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Influence of the Impact of Slurry Slag from a Single-Stage Process of Copper Production on the Exploitation of Ceramic Materials

Maciej Wędrychowicz*, Adam Bydałek

Department of Mechanical Engineering, University of Zielona Góra, Zielona Góra, Poland

Email address

maciej.wedrychowicz@gmail.com (M. Wędrychowicz)
*Corresponding author

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Abstract: This article presents the single-stage process used in the "Głogów II" copper smelter along with aspects of the impact of the chemical slurry slag on the structure of the lining of the flash furnace for the direct smelting of blister copper. Some aspects of the structure of the lining of the flash furnace for direct smelting of copper were also discussed, including the furnace hearth and the settler. This article presents the decisive factors for the selection of the technology of single-stage smelting of copper and characterizes the reasons for the wear of refractory materials. In order to assess the possibility of dissolution of the refractory material by the slurry slag, tests with the use of micro-analysis of the surface of the ceramic material made of Al_2O_3 and macroscopic analysis with the use of a scanning microscope were carried out. The obtained results allowed for the assessment of the possibility of the dissolution of the slurry slag in relation to the performed material. The discussed issues were summarized in the conclusion, stressing that the single-stage process requires continuous improvements.

Keywords: Slurry Slag, Single-Stage Process of Obtaining Copper, Ceramic Material

1. Introduction

In the first stage of its development the process of obtaining copper was based on the technology of the Finnish company "Outokumpu Oy", whose production was focused on obtaining copper matte and copper-nickel matte from chalcopyrite concentrate. Already at the stage of improvement of efficiency of the process based on the "Outokumpu" technology it was noted that "Polish copper concentrates" have in their chemical composition low iron and sulphur contents, i.e. Fe contents up to 4% and S contents up to 13%, which allowed for the introduction of a single-stage copper smelting process, that is without the operation of conversion of the copper matte used in the Finnish technology. High contents of organic carbon also contributed to a change in the nature of the application of the "Outokumpu" technology. For the first time the single-stage process for obtaining copper was launched at HM "Głogów II" on 8 January 1978. At the moment, due to the strict EU rules on CO_2 emissions both HM "Głogów I" and the modernized HM "Głogów II" are based on the single-stage process of obtaining copper.

2. Analysis of the Issue

The classic "Outokumpu" technology of obtaining copper based on smelting of copper matte from pyrite concentrates was characterized by low heat losses due to the use of multiple layers of insulation in the heart of the flash furnace and its insufficient cooling. Such a solution allowed for obtaining more favorable energy performance of the process and preventing the secretion of a thick layer of magnetite. The conditions of a single-stage process are entirely different, because the slag from Polish concentrates contains a significant amount of cuprous oxide and copper, which have direct contact with the refractory lining. Due to such a chemical composition, the slag is "aggressive" in relation to the furnace refractory lining. In other words, in the current technology there is no durable protective layer, which could ensure the continuity of the production process over a period of several decades. That is despite the improvement of the structure of the flash furnace in the years 1983-1990, which mostly involved the use of metal-ceramic caissons characterized by high durability.

2.1. Technological Process

Figure 1. shows the technological diagram of the process of obtaining copper at HM "Głogów II"

