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Pyrometallurgical Processing of Copper Slags into the Metallurgical Ladle

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ABSTRACT: The present study relates to non-ferrous metallurgy and can be used in the production of copper to decrease the loss of copper with slags in copper smelters. The objective of this study is the most complete decreasing in the loss of copper with slags and an increase in the productivity of copper smelters. Pyrometallurgical processing of copper slags into the metallurgical ladle by waste tires addition is that in the process of depletion of slags used semi-products and waste tires, as well as used as a reducing agent and sulfidization of oxidized copper compounds waste of crushed tires.

KEYWORDS: Copper slag, Copper matte, Processing, Reducing agent, Sulfidizing agent, Slag ladle, Waste of tires, Decreasing of copper loss, Magnetite, Hydrogen, Carbon, Coalescence.

I. INTRODUCTION

Resource-saving technology - such an organization of production, in which waste is minimized and processed into real secondary material resources. When resource-saving technology is supposed to create optimal technological schemes with closed material and energy flows [1]. However, not all industries have developed industrial technologies for the rational use of resources, economic and legal prerequisites for this have not been created. Such a task should and will be solved by the generation that today is entering into real economic activity. An alternative to this approach, as we have seen, is no longer today [2].

Resource-saving technologies allow:

- reduce or prevent the amount of damage caused to the environment by the release of waste;
- reduce the area of land occupied by dumps, accumulators, waste dumps;
- to reduce environmental pollution from the processing of primary raw materials, "compensating" the non-use of secondary material resources contained in the waste, as well as the heat contained in the secondary energy resources;
- to reduce thermal pollution of the environment;
- reduce emissions to the environment in the production of products from secondary resources compared with primary raw materials (due to the exclusion of a number of links from the technological chain);
- reduce the amount of fuel burned at power stations, boilers, industrial furnaces, and accordingly reduce the amount of pollution associated with the combustion products of the saved equivalent amount of fuel, as well as with its production, preparation and transportation [3].

The widespread use of resource-saving technologies in all sectors of the national economy should be a decisive factor in improving environmental protection, ensuring the greatest possible prevention of environmental damage. Resource-saving technologies, paying off in a short time, provide the highest yield of the final product per unit of raw materials, and given the high degree of automation of such technological processes [4-5].

II. RELETED WORK

As is known, slags of smelting processes in a suspended state contain significantly more dissolved copper than its equilibrium solubility over mattes of a given composition [6]. This is due to the fact that the loss of copper dissolved in slags is determined not by the composition of the matte, but by the copper content in the sulfide inclusions suspended in the slag melt. According to the electron probe analysis of factory samples, the composition of the slag of converting processes differs significantly from the composition of the bottom matte (Fig. 1.). In mattes containing 30–40% Cu, sulfide inclusions contain 40–50% Cu, and mattes containing 50–60% Cu, they are similar in composition to chalcocite. In addition, the total surface area of sulfide inclusions is several orders of magnitude greater than the surface area of the matte – slag interface in an industrial unit [7-8].

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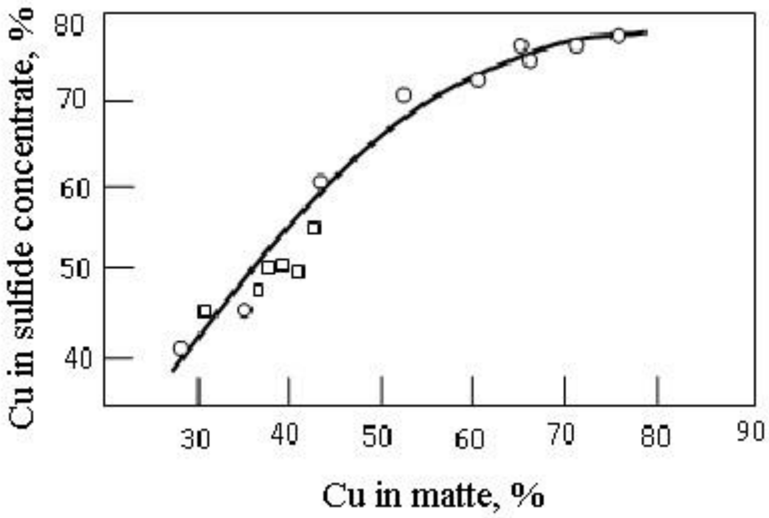

Figure 1. Curves of bonding of copper content of sulfide concentrates and copper content in matte

In all cases, such an approach, in which production waste is eliminated or reduced, should be prioritized as compared with the technical policy aimed at recycling, neutralization or burial of waste [9]. Speaking about priorities in the protection of the environment from waste, you should put different ways to eliminate them in the following row:

- prevention or reduction of pollution at the source of their formation;
- use of waste products;
- transfer of waste to a safe state for man and nature;
- disposal of waste in completely safe containers.

