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The Concept of Optimizing the Decopperisation of Slag Slurry in Electrical Furnace

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Abstract

This paper presents the idea of increasing the effectiveness of slag decopperisation in an electric furnace in the "Głogów II" Copper Smelter by replacing the currently added $CaCO_3$ with a less energy-intensive technological additive. As a result of this conversion, one may expect improved parameters of the process, including process time or power consumption per cycle. The incentives to optimize the process are the benefits of increasing copper production in the company and the growing global demand for this metal. The paper also describes other factors that may have a significant impact on the optimization of the copper production process. Based on the literature analysis, a solution has been developed that improves the copper production process. The benefits of using a new technology additive primarily include increased share of copper in the alloy, reduced production costs, reduced amount of power consumed per cycle and reduced time it takes to melt. At the conclusion of the paper, the issues raised are highlighted, stressing that mastering the slag slurry process in electric furnaces requires continuous improvement.

Keywords: Slag slurry, Manufacture optimization, Decopperisation

1. Introduction

Process optimisation involves the continuous improvement of the current manufacture procedures. Stages of work that do not create added value are being eliminated from the manufacturing process. Various types of process efficiency indicators, for example economic, environmental, thermodynamic, thermodynamic/economic, etc., are used to reveal process imperfections, as well as to help improve process quality [1]. Process improvements can also include legal requirements for environmental protection.

As shown in Figure 1 and the analysis of China Copper Market Analysis and Outlook, the manufacture of blister and cathode copper is growing year by year. This trend is most likely to last until 2020. According to the independent International Copper Study Group (ICSG), global copper consumption in 2014 increased by about 4% compared to 2013 [2]. ICSG data also showed a slight increase in demand for this metal by 0.3% in 2015. This means that world leaders in copper manufacture, including KGHM, will be forced to increase copper production and reduce their costs. According to one of the articles [3], publications and research papers on the processing of copper concentrates and deposits, as well as the amount of copper produced, are primarily focused on increasing copper mining and processing rather than improving the process itself. Difficulties with improving process efficiency may result from the fact that the larger the production process, i.e. the more developed the technology is, the more difficult it is to make changes in the process itself. To modify and improve upon this process, you need to identify a parameter that can be modified. In the process of slurry slag decopperisation in an electric arc furnace, such a changeable parameter is the addition that is present in the form of calcium carbonate.

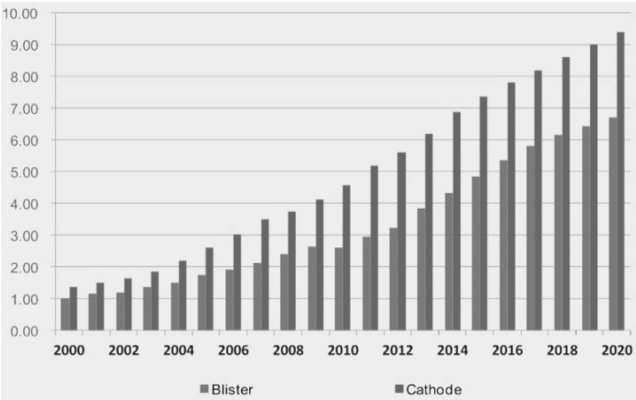

Fig. 1. Blister and cathode copper manufacture in 2000 - 2020 in tonnes [4]

