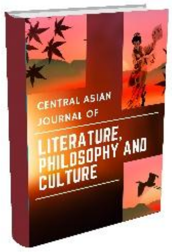

CENTRAL ASIAN JOURNAL OF LITERATURE, PHILOSOPHY AND CULTURE

Volume: 02 Issue: 02 | Feb 2021

Current State Of Copper Smelting Slags And Their Processing: A Review

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Received 22nd December 2020, Accepted 12th January 2021, Online 13th February 2021

Abstract: *The review article is devoted to the current state and ways of solving one of the most pressing and complex problems in copper metallurgy - the reduction of irrecoverable losses of metal with dump slags and the creation of environmental technology. A comprehensive solution to the problem with the use of physicochemical methods of influence on the melt is proposed. It is shown that the success of the depletion process depends on the sulfiding of oxidized copper compounds, the reduction of magnetite in the slag to wustite, and the creation of conditions for the coalescence of fine drops of matte. Creating these conditions makes it possible to reduce the residual concentration of copper to the level applied. This can be obtained poor matte, which is processed by pouring them into a melting furnace. Depleted slag is waste products and can be implemented in the construction industry. In fact, this makes it possible to abandon the creation of slag heaps.*

Keyword: *slags, depletion process, sulphidation of oxidized compounds, magnetite reduction, bubbling of a bath, coalescence of small particles, poor matte, waste product, construction industry.*

Introduction

The classical pyrometallurgical scheme for the production of blister copper at most plants in the world, including the Almalyk Mining and Metallurgical Combine, includes: melting the charge for matte in a reflective, electric or autogenous process furnace, oxygen-flare smelting, Vanyukov furnace, suspended smelting , flare-bobbin melting, matte converting.

With such a technological scheme, the production products are: blister copper, matte, reflective and electric smelting slags, autogenous smelting slags, converter slags.

Slags of copper production currently contain from 0.45 to 5.5% Cu and are not dump [1].

The waste of pyrometallurgical copper production at AGMK 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 [2,3].

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 [4].

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 [5].

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 amount of converter and dump slags per unit of output, ultimately increasing irrecoverable losses with dump slags. At the same time, there is a rapid accumulation of slag, and even being a recycled product, converter slag, only part of the resulting volume is processed, although the copper content in it reaches an average of 3%, the remaining amount is stored in special storage facilities [6].

For several decades, the attention of scientists and specialists has been directed to finding methods for processing slags from copper-smelting production. Many hundreds of technologies and recommendations have been developed, which, as a rule, are local in nature and are applicable to solving a specific problem. This is due to the variety of composition, properties and mechanism of slag formation, which require individual technology for processing. Currently, there is no unified technology applicable to solving all the problems of processing copper-containing slag [7].

All known methods of processing slags from copper smelting can be classified into the following main areas: hydrometallurgical, flotation, pyrometallurgical and combined. Each direction has its own advantages and disadvantages. Their applicability is determined both by the composition of the feedstock and fluxes, and by the specific conditions of the enterprise [8].

The hydrometallurgy of slag processing is based on the transfer of copper into a solution and its subsequent separation from it by one of the known methods. Dissolution is carried out by treating the slag with a solvent after crushing and grinding with the possibility of chemical treatment for additional conversion of copper into soluble forms or without it. The conversion of copper into soluble forms can be carried out by sulfatization, chlorination, biotechnological methods and other methods [9].

The advantage of slag hydrometallurgy is the ability to achieve high copper recovery into a highly concentrated sludge in the absence of process gases, thereby excluding air pollution. However, this method also has significant drawbacks: low leaching rate, the formation of a large volume of solutions per unit of production, difficulties with the extraction of noble metals and the removal of sulfur in elemental form. The complex of the above reasons leads to the fact that slag hydrometallurgy has not found practical application and technological developments are mainly limited by the framework of laboratory and semi-industrial tests [10].

Depletion of copper-containing slags by flotation has found a fairly wide application. Both rapidly and slowly cooled slags are subjected to flotation. Moreover, with a content of up to 18-20% silicon dioxide, the technical and economic indicators practically coincide. At a higher content of silicon dioxide, it is preferable to slowly cooled slag in ponds or ladles [11].

