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To Prevent the Loss of Copper with Slag during the Casting of the Converter Slag

Tursunoy Parkatovna Karimova[1], Shokhrukh Toshpo'latovich Khojiev[1], Malika Sayfullaevna Saidova[1], Nigora Qobilovna Bakhodirova[2]

[1]Senior Lecturer of the Department of Metallurgy, Tashkent State Technical University,
[2]Assistant of the Department of Metallurgy, Tashkent State Technical University,
E-mail: hojiyevshohruh@yandex.ru

Abstract: *Developed efficient technology of significant copper content in converter slag using inexpensive and non-scarce industrial waste - zinc clinker. The technology is new and makes a certain contribution to the development of science and technology for the integrated use of raw materials, the creation of low-waste technologies while simultaneously solving the problem of environmental protection. As a research hypothesis, it was established that the greatest influence on the copper content in the converter slag is exerted by the magnetite present in it in significant quantities. Magnetite heterogenizes the melt, increases the viscosity and density of the melt, as a result of which the reduction processes are very difficult. It is assumed that the carbon-thermal reduction of the melt magnetite should contribute to the successful reduction of the copper concentration in industrial waste. The developed technology of a significant reduction in the concentration of copper in the converter slag significantly increases the complexity of the use of raw materials, helps to remove part of the metal from the work in progress, reduces the ballast turnover of metal in the reverberatory furnace - converter cycle and can provide an economic effect of more than 10 million US dollars per year.*

Keywords— metallurgy, pyrometallurgy, copper, copper losses, slag, copper matte, converting, processing, automatic control, clinker, magnetite, recovery.

1. INTRODUCTION

The results of the socio-economic development of Uzbekistan for the first quarter of 2021 testify to the effectiveness of the measures taken to deepen the processes of economic reform and the implementation of the most important priorities of the country's socio-economic development for 2021, determined by the President of the Republic of Uzbekistan [1].

As a result of the measures taken to continue deepening the structural transformations of the economy, accelerated modernization, technical and technological renewal of production, the GDP growth rate in the first quarter of this year amounted to 7.6%. Economic growth was ensured by an increase in industrial production by 6.2%, agricultural products - by 5.8%, etc [2].

Thanks to the implementation of comprehensive measures to increase the competitiveness and strengthen the position of Uzbekistan in world markets, in the first quarter of this year, high economic activity was noted in the field of high-tech industries, which had a positive effect on the growth of industrial production [3,4].

As part of the implementation of the Program on the priority of industrial development of the Republic of Uzbekistan in 2017-2021, work continued to further deepen structural reforms in industry, aimed at the advanced development of such priority sectors as energy, non-ferrous metallurgy, etc [5,6].

Achievement of such high indicators became possible due to the continuation and deepening of reforming, renewal and modernization of the country, the unconditional implementation of the Anti-Crisis Program for 2017-2021 and, on this basis, ensuring high and sustainable economic growth rates, its efficiency and macroeconomic balance [7,8,9].

Uzbekistan possesses significant explored reserves of non-ferrous metals: copper, lead, zinc, tungsten, etc. Copper ores are accompanied by more than 15 types of non-ferrous metals, such as gold, silver, molybdenum and others.

The reserves of non-ferrous metal ores are mainly concentrated in the Almalyk ore field. Ore is processed at the Almalyk Mining and Metallurgical Combine (AMMC), which is one of the largest enterprises in Uzbekistan [10].

Almalyk Mining and Metallurgical Combine, like most plants in the world, uses the classic pyrometallurgical scheme for the production of blister copper, which includes:

- melting the charge for matte in a reverberatory furnace;
- melting the charge for matte in the oxygen-flame smelting furnace (OFSF);
- converting mattes.

With such a technological scheme, one of the by-products of production is man-made waste;

- slags of reverberatory melting;
- slags of oxygen-flare smelting;

- converter slags.

Slags of copper production contain from 0.45 to 3.5 Cu and are not dump. Slags of OFSF and reflective smelting are partially processed by flotation, and most of them are stored until an economically viable processing technology is developed. Converter slag, containing up to 3.5% copper, is a recycle product and, for the most part, is processed in a reverberatory furnace. However, in this case, almost all technical and economic indicators of reflective melting significantly deteriorate. In addition, with such a technological scheme, a significant amount of copper is in work-in-progress in the form of ballast circulation between the converter and the reverberatory furnace. In this regard, the topic of the master's thesis on reducing the copper content in the converter slag is very relevant.

