ANALYSIS OF SLURRY SLAGS IN TERMS OF COPPER EXTRACTION PROCESS FROM SYSTEM IN STATIC AND DYNAMIC CONDITIONS

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Abstract

Process production of copper in a slurry furnace (Outokumpu technology) is based on converting copper matte for a blister, and slag containing even 16% copper oxides. Such slag is tapped into the electric arc furnace in sequence. In this process liquid slag (slurry) is extracted by treatment reducers and technological modifiers. Through the process of refining, the copper content in the tapping slag is at the level approx. 0.4-0.8% Cu. Based on the results it's seems to be decreased this level, among others through comprehensive technological activities. The refining slag in arc furnace and industrial conditions is staying in static conditions and in strong step of mixing i.e. under electrode zone. The paper discusses the influence of selected technological additives on the reduction of copper oxides in slurry slag, coagulation of products and sedimentation in particular conditions. The tests were carried out under static and dynamic conditions of mixing molten slag at 1300 °C. Differences for the copper forms (like a products of reduction reactions) in the post-deposition slag were demonstrates and occurrence of the coagulation phenomenon.

Keywords: Copper metallurgy, reductions of copper oxides, slags

1. INTRODUCTION

The process of decoppering the suspension slag in an electric furnace has three different stages. They depend on the prevailing physicochemical phenomena in the process [1-3]. In the first stage, the furnace is filled with the use of spouts (directly from the flash furnace) with liquid slag at a temperature of about 1300 °C, coke and limestone. The duration of this stage is about two hours. During this period, about 80 % of the initial copper value is reduced [3-5]. In this step, the copper content drops to 2 %. The second stage is the longest and lasts 4-5 hours. Copper, iron, arsenic and lead oxides are reduced. There is also sedimentation and coagulation of the reduced metals, which creates a Cu-Fe-Pb alloy. At this stage, the reduction process is very slow and the copper content in the slag decreases to 0.8 % [4,6]. During the last stage, the Cu-Fe-Pb alloy and slag are triggered. It lasts 2-3 hours and the slag temperature is 1350-1380 °C. The final copper content in the slag drops to about 0.5 %. In general, one cycle lasts about 10 hours [1].

Throughout the process, intensive mixing of the slag occurs due to:

- CO_2 flow through the slag layer, which was formed by the decomposition of calcium carbonate.
- electromagnetic forces that arise from the flow of current through the slag between the electrodes
- kinetic energy of slag, during transfer from the furnace.

Mainly the reduction of slag in the electric furnace takes place in the zone where the slag meets the graphite electrode or adjacent to the coke. In this zone, the oxygen partial pressure is dependent on two reactions:

$$CO_2 = CO + 0.5 O_2 \tag{1}$$

$$CO_2 + C = 2 CO \tag{2}$$
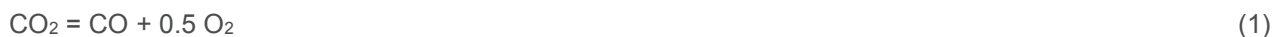
To calculate the required p_{CO2} / p_{CO} ratio, use the Boudouard reaction. According to the data, the oxygen partial pressure at 1300 °C is $1.81 \cdot 10^{-17}$ [3, 5]. On the basis of these equations it is possible to calculate equilibrium concentrations for respectively copper, iron and lead to which the slag in this zone can minimally reduce: Cu - 0.0067 %, Fe - 0.062 %, Pb - 0.023 %. It should also be taken into account that in the contact zone of the slag electrodes, strong overheating of the slag can occur. The temperature can be higher by 150 °C. It is assumed that in this zone there is almost complete reduction of the above-mentioned elements. Drops of the alloy that have formed will fall to the bottom of the furnace (**Figure 1a**). During this time, the role of the reducer will be taken over by iron, and at the beginning also lead (3), (4).

$$2\ (Cu^+)_{slag} + [Fe]_{metal} = (Fe^{2+})_{slag} + 2\ [Cu]_{metal} \tag{3}$$

$$2\ (Cu^+)_{slag} + [Pb]_{metal} = (Pb^{2+})_{slag} + 2\ [Cu]_{metal} \tag{4}$$

Unfortunately, the dropping time of the droplets is so short that it is impossible to reach the equilibrium. What causes that the above-mentioned reactions will continue to occur mainly at the slag-stop boundary [7].