Of considerable interest is also the production of highly basic ferrite-calcium slags, which have self-dispersing properties during melting and conversion. Work in this direction was carried out at the Institute of Metallurgy of the Academy of Sciences of Russia, the Ural Scientific Center, etc. The fundamental possibility of obtaining well-floatable CFP slags with self-dispersing properties was confirmed during pilot tests at the Gintsvet Meta OEMZ [12].

Volume: 02 Issue: 02 | FEB 2021, ISSN: 2660-6828

Flotation of converter slag is also carried out at almost all plants using electrothermal depletion of slag from suspended smelting. Electrothermal depletion of converter slags is used at the Onson factories (South Korea) and Nordoiche Arfineri (Germany). Slags from the Noranda and TVRS processes are processed by flotation. Slag flotation technology is similar at all enterprises. For example, at the Harjavalta plant (Finland) it includes: -separate three-stage crushing to a size of 4 mm; - two-stage joint grinding to a class yield of 0.053 mm (90-91%). The total flotation time is 40 minutes. When the copper content in the flotation tailings is at the level of 0.4 - 0.5%, copper recovery from slags is ensured up to 60-70%.

In [13,14], the possibility of joint processing by flotation of copper-containing slags with sulfide ores is shown. The extraction of copper into concentrate at the same time reached 80-85%, with a residual content in the tailings of 0.08 - 0.1%.

However, flotation processing of slags has a number of significant disadvantages: the heat of molten slag is not used, the hardness of the slag significantly exceeds this indicator of the original ore, which creates great difficulties in crushing and grinding, slag flotation does not allow solving the issue of extracting a number of other components, such as nickel, cobalt, zinc. All these disadvantages greatly limit the possibilities of using slag flotation technology and they are used only where other technologies, for whatever reason, are not effective.

Pyrometallurgical methods of depletion of slags from copper production are the most promising in comparison with the hydrometallurgical method. Because:

- they enter the processing with liquid slags and do not require fuel consumption for their melting;
- the consumption of fossil fuel for the process is minimized, etc.

Converter slags, being a circulating product, according to the technological regulations for obtaining blister copper in liquid form, are poured and processed in a reflective and electric furnace [15]. However, as noted above, due to the receipt of a large volume of converter slag per unit of output, only a part is processed, the other is stored. The processing of converter slags in a reflective and electric furnace due to the excess content of magnetite in them negatively affects the technology and technical and economic indicators of smelting when producing blister copper.

Depletion of converter slag with natural gas on a semi-industrial scale was carried out at the Almalyk Mining and Metallurgical Combine (AMMC) [16]. But this method has not found industrial application, due to the laboriousness and in the final products of obtaining slags rich in copper.

The authors of [17, 18] note the possibility of depletion of slags from the copper industry by reduction treatment under conditions of bubbling in liquid bath furnaces.

There are developments on slag depletion by mixing it both with a special extraction phase and with its own matte in order to change the equilibrium towards a lower content of magnetite and dissolved copper.

However, the process is applicable mainly for suspended smelting slags, in which there is no equilibrium between matte and slag [19].

The development of a technology for depletion of slags in top-blown reactors is underway. According to the authors' proposals, high-pressure gas is blown into the melt at great speed and sets it in rotational motion. A high initial velocity leads to good dispersion of the gas in the slag and high rates of mass transfer. This technology makes it possible to deplete the slag to 0.5% copper, regardless of the initial initial content. The technology of slag depletion by means of the upper blast is included in the Kontop process of the Humboldt company (Germany).

In the CIS, a similar technology is being developed with the use of additional solid reducing agents [20].

Converter slag according to the UPI scheme [21] is processed as follows: liquid converter slag is poured into an electric arc furnace, up to 10% lime and 2-3% coke are added to it. The matte enriched to 10-15% Cu is sent for conversion, and the slag containing 0.2-0.5% Cu is sent to the second electric furnace. In this furnace, 1-2% coke and 10% pyrite are added to the slag. Metallized matte (1.5-3% Cu) is fed into the first furnace, and slag with 0.07 - 0.1% Cu is fed into the third furnace. Lime and 12-15% of a reducing agent are loaded into the furnace. Recovery of copper from slag to matte is 85-90%, and iron to steel cast iron is about 90%. The process is energy-consuming and requires a large consumption of coke.

On an industrial scale, at the Harjavalta plant (Finland), converter slags were depleted in a three-phase electric furnace [22]; slags were poured into the furnace 4-5 times a day in portions of 40-50 tons. Due to the shallow reduction of magnetite (before depletion of 15% Fe_3O_4 after 12 %) and low copper recovery from slags (60%), the plant abandoned this method and switched to converter slag flotation.

