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Complex Reagent Efficiency in Reduction of Copper from the Slags in Conditions of the Smelter & Refinery Plant - Głogów

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Abstract

The copper droplets contained in the post-processing liquid slag are subjected to the treatment by the complex reagent. The complex reagent has been recently elaborated and patented in frame of the Grant No. PBS3/A5/45/2015. In particular, the complex reagent is dedicated to the post-processing slags coming from the Smelter and Refinery Plant, Głogów, as a product of the direct-to-blister technology performed in the flash furnace. The recently patented complex reagent effectively assists not only in agglomeration, and coagulation but also in the deposition of the copper droplets at the bottom of crucible / furnace as well. The treatment of the post-processing slags by the complex reagent was performed in the BOLMET S.A. Company as in the industrial conditions which were similar to those usually applied in the KGHM – Polish Copper (Smelter and Refinery Plant, Głogów). The competition between buoyancy force and gravity is studied from the viewpoint of the required deposition of coagulated copper droplets. The applied complex reagent improves sufficiently the surface free energy of the copper droplets. In the result, the mechanical equilibrium between coagulated copper droplets and surrounding liquid slag is properly modified. Finally, sufficiently large copper droplets are subjected to a settlement on the crucible / furnace bottom according to the requirements.

Keywords: Solidification process, Copper droplets, Complex reagent, Post-processing slag, Thermo-chemical treatment

1. Introduction

The analysis connected with the efficiency of the stimulators and reagents on the agglomeration, coagulation and sedimentation of the copper droplets in the liquid post-processing slags is continued. The experiment was dealing with the so-called direct-to-blister process which is in reality an extraction technology. The mentioned process delivers the primary suspension of the copper droplets in the liquid slag (Fig. 1). Agglomeration, coagulation and sedimentation, all above phenomena are strongly influenced by the extraction technology [1] and [2].

A comparison between industrial process of decopperisation and the current one was the subject of the performed experiments in the industry scale.

An additional problem which accompanies the decopperisation is the removing of lead and iron from the copper droplets [3]. Moreover, carbon is also frequently present in the copper droplets, especially, when reduction of oxides is not sufficiently effective in the direct-to-blister process [4] [5] and [6].

Surprisingly, the copper droplets geometry is strictly connected with the copper concentration [7]. Therefore, an evolution of droplet shape is expected during droplets coagulation (Fig. 1).

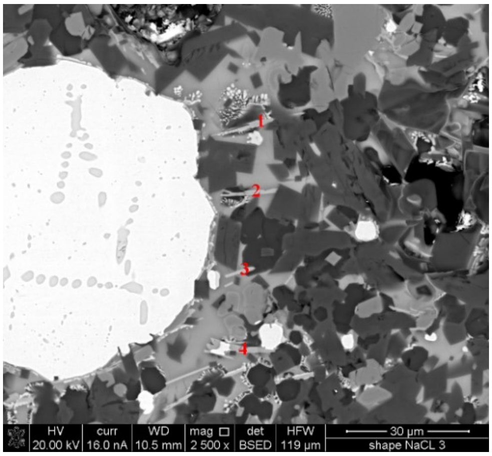

Fig. 1. Copper droplets shape; a/ (1,2,3,4 - rods) - containing below 15 wt.% Cu tend towards the main copper droplet, b/ main / large copper droplet (irregular in shape) in the course of coagulation [7]

When the copper droplet geometry is similar to the shape of a star then this droplet contains about 25 wt.% Cu. When the copper droplet evinces irregular spherical geometry, Fig. 1, then it contains almost 50 wt.% Cu. Fully spherical shape of the copper droplet is connected with the highest purity. This kind of droplet contains about 70 wt.% Cu or more (Fig. 2).