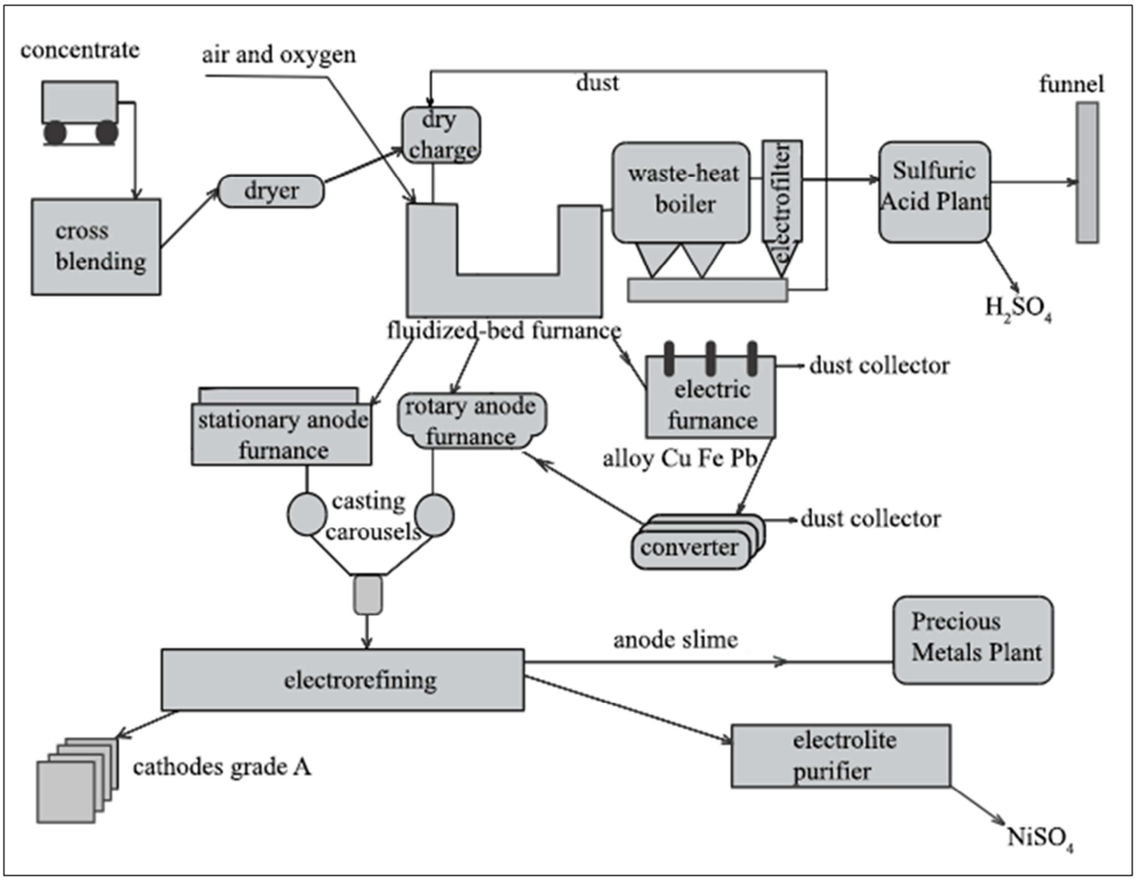

Figure 1. *Diagram of the process of obtaining copper at HM "Głogów II" [1].*

The mineralogical concentrate derived from "ZWR Polkowice" and "ZWR Rudna" is subjected to processes generally referred to as preparatory operations which include [2]:

Drying of the concentrate to a level of 0.3% H_2O

Selection and grinding of the dried concentrate to granules with a size exceeding 0.75 mm

The dry charge is transported with a pneumatic conveyor to the feed tank and is then fed by four concentrate burners into the reaction shaft of the flash furnace. Exothermic reactions of oxidation of sulphides occur in the reaction shaft of the flash furnace, and reactions between the oxide and the copper sulphide occur in the settler, in accordance with reaction (1) [3].

$$Cu_2O + Cu_2S = Cu + SO_2 \quad (1)$$

Oxygen is also supplied to the reaction shaft of the flash furnace shown in Figure 2, and the blister copper created in the settler is discharged into a ladle where it is directed to a stationary or rotary anode furnace. In the subsequent stages the copper from the anode furnace is poured to the rotary casting machine, and then subjected to the process of electrorefining in settlers. As a result of purification of copper using electrolysis, copper with a purity exceeding 99.9% is obtained [4, 5]. Slag from the flash furnace is directed into an electric furnace where an alloy of copper, iron and lead is obtained. In subsequent production stages this alloy is directed to the Hoboken converter, and then to the anode furnaces. The decoppered waste slag is granulated, and following the burning of the carbon monoxide to CO_2 the process gases from the electric furnace are cooled and dedusted in the pulse bag filter [6].

