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# PROCESSING OF SLAGS OF COPPER MANUFACTURING WITH THE USE OF IDEAL MIXING EQUIPMENT

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***Abstract:*** *The article discusses the issues of processing slag of copper production using devices that model ideal mixing. It has been shown that the use of this type of apparatus increases the efficiency of physical and chemical processes and significantly reduces the copper content in dump slags. It has been found that the process of reduction of ferric iron oxide by the clinker in the initial period takes place in the kinetic mode. After reducing the concentration of magnetite (3-5%) in the slag, the process of reducing it passes into the diffusion region, that is, restoring the excess content of ferric iron in iron silicate melts takes a short period of time during which the process can be carried out, without significantly delaying the operation time of the main industrial equipment. The optimal slag magnetite reducing agent is determined to be zinc production waste.*

***Keywords:*** *slag, processing, reducing agent, zinc-clinker clinker., chemical reactions, depletion, flotation, ideal mixing apparatus, low-waste production.*

Processing of copper production slags remains one of the most complex and unresolved problems of modern non-ferrous metallurgy. This problem has not been comprehensively solved in any country in the world. This issue is particularly acute for the conditions of Uzbekistan. This is because the concentration of copper in the slag is significantly higher than its concentration in the original ore and cannot be allowed to lose it irretrievably.

Our strategic objective is the integrated use of raw materials, the extraction of all valuable components, and the use of residues in cement production or road construction. Together, this will make it possible to organize low-waste production with high technical and economic indicators.

In recent years, extensive studies have been carried out to recover the valuable metals from copper slag. Basically, they can be classified into three main categories, namely physical separation process, pyrometallurgical process and hydrometallurgical process, such as flotation [1–4], roasting [5,6] and leaching [7,8].

A large number of different slag processing technologies have been developed and recommended in world practice [9]. However, most of them did not go beyond the laboratory and semi-industrial tests. They introduced technologies may make exceptions for slag flotation at the Haryavalta plant (Finland) and Almalyk mining and metallurgical plant.

At the Finnish plant, the technology includes:

- Separate three-stage crushing to 4 mm size;

- Two-stage combined grinding to yield -0.05 mm (90-96%). The total flotation time is 40 minutes to produce a concentrate containing about 20% copper. At copper content in flotation tailings at the level of 0.40- 0.50% copper extraction from slags up to 60-70% is provided [10]. Similar values were obtained using this method and in AGMC.

Flotation enrichment has some significant disadvantages, the main ones being:

- High consumption of electric power, grinding balls and wear of lining during slag grinding;

- Low extraction of copper, since sulfide and partially metallic copper, whose contents are not high, are mainly extracted into concentrate. At the same time, the oxidized copper mainly passes into slag rods and is irretrievably lost;

Flotation does not allow removal of some associated elements (Ni, Co, Zn, etc.), which reduces the efficiency of the process;

- It is challenging to use iron-silicate part of tails for metallurgical purposes, which affects complex use of raw materials;

- The heat of the molten state is not used.

The above and some other disadvantages reduce the prospect of a comprehensive introduction of the flotation processing of copper production slags.

Slag processing technologies based on molten heat may be the most promising. In our view, the intelligent technology of slag processing can be developed based on studying the structure and properties of melts, thermodynamics, and kinetics of chemical reactions taking place in the system. To this end, the Department of Metallurgy of Tashkent State Technical University developed a concept for the development and introduction of copper slag processing technology. At the same time, the following [11] was established as the main requirements for the technology:

- Focus on increasing the sophisticated use of raw materials, preventing loss of valuable components with waste products;

- Orientation towards the use of only local materials as additives, preferably secondary human-made formations of local industrial enterprises;

- Absence of environmental contamination by melting products beyond the permissible limits;

- Technology should have prospects for further transition to low-waste;

- Implementation of the technology should be carried out on the operating equipment with minimum costs for reconstruction and changes in technological regulations.

