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USE OF ZINC PLANT CLINKER AS A REDUCING AGENT IN THE PROCESSING OF COPPER SLAGS

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Abstract:
The study was carried out for the purpose of theoretical substantiation and obtaining some data on the basis of laboratory semi-industrial and industrial tests, to select the optimal technological mode (improved) for the production of blister copper with the receipt of dump slag containing copper in it up to 0.35%. Waste slags with such a copper content can be transferred to the construction industry, thereby stopping the accumulation of slags that occupy more and more hundreds, thousands of hectares of fertile land for storage.

Keywords: metallurgical slag, magnetite, copper losses, reduction, zinc plant clinker, reducing agent.

At present, the enterprises of the CIS and Uzbekistan, as noted above, receive slags containing 0.45-0.60% copper, which must be depleted. The waste and semi-products of the Almalyk Mining and Metallurgical Combine (AMMC) have accumulated a large amount of tailings from concentrating plants, copper production slags and clinker from the processing of zinc cakes. These materials contain non-ferrous, precious metals and are actually outside the production cycle. Their involvement in processing will allow the plant to significantly expand its raw material base without increasing capital expenditures for geological and mining operations [1,2,3,4,5].

Thus, at present, the AMMC tailings have accumulated over 800 million tons of tailings from concentrating plants with a copper content of 0.07-0.112%. They contain over 800 thousand tons of copper, 10 thousand tons molybdenum, 182 tons of rhenium, 500 thousand tons zinc and many other valuable components [6,7].

The waste of pyrometallurgical copper production at AMMC has already accumulated over 12 million tons of dump slags of reflective processing and oxygen-flare smelting. Even with an average copper content in them of about 0.6%, it can be calculated that more than 70 thousand tons are not involved in the national economic turnover. Copper More than 1000 tons of such slag are additionally formed daily [8,9].

Special storage facilities have accumulated tens of thousands of tons of solid converter slag, in which the copper content is 2.5-5.5%. These slags contain thousands of tons of valuable metal unused. It should be especially noted that about 24,000 tons of such slag are additionally formed annually [10].

Zinc production clinker contains over 2.2% copper, 2.40% zinc, 0.01% cadmium, 1-10 g / t gold, 100-500 g / t silver and many other valuable components. About 600 thousand tons of such clinker have already been accumulated in dumps, and, with a full load of the plant, an additional 70 thousand tons of such valuable material is generated per year [11].

The involvement of these materials in production will allow the plant to additionally obtain thousands of tons of copper, a significant amount of precious metals and other valuable products [12].

The classic pyrometallurgical scheme for the production of blister copper at most plants in the world, including the Almalyk Mining and Metallurgical Combine, includes:

- melting of the charge for matte in a reflective and electric furnace, in furnaces of the autogenous process of oxygen-flare smelting, Vanyukov's furnace, suspended smelting, flare-boring smelting [13];
-converting mattes.

With such a technological scheme, production products are:

- rough copper;
-matte;
- slags of reflective and electric melting;
-slag of autogenous smelting;
-converter slags.

Slags of copper production contain from 0.45 to 5.5% Cu and are not dumps. Slags of KFP and reflective smelting are stored until an economically viable processing technology is developed. Converter slag, containing about 3.5% copper, is a recycled product and, for the most part, is processed in a reflective and electric furnace [14].

The loss of copper with slags is influenced by many reasons. These are, first of all, the deposition of charge dust on the surface of the bath, an increase in the viscosity of slags, a high content of magnetite in melts and oxygen in the gas atmosphere of the furnace, dissolution of metal, etc [15].

It is known that all possible types of copper losses with slags can be conditionally classified into chemical, physical and mechanical [16].

Chemical losses of non-ferrous metals owe their origin to the reversibility of the reduction or sulfidation reactions of copper oxides:

$(Cu_2O) + CO(C) = 2[Cu] + CO_2(CO)$

$(Cu_2O) + [FeS] = [Cu_2S] + (FeO)$

The amount of copper loss in dissolved form (Cu_2S) in this case is determined by the thermodynamics of the process. Under industrial conditions, the reactions may not reach an equilibrium state, which will lead to an increase in the chemical losses of copper with slag [17].