2. Issue analysis

Slag slurry from "HM Głogów II" contains a large amount of copper (about 14% of weight), which is why it is subjected to a reflow process in an electric furnace to recover as much of it as possible. The slag decopperisation process is cyclical and occurs as a result of two phenomena. In the first one, the copper is released from the slag as a result of a reduction, while in the second, due to favorable conditions for coalescence and deposition of copper particles at the bottom of the electric furnace. The presence of copper oxides in liquid slag has a direct effect on its viscosity. In the metal recovery from metallurgical slags, the increase in viscosity of the slag occurs as a result of polymerization. In the case of slurry decopperisation, polymerization mainly affects oxy-aluminosilicate anions [5]. The more polymerized the slag is, the higher its viscosity. Slags that are too viscous cause inhibition of the coalescence and sedimentation of the reduced metal to the alloy, which results in a reduction in the yield of this metal in the alloy. The solution to this problem in the slurry technology of "Głogów II" involves introducing into the slag 10% to 15% calcium carbonate, which is thermally decomposed into calcium oxide and carbon dioxide [6]. On the one hand, calcium oxide effectively lowers the viscosity of the slag slurry and thus contributes to an increase in copper yield in the alloy, but on the other hand, it increases the weight of the slag by artificially lowering the concentration of this metal. In addition, decopperisation of slag slurry is considered to be highly energy intensive. In this process, about 1/3 of the energy from the whole process is consumed by the decomposition of calcium carbonate. An example of the amount of energy consumed by type is shown in Figure 2.
Moreover, the amount of slag that is produced after decopperisation is increasing year by year, as shown in Table 1. This will mean some problems with the storage of this waste, and the annual loss due to the non-recovery of copper waste from slag can amount to more than $2 billion annually [7].

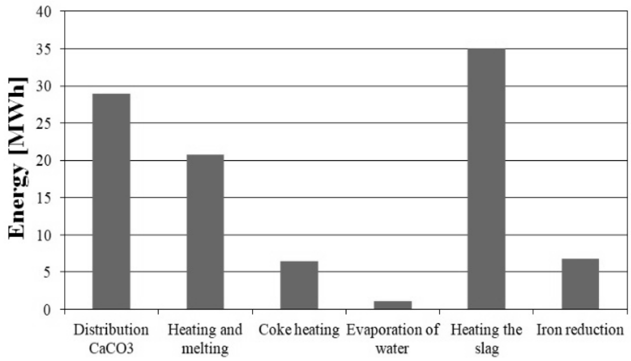

Fig. 2. Energy consumption in electric furnace by type

Table 1.
The amount of slag produced in the years 1991 - 2012 and its anticipated quantity in 2018 at KGHM Polska Miedź S.A.

Year	1991	2001	2006	2012	2018
Quantity [t]	259632	394700	390000	400000	1mln

Thus, the main problem in the slag decopperisation technology is calcium carbonate. In addition, after the decopperisation process, there are also problems with the storage of the granular slag itself, and the decline in interest in many non-environmentally friendly products may have a significant impact on the sale of metallic copper. The above analysis of the decopperisation process, together with a description of its stages, induces reflection on the possibility of technological changes of the slag slurry in electric furnaces, including: replacing the limestone addition with another less energy-intensive basic oxide, which in small amounts will significantly reduce the viscosity of the slag coming from the electric furnace

2.1. Optimizing the decopperisation process

Optimization is the search for the best solution from a set of permissive solutions [8]. The effectiveness of process optimization depends not only on the adopted quality control criterion, or on the type of technological parameters, but also on the characteristics of these parameters. The practical purpose of optimization is to find a solution to the problem and to optimize the decision. The most commonly used synthetic optimization criteria in manufacturing engineering are:

– minimizing the cost of the product, with a time limit,
– minimizing product manufacture time under specific conditions.

One of the important stages of optimal design involves choosing the right optimization procedure as a tool to solve an engineering problem. The choice of this method is not simple, as there is no one universal method equally effective for all engineering problems. An example of a solution to the issue of decopperisation is presented in Figure 3.