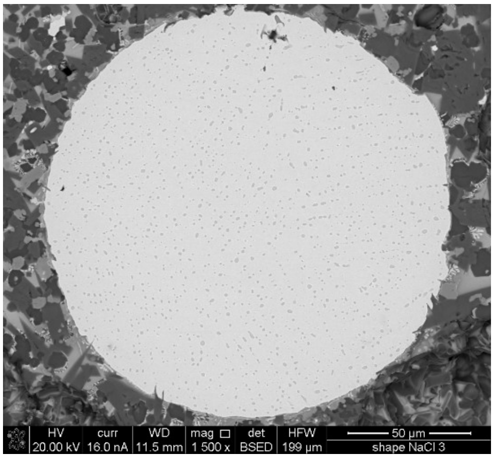

Fig. 2. Fully spherical coagulated droplet which contain about 85 wt.% Cu and some precipitates of the Cu-Cu_2O – eutectic [7]

It is obvious that the copper droplets are subjected to the purification (droplets lose lead and iron due to centrifugal force accompanying their rotation) during the evolution of their shape.

Moreover, this evolution leads to substantial improvement of the mechanical equilibrium between copper droplet and surrounding different particles of the liquid slag (Fig. 1). Locally, the copper droplet is convex (in the contact with the bright particles of the liquid slag) or rather concave (when its periphery is in the contact with the dark particles of the surrounding liquid slag).

It is well visible in (Fig. 1) that the planetary arrangement of the copper droplets suspend in the liquid slag seems to be typical for these systems. So, the small droplets (rod-like in shape) tend to be swallowed by the dominant / main copper droplet in order to diminish its specific surface free energy (surface tension). So, small, rod-like droplets tend to join the dominant droplet, to support its coagulation.

The droplets coagulation is significantly easier when the viscosity of the liquid slag is decreased [8]. Therefore, the elaborated and patented complex reagent not only promotes the coagulation but first of all changes positively the liquid slag properties [9]. The mechanism of coagulation is well illustrated in (Fig. 1) where the small spherical droplets or rod-like droplets tend to be swallowed by the dominant droplet which is growing due to the smaller droplets feeding [1]. When buoyancy force is smaller than gravity then a given droplet is settled on the furnace / crucible bottom as desired [7]. However, when the buoyancy force is the winner in this competition then the copper droplets are situated at the liquid slag surface (Fig. 3).

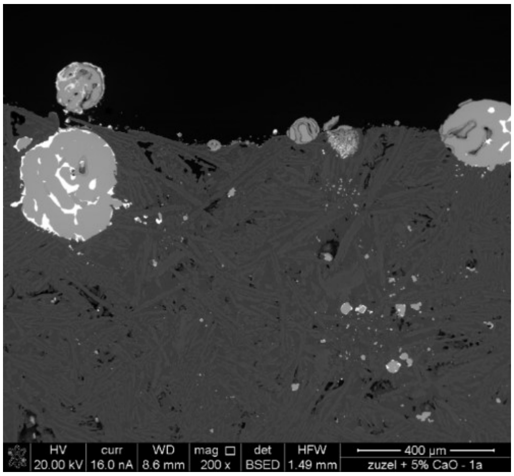

Fig. 3a. Some copper droplets (even containing lead – white areas) localized at the liquid slag surface after industrial chemical treatment (Smelter and Refinery Plant – Głogów) [7]

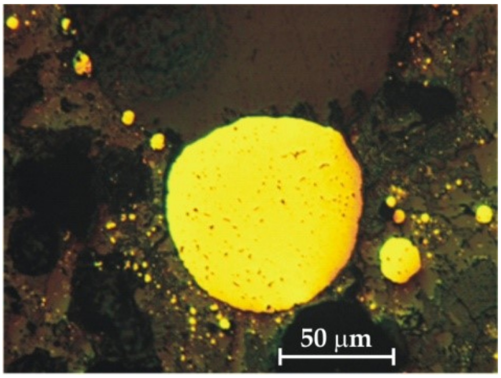

Fig. 3b. Copper droplets localization at the liquid slag surface; even an enough large droplet tends towards the liquid slag surface (not to the crucible bottom) since the industrial chemical treatment is not sufficiently effective; however, the main copper droplets is surrounded by some very small droplets (phenomenon of agglomeration) [7]

When carbon added to combustion reactor in the flash furnace is dispersed uniformly in the furnace shaft and completely consumed in the process under investigation then some particles of this element would be visible in the slag coming from the direct-to-blister process. Otherwise, these particles are localized inside the copper droplets [10] and [11]. So, in some cases the carbides can be revealed within both liquid slag and droplets [12] and [13].

