reduction potential in the presented stirring reactors in the laboratory of department of "Metallurgy" (TSTU, Tashkent, Uzbekistan) will be made at the end of this year.

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REASONS OF COPPER LOSS WITH SLAG

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Abstract. The main problems of increasing complex-using from raw materials during processing of copper sulfide concentrates have been shown in this article. In implementing this process on an industrial scale, it is recommended for decreasing amount of copper in waste materials with method of working with different reducing agents. As these components it has been installed what addition different secondary technogenic products of local industrial enterprises which consist of copper and other valuable components for changing physical and chemical properties of slags and lower general losing of copper.

Keywords: copper loss, pyrometallurgy, smelting, molten copper slag, depleting.

ПРИЧИНЫ ПОТЕРИ МЕДИ СО ШЛАКАМИ

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Аннотация: В статье рассмотрены проблемы комплексного использования из сырьевых материалов в металлургии. Даны полезные информации о теоретических основах процессов, которые происходят при плавлении сырьевых материалов. Также, определены основные технологические параметры получения расплава, образующейся при процессе плавления медных концентратов.

Ключевые слова: потеря меди, пирометаллургия, плавление, жидкий медный шлак, обеднение

Introduction. As already it was marked above, one of the basic components of economy of Uzbekistan is nonferrous metallurgy. Formation and development of the given industry were promoted by rich mineral stocks and presence of energy sources. Technologically it meant reception of one component of the raw materials, at the best two, and other valuable metals a concentrate or half-finished product kind went on others the branch enterprise. As a result in many mining-metallurgical enterprises the quantity of a waste which it is necessary to consider as technogenic raw materials has accumulated hugely [1, p 255].

So, now, in tailings of Almalyk Mining and Metallurgical Complex (AMMC, Uzbekistan) it is saved up over 800 million tons tailings of concentrating factories with the maintenance of copper 0.07 - 0.12 %. In them is over 800 thousand tons Copper, 10 thousand tons Molybdenum, 182 tons Rhenium, 500 thousand tons Zinc and many other valuable components.

Materials and Methods. In a waste of pyrometallurgical copper manufactures it is saved already up over 12 million tons waste slags of reflective repartition and an oxygen-torch fusion. Even at the average maintenance of copper in them about 0.6 %, it is possible to count up that in it is national economic circulation

it is not involved over 70 thousand tons copper. Daily such slags it is in addition formed from above 1000 tons.

In special storehouses are saved up ten thousand tons firm converting slags in which the copper maintenance makes 2,5 - 3,5 %. In these slags not demanded there are thousand tons of valuable metal. Especially it is necessary to notice that annually such slags it is in addition formed about 24 thousand tons.

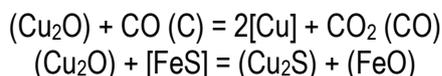
Waelz clinker of zinc manufacture contains over 2.2 % of copper, 2.4 % of zinc, 0.01 % of cadmium, 5-8 g/t gold, 250-500 g/t silver and many other valuable components. About 300 thousand tons such as clinker it is saved already up in sailings, and, at a factory total load, in a year it is formed in addition about 70 thousand tons such valuable material.

Involving of these materials in manufacture will allow industrial complex to receive in addition thousand tons of copper, a significant amount of precious metals and other valuable production.

Results and Discussion. Losses of copper with slags are influenced by many reasons. It, first of all sedimentation on a bath surface concentrate a dust, increase of viscosity of slags, the high maintenance of magnetite in bullion and oxygen in gas atmosphere of the furnace, dissolution of metal, etc.

It is known that all possible kinds of losses of copper with slags can be classified conditionally on chemical, physical and mechanical [2, p 7].

Chemical losses of nonferrous metals are obliged by the origin of convertibility of reactions of restoration or sulfidizing of oxides of copper:



The size of losses of copper in the dissolved form (Cu_2S) in this case is defined thermodynamic process. In industrial conditions of reaction can not reach an equilibrium condition that will lead to increase of chemical losses of copper with slag.

Physical losses is bonded with dissolution in slag of sulphides or metals also are defined by laws of distribution of substance between two not mixing up phases. The first and second kind of losses differs from each other only the mechanism of transition of metals through interphase border and consequently they can be united in uniform group under the name electrochemical losses which metals being in slag in the form of ions concern.

Mechanical losses take place at incomplete division of phases and arise owing to complication in slag of the smallest drops liquid matte or metal. Mechanical losses are presented by drops of matte or metal various size which had not time to be allocated from a slag phase in molten matte during stay bullion in the furnace. The sizes of such drops fluctuate within 0,5 microns to 0,2 mm. The great bulk has the sizes 10 - 100 microns [3, p 112].

Electrochemical and mechanical losses are caused by the nature pyrometallurgical way of reception of copper and to avoid them in actual practice operating enterprise it is absolutely impossible. Necessity of searches of other methods and ways for decrease in negative influence of these factors on technic - economic parameters of process from here follows.

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