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Reagents Activity in a Copper Droplets / Post-Processing Slag Suspension

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Abstract

The suspension of the copper droplets in the post-processing slag taken directly from the KGHM-Polska Miedź S.A. Factory (from the direct-to-blister technology as performed in the flash furnace) was subjected to the special treatment with the use of the one of the typical industrial reagent and with the complex reagent newly patented by the authors. This treatment was performed in the BOLMET S.A. Company in the semi-industrial conditions. The result of the CaCO_3 , and Na_2CO_3 chemicals influence on the coagulation and subsequent sedimentation of copper droplets on the crucible bottom were subjected to comparison with the sedimentation forced by the mentioned complex reagent. The industrial chemicals promoted the agglomeration of copper droplets but the coagulation was arrested / blocked by the formation of the lead envelope. Therefore, buoyancy force forced the motion of the partially coagulated copper droplets towards the liquid slag surface rather than sedimentation on the crucible bottom. On the other hand, the complex reagent was able to influence the mechanical equilibrium between copper droplets and some particles of the liquid slag as well as improve the slag viscosity. Finally, the copper droplets coagulated successfully and generally, were subjected to a settlement on the crucible bottom as desired / requested.

Keywords: Copper droplets, Coagulation, Sedimentation, Liquid slag

1. Introduction

The so-called direct-to-blister process which is an extraction technology delivers the primary suspension of the copper droplets in the liquid slag, Fig. 1. Coagulation and sedimentation, both are strongly influenced by the extraction technology, [1], and [2]. Usually, the copper droplets contain lead and iron, [3]. These two elements, that is iron and lead cannot be easily removed from the droplets. In the case of carbon, this element is also present there, especially, when reduction of oxides is not sufficiently effective in the direct-to-blister process, [4], and [5].

The copper content in the droplets is strictly connected with the evolution of droplet shape which changes during droplets'

coagulation, [6]. The droplets coagulation is significantly easier when the viscosity of the liquid slag is decreased, [7]. Thus, it is expected that the complex reagent should not only promote the coagulation but first of all to change positively the liquid slag properties, [8]. 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].

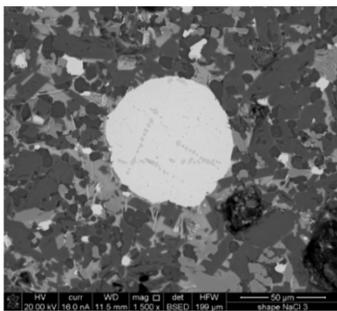


Fig. 1. Planetary arrangement of the copper droplets suspend in the liquid slag; small droplets tend to be swallowed by the dominant copper droplet in order to diminish its surface tension; also rod-like droplets tend to join the dominant droplet, to support a coagulation

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 taken from the direct-to-blister process and even inside the copper droplets, [9], [10], and [11]. In some extremal cases even some carbides can be formed within the liquid slag and copper droplets suspension, [12].

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 and second is the complex reagent recently patented, [13].

2. Reagents activity in the Cu coagulation

The experiments dealing with the copper droplets coagulation were performed in the semi-industry scale with the use of a proper crucible situated in the furnace and initially heated up to 1300°C . The slag was inserted into the crucible and next the industrial chemicals CaCO_3 , and Na_2CO_3 or some components of the complex reagent were introduced into the suspension of copper droplets, respectively.



Fig. 2a. Results of the copper droplets coagulation after the St1 (5%) - chemical treatment performed for 10 minutes

The following stimulators (St), and reagents (R) were applied: to this semi-industrial examination: St1 = CaCO_3 , St2 = Na_2CO_3 , St3 = K_3PO_4 , St4 = NaCl , R1 = Mn_3C , R2 = CaC_2 , R3 = calcium cyanamide.

Particularly, the complex reagent should be very effective in the copper removal (copper droplets coagulation, growth and subsequent settlement) from the slag, as expected. The results of the performed test is presented in Fig. 2, respectively.