The processing of slags from copper smelting is dealt with in almost all countries and continents that have a corresponding industry. Numerous technologies and recommendations have been developed in relation to specific production conditions. This is due to the variety of composition, properties and mechanism of slag formation, requiring individual technological solutions for their processing [11-20].

All known methods of processing slags from copper smelting production can be classified in the following main directions: [21].

- hydrometallurgical;
- flotation;
- pyrometallurgical;
- combined.

Each direction has its own specific advantages and disadvantages. Their applicability is determined both by the composition of the feedstock and fluxes, and by the specific conditions of enterprises [22-29].

The analysis of the developed technologies shows that none of them can be applied in AMMC conditions with acceptable technical and economic indicators. Consequently, the development of an optimal slag processing technology in the AMMC conditions based on the technology used and the operating equipment is necessary.

This research work was carried out in accordance with the State Budgetary Research Topic of the Department of Metallurgy: "Improving the technology of processing ores and concentrates of ferrous and non-ferrous metals, aimed at increasing the complexity of the use of raw materials, environmental protection and environmental issues", as well as in within the framework of the fundamental grant: OT-F 6 - 008 "Development of the fundamental foundations of a fundamentally new technology for the processing of sulfide copper concentrates, aimed at increasing the complexity of the use of raw materials and environmental protection in 2017-2021" [30-35].

The purpose of this dissertation work is to develop an effective technology for converting copper mattes, aimed at reducing metal losses with man-made waste.

Within the framework of this goal, the following scientific and technical tasks were solved:

- various methods of matte production during sulphide copper concentrate smelting in reflective, electric and autogenous furnaces are considered;
- it is shown that the only way to obtain blister copper from mattes is to convert them;
- selected objects and determined the conduct of research;
- studies were carried out to reduce the copper content in converter slags;
- studied the reduction processes in the converter slag - clinker scheme;
- the processes of interaction of liquid slag and solid carbon have been studied;
- determination of electrical conductivity of liquid slag and mattes in converting;
- development of an effective technology for reducing the copper content in converter slags when they are discharged from the furnace.

The subject of the study is to establish the possibility of a significant reduction in the copper content in the converter slag by means of coal-thermal reduction of slag magnetite with added clinker from zinc production, as well as to study the reduction of metal losses with industrial waste when the melt is drained from the furnace [36-47].

2. Materials and Methods

The object of research was the current technology, processed matte and converting products. The materials of the research work were the same charge materials that are used in reflective smelting and an oxygen-flare furnace of the Almalyk Mining and Metallurgical Combine. To study the processes occurring in the layer of charge materials during heating, the change in the electrical resistance of the sample prepared from the initial components was determined. The electrical resistance was measured using a voltmeter-ammeter circuit, which makes it possible to measure the resistance of the circuit continuously and with great accuracy. The setup diagram is shown in Fig.1. The circuit was powered from an alternating current network through a GZ-7A signal generator. The generator allows you to adjust the output voltage from 100 μV to 30V, and the frequency in the range from 20 Hz to 10 MHz [48-53].

The generator output voltage was monitored with a V3-5 tube millivoltmeter. The range of measured voltages varies from 10 μV to 1 V. If it was necessary to establish a voltage in the circuit above 1 V, the millivoltmeter was turned off and the output voltage was set using a millivoltmeter mounted in the generator [54].

The current in the circuit was measured using an F-58 electronic milliammeter. If it was necessary to measure smaller effective values of the current, an F-58 milliammeter was used, which makes it possible to make measurements with 0.001 mA [55].

To measure the electrical resistance, electrodes were introduced into the sample. The introduction of electrodes separately into the core and into the shell made it possible to control the processes in the entire volume of the sample. The core and shell of the sample, in order to study the processes of their interaction during heating and melting, were made from various initial materials. The introduction of both electrodes into the core of the sample makes it possible to obtain information on the parameters of chemical interaction and melting in the center of the materials under study in conditions of their protection from the influence of the external environment [56].