According to various analyzes [7, 8], it can be concluded that the biggest gauging of slag occurs in zones I and III (**Figure 2**), which unfortunately does not give satisfactory results. It is concluded that the main reason for this state of affairs is the slow transport of Cu + and Cu_2O ions to zones I and III from zone II.

The main factor that has the most important impact on the amount of copper losses in the slag is the dropping speed of Cu-Fe-Pb droplets in the slag. After applying the equation (to Stockes model) described in **Figure 1b**, it can determine the movements of drops speed/rate depending on its diameter.

a)   b)
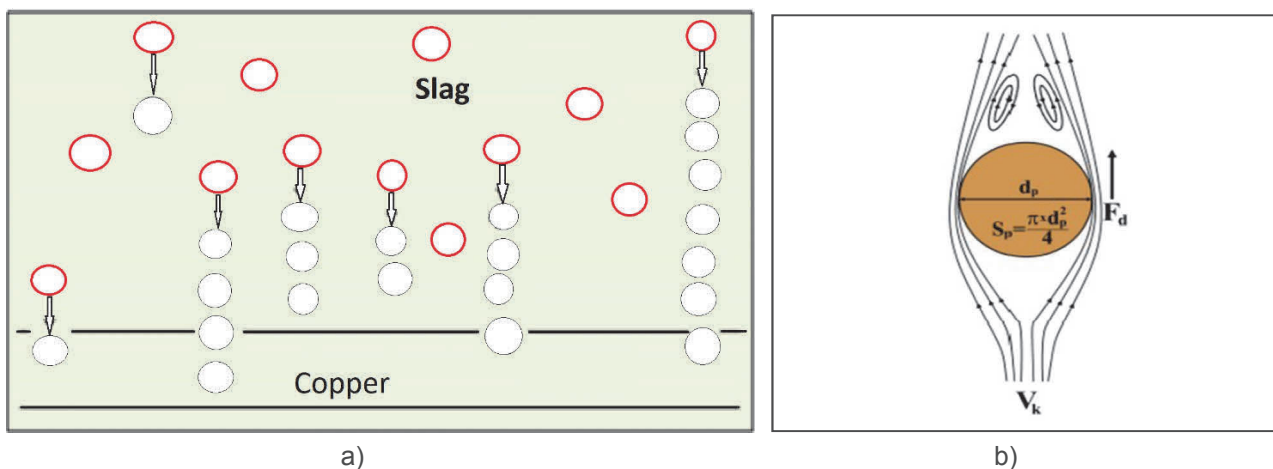
Figure 1 a) Diagram of dropping phenomenon of metallic Cu-Fe-Pb alloy from slag in the direction of continuous metallic phase on the bottom of settling tank, b) Pattern of drop falling in fluid [9], where: F_d - buoyancy/resistance coefficient; S_p - area of the cross section of the molecule/particle; d_p - diameter of molecule/particle, V_k - relative rate between liquid and particle