Detailed familiarization with the existing literature on slag processing, as well as the study of the experience of advanced metallurgical enterprises, has made it possible to establish that the success of the depleted process is mostly determined by the solution of the following problems [12]:

- Reduction of slag magnetite to cystitis;

- correction of the composition of slag and work on the optimum maintenance of such components, as $SiO_2$, CaO, FeO, $Fe_3O_4$, etc.;

Sulfiding the oxidized copper compounds and converting them to the matte phase;

- Bubbling the melt to create conditions for the coalescence of beautiful matte drops;

Converting the matte fines into the bottom phase by stirring with inert gas or with a recovery phase;

- Sulfur bonding into the condensed phase, which will simultaneously reduce desulfurization and convert it to matte.

Solving these problems could ideally solve the issue of processing copper-made slags. In practice, however, this is a difficult-to-implement problem because it requires the involvement of a large number of materials and equipment. It is advisable to carry out the work in stages to study the effect of each factor on the result of the decapitation.

At this stage of the studies, the effect of the degree of reduction of magnetite on copper release from slag was studied. Solid carbonaceous materials (coke, petroleum coke, coal, zinc plant clinker), as well as natural gas, can be used in real-world conditions of Almalyk MMC [13].

Based on the developed concept of depletion, the authors selected as reducing agent clinker Almalyk zinc plant, the composition of which is given in Table 1.

**Table 1**

**Chemical composition of clinker Almalyk zinc plant (on the main components)**

| Type of clinker | Content, % | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cu | Zn | Fe | C | Pb | Cd | In | $SiO_2$ | As | Au, g/t | Ag, g/t | Glass - visible silicate phase |
| CL-1 | 2,34 | 2,45 | 32 | 15 | 0,6 | 0,02 | 0,001 | 1,6 | 0,3 | 3-5 | 300-500 | The rest |
| CL-2 | 2,11 | 2,69 | 36 | 16 | 0,7 | 0,02 | 0,009 | 19 | 0,3 | 2-5 | 250-300 | The rest |

The choice of clinker as the reducing agent was due to the following circumstances:

1) in clinker composition in sufficiently large amounts there are such active, reducing agents as carbon (12-20%) and metallic iron (18-24%);

2) clinker contains more than 2% copper, a significant amount of noble metals. Their extraction into the finished product will significantly improve the technical and economic performance of the whole process;

3) in Almalyk MMC clinker is available in quite large quantity, and the form ready for use in technology;

4) To date, the clinker processing technology has not been developed in a separate cycle with acceptable techno-economic and technological indicators. Therefore, its use as a reducing agent is justified.

Various chemical reactions may occur when the clinker is added [14].

The process of reducing iron from oxides according to Baykov 's principle on the sequence of transformations proceeds stepwise by the successive transition from higher oxides to lower oxides according to the scheme [15]:

$Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$ (higher than 570 $^0$C) or $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow Fe$ (lower than 570 $^0$C).

Following the Fe-O diagram, not only lower oxides and metal are formed in the system, but also reliable solutions.

Reduction of iron oxides by hard carbon clinker is possible by the following reactions:

$$3Fe_2O_3 + C = 2Fe_3O_4 + CO$$

$$Fe_3O_4 + C = 3FeO + CO$$

$$FeO + C = Fe + CO$$

Clinker metallic iron, as well as CO reaction gas, is also involved in reducing processes by reactions:

$$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2 + 37.25 \text{ MJ}$$

$$Fe_3O_4 + CO = 3FeO + CO_2 -20.96 \text{ MJ}$$

$$FeO + CO = Fe + CO_2 + 13.65 \text{ MJ}$$

$$Fe_3O_4 + Fe = 4FeO$$

The $CO_2$ released by these reactions in the presence of clinker carbon can again be converted to CO:

$$CO_2 + C = 2CO -166.32 \text{ MJ}$$

The average sample of converter slag of the following composition, %: Cu – 2,30, was selected for research on magnetite reduction by zinc clinker; $Fe_{(total)}$ – 48.50; $SiO_2$ – 19,89; $Al_2O_3$ - 3,16; CdO – 0,75; $Fe_3O_4$ – 16,30; S – 1,39; MgO – 0,46.