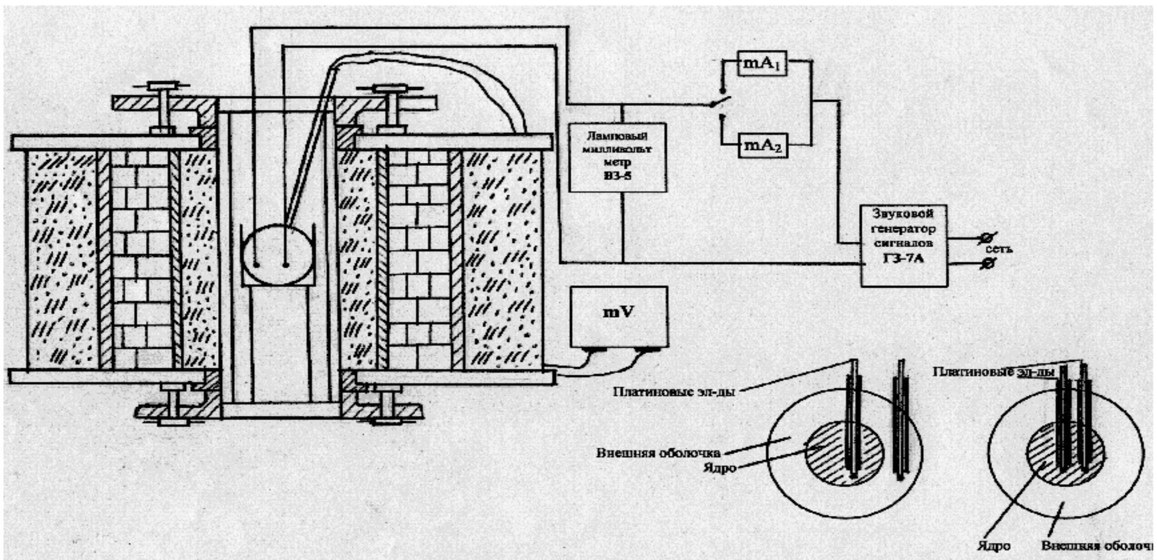

Fig.1. Installation for determining the electrical resistance of materials and a diagram of the introduction of electrodes into the sample

Particular attention was paid to the choice of material for the electrodes. The following requirements were presented to him:

a) low value of its own electrical resistance;

b) weak influence on the characteristics of the material of temperature and composition of the gas phase;

c) low reactivity with respect to the materials that make up the charge.

Platinum meets these requirements most of all. Platinum electrodes were inserted into the sample in quartz sheaths, and only the ends of the electrodes were not protected.

Evseev N.V., Yaskin V.N., Tokovoy O.K. and others Used a similar method to determine the stages of melting the charge in the smelting furnace [57].

Thermographic analysis was performed using well-known and widely used techniques.

Thermograms were taken of both pure substances CaO, SiO_2, Fe_2O_3, Fe_3O_4, and various compositions of the initial components of the depletion mixture. In necessary cases, we also used X-ray phase analysis [58].

3. Results and Discussion

The main circulating products of copper-smelting production are converter slags. With their traditional processing by pouring into a reflective furnace, the extraction of copper from them is ~ 70%. They are also the main source of magnetite entering the melting unit, which significantly worsens the melting performance. Recovery of converter slags in order to reduce the content of magnetite and copper in them has a positive effect on the process of their subsequent processing. It is of interest to evaluate the possibility of using one of the wastes of zinc production - the Waelz clinker for the recovery of converter slags. As you know, up to 30 - 35% of the clinker mass is made up of highly effective reducing agents - finely dispersed solid carbon, cast iron carbon and metallic iron [59].

Laboratory experiments of the authors and previously published data have shown that the addition of clinker in an amount of 10 - 30% of the matte mass does not reduce the copper content in the slag from 2.95 - 3.25 to 0.5-1.0% with a decrease the content of magnetite in the slag is from 20 to 3 - 5%.

Pilot tests on the supply of clinker to an industrial converter were carried out at one of the copper smelters. During the tests, 420 tons of clinker of the following composition,%, were processed: 2.6 Cu; 0.9 Zn; 37.6 Fe; 8.2 S; 18.9 SiO2; 5.0 CaO; 12.0 C; 4.8 g / t Au; 250 g / t Ag. The clinker was fed into the converter together with quartz flux during the entire blowdown. The amount of supplied clinker is 5 - 15% of the amount of processed matte.

During pilot industrial tests, it was established:

when loading clinker, the temperature in the converter rises by 50-100 ° C, which makes it possible to process an additional amount of recycled materials (Table 1). Over the entire testing period, the volume of recycled recycled materials amounted to 22% of the matte mass instead of 10% in the previous month.

