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Analysis of Multicriteria Optimisation in the Decopperisation Process of Flash Smelting Slags

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Abstract

This article presents results of studies on multicriteria optimisation in the decopperisation process of flash smelting slags coming from the process of decopperisation at the "Głogów II" Copper Smelter. Measurements of viscosity were conducted using a high-temperature viscometer manufactured by Brookfield company. An addition in the form of calcium fluoride has an advantageous influence on decreasing the liquidus temperature of slag, and the effect of decreasing viscosity at the participation of calcium fluoride is significant. A motivation to conduct studies on viscosity of decopperised slags is an optimisation of the process of decopperisation at an improvement of this process parameters, i.e. the time of melt per one production cycle and consumption of electric power in the whole process. The efficiency of optimisation of the process course depends not only on an accepted criterion of the quality of controlling, a type of technological parameters, but also, to large extent, on characteristics and features of these parameters. $CaCO_3$ currently added to the process of decopperisation efficiently decreases viscosity of flash slag, at the same time has influence on an increase of the yield of copper in alloy, but on the other hand, it increases the mass of slag, artificially under representing concentration of this metal. The article is completed with a conclusion of discussed issues, stating that a search for a new technological addition is still necessary,

Keywords: Calcium fluoride, Viscosity of slag, Flash slag, Decopperisation

1. Introduction

Information in the existing references about viscosity of flash smelting slags and decopperised slags is quite differentiated. It mainly results from the fact that at slight changes of particular components of slag, there take place a significant change of its viscosity. Influences of particular components on viscosity of flash smelting slags were well presented in a publication by A. Zajączkowski et al. [1]. In the article, the authors presented results of studies on viscosity of two flashsmelting slags and six synthetic slags, various as far as their chemical compositions are concerned. The first of slags, in the temperature of 1200°C has viscosity of 1969 mPa·s, while the second one, having about 5% copper more, has viscosity at the level of 1573 mPa·s. In case of synthetic slags, their viscosity ranges from about 4000 mPa·s to 10 000 mPa·s at the temperature of 1300°C. S. Bratek [2], analysing the influence of additions modifying a composition of flash slag on its melting temperature achieved viscosity of 1224 mPa·s at the temperature of 1200°C, but it must be noted that the basicity index was 0,76. M. Kucharski et al. [3], studying synthetic slags of three-component set SiO_2-CaO-FeO, at the Fe to Si proportion of 2,1, achieved viscosity of 141 mPa·s at the temperature of 1300°C. The same author, when analysing viscosity of flash smelting slags during the process of decopperisation, achieved viscosity at the level of 2185 mPa·s at the temperature of 1200°C [4]. M. Wędrychowicz [5], marking viscosity of flash smelting slags depending on temperature and partial pressure of oxygen in the oxidising condition, achieved viscosity at the level of 1750 mPa·s. Results in the reducing conditions were, respectively: 1704 mPa·s and 1691 mPa·s. A monograph by KGHM [6] presents graphical results of viscosity of flash slag during decopperisation of it depending on temperature. Reading values from the chart, one can state that viscosity of slag in the temperature of about 1200°C at the copper content of 14,7% have the values of about 1000 mPa·s, whereas authors do not provide the chemical composition of the analysed flash slag. Bockris and Kozakevitch, analysing viscosity of three-component set of $CaO–SiO_2–Al_2O_3$ in the range of temperatures of slag cast of slag, i.e. 1400–1500°C, obtained viscosity in the range of 70–2000 mPa·s [7]. They presented results of their works within the concentration triangle of the three-component set. Machin and Potatin [8, 9], studying synthetic slags of a four-component set achieved viscosity at the level of 4000 mPa·s. Slags acquired from melting of Polish concentrates of copper in a fluidised-bed oven and in the course of reduction of flash slag in an electric oven were a subject of systematic studies of the Institute of Non-Ferrous Metals, results of which are presented in work [10]. Depending on the chemical composition, these slags had viscosity of 500 mPa·s to over 20 000 mPa·s. in the temperature of 1300°C.

2. Multicriteria optimisation of the process of decopperisation of flash slag

Studying physical and chemical characteristics of slags, including viscosity, provides the possibility to draw conclusions concerning their structure, providing information about the amount of energy of activating laminar flow, as well as the influence of particular cations on the structure of slag. For example, Table 1 presents several types of measurements enabling acquirement of detailed information concerning the structure of slags.

Table 1.
Structural information about various measurement methods

Method	Measurement	Structural information
Measurements of physical characteristics of slags	Density, molar volume	Packing and coordination of atoms
	Molar refraction	Concentration of O^{2-}, O^{0} oxides
	Viscosity	Activation energy an related bond strength
	Thermal and electric conduction	Ionic conduction of Li^{+},Ca^{2+} etc.