The present study relates to methods for processing copper slags and can be used in copper metallurgy in order to reduce metal losses from slags [10-11].

The aim of the study is to increase the degree of copper extraction in the application of low-waste technology, reducing overall costs in the production of copper. Along with this requires the extraction of metal cord from waste tires [12].

This goal is achieved by the fact that instead of clinker, which acts as a reducing agent and instead of pyrite-containing tailings from Lead-Enrichment Factory, which play the role of sulfidization, waste tires are used, containing a large amount of hydrocarbon and sulfur, which play the role of reducing agent and sulfidization [13].

III. MATERIALS AND METHODS OF RESEARCH

The composition of the materials of the proposed study is illustrated in tables, where table 1 presents the chemical composition of the converter slag and table 2 presents the chemical composition of the waste tires [14].

Table 1. The chemical composition of the converter slag of AMMC (Almalyk Mine-Metallurgical Combine)

	Chemical composition, %							
№	Cu	Fe (total)	SiO_2	Al_2O_3	CdO	Fe_3O_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	-

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Table 2. The chemical composition of waste tires, %

№	Chemical composition				
	C	H	S	O	Others
1	83,75	7,58	4,62	2,31	1,74
2	78,61	7,11	8,35	1,57	4,35
3	74,33	6,72	12,43	2,82	3,7
4	70,46	6,37	19,57	1,95	1,65
5	64,42	5,83	26,63	1,77	1,35

The main criteria for minimizing the loss of copper with slags is that the reducing agent and the sulfidizing agent are located at the same source and reducing the mass of the slag formed. For the smallest possible slag yield, you need to add the optimal amount of tire waste.

The processing of copper slags using waste tires is carried out as follows: the process consists of two stages. At the first stage, the preliminary slag depletion is performed. Before it is drained from the converter into the bucket, waste tires must be loaded into the bucket.

Crushed tires, pre-loaded into the slag ladle in the amount of 3 to 5% by weight of slag (Fig. 2). When slag is drained, the car tires heat and decompose, which is accompanied by the formation of a reducing agent — solid carbon and a gaseous reducing agent — hydrogen. In addition, sulfur in the composition of the tire contributes to the sulfidation of oxidized copper compounds and their transition to the bottom phase. The gases released during these reactions contribute to the coalescence of the fine drops of matte.

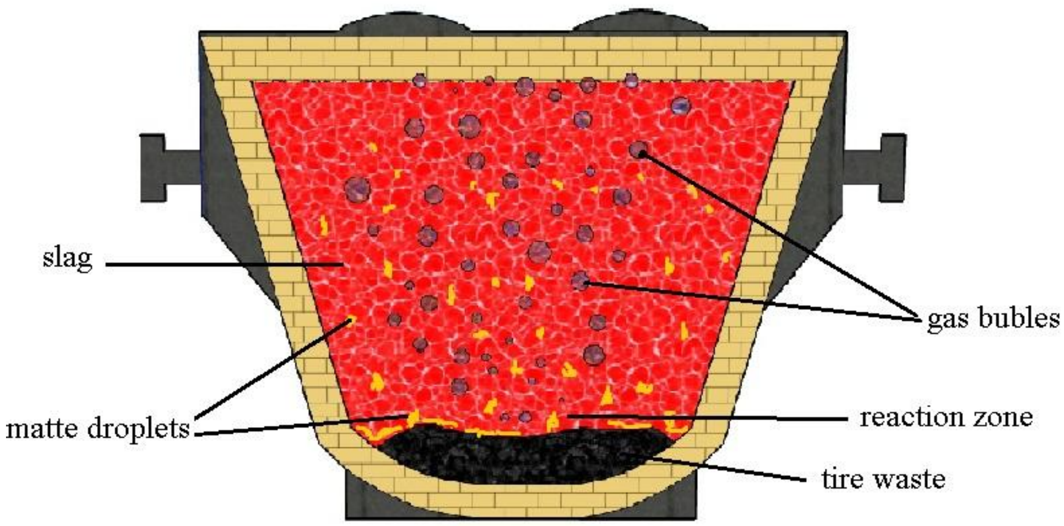

Figure 2. Scheme of pyrometallurgical processing of copper slag into the ladle

After the slag is poured from the converter into the ladle, the following chemical reactions take place (at 1100 - 1200 °C):