By stoichiometric calculations, a 5% clinker of slag weight is sufficient to reduce magnetite to the equilibrium value [16]. For an increase in the extent of restoration, the reducer consumption of up to 10% was increased. The results of the performed studies are given in Table 2

**Table 2**

**Results of converter slag depletion with clinker**

| № | Loaded, % | Matte yield, % | Matte content, % | | | | Slag yield, % | Slag content, % | | | | Copper extraction in matte, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Cu | Fe | S | Zn | | Cu | Fe | $SiO_2$ | S | |
| 1 | 5 | 1,70 | 66,30 | 7,1 | 17,2 | 0,4 | 87,9 | 1,20 | 46,5 | 18,6 | 2,6 | 51,2 |
| 2 | 5 | 1,67 | 70,70 | 4,8 | 18,1 | - | 87,2 | 1,00 | 47,5 | 20,1 | - | 52,3 |
| 3 | 5 | 1,60 | 71,20 | 5,3 | 18,9 | - | 83,3 | 1,13 | 49,0 | 18,6 | - | 50,9 |
| 4 | 10 | 1,50 | 71,60 | 4,5 | 18,2 | - | 84,5 | 1,13 | 48,2 | 19,4 | 1,9 | 58,3 |
| 5 | 10 | 1,43 | 72,80 | 5,7 | 17,3 | 0,6 | 81,2 | 1,20 | 42,5 | 20,1 | 2,7 | 49,7 |
| 6 | 10 | 1,54 | 72,16 | 4,4 | 19,3 | 0,5 | 83,8 | 1,56 | 40,1 | - | - | - |

Experiment conditions: slag overhang 100 g, slag tempering 1300 $^0$C, holding time 120 min.

Analysis of the data given in Table 2 shows that the extraction of copper in matte does not exceed 50-55%, which will lead to significant losses of metal with waste slags. We considered it inappropriate to increase clinker consumption for the following reasons:

- The addition of a large amount of cold material cools the melt and slows down all physical and chemical conversion;

- Obtained clinker dilutes slags, increases their quantity, which creates additional difficulties in their subsequent processing.

Experiments were carried out according to known, widely spread methods [17]. During the experiments, the clinker was filled on the surface of the slag melt. It has been observed that a significant portion of the powder clinker burns from the surface; relatively large particles (3-5 mm) float on the surface of the bath. All of this results in a low degree of clinker acquisition of the bathroom, which accordingly leads to insufficient recovery of magnetite [18-19].

Bath stirring experiments were conducted to increase clinker absorption. Argon was used as the stirring phase. The results of the study are shown in Table 3.

**Table 3**

**Results of experiments on converter slag depletion with argon stirring**

| № | Mixing time, min | Matte yield, % | Matte content, % | | | Matte extraction, % | Slag yield, % | Slag content, % | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Cu | Fe | S | | | Cu | Fe | $SiO_2$ | CaO | S |
| 1 | 10 | 10,0 | 14,9 | 70,6 | 6,07 | 69,8 | 88,2 | 1,09 | 43,7 | 20,6 | 1,48 | 2,56 |
| 2 | 15 | 10,0 | 12,7 | 44,8 | 5,60 | 60,2 | 87,7 | 1,02 | 39,4 | 24,7 | 1,29 | 2,70 |
| 3 | 20 | 10,4 | 15,3 | 64,3 | 5,10 | 69,1 | 87,9 | 1,39 | 42,6 | 23,7 | 13,0 | 2,10 |
| 4 | 30 | 14,7 | 12,1 | 70,1 | 5,60 | 76,8 | 84,4 | 1,08 | 35,4 | 25,6 | 1,80 | 1,20 |
| 5 | 40 | 10,35 | 17,28 | 54,9 | 13,8 | 77,5 | 88,1 | 0,97 | 32,4 | 30,61 | 1,88 | 1,57 |

Experiments were carried out under the following conditions: clinker loading - 10% of the initial slag weight, settling time - 20 min, temperature 1300 ° C.