Although pyrometallurgy of metals is known, modern science about the structure of liquid slags is still not beyond the stage of collecting experimental data. Thus, it is difficult to determine what structural criteria liquid slags should have. However, these criteria should include size of ions, as well as forms of their occurrence. In most of cases, slags from Polkowice or Rudna contain mainly large silicon and oxygen, alsifer ions, forming a compact and glassy structure of slag at its fast cooling. A large density of these slags, as well as a retarded process of connection of drops of metals into larger clusters is not desirable. Slags with smaller ions and having oxides of alkaline metals, reveal a trend to so called silicate decomposition. The latter most often occurs in the course of polymorphouos transformations of calcium orthosilicate $CaO·SiO_2$ bęing coooled. Decomposition of slag can be retarded by adding acid oxides that stabilize slag, i.e. Al_2O_3, MgO or P_2O_5. Many authors think [11], that the best quality of slag should be obtained in the course of mixing main slag with other slags of a similar composition. It is also worth to note that during casting slag from a hot ladle, residues of it contact much cooler air, while a very hot mass drifts to directly poured slag. Due to such pouring of slag, on its surface, there forms a brittle layer, while internally it maintains more compact and porous layer. The upper part of these layers makes a recovery of metals from liquid top difficult, thus, in order to counteract this phenomenon, upper parts of layers of slag in a ladle should be overheated in order to obtain a better structure and quality of lasg. Another example of the influence of a composition of slags on their quality is a work by T. Karwan, J. Nowakowski, Z. Gostyński, and R. Konefał [12]. They show the way that a change of flash technology from four-burner to one-burner has the influence on a structure of slag in the flash process. Below presented microsope images from this work show that in case of four-burner technology, regular and spherical inclusions of copper are obtained, while in case of the one-burner technology, surfaces are irregular, less close to spherical (presented in figures 1 and 2, respectively).

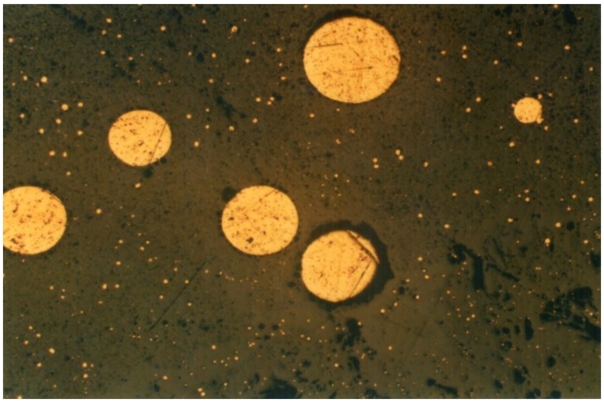

Fig. 1. Microphotography of the structure of slag from four-burner process [12]

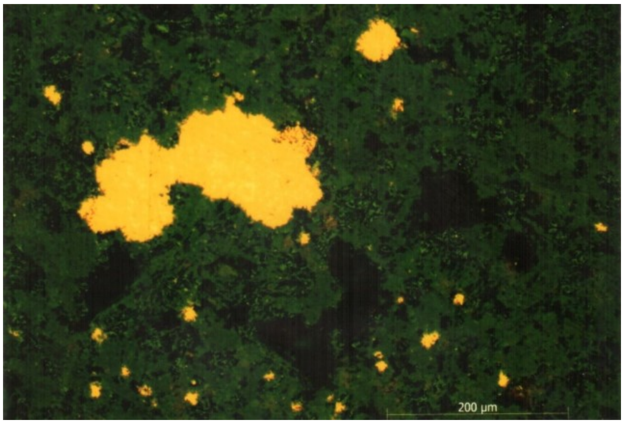

Fig. 2. Microphotography of the structure of slag from one-burner process [12]

Authors perceive a reason of the presence of an irregular shape of copper in the pace of supplied stream of gas, driving conversed and not conversed molecules of the concentrate into slag. Formation of so irregular surfaces results also from graining of the mixture components. Coagulation and sedimentation of these molecules to the metallic phase will be difficult not only in the suspension process but also in further processes, including the process of decopperisation of slag. Too fast supply of air enriched in oxygen has a contribution in a large amount of technological gases which should be carried away.

To sum up, on the quality of slag as far as its composition is concerned, decisive shall be factors such as:

- forms and sizes of presence of ions, related with the chemical composition of the concentrate, as well as their amount;
- a way of moving liquid slag from a ladle to a furnace and related losses of thermal and electric energy;
- a technological way of conducting the penetration of slag, which can lead to excessive emission of technological gases.