$$(C_4H_6S_{0,25})_n \rightarrow 4nC + 6nH_2 + 0,25nS$$
$$C + 2S \rightarrow CS_2$$
$$S + H_2 \rightarrow H_2S$$
$$Cu_2O_{slag} + C(H_2) \rightarrow 2Cu_{metallic} + CO(H_2O)_{gas}\uparrow$$
$$Fe_3O_4 + C(H_2) \rightarrow 3FeO + CO(H_2O)_{gas}\uparrow$$
$$FeO + C(H_2) \rightarrow Fe_{metallic} + CO(H_2O)_{gas}\uparrow$$
$$Fe_3O_4 + Fe_{metallic} \rightarrow 4FeO$$
$$3FeO + 4C \rightarrow Fe_3C + 3CO_{gas}\uparrow$$
$$Fe_3O_4 + CO \rightarrow 3FeO + CO_{2\ gas}\uparrow$$

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$$C + CO_2 \rightarrow 2CO_{gas}\uparrow$$
$$C + H_2O \rightarrow CO_{gas}\uparrow + H_{2\ gas}\uparrow$$

The chemical reactions occurring are exothermic, therefore, when performing work, the temperature of the slag does not decrease (1100 - 1200 °C). At 1000 - 1100 °C, hydrocarbons, which are present in the composition of car tire waste, decompose to form carbon and hydrogen. Both reagents reduce copper and iron from their oxides. Sulfur present in the composition of automobile tire waste sulphide copper and iron oxides:

$$2Cu_2O_{slag} + 3S \rightarrow 2Cu_2S_{matte} + SO_{2\ (gas)}\uparrow$$
$$2Fe_3O_4 + S \rightarrow 6FeO + SO_{2\ (gas)}\uparrow$$
$$2FeO + 3S \rightarrow 2FeS + SO_{2\ (gas)}\uparrow$$
$$Cu_2O_{slag} + FeS \rightarrow Cu_2S_{matte} + FeO$$
$$2Cu_2O_{slag} + CS_2 \rightarrow 2Cu_2S_{matte} + CO_{2\ (gas)}\uparrow$$
$$Cu_2O_{slag} + H_2S \rightarrow Cu_2S_{matte} + H_2O_{vapor}\uparrow$$

After the reduction of magnetite, the density and viscosity of the slag is decreased and this allows the formation of a slag-matte phase in the system.

IV. RESULTS OF THE RESEARCH AND THEIR DISCUSSION

In the course of the experiments, matte and slag were completely released from the furnace into a ladle, where they were mixed with tires waste. The amount of matte was 100-400 kg, slag - 1200-1500 kg. Tires waste consumption in the experiments was chosen so as to obtain a different copper content in the final matte. The duration of mixing was 10–15 min. The results of the experiments are given in the tables. The copper content in sulfide inclusions suspended in the slag obtained during smelting varied (according to electron probe microanalysis) from 65 to 75%. In the process of mixing, the composition of sulfide inclusions approached the composition of the bottom matte. As the compositions of bottom matte and sulfide inclusions converge, slag depletion on copper occurred, and the smaller the difference in copper content in sulfide inclusions and in the bottom matte, the poorer in copper slag was obtained.

As a result of the experiments, a coincidence of the copper content in the slag after mixing with the equilibrium solubility of copper, i.e., a decrease in its loss, was obtained. This suggests that with autogenous suspended smelting, slag can be obtained, which is close to the state of equilibrium with bottom matte. The content of magnetite in the slag decreased by 1.5-2.0 times, which ensures the effectiveness of the subsequent deep depletion of slag by any of the known methods. Further de-mixing of slag is possible only by contacting it with a copper-poor sulfide extraction phase.