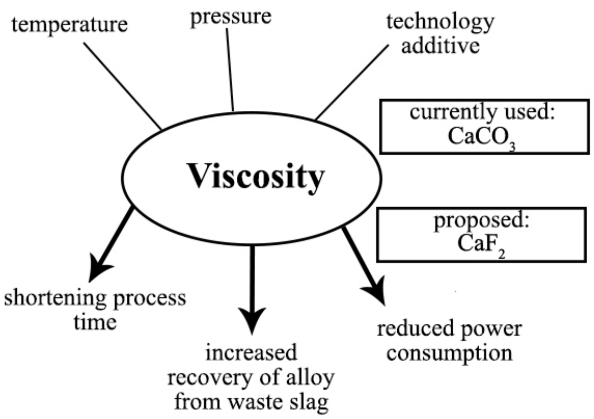

Fig. 3. The idea of possible improvement in slag decopperisation

Of all the possible optimization solutions in an electric furnace, i.e., increasing the slag temperature, reducing pressure in the electric furnace, the optimal and most commonly described by literature sources involves replacing the currently introduced technological additive in the form of calcium carbonate. Literature on the subject speaks of several substitutes that could replace the presently added calcium carbonate [9,10]. Of all possible technological alternatives i.e. FeO, CaF_2, Na_2O, CaO, it seems that CaF_2 is the most optimal technological additive, since it is mainly due to its physicochemical properties.

3. The analysis of the impact of CaF_2 on structural cross-linking

According to the theory of discrete anions [11], viscous flow is determined by the type of polyanion rather than the type of metal oxide present in the slag. Calcium fluoride has two fluoride ions that accelerate the removal of silicon oxide chains in the slag structure. Just as the Ca^+ ion, the F^- anion can destroy grid bridges and the fluorine reaction within the slag structure can for example occur in the following bonds (1), (2):

$$(Si_3O_9)^{6-} + 2F^- = (Si_2O_6F)^{5-} + (SiO_3F)^{3-} \quad (1)$$

$$(Si_2O_6F)^{5-} + (SiO_3F)^{3-} + 2F^- = 2(SiO_3F)^{3-} + (SiO_2F_2)^{2-} + O^{2-} \quad (2)$$

This may mean that lower amounts of CaF_2 added to the slag may increase the production of metallic copper. Whereas the mechanism of breaking the slag grid structure in the case of Ca can be represented as follows:

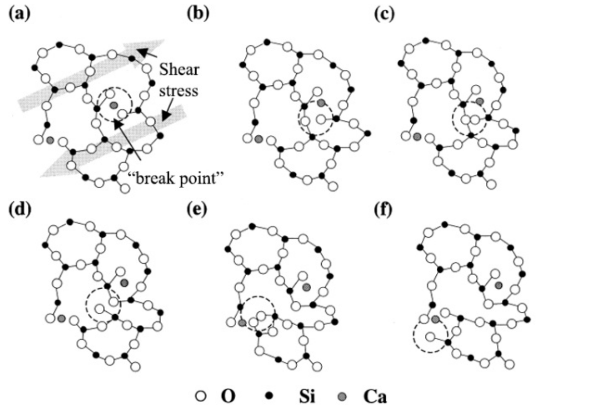

Fig. 4. Mechanism of breaking silicon-oxygen anions according to Tanaka [13]

The mobility of oxide ions that closely adhere to "break points" is high because cross-linking is weakened there. When the slag is affected by shear forces, there is displacement in the so-called "break points" that cause the subsequent slag grid to break. This process is repeated cyclically and the number of break points depends on the amount of oxygen that is not bound with the silicon-oxygen grid (so-called free oxygen). The model assumes that each "break point" moves in any direction along the slag grid structure. The total path traveled through the "break points" can easily be derived from the random walk hypothesis. As the authors of the publication [13] note, the addition of basic oxide with a "break point" has a significant effect on the change in the proportion of structural units, i.e. $Si_2O_7^{6-}$ to e.g. $Si_2O_6^{4-}$ i.e. only the proportion between longer and shorter silica chains is changed. It is possible that the mechanism of movement of ions inside the system may consist of several stages. Toplis and Webb state that in a ternary system Na_2O – Al_2O_3 – SiO_2 the flow mechanism is more complex [14,15]. In their mechanism, they assume that the disintegration occurs at the point where the Na^+ cation balances the charge in the chain. They also assume that the transition energy of the molecule in the flow direction is so small that a break in the grid is possible.

