

Determining the Degree of Removal of Copper From Slag

A.W. Bydalek *^a, P. Migas^b, W. Wolczyński^c, S. Biernat^d, A. Bydalek^d, K. Jasińska^d, P. Kwapisiński^e

^a University of Zielona Góra, ul. Podgórna 50, Zielona Góra

^b AGH University of Science and Technology, Mickiewicza 30, Kraków

^c Institute of Metallurgy and Materials PAN, Reymonta 25, Kraków

^d PWSZ Głogów, Piotra Skargi 5, Głogów

^d Metallurgy Department, KGHM Polska Miedź, M. Skłodowskiej-Curie 48, Lubin

*Corresponding author. E-mail address: adam_bk@poczta.onet.pl

Received 04.04.2016; accepted in revised form 09.05.2016

Abstract

The scope of work included the launch of the process of refining slag suspension in a gas oven using a variety of technological additives. After the refining process (in the context of copper recovery), an assessment of the effect of selected reagents at the level of the slag refining suspension (in terms of copper recovery). Method sieve separated from the slag waste fraction of metallic, iron - silicate and powdery waste. Comparison of these photographs macroscopic allowed us to evaluate the most advantageous method of separating metallic fraction from the slag. After applying the sample A (with $KF_2 + NaCl$) we note that in some parts of the slag are still large amounts of metallic fraction. The fraction of slag in a large majority of the elements has the same size of 1 mm, and a larger portion of the slag, the size of which is from 2 to 6 mm. Definitely the best way is to remove the copper by means of the component B (with $NaCl$) and D (with KF_2). However, as a result of removing the copper by means of component C (with CaO) were also obtained a relatively large number of tiny droplets of copper, which was problematic during segregation. In both cases we were able to separate the two fractions in a fast and simple manner.

Keywords: Post-process slag, Copper recovery, Coagulation

1. Introduction

The discussed concept takes into consideration the impact of the non-carbon reagents, and this constitutes the next aspect of its originality [1-3]. Most of the methods of pyrometallurgical recovery of copper from post-process slag, including those applied in copper smelter in Głogow (Poland), employ coal in the form of coke or coal briquettes [4-9]. It is used in conjunction with the fluxes that correct physic - chemical properties of processed slag. However, in the light of the experience of the authors and other scientists, as well as theoretical analysis, that

form of carbon reagent appears to be very inefficient. Reacting only with the agents of the melting atmosphere, solid carbonaceous/carbon does not dissolve itself, and, therefore, it does not react in the slag. That is why some different reagents, such as the carbon - nitrogen - carbide ones, have been introduced. The article presents an outline of the new technology of pyrometallurgical processing of slag in the direct-to-blister process. A new way of implementing the technology of recovery of copper from the flash furnace slag by means of different feedstocks has been proposed [3, 6, 9, 13-16]. A core of the paper is focused on a method for an assessment the effect of selected

reagents on the slag's state after its refining. The presented concept intensify the reduction reactions, using the Carbo-N-Ox method [10, 13], of copper compounds to forms of metallic phases in the slag. The processes of coagulation are accelerated and the processes crystallization of metallic phases are under control. The formation of the chilled grains zone is the result of unconstrained rapid solidification and was not subject of simulation [14-16].

Sieve analysis is a method that aims to separate the test material into grains of different sizes and to determine the weight and the percentage of each fraction. Is also done grading curve. The percentage of individual grain fractions shall be calculated using the following formula:

$$Z_i = \left(\frac{m_i}{m_c} \right) \times 100\%$$

where:

z_i – the percentage of a fraction [%],

m_i – weight corrected for the fraction of soil remaining on the sieve, [g],

m_c – the total mass of the sample [g]