Comparative experiments on settling the slag in the ladle after releasing the Reverberatory furnace in the presence of matte without mixing showed that in 30 minutes the copper content in the slag decreased by 7 - 15%. The copper content in the sulfide suspension at the sludge almost did not change and significantly exceeded the copper content in the bottom matte.

The results of slag purging Convertor confirmed the results obtained in the laboratory and showed the fundamental possibility of the depletion of slags from the converting by the proposed method.

Stirring the smelting products inside a melting unit is a technique known in metallurgy. Nitrogen, natural gas, or an air-oxygen mixture are used as a mixing reagent. The amount of gaseous reagent required for mixing the smelting products is determined by the required mixing intensity. In the industrial implementation of the process, the amount of gaseous reactant will also be determined by the degree of dilution of exhaust gases by combustion products or neutral gases, and in the case of mixing with oxidizing gases, by the degree of additional enrichment of the matte obtained.

The main constructive task in the organization of the mixing process is to determine the installation location of the tuyeres for supplying the gaseous reactant to the melt. Tuyeres should be installed in such a way as to ensure the most rapid course of the processes of phase mixing, averaging sulfide droplets by composition, coalescence of droplets and establishing a state close to equilibrium.

Usually in the slags of suspended smelting of copper sulphide concentrates on matte containing 60% Cu, the copper content is ~ 1.2%, and in the Oxygen-Torch Furnace slags - 0.7– 0.9% with a matte content of 40–45% Cu. In the Vanyukov smelting slag, the copper content is 0.3-0.4% lower when working on mattes of identical composition.

The study can be useful when developing methods for the depletion of slags from various autogenous processes. The results of laboratory analysis of the chemical composition of matte and slag are shown in Tables 3 and 4.

Table 3. The chemical composition of the resulting copper matte into the ladle

№	Time of mixing, min	Matte forming, %	Content of copper matte, %			Extraction of copper into the matte, %	Slag forming, %
			Cu	Fe	S		
1	10	10,31	14,9	70,6	6,07	69,8	88,2
2	20	10,9	12,7	44,8	5,6	60,2	87,7
3	20	10,4	15,3	64,3	5,1	69,1	87,9
4	40	10,35	17,2	54,9	13,8	77,5	88,1
5	40	11,02	15,1	42,5	28,0	82,57	86,2

Table 4. The chemical composition of the slag after pyrometallurgical processing into the ladle

№	Time of mixing, min	Chemical composition of slag, %					
		Cu	Fe	SiO_2	CaO	S	Zn
1	10	0,89	43,7	22,0	1,48	2,56	0,37
2	20	1,02	39,4	24,7	1,29	2,7	0,09
3	20	0,79	42,6	23,8	1,3	2,1	0,10
4	40	0,61	35,4	25,6	1,8	1,2	0,04
5	40	0,57	32,4	30,61	1,88	1,57	0,03

Due to the high density, the sulfides formed and the metallic composition of iron and copper is deposited in the depth of the ladle and a matte phase is formed. The gases formed during the reduction and sulphidation processes bubble and melt the mixtures and this makes it possible to increase the process of coalescence. In the process of coalition, small drops of matte are associated with each other and a large drop of matte with a large radius is formed. An increase in the radius of a matte drop accelerates their precipitation into the bottom phase. The main mass has dimensions of 10 - 100 microns (0.01 - 0.1 mm).

The residence time of the melt in reflective furnaces or electric furnaces does not exceed 2-2.5 hours. From here it follows that the main quantity of metal or matte drops larger than 0.1 mm will have time to settle in the bottom phase, while smaller drops will remain in the slag in suspension .

At the second stage, products obtained in the optimal amount are processed in a Reverberatory furnace or in a Vanyukov furnace.

V. CONCLUSION

It is the implementation of this method that is based on the fact that the composition of the zinc production clinkers contains a large content of the main carbon as a reducing agent and sulfur, the main copper sulphidizer. Due to the formed gases CO_2 and H_2O, when the hematite and magnetite interact with carbon and hydrogen, the slag mass does not increase. When magnetite is reduced, the viscosity of the slag decreases and this makes it possible to increase the sedimentation rate of the matte drops to the bottom phase. All of the taken results show that, implementing this research on an industrial scale it will increase the coefficient of productivity of copper producing plants.

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