Analysis of the results shown in Table 3 shows that the recovery of copper to matte with an increase in mixing time slightly increased from 69,8 to 77,5%. However, the residual copper content of depleted slag remains quite high (0,97 -1,39%), which can lead to significant metal losses with production waste. These results have shown that mixing the melt with argon does not produce the expected results for slag depletion, and this process requires further improvement.

We conducted particular experiments on the parallel loading of melt and clinker. However, the results of the experiments remained virtually unchanged. This method concentrated all the disadvantages of the previous series of experiments, and they were suspended.

In search of the complete contact between the melt component and the reducing agent, several experiments were carried out using an ideal mixing apparatus [20].

Mixing in liquid media is widely used in the chemical industry for the preparation of emulsions, suspensions, and the production of homogeneous systems, as well as for the intensification of chemical, thermal, and diffusion processes. In the latter case, mixing is carried out directly in devices equipped with mixing devices intended for carrying out these processes.

In the case of homogenization, suspension preparation, heating, or cooling of the stirred heterogeneous medium, the purpose of mixing is to reduce the concentration or temperature gradients in the volume of the apparatus.

When mixing is used to intensify chemical, thermal, and diffusion processes in heterogeneous systems, better conditions are created to supply the substance to the reaction zone, to the phase interface, or the heat exchange surface.

The increase in the degree of turbulence of the system achieved by stirring leads to a decrease in the thickness of the boundary layer, an increase, and continuous renewal of the surface of the interacting phases. This causes a significant acceleration of heat and mass exchange processes [21].

Any metallurgical process is generally accompanied by the movement of material streams of liquid, gas, or solid particles. Flows can be single-phase, i.e., consist entirely of only one phase moved in some volume of the apparatus, and multiphase in our case this liquid is a solid body. The efficiency of metallurgical conversion depends to no small extent on the rational organization of flows. In our case, the description of the flow of flows makes sense for the most part, only about the movement and distribution of substances in these flows.

The main problem of the process of slag depletion and magnetite reduction with dependable reducing agents in the provision of dense and uniform contact of reactive substances. This condition can be achieved if the process is carried out in machines providing perfect mixing.

The physical feasibility conditions of this model are met if the total (ideal) mixing of the flow particles occurs in the entire flow or the section under consideration. In this case, any change in the concentration of the substance at the inlet of the flow into the ideal mixing zone will be instantly distributed throughout the entire volume of the zone. The equation describing the change in concentration in the ideal mixing zone is:

$$V\frac{dx}{dt} = v(x^{(0)} - x),$$

Where $V$ - the volume of the ideal mixing zone, $m^3$;

$v$ - flow rate entering and leaving the ideal mixing zone, $m^3/h$;

$x^{(0)}$ Is the concentration of the substance at the inlet and outlet in the ideal mixing zone, $kmol/m^3$; T - time, h.

In hydrometallurgical processes, it is often sought to approach the conditions of ideal mixing by installing special stirrers, bubbling, or other methods in the apparatus. The recommended diagram of one of these sets is shown in Figure 1.

In its design, slag ladles are well suited to the ideal mixing apparatus. However, in the actual operating conditions of slag ladles, it is difficult to use mechanical and aerodynamic mixing.

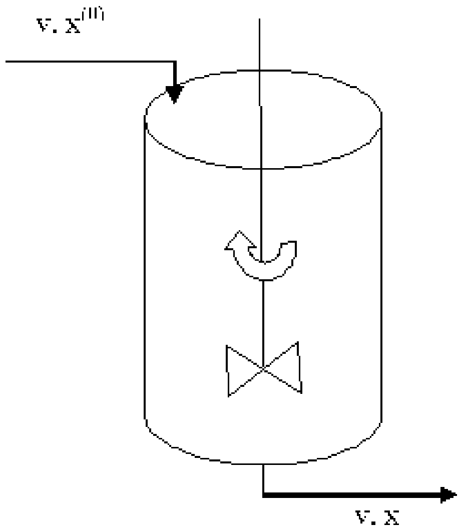


**Fig.1** Schematic diagram of the ideal mixing apparatus

For this reason, to create conditions for perfect mixing, we propose to use the energy of the falling and reflected jet. The diagram of the proposed cutting is shown in Figure 2.