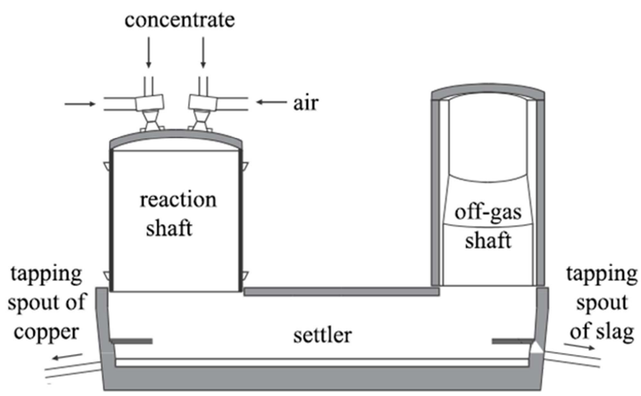

Figure 2. *Diagram of the flash furnace [8].*

2.2. Operating Conditions

Despite the large differences in the construction of melting furnaces used in the metallurgical industry, in each of them we can notice the presence of four generally destructive impacts, which include:

1) High temperature
2) Thermal stresses
3) Mechanical impact
4) Corrosive effect of the slag

The diagram of the behavior of the refractory walls of the furnace in conditions of strong heating is shown in Figure 3. A magnesium-chromite refractory shape heated from one side will expand under the influence of heat in accordance with the prevailing temperature gradient. The expansion of the shape will be limited by the adjacent shapes, as a result of which it will crack and deform [10]. Stresses in the adjacent fittings will increase and will move over the entire wall surface causing further cracking in the furnace lining. In addition, the impact of charge dusts and the abrasive motion of the moving charge in the furnace will also result in the deformation of furnace linings, for example in the form of the ovalization of the cooling shell. In the case of slurry slag, however, it is the corrosive effect of the slag that is the most important. The corrosion processes may occur on the surface of the refractory lining or penetrate to the inside of the furnace walls. Process gases will contribute to this corrosion, because they have the highest penetration ability, mainly under the influence of SO_2 and SO_3. The areas most vulnerable to corrosion are located in the molten slag area. The most aggressive slag reactants include: oxygen, carbon monoxide, hydrogen and hydrocarbons, sulfur oxide and vanadium oxide along with zinc and lead compounds. In addition, in the temperature range of 500°C to 600°C carbon monoxide undergoes thermal decomposition into carbon dioxide and carbon [7]. Fixed carbon and the carbon resulting from decomposition builds up in the interior of the furnace lining, blowing it up from the inside. In addition, the iron oxides present in the slag can undergo so-called inversion, i.e. pass from the oxide phase to the spinel phase, and these reactions are accompanied by uneven changes in volume of the slag which in turn leads to cracking and layered flaking of the walls.

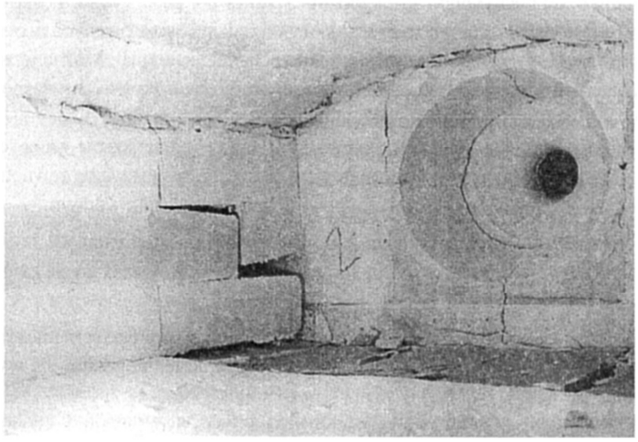

Figure 3. *Example of damage to the lining of the furnace walls due to overheating [9].*

Dolnośląskie Zakłady Magnezytowe (The Lower Silesian Magnesite Plants) supply the products for the flash furnace for the Głogów II Copper Smelter. These are mainly two magnesite products: MC5-20 and M94. An example of the chemical composition of the products manufactured at the Dolnośląskie Zakłady Magnezytowe is shown in Table 1.