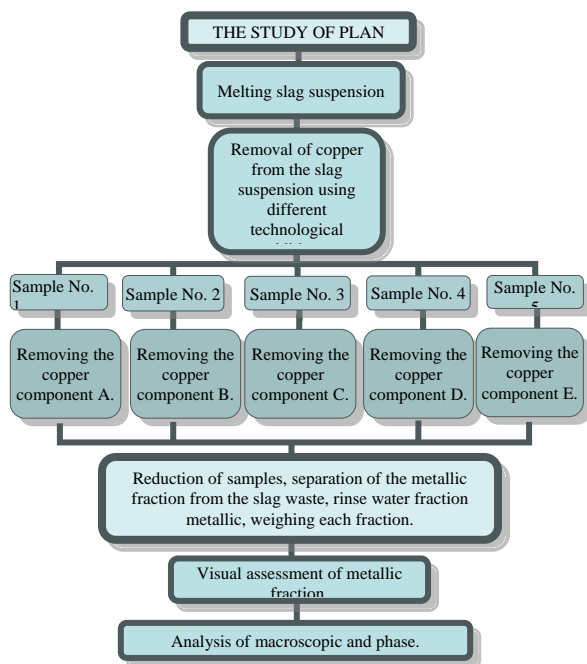


Fig. 1. Schematic plan of study

2. The research program

The aim of the study was to establish a simple method to assess the slag after refining (for removing a copper). Cognitive criterion will attempt to distinguish three different fraction: metallic fraction, fraction of iron - silicate and dusty fraction. Detailed analysis will focus on the type of obtained fractions for selected samples of slag obtained during the removal of copper in industrial conditions.

The study area included analysis of the process of removing copper from suspension slag using five different technological additives. Additives have been proposed as part of a research project carried out at AGH by a consortium under the name "Odmiedziowanie 2014". It was assumed that a detailed analysis will focus on the type of selected samples obtained fractions of slag obtained during the removal from copper in industrial conditions. Starting material for research was the slag obtained from a suspension process with additions of technological labeled respectively A, B, C, D, E. The study design is shown in the figure below (Fig. 1).

2.1. Removal of copper from the slag suspension

The process for removing copper from the slag suspension consisted of three basic steps: melting slag slurry, removing the copper from the slag and to release the slag-free copper.

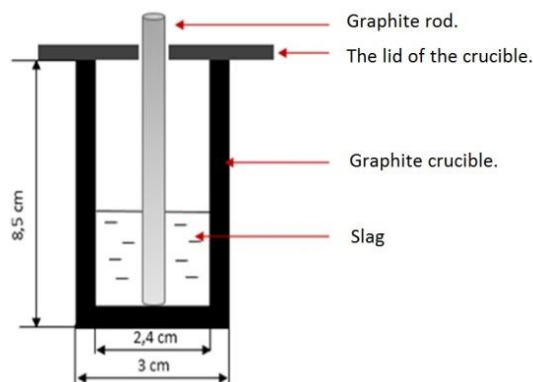


Fig. 2. Graphite crucible, which was cast slag after the removal of copper from the slag suspension

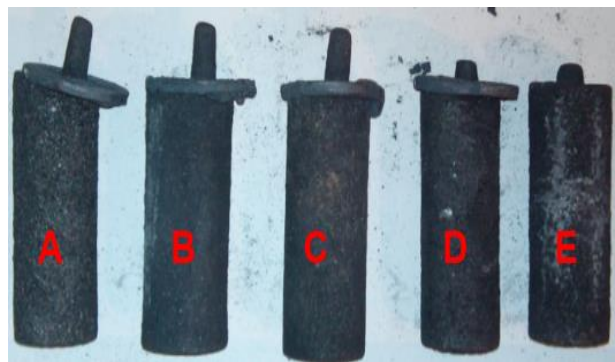


Fig. 3. Collected samples for test: Slag suspension without copper in the graphite crucibles (A, B, C, D, E - Preparations added to the process to remove the copper)

2.2. Preparation of test samples

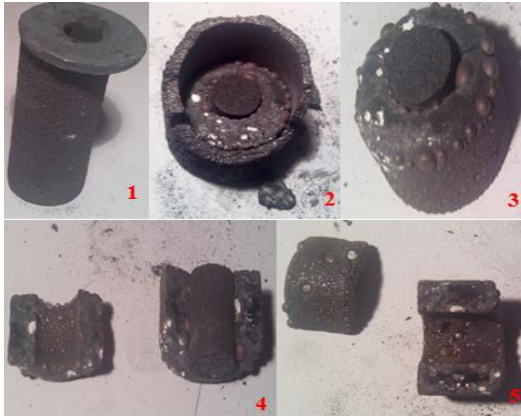


Fig. 4. The steps of separating the sample from the graphite crucible, with lid and a measuring rod

In a first step, the lid and the graphite rod were removed, then the crucible was cut and separated it from the slag, as shown in Fig. 4.

Samples were taken from four heats. The test material was prepared slag are poured into crucible - as shown in Figure 3. The samples for analysis had a mass of about 50 g (the accuracy 2g) – Tabl. 1

The next step was to break and trituration of the sample, and then separating the metallic fraction of remaining slag. Certain parts of the same samples were temporarily disrupted with equal force, then screened by two different sieve 0.05 mm and 1 mm. This operation is repeated until obtaining the fractions of desired size. Part of the grain fraction could not be more break, which was caused by high hardness of the material. Figure 5 (Fig. 5) shows the overall scheme of separation of metallic fraction of crushed slag waste. At the end of the metallic fractions rinsed with water.