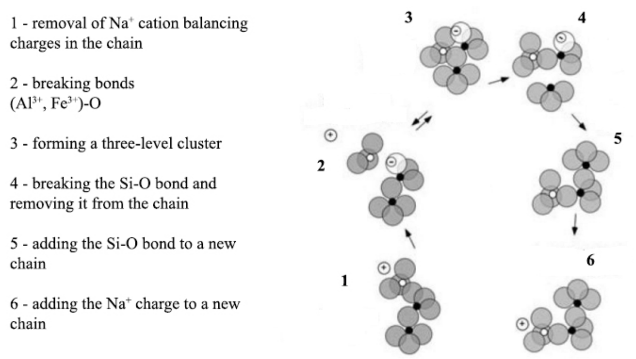

Fig. 5. Formation of chains according to Toplis and Webb [16]

The next step is the breakdown of Al-O binding and the formation of a three-level cluster composed of SiO_2 and Al_2O_3 ions. The authors of the paper do not accurately explain the mechanism behind the formation of SiO_2 and Al_2O_3 clusters. In turn, this cluster decomposes as a result of internal friction into single tetraedra which, in subsequent stages, merge into silicate chains. In the last step, the cation balancing the charge across the chain is added into the silicate chains. The mechanism behind chain formation for the ternary system is shown in Figure 5.

4. The effect of the amount of fluorite added on its viscosity

The introduction of fluorite into the decopperisattion process favors the recovery of copper from the slag. The impact of the amount of added calcium fluoride on its viscosity has already been studied by the authors [17] and is shown in Fig. 6. As a result of this study, it can be stated that the conventional limit for the amount of calcium fluoride added is just over 10%. In other words, exceeding this value will not affect significantly the improvement of slurry technology. Nevertheless, this is far less than in the case of currently added calcium carbonate, with a limit value of 15% as shown in Figure 7.

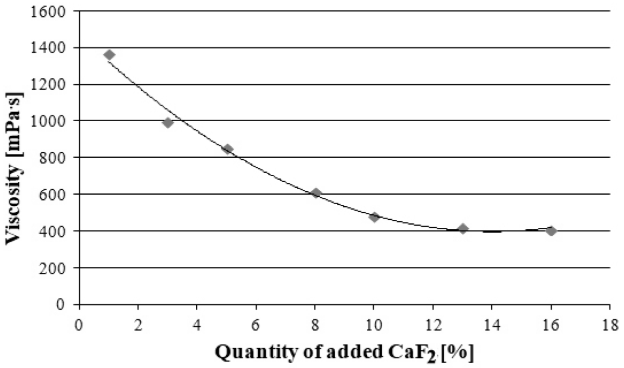

Fig. 6. The effect of the amount of fluorite added on its viscosity at 1300°C [17]

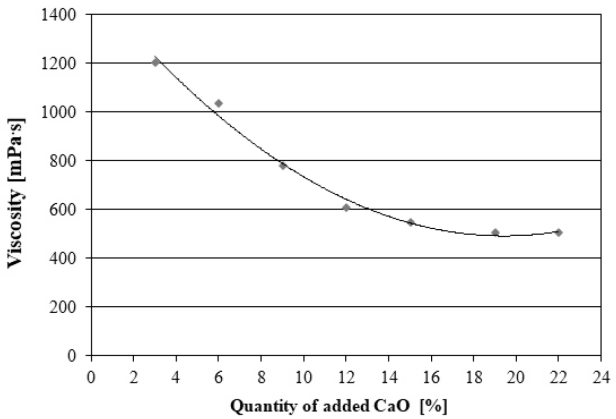

Fig. 7. The effect of the amount of calcium oxide added on its viscosity at 1300°C [17]