Table 1. *Chemical composition of the products used in copper metallurgy [11].*

	Chemical Composition [%]					
Manufacture	**SiO_2**	**Fe_2O_3**	**Al_2O_3**	**Cr_2O_3**	**CaO**	**MgO**
CM3	4.0	12.4	12.6	33.0	0.6	35.0
MC5-20	2.0	7.0	4.0	17.0	-	62.0

3. Determination of the Impact of Slurry Slag on the Refractory Material Lining

3.1. Research Plan

The purpose of the research is to demonstrate the chemical interaction of the slurry slag with the refractory material made of aluminium oxide. After prior grinding in a vibratory crusher and selection to fractions smaller than 0.1 mm, the slurry slag was placed in a ceramic crucible. Slurry slag in the amount of about 80 g was placed in a corundum crucible, and then melted in a resistance furnace in the temperature range from 1200°C to 1380°C every 20°C. After the removal of the studied sample and cooling of the slag the crucible was broken and its fracture was studied macroscopically and microscopically.

3.2. Results of the Conducted Research

The meaning of this research is to find the answer, what kind of material in the flash smelting furnance. The slag from the single-stage process of obtaining copper, but also the dusts and the process gases are characterized by high chemical aggressiveness towards the lining of the flash furnace [12]. According to the KGHM monograph in contrast with the classical "Outokumpu" technology, the slurry slag containing about 14% Cu_2O and having direct contact with the flash furnace lining causes the rapid wear of refractory (ceramic) materials and the deformation of the furnace hearth. In order to confirm the erosive effect of the slag, a test of the effect of the chemical slurry slag on a ceramic material made of Al_2O_3 was carried out. Figures 4 - 7 show a macroscopic image of the slurry slag penetrating into the corundum crucible. Figures 8 and 9 shows an image from a scanning microscope.

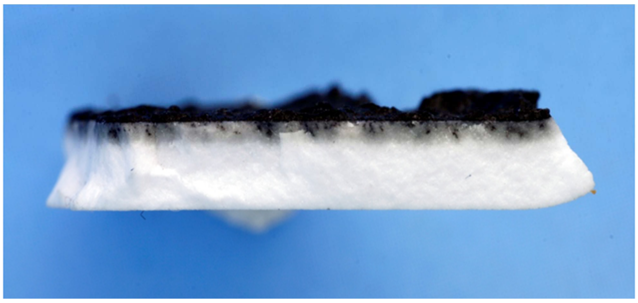

Figure 4. *View from the side of the corundum crucible after the measurement of slurry slag at 1360°C (natural size).*

Figure 5. *View from the top of the corundum crucible after the measurement of slurry slag at 1360°C (natural size).*

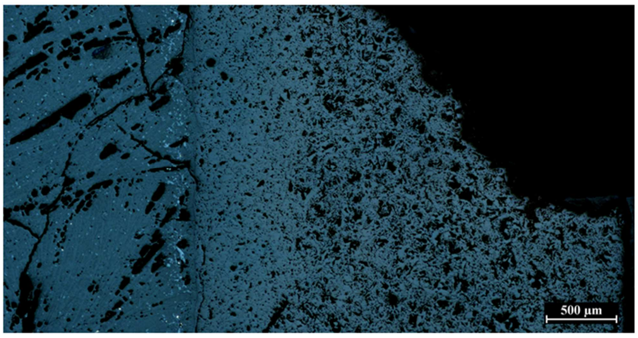

Figure 6. *Image of the corundum crucible after measurement made in polarized light.*