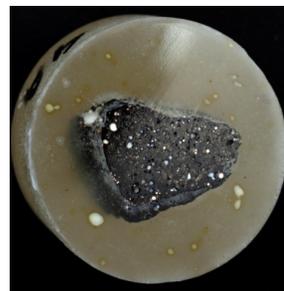


Fig. 2b. Results of the copper droplets coagulation after the St1 and St2 (5% of each) - chemicals treatment performed for 10 minutes



Fig. 2c. Results of the copper droplets coagulation after the St1, St2, and R2 (5% of each) - chemicals treatment performed for 10 minutes

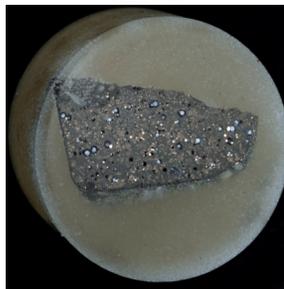


Fig. 2d. Results of the copper droplets coagulation after the St1, St2, (5% of each) and St4 (2%) - chemical treatment performed for 10 minutes



Fig. 2e. Results of the copper droplets coagulation after the St1, St2, R2 (5% of each), and St4 (2%) - chemical treatment performed for 10 minutes

Some copper droplet agglomerations are well visible in the samples presented in Fig. 2c, Fig. 2d, Fig. 2e.

However, it seems that expected / required further coagulation of the copper droplets is blocked by the envelopes formed closely around these droplets.

Usually, the envelopes are formed by the (Cu,Fe) – solution, and the (Pb) – solution containing elements, like: Ca, Fe, Cu, and Si.

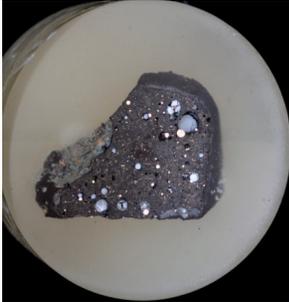


Fig. 2f. Results of the copper droplets coagulation after the St1, St2, St3, and R2 (5% of each) and St4 (2%) - chemical treatment performed for 10 minutes



Fig. 2g. Results of the copper droplets coagulation without the chemicals treatment performed for 20 minutes

Particularly, in the case of sample treated by the St1, St2, St3, St4 and R2, Fig 2f, the copper droplets are not yet enough large to be settled on the crucible bottom (they are also blocked).



Fig. 2h. Results of the copper droplets coagulation after the R1 (5%) - chemical treatment performed for 20 minutes

Some additional observations dealing with the copper droplets coagulation (growth) deliver a new information. According to these observations the industrial chemical is rather effective in the formation of some agglomerations, only, Fig. 3. It is well visible that a dominant droplet is rather large and situated in the agglomeration centre, Fig. 3a. It attracts other droplets since it has

the least of all surface tension among other copper droplets. The smaller droplets tend to be swallowed by this dominant droplet



Fig. 2h. Results of the copper droplets coagulation after the R2, R3, St1, St2, St3 (5% of each), and St4 (2%) - chemical treatment performed for 20 minutes

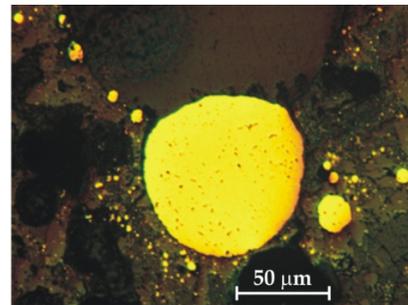


Fig. 3a. Agglomeration of the copper droplets at the liquid slag's surface due to buoyancy force effect on the studied suspension

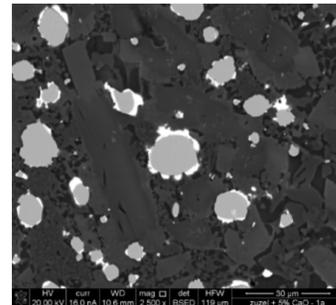


Fig. 3b. Agglomerations of the copper droplets as a positive result of the industrial chemical interaction with the suspension

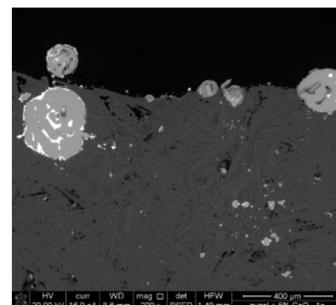


Fig. 3c. Copper droplets localization at the liquid slag's surface; even a distinguished large enough droplet tends towards the liquid slag's surface (not to the crucible bottom), (industrial chemical)

3. Concluding remarks

The comparison of the interaction of both industrial chemicals and complex reagent with the studied suspension proves that the complex reagent is satisfactorily effective in the process of coagulation and further sedimentation of the copper droplets suspend in the liquid slag.

However, in the case of the industrial chemicals application, some copper droplet's agglomerations are formed, generally.

Subsequently, the copper droplets are subjected to the self-cleaning by the centrifugal force and lead which was contained inside a given droplet is forced to form an envelope, Fig. 3b.

This phenomenon was also confirmed previously during the examination of the droplets settlement in the laboratory scale, [14].