Table 1.

Statement of mass fraction, the share of metallic fraction and mass% Cu content in the waste dusty fraction

	Mass [g]					% Cu mass in dusty fraction.
	Metallic fraction	The fraction of iron - silicon	Fraction dusty	Sum	Percentage of metallic fraction [%] mass.	
Sample No. 1 (removal of copper with component A with $\text{KF}_2 + \text{NaCl}$)	2,9	8,8	13,3	25	11,6	2,50
Sample No. 2 (removal of copper with component B with NaCl)	8,3	20	20,5	48,8	17	3,03
Sample No. 3 (removal of copper with component C with CaO)	4	18	25,5	47,5	8,4	3,06
Sample No. 4 (removal of copper with component D with KF_2)	4,5	10,1	32	46,6	9,7	2,46
Sample No. 5 (removal of copper with component E with Na_2O)	4	20,7	22,8	47,5	8,4	3,93



Fig. 5. (Picture left) Separation of the fraction of metallic from the slag: 1 - droplets of copper or a copper alloy drops separated from the slag; 2 - waste slag with copper droplets; 3 - greater fractions were re-fragmentation; 4 - waste slag

3. Results of research and analysis

As a result of testing samples were obtained, which consisted of three different factions: metal, iron - silicate and dusty. Collected fractions were collected for each sample is weighed on a laboratory scale with an accuracy of 0.1 g. The slag analysis was performed on the device ARL QUANT'X EDXRF Thermo Fisher Scientific. Table 1 shows the results obtained.

From Table 1 it can be noted that the largest fraction obtained during the removal of metallic copper component B, and the lowest in the case of sample No. 3 and No. 5.

3.1 Visual assessment of metallic fraction

In Fig. 6a) - 6e) is a photograph obtained metallic fraction of each sample, on a linear scale [cm] which allows us to estimate and compare the individual grains in terms of their size.

As a result of removing the copper from the slag from the furnace suspension by means of component A (Fig. 6a) to give 9 droplets of diameter between 2-5 mm, while the rest of the

metallic fraction with a diameter of less than 2 mm and is the most significant. All elements have a characteristic rounded, spherical shape providing a high metal content (characteristic high contact angle on the border of metal - slag). Fig. 6b, we can see that there is a significant difference in size between the different fractions.

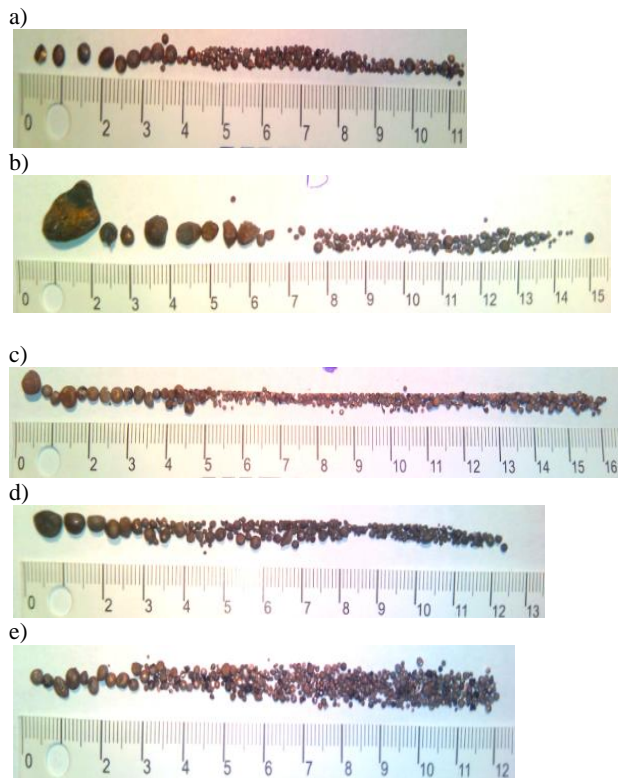


Fig. 6. a) Metallic fraction obtained from the sample No. 1 - removing copper using the component A; b) a metallic fraction obtained from the sample No. 2 - Copper removal using the component B; c) a metallic fraction obtained from the sample No. 3 - Copper removal using the component C; d) a metallic fraction obtained from the sample No. 4 - Copper removal using the component D; e) a metallic fraction obtained from the sample No. 5 - removing copper using the component (centimeter an auxiliary scale of 1 mm)