The global production of calcium fluoride (fluorite) has been growing strongly until 2009. The largest supplier of fluorite in the world is Mexico, which exports about 1 million tonnes a year. Its price in 2013 ranged from 200 USD/t - 230 USD/t. In contrast, calcium carbonate currently used in slurry technology is not subject to price quotes, but the price is instead set in contracts between the seller and the purchaser. Typically, calcium carbonate prices range from $200 - $290/t. So we can say that prices of calcium carbonate and fluorspar are comparable. The demand for fluorspar in Poland is 100% covered by import, which amounted to 11.4 thousand tons in 2012 [18]. This raw material was mainly imported from Mexico, with some smaller batches brought in from Germany. Nevertheless, it still seems possible to limit the import of this raw material, provided that more domestic sources are used. Fluorite concentration in Poland was documented in the deeper parts of the Stanisławów Baryt deposit, and the overall resource balance as of 31 December 2013 is 543 thousand tonnes. The main recipients of fluorspar were, e.g. Aluminium Konin and the ironworking industry, chemical and glass industry. After shutting down the mill, the demand for fluorite has decreased drastically. The price of fluorspar in the years 2009-2013 is shown in Table 2.

Table 2.
Prices of Mexican fluorspar in the years 2009-2013 expressed in USD/t [18]

Year	2009	2010	2011	2012	2013
CaF_2	140-195	170-200	230-270	230 -270	230-270

As a result, 500 tonnes of slag slurry will consume about 50 tonnes of fluorite per processing cycle, rather than the current 75 tons of calcium carbonate, which translates into a reduction in the cost of the technological additive. Moreover, the thermodynamic calculations of the change in enthalpy of the free reaction of calcium fluoride decomposition show that its decomposition during the introduction of the new technological additive consumes much less energy [19]. During the course of the decopperisation process, the droplets falling time to the setter bottom in an electric furnace is also important. Based on our own calculations [20], it was found that the drop time of 0.1 mm radius drops at 1300°C in the slag after adding fluorite decreases by about two hours compared to the present technology, as illustrated in Fig. 8. The calculations were based on the Stokes equation (3) and some assumptions regarding the droplet and slag density as well as the slag viscosity.

$$V = \frac{2}{9} \cdot \frac{\rho_1 - \rho_2}{\eta} \cdot g \cdot r^2 \quad (3)$$

ρ_1 – droplet density,
ρ_2 – slag density,
η – slag viscosity,
g – gravitational acceleration,
r – radius of copper drop,
V – speed of descent.

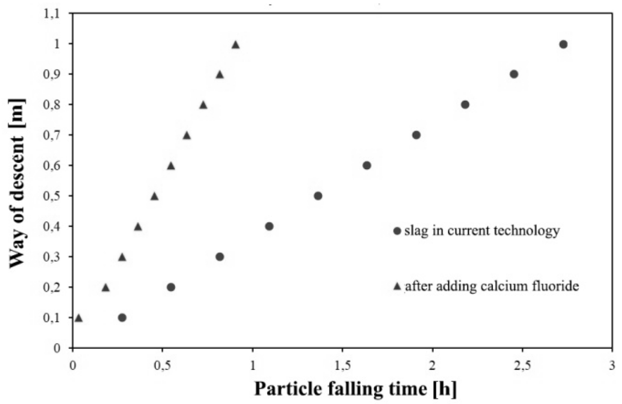

Fig. 8. Dropping time of melt drop with radius φ = 0.1 mm at 1300°C after adding calcium fluoride

4. Summary and conclusions

Production processes in Copper Mining and Metallurgy Copper Complex are complicated processes and require customers to provide ever higher quality products at relatively low prices. This situation increases the importance of process optimization. As technology and products change very quickly, the technicians of Glogow Combinate have less and less time to optimize it based on their own experience. Analyzing a specific process, we can detect e.g. interference in the process, find the causes of issues with process quality, choose optimal settings for the process or compare different manufacturing procedures. The basis of process optimization is the analysis of the production process. In the case of slag slurry decopperisation, the process was analyzed, as were the main drawbacks and advantages, and the possibility of modifying the presently added calcium carbonate as a highly energy-intensive additive. Based on the literature analysis, a solution has been developed that improves the copper production process. The benefits of using a new technology additive primarily include increased share of copper in the alloy, reduced production costs, reduced amount of power consumed per cycle and reduced time it takes to melt.

Acknowledgements

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