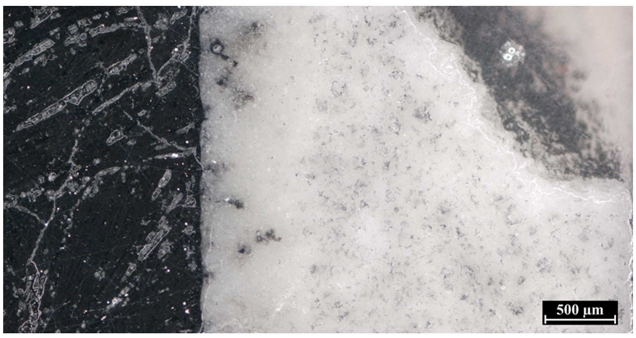

Figure 7. *Image of the corundum crucible after measurement made in darkfield.*

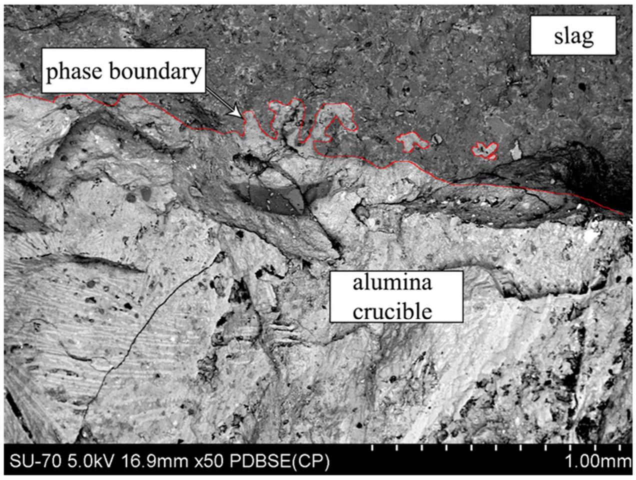

Figure 8. *Image from a scanning microscope of the corundum crucible after the measurements.*

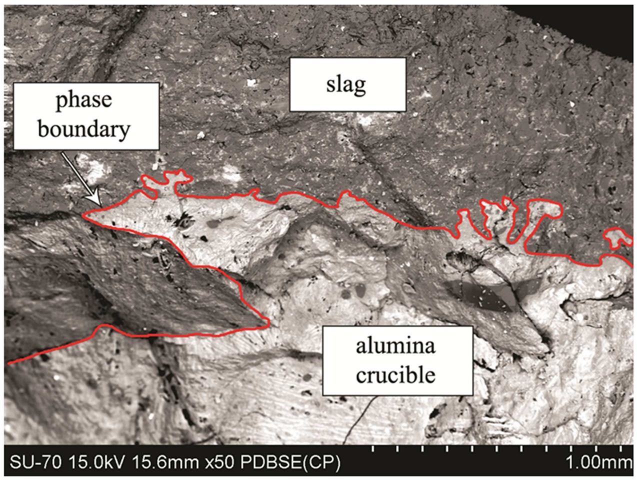

Figure 9. *Image from a scanning microscope in different side of the crucible.*

The results of the conducted microscopic and macroscopic analysis clearly indicate the dissolution of the crucible material by the slurry slag and the movement of the slag - crucible phase boundaries deeper into the slag. According to one of the authors [13, 14] this dissolution likely begins at the temperature of 1360°C with hardly visible solid phase separations in the form of mullite $Al_6Si_2O_{13}$. The mullite phases are present in the form of "needles" and their length mainly depends on the slag cooling rate. The faster the cooling, the larger the size of the "needles". During the dissolution of the material, small pieces of Al_2O_3 pass to the slag and a clear boundary is outlined in the crucible separating the slag from the aluminum oxide. Penetrating deeper, the slag fills the surface of the aluminum oxide which can be seen in Figure 6. Raising the temperature of the slag to 1380°C, we notice a significant increase in the rate of dissolution of the ceramic material in the slag. The formation of mullite in accordance with the SiO_2 – Al_2O_3 balance proceeds in a very narrow chemical composition range, which may indicate that at temperatures lower than 1360°C chemical corrosion may occur through the slag components [15]. Due to saturation with slag reagents, the surface layer of the crucible softens and is then washed out and moves to the slag in the solid form.

4. Conclusion

In all types of flash furnaces the furnace reaction area is among the least durable elements of the furnace and it is decisive in its renovation cycles. Despite the use of the best refractory materials in this area, their durability does not exceed 10 months. The research results presented in the article indicate not only the possibility of dissolution of the ceramic material in the molten slag, but also on the possibility of erosive activity of the slag on that material. Therefore, it is important to conduct further research and works on the development of refractory materials which could allow for extending the cycle of works between the renovations of the flash furnace.

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