One grain has a diameter of about 15 mm, then about 10-12 particles are in the range 2-5 mm and the balance of fine particles having a diameter of less than 2 mm. It is also important that in terms of mass, the smallest fraction is only a small part of all the pieces of metal. The high roughness and irregular shapes is likely that there are large non-metallic admixtures. In the case of removing the copper from the slag suspension using component C (Fig. 6 c) to give about 15 particles with a diameter of 2-5 mm and a residue fraction below 2 mm predominantly fine-grained. The color of most of the grains is similar to the color of the copper. The application of the reducer D (Fig. 6 d) as in the method of removing copper reducer B, results in a fraction of a large difference in size between the grains, as shown in Fig. 6 b.

However, in this case grains are smooth and as far as the shaped pattern of drops. The largest grain has a diameter of approx. 7-8 mm. The fraction of metal shown in Fig. 6 E (with component E) is characterized by a very high fine particle size. By far the majority of grain fluctuates diameter of 1 mm. The remainder of the precipitates with a diameter of in the range of 2 - 5 mm. Variegated and moderate graininess, can mean zonal secretion droplets in the crucible. There are grains of colored tight copper, very dark and the colors in between.

3.2. Macroscopic analysis of the slag

The particulate waste slag, which is a material iron - silica was photographed macroscopically larger 50. This procedure aims to assess the amount of metallic fraction, which failed to extract the stage of breakdown and segregation of the material. The resulting photographs are a descriptive analysis of the material.

After applying the sample A (Fig. 7 a, b) we note that in some parts of the slag are still large amounts of metallic fraction. The fraction of slag in a large majority of the elements has the same size of 1 mm, and a larger portion of the slag, the size of which is from 2 to 6 mm. Mainly in those areas there is a lot of tiny droplets of metal and flux residues. The whole is characterized by high roughness and sharp edges. In the case of removing the copper component B (Fig. 7 c, d) indicated that residues do not see any metallic fraction in the resultant slag. This demonstrates the high efficiency of reagent B, by which easily managed to separate the two fractions. Figure 7 d is a photograph of selected portions of the slag-free copper which can be seen unreacted technological additives.

Following removal of copper by component C was observed similar results as for reagent A. There was a lot of copper drops of 0.1 - 0.4 mm, which are separated from the fraction of the slag impossible. Major concentrations of copper are in larger parts of the slag, have not been able to more comminuted. This fraction is the size of 2 - 5 mm. The slag obtained by "D" is very similar to slag from the method "B". Macroanalysis (Fig. 7 e, f) showed the lack remnants of the reactants and practically absence of copper. On the pictures above we see only 2 very small drops of metallic fraction. The material is the same in most of the order of 1 mm. The isolated major elements shown in figure 7 f) have a diameter in the range of 3-5 mm. Unable to crush more of these fragments, which demonstrates the variable hardness of the slag. This may be due to the irregular distribution of phases, where the harder elements are richer in iron.

After applying the reagent E was observed low-metallic inclusions, and the observed structures were similar to samples obtained after the reactants A and C. Inclusions in the phase of iron - silicate most are in the form of droplets of about 0.4 mm and a cluster of tiny droplets of up to 0.01 mm. There was also white, rough parts, which are unreacted flux.



Fig. 7 a, b) Photographs gross fraction of the iron silicate slag-free copper by means of component A; c, d) Macroscopic photographs fraction of the iron silicate slag-free copper by means of component B; e, f) Photographs of gross fraction of the iron silicate slag-free copper by means of component D (scale division correspond with 1 mm)

4. Summary and Conclusions

Comparing samples, we note that in the case of removing copper by component B are larger pieces of metallic fraction of a different from the other grains irregularly shaped. We can assume that this is an alloy which in its composition contains copper. In the case of the removal of copper using a component A (sample 1), we see that it is quite beneficial because it created quite large drops of metal which could be easily separated from the crushed slag. The situation is similar in the case of sample number 3 and 4. However, as a result of removing the copper by means of component C were also obtained a relatively large number of tiny droplets of copper, which was problematic during segregation.

Comparison of these photographs macroscopic allowed us to evaluate the most advantageous method of separating metallic fraction from the slag. Definitely the best way is to remove the copper by means of the component B and D. In both cases we were able to separate the two fractions in a fast and simple manner.