Most of the plants that use suspended smelting, depletion of the slags of the main smelting unit is carried out in electric furnaces. These include "Aseno", "Kosaka", "Saganoseki", "Toyo", "Tamano" (Japan), "Gatsila" (India), "Glogow-P" (Poland), "Nordoiche Affineri" (Germany), Uelova (Spain), Hidalgo (USA), Onsoy (South Korea), Passar (Philippines), NMMC (CIS), etc. In slags, the copper content is reduced to 0.4 - 0.6%. Coal or coke is used as a reducing agent, pyrite, concentrate or other sulfur-containing materials are used as a sulfidizer. Slag depletion is carried out, as a rule, in one stage in a separate round or rectangular electric furnace. In the combined process of Mitsubishi (Japan), a three-electrode oval electric furnace is used [23].

Plants "Tamano" (Japan) and "Passar" (Philippines) have in-furnace electric settling tanks, combined with the settling zone of the furnace itself. This design makes it possible to reduce the consumption of electricity by 25%, eliminate the difficulties with the transport of depletion matte and reduce the volume of waste gases by 14% [24].

The copper content in slags after electrothermal depletion at the level of 0.5 - 0.6% is an economic minimum. Its further decrease is possible with an increase in the degree of reduction and sulfidation, or by increasing the number of stages of the depletion process. In this case, a significant increase in energy consumption, consumption of fluxes, reagents and the complication of technology inevitably occurs [25].

From the literature, there are also many other developments that have passed semi-industrial and industrial tests of electric furnace depletion of copper-containing slags, but electrothermal depletion has a number of significant drawbacks: high power consumption per unit of commercial product obtained, emission of sulfur-containing slags into the atmosphere. gases, i.e. the need to solve the same problems as in reflective melting, albeit in smaller volumes, the impossibility of obtaining deep depletion, and limitation only to the economic minimum (0.5 - 0.6% copper), the impossibility of using waste-free technology.

These and some other disadvantages make the technology of electro-thermal depletion of copper-containing slags unpromising.

Technologies for depletion of copper-containing slags of copper production have been developed at the Tashkent State Technical University. According to one of them, which became the winner of the competition among the CIS countries for the creation of a technology that provides effective and large-scale complex processing of copper-containing protection of stale slags, the maximum use of the existing smelting capacities, reconstructed for units with upper air-oxygen blast, is provided. According to this technology, clinker is added to the composition of the reducing-sulphidizing compositions during the complex processing of converter slags from AMMC in reverberatory furnaces, converted into a depleting unit.

Another technology provides for the maximum use of the reduction potential of carbon and metallic iron that make up the clinker for the reduction of magnetite in the converter slag, with the subsequent production of waste slags with a low copper content in them. At the same time, several problems are being solved for the processing of difficult-to-process types of technogenic raw materials: extraction of valuable components from clinker, depletion of converter slag in copper, conditions are created for obtaining dump slags with a copper content of 0.35%.

These tasks are achieved by reducing the excess content of ferric iron (magnetite) of the converter slag in the process of converting copper mattes. The high content of ferric iron in iron silicate slags increases the copper content in them both in dissolved and in mechanical form.

Reduction of excess magnetite of the converter slag with a solid reductant (zinc production clinker) to a residual content of 2-7%, followed by pouring into a reflective and electric furnace, should reduce the copper content in the waste slag to 0.35%, since during operation of reflective furnaces without pouring the converter slag, dump slags contain 0.1-0.35% copper, 1-5% magnetite. It follows that when pre-reduced converter slag is poured into a reverberant furnace with a residual magnetite content of 2-7%, part of the latter is reduced by iron sulfides of the charge to 1-5% during reflective melting, the slag will contain 0.145-0.35% copper. On the basis of the above, laboratory studies were carried out, smelting of sulfide concentrates, fluxes and pre-reduced converter slags in conditions close to reflective smelting and slags with a copper content of 0.19 - 0.35% were obtained. Such slags can be transferred to the construction industry, creating waste-free technologies for producing blister copper.

Thus, with the implementation of both technologies, the problems of the copper plant may be solved: according to the first technology, the accumulated slags in the dumps of the copper smelting production are processed, according to the second technology, slags are obtained that do not require their storage, but transfer them for use as building material.

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