The current analysis makes effort to show the comparison between the effectiveness of two chemicals on the copper droplets coagulation and finally on their sedimentation. The first chemicals are $CaCO_3$, and Na_2CO_3 compounds (industrial treatment) and second chemical is the complex reagent recently patented [9].

2. Efficiency of the complex reagent

The experiments dealing with the copper droplets coagulation preceded by agglomeration were performed in the industry scale with the use of a proper furnace initially heated up to 1320 ^{0}C. The slag was melted and subsequently treated by the industrial chemicals like: fine coal, CaO from the $CaCO_3$ decomposition, and Na_2CO_3, or, by some components of the patented complex reagent, respectively.

The treatment of the liquid slag by the industrial chemicals is not so efficient, Fig. 4. The cooled slag (after chemical treatment) contains many copper droplets gathered in some agglomerations, (about 0.86% of Cu in the slag).

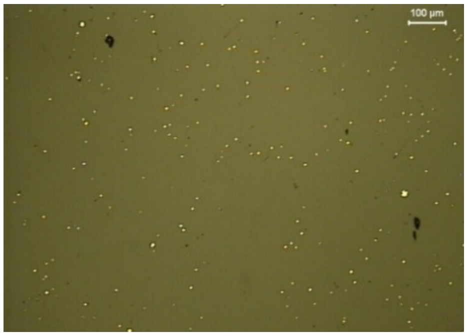

Fig. 4. Agglomeration of the copper droplets in the cooled slag

When the suspension of the copper droplets in the liquid slag is subjected to activity of the patented complex reagent, however, without NaCl, K_2PO_4, and CaC_2, but with an addition of Na_2CO_3, then the efficiency of the decopperisation is more visible than in the case of the industrial chemical treatment (Fig. 5).

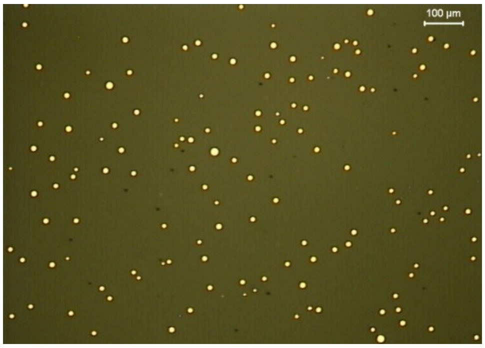

Fig. 5. Agglomeration and coagulation of the droplets in the slag

In the subsequent experiment, the slag was subjected to activity of the complex reagent, however, without K_2PO_4, and CaC_2, but with an addition of Na_2CO_3 (Fig. 6). In this case both agglomeration and coagulation of the copper droplets were more efficient than that shown in (Fig. 4) and (Fig. 5). Many droplets were subjected to sedimentation on the furnace bottom.

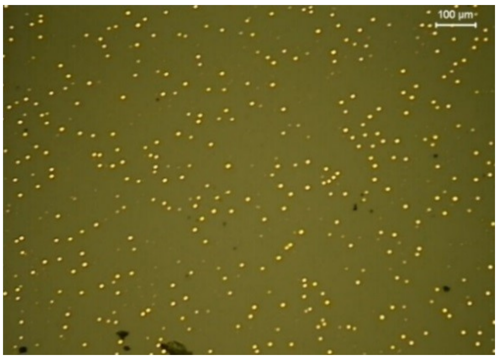

Fig. 6. Agglomeration and coagulation of the droplets in slag

Next, the patented reagent was enriched in Na_2CO_3, but CaC_2 was removed from the reagent. The resultant agglomeration and coagulation is shown in (Fig. 7). Agglomeration and coagulation were better than in the case of the treatment by the industrial chemical (Fig. 4). Many droplets are situated on the furnace bottom due to action of gravity on the studied suspension.