3. Influence of changes of slag viscosity on the quality of the process of decopperisation

The decopperisation process significantly facilitates a decrease of viscosity of slag, after an introduction of a proper technological addition. However, it is important that such addition allowed an easy separation of liquefied slag from metal and would not artificially underrepresent the concentration of metal in slag. Each unexpected change of slag viscosity during the process can lead to increasing the time of settling of reduced copper (even to several weeks). What is more, too viscous slag disturbs the run of gases going through the layer of slag what impedes their degassing. Another factor having an influence in the quality of decopperisation is an increase or a decrease of the activation energy of laminar flow, which can take place thanks to a presence of undesired compounds, i.e. Ca_2SiO_4, Mg_2SiO_4 or $Ca_3MgSiO_2O_3$; they occur due to changes of slag's chemical composition. Additionally, some authors [13] claim that copper ferrates $Cu_2O{\cdot}Fe_2O_3$ included in flash smelting slag cause a resistant course of reduced in an electric furnace. This takes place in the course of an intensive reduction of iron in the range of temperatures of 1300–1360^{o}C. As viscosity of slag depends also on temperature, it is worth to note that at high temperatures, all bounds between ions of metals become too weak due to intensive heat movements, in the course of which, viscosity of slag decreases [14-16]. Thus, maintaining temperature in the range of 1300-1400^{o}C is also required.

Metallurgical slags are multi-component and multi-phase systems, containing mainly oxides of metals, i.e.: Al_2O_3, CaO, MgO, MnO, SiO_2 as well as FeO. Oxides such as SiO_2, P_2O_5 and B_2O_3 are so called network formers, thus oxides forming the net structure of slags. A very strong metal-oxygen covalence occurring in the oxides impacts results in high viscosity of slags. In comparison to other oxides such as oxides of alkaline metals and alkaline soils, i.e. Li_2O, Na_2O, K_2O, MgO, CaO as well as MnO and FeO they cause a disruption on the net structure of slags, what leads to decreasing their viscosity. These are so called formers breakers. The scale of decreasing or increasing viscosity closely depends on the composition of slag and their proportions in slag. Amphoteric oxides such as Al_2O_3, Fe_2O_3, can behave both as oxides decreasing as well as increasing viscosity. In case of transition metals such as Fe, Cr, it is important to have knowledge about the level of oxidation of these metals, as the way of influence on viscosity is of iron of the +2 grade of oxidation is different than in case of iron at the +3 grade. Iron (II) oxide in decopperised slag decreases its viscosity, while iron (III) oxide increases it. According to the above discussion, an essential criterion of the quality of slag is its chemical composition, having a direct influence on slag viscosity. To sum up, flash slag should be characterised by:

- a lack of precipitation of metallic phase or other compounds having a direct influence on a change of slag viscosity;
- a drop of viscosity during the process due to a decrease of the module of slag acidity at increasing the content of basic oxides, i.e. FeO, ZnO, CaO, PbO.

4. Methodology of studies

4.1. Measurement of viscosity of decopperised slags with the use of calcium fluoride

Flash smetling slag obtained from “Głogów II” plant in the form of congealed lumps of dimensions not exceeding 40 cm was broken into smaller fractions using a clinker grinder. Next, smaller fractions were crushed using a ball mill, and next screened to particulate fractions of the size of particles not larger than 0,01 mm. Next, flash slag was precisely averaged and additionally dried at the temperature of 300^{o}C for 12 hours in order to eliminate moisture. A weighed sample of decopperised slag with calcium fluoride of the total mass of about 70 g was put into a molybdenum crucible, and next put into a rotating-cylinder viscometer. Any working tools of the viscometer i.e. suspension of the spindle and the spindle itself were made of molybdenum. Measurements of viscosity of decopperised slag were conducted at a low partial pressure of oxygen in the atmosphere of CO-CO_2 gases. After connecting a furnace to a chamber of a head of viscometer, pure nitrogen of the intensity of 20 l/h was transferred through the system for 12 hours and next the furnace was switched on and its temperature controller was set to 300^{o}C. After 12 hours, the temperature was increased to 1200^{o}C, waiting for a stabilisation of temperature for about an hour. After achieving a set temperature level, CO-CO_2 were transferred and the viscometer spindle was lowered to its complete immersion, and next, the number of turns of a penetrator was calculated and the viscometer was switched on. In the course of a turn of the penetrator in slag, the controller of the viscometer gave the necessary torque as a part of the maximal torque, expressed in percents. Viscosity of analysed slag was determined by comparing the obtained readings with a calibration line. A detailed description of the procedure is presented in the work [14]. Figure 3 presents the viscometer by Brookfield company used in the research, while figure 4 presents crumbled flash slag obtained in a clinker grinder.