2.   OWN RESEARCH AND ANALYSIS

Conditions resulting from the difficulty reductions of copper oxides and subsequent entry of reduced metallic phase settling to the bottom of the electric furnace (**Figure 1a**) were the basis for making analysis and testing of coagulation and crystallization of copper under dynamic conditions. It was decided to take into account and analyze the turbulent movement of the slag during its discovery. The results of the first analyzes are presented in the work [10], indicating in it the possibility of obtaining the effects of decoppering by inclining the electrode.
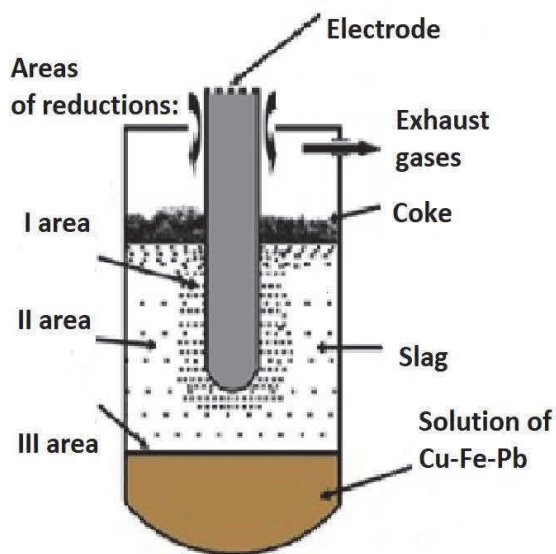
Simplified electrode diagram in a furnace for decontamination of slag

Research position

Figure 2 Description of the scheme of interactions in the electric furnace (a) and tests unit (b)

A stand consisting of a Tammana tubular resistance furnace and a mixer with regulated speed was made for the tests (**Figure 2b**). Dynamic tests were carried out at 1300 °C. The residence time in the assumed temperature was 20 min. The rotation speed was adjustable from 10 - 30 rpm. The slag from the flash furnace was modified with stimulants and reagents. **Table 1** shows the types of stimulators and reducers used. For comparison, samples were made under the same conditions for static state. For the dynamic tests, samples were selected for which, in static conditions, the largest contents of the copper alloy after the reduction process were identified. After cooling the samples reduced under dynamic conditions with the furnace, the obtained products were weighed (slag + metal), then they were ground in a mortar, sieve analysis of obtained fractions was performed subsequently. **Figure 3** presents an example of a sample obtained during dynamic coagulation. There is a large mass fraction of the product of reduction and sedimentation in the form of a "copper" alloy, which is presented in **Figure 4** in numerical form.

Table 1 The results of experimental research

Identification and type of reagent						
W1	W2	W3	M1	M2	M3	M4
FeC	CaC_2	$CaCN_2$	$CaCO_3$	Na_2CO_3	K_3PO_4	$NaCl_2$

Types of composition stimulators and reducers used for selected samples

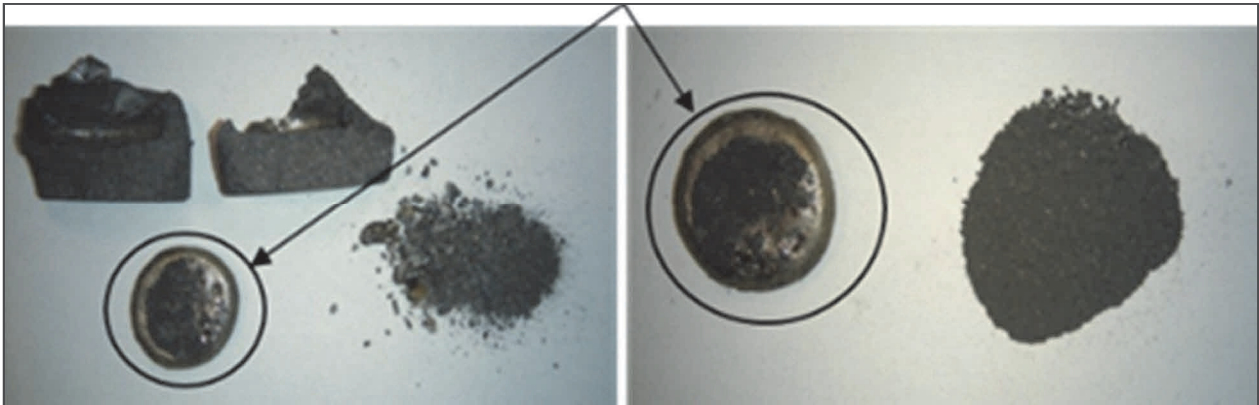| Sample no.	4	11	11,1	13	7
(%)	66	69	27	27	60

Percentage of metal (%) after coagulation under dynamic conditions in slag

where:

W1, W2, W3 - compounds that input carbon (reacting) to the slags system = 5% in sample.
M1, M2, M3, M4 - modifiers chemical compositions of slags = 2% in sample.