Usually, the envelope is so tight and hermetic that it blocks further growth of the droplet itself. In the consequence, the droplets go to the liquid slag's surface, Fig. 3c, from these agglomerations due to the victory of the buoyancy force over gravity force effect as both forces are in the continuous competition with each other, [15].

Other elements which are present in the liquid slag suspension with the copper droplets are subjected finally to solidification and frequently form some eutectic precipitates, according to the non-equilibrium solidification well described (in details), [16].

In fact, the performed experiments demonstrated that in the case of the application of the complex reagent, recently patented, [13], majority of the copper droplets subjected to the competition between buoyancy and gravity force were settled on the crucible bottom due to the successful, effective coagulation.

It is obvious, that the patented, complex chemical should be recommended for the industrial practice in the near future, especially to the KGHM- Polska Miedź Company.

The chemical is satisfactorily effective not only in coagulation but in the required sedimentation of the copper droplets on a crucible bottom as well.

It contains some stimulators which improve the surface tension of the copper droplets as well as viscosity of the liquid slag suspension, in general.

The patented chemical also contains some reagents which are effective in coagulation itself and further sedimentation of sufficiently large droplets.

The addition of the stimulators and reagents contained in the patented chemical can be controlled by the computer assisted system / program which analyze the current composition of the liquid slag suspension and informs about quantities of stimulators and reagents required to be inserted into a given suspension.

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References

- [1] Bydałek, A.W., Wołczyński, W., Bydałek, A., Schlafka P. & Kwapisieński, P. (2015). Analysis of separation mechanism of the metallic phase of slag in the direct-to-blister process, *Archives of Metallurgy and Materials*. 60, 2347-2353.
- [2] Bydałek, A.W., Bydałek, A., Wołczyński, W. & Biernat, S. (2015). The concept of slag decopperisation in the flash furnace process by use of complex reagents. *Archives of Metallurgy and Materials*. 60, 319-322.
- [3] Nowakowski, J. (1976). Thermodynamic problems in copper fire refining. *Meturgia i Odlewnictwo*. 2, 3-14.
- [4] Bydałek, A.W. (2011). Role of carbon in melting copper processes. *Archives of Foundry Engineering*. 11(special 3), 37-42.
- [5] Migas, P. & Karbowniczek, M. (2010). Interactions between liquid slag and graphite during the reduction of metallic oxides. *Archives of Metallurgy and Material*. 55. 1147-1157.
- [6] Gierek, A., Karwan, T., Rojek, J. & Szymek, J. (2005). Results of test with decopperisation of slag from flash process. *Ores and Non-Ferrous Metals*. 50, 669-680.
- [7] Migas, P. (2015). Analysis of the rheological behavior of selected semi-solid slag systems in blast furnace flow conditions. *Archives of Metallurgy and Materials*. 60, 85-93.
- [8] Bydałek, A.W., Bydałek, A., Najman, K. & Schlafka, P. (2008). The estimation of slag refining features for the Cu-Si alloys melting process. *Archives of Foundry Engineering*. 8(special 1), 41-44.
- [9] Takeda, Y. & Yazawa, A. (1988). Fire Refining of Gruel Copper by Alkaline Carbonate Fluxes. *Transactions of the Japan Institute of Metals*. 29, 224-232.
- [10] Bydałek, A.W. (1995). The thermal analysis of the carbides slags solutions. *Journal of Thermal Analysis*. 45, 919-921.
- [11] Bydałek, A.W. (2000). The liquid surface during copper melting with carbon monoxide slag, Proceedings of the 3rd Conference "High Temperature Capillarity", Kurashiki, 157-158.
- [12] Krasicka-Cydzik, E. (2001). Copper de-oxidation with calcium carbide melts: electrochemical reactions. *Journal of Applied Electrochemistry*. 31, 1155-1161.
- [13] Bydałek, A.W., Bydałek, A., Bydałek, F., Kurzydłowski, K.J., Wołczyński, W.S. Reagent for the copper removal from the metallurgical slags, Polish Patent: P 404363/2015.
- [14] Wołczyński, W. & Bydałek, A.W. (2016). Sedimentation of Copper Droplets after their Coagulation and Growth. Laboratory Scale. *Archives of Foundry Engineering*. 16(1), 95-99.
- [15] Wołczyński, W. & Bydałek, A.W. (2015). Gravity / Buoyancy Competition within Coagulation of Copper Droplets in Slag. *Archives of Materials Science and Engineering*. 76, 35-45.
- [16] Wołczyński, W. (2015). Back-diffusion in crystal growth. Eutectics. *Archives of Metallurgy and Materials*. 60, 2403-2407.