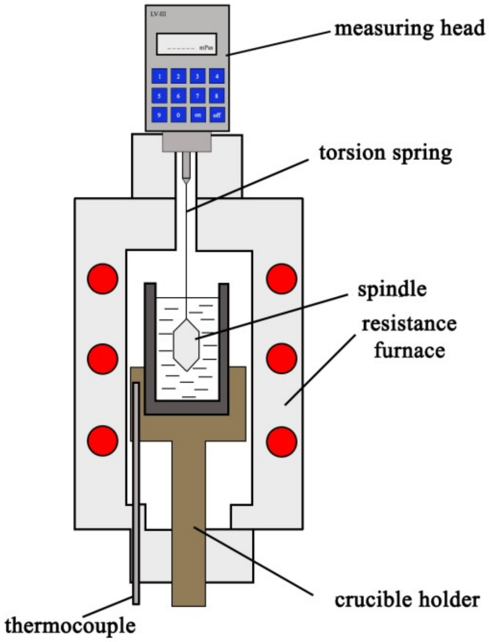

Fig. 3. Diagram of a rotating-cylinder viscometer

Fig. 4. Powdered flash slag

Table 2.
Main components of decopperised slag

Component	SiO_2	CaO	Cu_2O	MgO	Al_2O_3	Na_2O	ZnO
[%] wt.	37,8	12,0	12,4	2,89	12,8	0,6	2,0

5. Results of measurements

In the course of conducted studies, it was stated that the maximal amount of added calcium fluoride should not exceed 10% and this is an optimal value of the amount of added calcium fluoride. Figure 5. presents results of viscosity of decopperised slag at addition of 1%, 3%, 5%, 8%, 10% of CaF_2 in the range of temperatures of 1200^{o}C - 1360^{o}C. Figure 6. presents results of viscosity of decopperised slag at the further addition of calcium fluoride amounting to 13% and 16%.

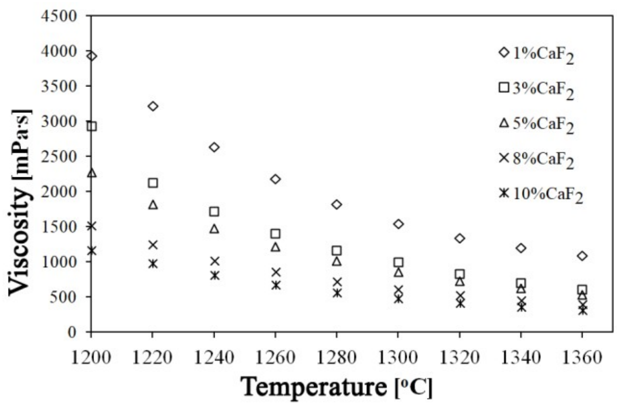

Fig. 5. Influence of added CaF_2 on viscosity of decopperised slag

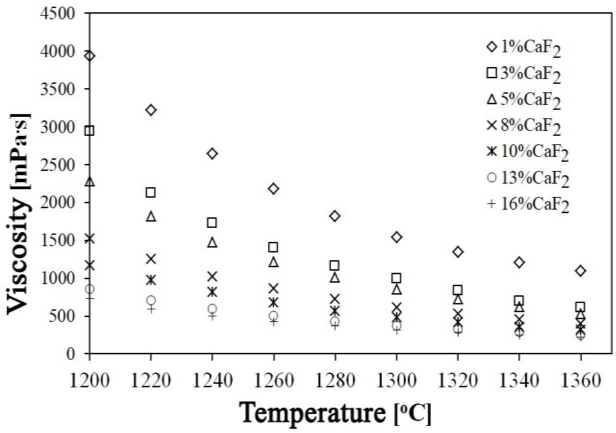

Fig. 6. Influence of further addition of calcium fluoride on viscosity of decopperised slag

In practice, further amount of added calcium fluoride does not have an influence on viscosity of analysed slag, so we can observe slight decreases of viscosity of the range of 100 mPa·s at additions of 13% and 16%. It seems that a further addition of CaF_2 can be regarded as unjustified. Nevertheless, it is significantly less than in case of calcium carbonate added in the present technology, limit value of which can be assumed at 15%.

6. Summary and conclusions

Attempts of perfecting the production process at „Głogów II" copper mill require continuous works. One of essential stages of an optimal designing is a selection of a proper optimisation procedure as a tool to solve the engineering problem. A selection of such method is not easy as there is no universal method that can be equally efficient for all engineering problems. In order to find the best solution for the process of decopperisation, the main related problem was formulated: in the present process of decopperisation of flash slag, calcium carbonate is added, which has an influence on the recovery of copper from flash slag on the one hand, and on the other hand:

– it is a highly energy-consuming addition,
– artificially decreasing the content of copper in slag,
– increasing the mass of slag.

On the basis of the main problem, an option of a solution was developed, an effect of which can be an increase of the process of copper manufacturing through an introduction of calcium fluoride into the process of decopperisation. What is more, this article presents also factors which have an influence on the quality of slags.

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