Figure 3 Photographs of the selected sample after dynamic coagulation

Figure 4 shows the weight comparison of samples in grams after the dynamic test. The proportion of the metallic phase is much greater than in the case of static conditions. The quantitative analysis of the slags was carried out on the ARL QUANT'X EDXRF from Thermo Fisher Scientific.
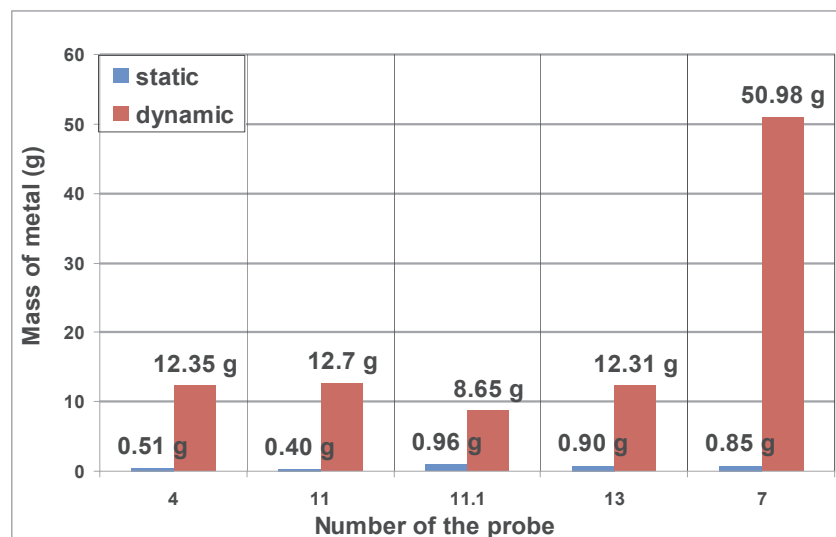

Figure 4 Lists of results of the obtained metallic mass (% by mass) on the bottom of the settling tank in static and dynamic tests

3.   RESULTS AND DISCUSSION

The tests carried out showed that during the process of pushing in dynamic conditions much more "Cu-Pb-Fe" alloy were obtained than during the reduction in static conditions. The highest efficiency of the reduction and coagulation process was obtained at 20 rpm. The impact of system dynamics on the efficiency of the reduction process is at least ten times greater in favor of dynamic conditions. This confirms that the intensity of refining of slag slag will be the most intense in terms of the operation of the electric arc, but also in the situation of the flow of slag (its movement).

Structural analysis of slags prior to the use of reducers (cycle I) showed a large number of fine separations of the Cu-Pb-Fe alloy (so-called copper plugs) with dispersion values (below 1 μm), and inclusions with dimensions in the range of 1 ÷ 10 μm inclusions with dimensions 10 ÷ 100 μm. Separations of copper were also trapped in the silicate - iron framings. The results are illustrated by pictures a, b (Figure 5) - smelting I.

a)

b)

c)