Physical losses are associated with the dissolution of sulphides or metals in the slag and are determined by the laws of the distribution of matter between two immiscible phases. The first and second types of losses differ from each other only in the mechanism of transition of metals through the interface and therefore they can be combined into a single group called electrochemical losses, which include metals in the slag in the form of ions [18,19].

Mechanical losses occur at incomplete phase separation and arise as a result of entanglement in the slag of the smallest droplets of liquid matte or metal. Mechanical losses are represented by drops of matte or metal of various sizes, which did not have time to precipitate from the slag phase into the matte phase during the residence of the melt in the furnace. The sizes of such droplets range from $0.5x10^{-6}$ m to $0.2x10^{-6}$ m. The bulk has dimensions of $1.0\text{-}10.0x10^{-6}$ m.

Electrochemical and mechanical losses are due to the very nature of the pyrometallurgical method for producing copper and it is absolutely impossible to avoid them in the real conditions of an operating enterprise. Hence the need to search for other methods and ways to reduce the negative impact of these factors on the technical and economic parameters of the process [20].

A detailed study of the theory, technique and technology of metal production made it possible to establish that numerous factors affect the copper content in slags, of which the following should be considered the most important: preparation of the charge, parameters of the technological regime of smelting, physicochemical properties of melts, high content of magnetite in slag melts, design of units, organization of work, etc. It is very difficult and hardly possible at all to give an unambiguous assessment of the influence of all parameters acting separately or in aggregate. In this regard, we will try to assess individual process parameters from the point of view of their influence on depletion indicators and the possibility of changing their values in real metallurgical smelting [21].

Batch preparation plays a very important role in any metallurgical process. It would be ideal to use a bedding system for this purpose. However, this will require large capital investments for the construction of the charge house and the presence of significant free areas is required, which is not feasible under the conditions of the operating Almalyk copper smelter [22].

The organization of work makes a certain contribution to the efficiency of the depletion process. However, there is practically no opportunity for a significant change in the currently used production organization system.

From the above it follows that the real lever for controlling the quality of the depletion process is the selection of the optimal technological mode of melting and, closely related to it, the physicochemical properties of slag-matte melts.

Under the technological regime of melting, first of all, it means: optimal compositions of matte and slag, oxidation potential of the gas phase, temperature, as well as physicochemical properties of melts, which are closely related to each other [23].

All of the above technological parameters have a significant effect on the copper content in the slags. However, not all of them can vary widely, providing an opportunity to influence the final results of depletion. For example, the upper temperature limit is limited by the resistance of refractories in an aggressive environment and the increase in the solubility of copper under these conditions. The lower limit is limited by the fluidity of the melts, the difficulty of separating slag and matte due to a sharp increase in viscosity with decreasing temperature, etc. Therefore, in real conditions of a metallurgical furnace, the temperature of the melts can vary within 1423-1573 K, i.e. this factor cannot be used to effectively control the copper content in slags.

The composition of the gas phase is a very important factor affecting the copper content in the slag. Working in a neutral or reducing atmosphere is considered ideal. However, in a really operating metallurgical unit, it is practically impossible to eliminate harmful leaks of secondary air. For this reason, the gas atmosphere inside the furnace above the melt will always be oxidizing and special measures must be taken to reduce its harmful effect.

The composition of the matte directly affects the copper content in the slags. The general principle applies: the richer the matte, the higher the copper content in the slags. However, it is almost impossible to use this principle to reduce copper losses. The fact is that in order to obtain a unit of production, working on a poor matte increases its volume and causes large losses of copper during the subsequent conversion operation.

As a result, metallurgists are limited to work on matte containing 20 - 50% copper.

However, according to the majority of metallurgical scientists and the experience of leading enterprises, they showed that the main reason for the high copper content in the dump slags of reflective and electric furnaces is the high magnetite content (18-29%) of converter slags poured into the unit. The pouring of liquid converter slag is envisaged by the existing technology for producing blister copper.