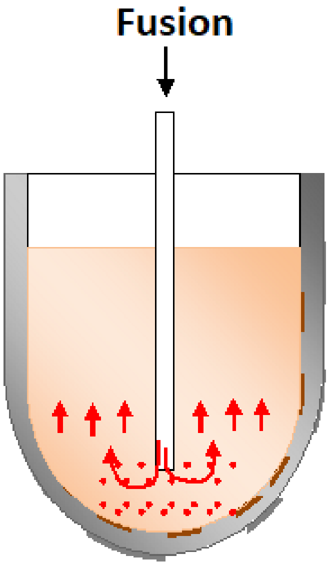


**Fig. 2.** Slag ladle scheme simulating ideal mixing apparatus

On the bottom of the slag ladle, we fill a certain amount of powdered clinker. Then we start pouring slag according to the accepted technological scheme. Slag jet, reflected from ladle bottom, rises upwards and takes with it particles of reducing agent. At the same time, practically ideal conditions are created for the mixing of components and the performance of reducing processes.

One series of experiments was conducted to test the feasibility of theoretical proposals. The results of the experiments are shown in Figure 3.

Analysis of the data in Figure 3 shows that the reduction of slag magnetite by clinker according to this technique is more successful, and the residual copper content in the slag is in the range of 0,6-0,7%. A comparison of these data with the results shown in Tables 1 and 2 shows a significant decrease in the copper content of the slag.

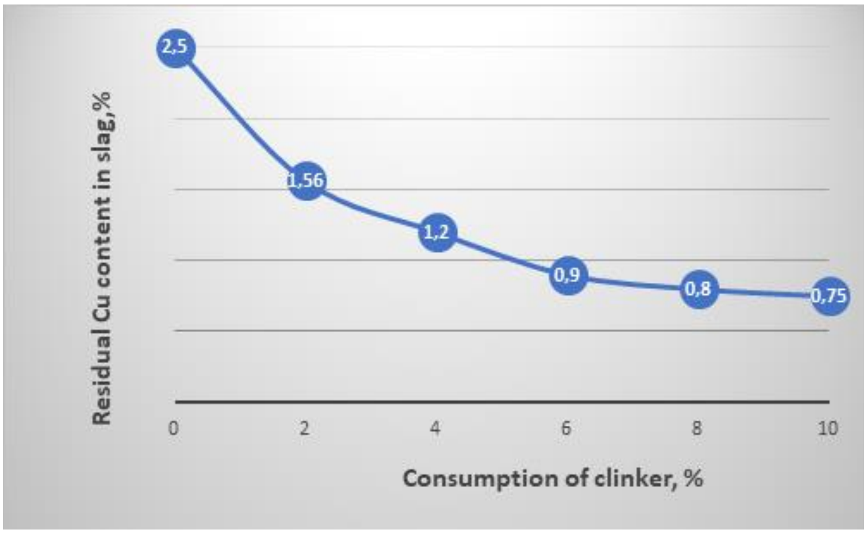


**Fig. 3.** Effect of clinker flow on residual copper content in slag

However, this content is still quite high and requires further processing. Mineralogical analysis of the depleted slag sample showed the presence of a large amount of oxidized copper and fine matte particles in it, which did not have time to settle into the bottom phase. The technology being developed requires further development in terms of sulfidation of oxidized copper compounds and the creation of conditions for the coalescence of beautiful matte drops.

Based on the studies carried out, it can be concluded that the use of ideal mixing devices will make it possible to most effectively carry out the process of extraction of copper, gold, silver and other elements from slag, to obtain a significant number of additional products and to switch to low-waste technology.

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