Conclusions:

1. The proposed method allowed the sieve analysis of the number produced three factions: metal, iron - silicate and

dusty. Macroscopic observation allows the evaluation of the suspension of the fraction of metallic iron - silicate.

2. Dusty fraction were found to be the equivalent of the main mass of slag - containing no micro separation of metal.
3. The type of additive technology in the removal of copper from the slag suspension process significantly influence the amount remaining in the metallic fraction and the size and hardness of all fractions were obtained.
4. Most metallic fraction collected at the interface between the graphite rod, the outer part and the bottom of the sample on the border of the graphite crucible.

Acknowledgements

Support provided by "Narodowe Centrum Badań i Rozwoju" under a grant No. PBS3/A5/52/2015 (PBS3/244864/PP/MMB).

References

- [1] Czarnecki, J., Śmieszek, Z., Miczkowski, Z., Bratek, S., Kubacz, N., Ostrowski, T., Gostyński, Z. & Warmuz, M. (2006). Two-stage process of flash slag decopperisation. *Ores and Non-Ferrous Metals*. 51(7), 405-411 DOI: bwmeta1.element.baztech-article-AGH6-0005-0020 (in Polish).
- [2] Burzyńska, L., Gumowska, W., Harańczyk, I. & Żabiński, P. (2002). Some aspects of copper electrorafining process. *Non-ferrous Metals. WMN AGH*. 29-47 (in Polish).
- [3] 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(1), 323-326. DOI: 10.1515/amm-2015-0052.
- [4] Łędzki, A., Migas, P., Stachura, R., Klimczyk, A. & Bernasowski, M. (2009). Dynamic viscosity of blast furnace primary and final slag with titanium and alkali admixtures. *Archives of Metallurgy and Materials*. 54(2), 499-509.
- [5] Migas, P. & Karbowniczek, M. (2010). Interactions between liquid slag and graphite during the reduction of metallic oxides. *Archives of Metallurgy and Materials*. 55(4), 1147-1157. DOI: 10.2478/v10172-010-0018-0.
- [6] Wołczyński W., Bydałek A.W., (2015), Gravity/buoyancy competition within coagulation of copper droplets in slag. *Archives of Materials Science and Engineering*. 76(1/2015), 35-45.
- [7] Kucharski, M., Sak, T., Madej, P., Wędrychowicz, M. & Mróz, W. (2014). A Study on the Copper Recovery from the Slag of the Outokumpu Direct-to-Copper Process. *Metallurgical and Materials Transactions B*. 45(2), 590-602 DOI: 10.1007/s11663-013-9961-2.
- [8] 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(12), 669-680 (in Polish).
- [9] Bydałek, A. W., Biernat, S., Bydałek, A. & Schlafka, P. (2014). The Innovative Analysis of the Refinement Ability Extractive Slag. *International Journal of Engineering and Innovative Technology*. 4(5), 186-197. ISSN: 2277-3754.

- [10] Biernat, S., Bydałek, A.W. & Schlafka, P. (2012). Analysis of the possibility of estimation ecological slag propriety with use the DATA Base. *Metallurgija-Metallurgy*. 51(1), 59-62.
- [11] Kowalczyk, J., Mróz, M., Warczok, A. & Utigard, T.A. (1995). Viscosity Viscosity of copper slags from chalcocite concentrate smelting. *Metallurgical and Materials Transactions B*. 26(1), 1217-1223 DOI: 10.1007/BF02654007.
- [12] Bydałek, A.W. (2011). Role of carbon in the melting copper processes. *Archives of Foundry Engineering*. 11(SI 3/2011), 37-42.
- [13] Migas, P. (2015). Analysis of the rheological behaviour of selected semi-solid slag systems in blast furnace flow conditions *Archives of Metallurgy and Materials*. 60(1), 85-93, DOI: 10.1515/amm-2015-0014.
- [14] Wołczyński, W., Himemiya, T., Kopyciński, D. & Guzik, E. (2006). Solidification and solid/liquid interface paths for the formation of protective coatings. *Archives of Foundry Engineering*. 18(1/2), 359-362.
- [15] Wołczyński W., Bydałek A.W. (2016), Sedimentation of copper droplets after their coagulation and growth, *Archives of Foundry Engineering*. 16(1/2016). 95–98.
- [16] Kalisz, D., Rzadkosz, S. & Piękoś, M. (2012). Computer simulation of liquid slag reduction process. *Archives of Foundry Engineering*. 12(SI 1/2012), 91-96. (in Polish).