It should be noted that due to the continuous decrease in the base metal in the ore, a concentrate with a low copper content is obtained, respectively, and the matte turns out to be poor, increasing the number of converter and waste slags per unit of output, ultimately increasing irrecoverable losses with waste slags. At the same time, there is a rapid accumulation of slag, and even being a recycled product, converter slag is processed by only 30% of the volume obtained, although the copper content in it reaches an average of 3%, the remaining amount is stored in special storage facilities. This is due to the violation of the technological regulations of smelting furnaces when pouring more than 30% of the resulting volume of converter slag. Even with such a volume of conversion of converter slag in smelting furnaces, dump slags with a high copper content of 0.45-0.60% are obtained.

Taking into account the negative effect of converter slags in the operation of the smelting unit and the role of magnetite in this process, in our opinion, it will be very effective to pour pre-reduced slags from the process of converting copper mattes of the 1st period into a reflective or electric furnace.

During the operation of reflective and electric furnaces of the copper industry without pouring converter slag, the residual copper content in the waste slag is 0.145-0.35%, magnetite 1-5%. Hence, it follows that with the preliminary reduction of excess magnetite of the converter slag to a residual content of 2-7%, followed by pouring into a reflective and electric furnace, in principle, it is possible to increase the processing of converter slag without violating the technological regulations and without increasing the copper content in the waste slag. In reflective and electric smelting, the presence of sulfides in the concentrate ensures the reduction of a part of magnetite to wustite, with iron, copper and zinc sulfides. A decrease in the content of magnetite (1-5%) in the final slag leads, in turn, to a decrease in the content of copper in the waste slag, both in dissolved and in mechanical form.

Thus, one of the real effective levers for controlling the quality of the depletion process is the selection of an effective slag composition that has optimal physicochemical properties.

The complex of these measures will make it possible to reduce the solubility of copper sulfide in the slag, extract dissolved copper into matte, convert oxidized copper into a sulfide form, create conditions for the deposition of the formed fine suspension of sulfides into the bottom phase, i.e. the necessary conditions will be created for the extraction of the valuable component with a significant reduction in the copper content in the slag and the practical implementation of waste-free technology in industry.

The depletion process can be successfully implemented with the simultaneous implementation of all of the above processes.

Before embarking on the solution of such a complex multifactorial problem, we developed a concept for the process of depletion of slags from copper smelters.

The concept developed by us was based on the following basic provisions:

- reducing agents should be preferably from local, not expensive, scarce and unclaimed resources and waste;
- the technology must ensure the absence of environmental pollution by smelting products outside the existing standards;
- the technology should have prospects for further transition to zero-waste;
- implementation of the technology should be carried out using existing equipment with no or insignificant reconstruction costs;
- the technical level of the technology must comply with the best world standards in relation to the real conditions of the AMMC.

To implement the developed concept in production, we have studied in detail numerous waste, semi-finished products and unclaimed materials from mining and metallurgical enterprises.

As a result of this work, zinc clinker was chosen as a reducing agent, containing, in addition to the reducing agent, a significant amount of valuable components and being a reactive substance.

The use of clinker as a reductant, magnetite contained in the slag melt, will allow AMMC not only to solve the problem of processing converter slags, but also to obtain a significant amount of copper, gold, silver and other valuable components.

Further, it was necessary to conduct theoretical and laboratory studies:

- study of phase equilibria in complex oxide systems close in composition to converter slags and reflective smelting associated with the behavior of magnetite (heteronization conditions in a wide range of gas atmospheres);
- study of the effect of ferric iron - magnetite, on the physicochemical characteristics of slag-matte melts in real conditions of metallurgical processes;
- carrying out theoretical studies and calculations on the interaction of components in the liquid and solid state of the process of carbon-thermal reduction of ferric iron of an iron silicate melt;
- substantiation of the possibility of depletion of copper-containing slags during the reduction of magnetite in the slag melt.

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