d)
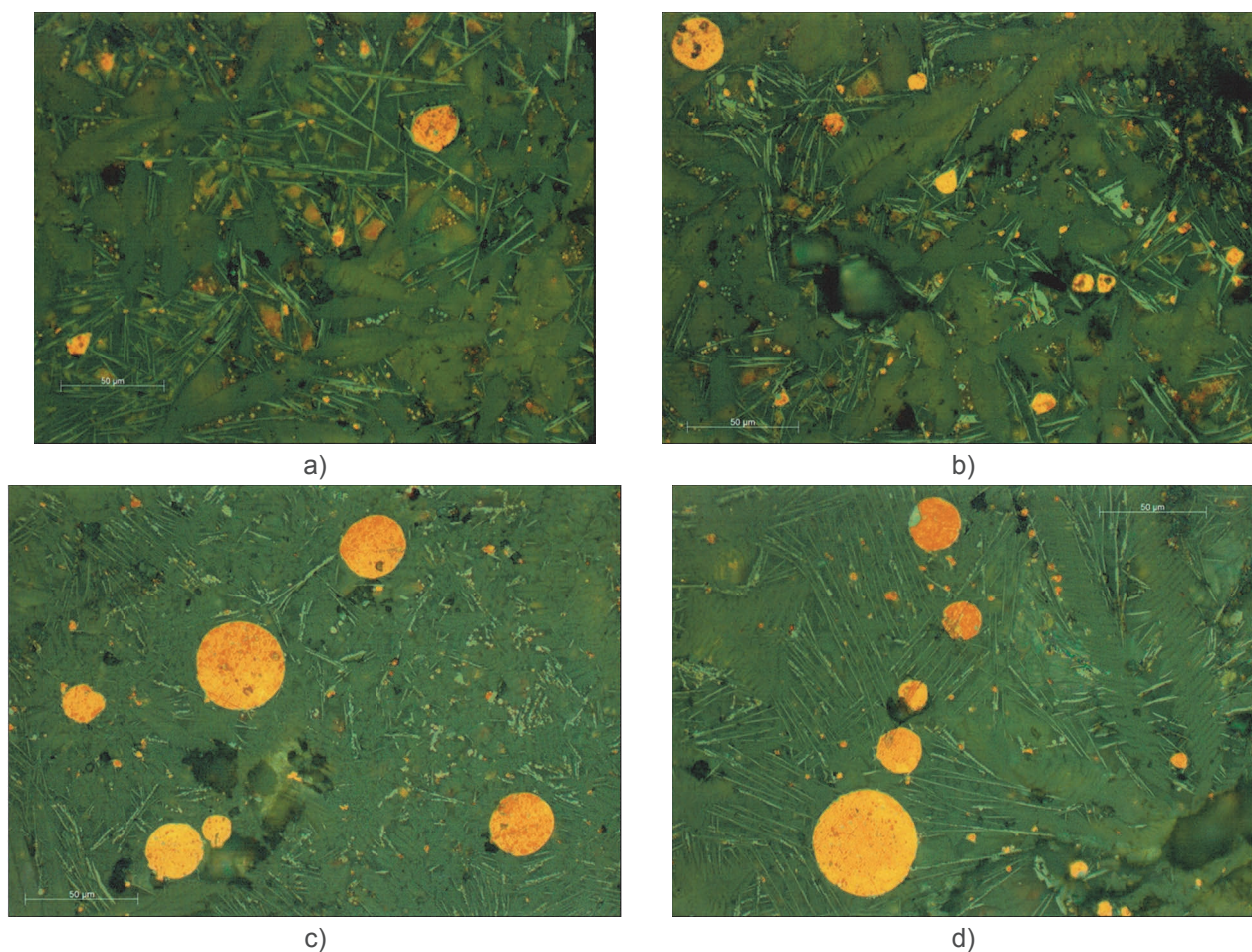
Figure 5 Structure of precipitations of the metallic phase of the Cu-Pb-Fe alloy for: a, b - static conditions, c, d - for dynamic conditions

The use of dynamic conditions, with the simultaneous use of carbide reagents and stimulants, influenced the appearance of spherical precipitates with dimensions over 100 μm - against the background of dispersed inclusions, mainly of dimensions 10 ÷ 100 μm (**Figures 5 c, d** - smelting II). Compared to static conditions, using the same reagents, more than tenfold increase in the size of metallic precipitates was obtained - in static conditions (**Figures 5 a, b**), the secretion had from a few to 20 μm in size.

4.   CONCLUSIONS

Based on the obtained results, it can be stated:

- reduction of copper oxides, coagulation of products and their sedimentation (dispersal of slag) in dynamic conditions is more efficient than in static conditions,
- in dynamic conditions not only much more "Cu" alloy was obtained, but also this alloy has coagulated and sediment to the bottom of the crucible, which is a very desirable phenomenon and beneficial from the point of view of industrial technology.

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