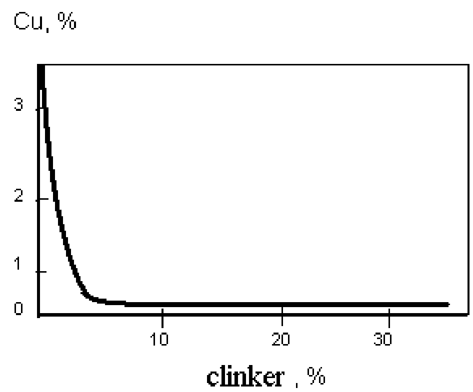

Fig.2. Dependence of the copper content in the converter slag on the amount of contaminated clinker

Additionally, 300 tons of previously accumulated recycled materials were processed;

the copper content in the converter slag ranged from 1.2 to 2.3% and averaged 1.8% with a reported grade of 3.5%;

- no decrease in the efficiency of the converters, additional wear of the lining and changes in the composition of the exhaust gases in terms of SO2 were not observed [60].

The second stage of pilot testing was carried out on all working converters of the plant; 993 tons of clinker were processed. The copper content in the converter slag during clinker loading was 1.4-2.5%.

Table 1. The effect of adding clinker to matte on the amount of recycled materials processed (the ratio of the amount of matte to the amount of clinker is 9: 1)

Blast 103 nm g/h	Matte g/h	Clinker g/h	Recycled materials	
			t/h	% by weight of matte
30	38,64		7,13	18,4
30	30,0	3,3	7,7	25,6
36	46,09		9,53	20,7
36	36,70	4,0	10,2	28,4
42	53,45		11,9	22,26
42	41,50	4,6	12,7	30,3
48	60,92		14,3	23,47
48	47,35	5,3	15,2	32,3

It should be noted that in addition to a significant decrease in the content of copper in converter slags, there is also a sharp decrease in the content of noble metals in them.

When converting without supplying the clinker, the content of gold and silver in the slags ranged from 2.5-9.0 and 12-43 g / t, respectively. When loading clinker, the content of gold and silver in slags was at the level of 0.4-1.3 and 2.8-7.6 g / t, respectively. The heat balances of the process showed that the heat input from the combustion of coke and the oxidation of the metallic iron of the clinker in general, the heat input is ~ 14%, i.e. the introduction of clinker into the conversion process makes it possible to significantly increase the amount of recycled materials processed [61].

Table 2. Composition of the obtained converter slags, %

Cu	Au, g/t	Ag, g/t	SiO_2	S	Fe
Without clinker feed					
3.0	2.8	12.2	19.2	1.2	60.3
3.4	9.0	43.2	21.3	1.0	59.1
3.2	2.5	22.8	23.6	0.8	58.1
3.4	3.2	17.6	19.5	1.8	56.8
3.4	3.2	17.6	19.0	1.8	61.5
With clinker feed					
2.4	1.0	4.8	19.1	1.9	66.6
2.0	1.2	6.0	24.2	1.8	60.6
1.9	0.8	5.0	21.0	1.0	64.3
1.2	0.4	6.2	24.8	0.4	61.2
1.4	0.4	4.8	26.0	0.9	63.0

The result of industrial tests showed the technological feasibility and high efficiency of continuous processing of clinker in converters due to the additional extraction of copper, gold and silver.

The present method makes it possible, without adding fuel, to process rich mattes of autogenous smelting processes and to obtain reduced converter slags, which are relatively poor in the content of copper and noble metals, suitable for deep depletion in a reverberatory furnace.

At present, the processing of clinker in converters has been introduced at two plants in the industry.

4. Conclusion

Large-scale laboratory tests using the developed effective technology for reducing the copper content in the converter slag were carried out on a unit mounted in the laboratory of the Metallurgy Department. Tashkent State Technical University together with employees of the Navoi State Mining Institute. The developed technology can be implemented in the copper-smelting plant AMMC.

Key points: - chemical reactions in a heterogeneous system for the reduction of magnetite of converter slag with solid carbon, which is part of the clinker of zinc production;

- influence and choice of optimal parameters of coal-thermal reduction in the converter slag - clinker system;
- developed technology for reducing the concentration of copper in the converter slag by reducing the melt magnetite;
- change in the technology of discharging the converter slag in order to reduce the ballast turnover of metal in the reverberatory furnace - converter system.

Scientific novelty:

- the chemical reactions of reduction of magnetite of converter slag by clinker of zinc production have been studied;
- it was found that the reduction processes in the heterogeneous system melt - solid carbon flow in both direct and indirect mechanisms in two stages;
- an effective technology has been developed to significantly reduce the copper content in the converter slag and reduce the ballast turnover of metal in the reverberatory furnace-converter cycle;
- a developed system for automatic detection of the end of the scale discharge and prevention of the discharge of the rich mass into the slag.

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