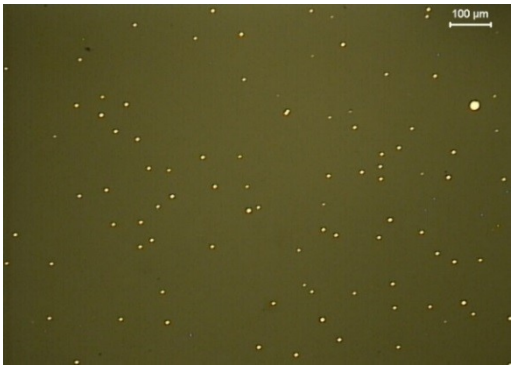

Fig. 7. Agglomeration and coagulation of the droplets in slag

In the last experiment, the full content of the complex reagent was introduced into the liquid slag, however, with a small addition of Na_2CO_3.

In this case not only agglomeration, and coagulation but sedimentation were very efficient (Fig. 8). Almost all copper droplets were situated on the furnace bottom. Few of them remained in the slag, only. The studied image / morphology of the cooled slag, after the treatment by complex reagent with the small addition of Na_2CO_3 evinces one fully coagulated copper droplet, only. The other droplets are situated on the furnace bottom.

Other studied images show also a little content of very small copper droplets which were not subjected to agglomeration and coagulation. Thus, efficiency of the patented reagent is estimated as equal to (0.86% - 0.3%)/0.86% and is equal to about 65%.

It means that content of copper in the slag was reduced from 0.86% to 0.3% in the analyzed suspension.

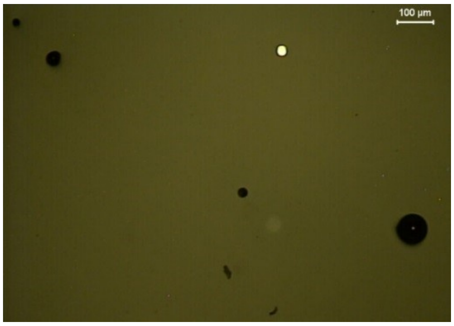

Fig. 8. Remaining, well coagulated individual copper droplet in the cooled slag after treatment by the patented, complex reagent with the small addition of Na_2CO_3

The copper deposited on the furnace bottom (Fig. 9) was subjected to further observation / analysis.

Fig. 9. Copper deposited on the furnace bottom due to activity of bot the complex reagent and gravity

3. Concluding remarks

The comparison of the activity of both industrial chemicals (Fig. 4) and complex reagent (Fig. 8) within the studied suspension proves that the complex reagent is substantially effective in agglomeration, coagulation and subsequent sedimentation (Fig. 9).

However, it should be emphasized that in the case of the industrial chemicals use, some copper droplet agglomerations are formed, mainly (Fig. 4). During the complex reagent activity, the copper droplets are subjected to the self-cleaning by the centrifugal force imposed on the droplets, usually. The mentioned force allows to remove lead and iron contained inside a given droplet (Fig. 10).

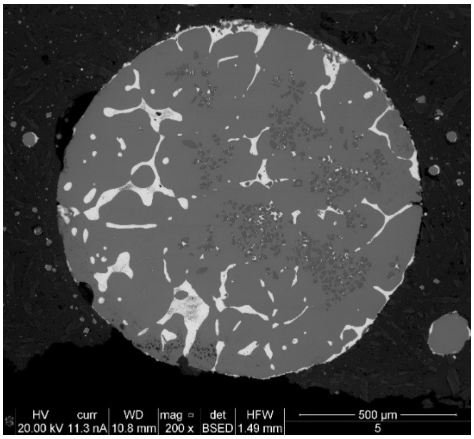

Fig. 10. Fully coagulated copper droplet before the self-cleaning; the droplet contains lead, iron (white areas) and Cu-Cu_2O (grey dots)

Surprisingly, the rod-like eutectic (Fig. 10) promotes a decrease of the specific surface free energy of the copper droplet. This is desired phenomenon which is conductive to coagulation and accompanying purification of droplet. On the contrary, the Cu-Cu_2O lamellar eutectic is not favorable to coagulation.

It is obvious, that the patented, complex chemical [9] should be recommended for the industrial practice in the near future, especially to the KGHM- Polish Copper Company S.A.

Acknowledgements

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