THE EFFECT OF SMELTING AND GRANULATION ON SOME PROPERTIES OF SMELTER SLAG**

Abstract

The technogenic copper deposit of slag Depo 1 is located in the industrial district of the Smelter and Refineries of RTB Bor. Exploitation reserves are 9 190 940 t of slag with the average copper content of 0.715%. Sample of this deposit was melted in a furnace and then cooled with a jet of water when it was poured into a thin jet, whereby the small - granulated pieces were formed. Comparison of some properties of this sample was done with the sample in the form in which it was deposited in the deposit. This paper presents the chemical analysis, SEM - EDS analysis, Bond working index in a rod and ball mill, grinding kinetics and experiments of flotation concentration of copper depending on the grinding fineness in the range of 60 - 95% -0.075 mm.

Keywords: slag, granulation, properties

INTRODUCTION

A large amount of slag, formed in the processing of copper concentrate, is an ecological problem because it takes up the space for disposal. In the literature [1], it is stated that 2.2 t of slag are formed for each ton of the obtained copper, and it is estimated that around 24.6 million tons are produced annually in the world. In the past, this slag was seen as a waste, but today there are the great possibilities for its use.

Depending on the properties, the slag can be recycled, i.e. copper can be flotated again from the slag, because the copper content in the slag is higher than in the ore that are now exploited. Also, the slag can be used for making cement as an aggregate for making asphalt road covers and concrete because it has the excellent physical characteristics. It is also used as an abrasive material for the machine processing of objects. Further use of slag depends on its characteristics. Some of them can be influenced by the cooling method.

The deposit of slag Depo 1 is a technogenic deposit located within the Mining Smelting Basin Bor, Serbia. It was formed from a flame furnace slag resulting from the copper concentrate melting. On the site, this material in a melting state was poured out of the containers for transport. It was cooled, so it was poured and formed a relatively solid mass of semi-crystalline structure. The upper limit of the slag size class is 150 mm.

On the basis of qualitative mineralogical analysis, the following mineral composition of slag was determined: solid sulfide solution (Cu-Fe), chalcocite, pyrite, copper, cuprite, magnetite and waste minerals. Non-
metallic minerals (waste) are represented by glass with the appearance of various eutectic dendrites (fayalite et al.). The most prevalent ore mineral is the sulphide phase "solid sulphide solution Cu-Fe" [2].

EXPERIMENTAL PART

For the purposes of testing, a slag sample was taken from the slag deposit Depo 1 from the technological process of slag processing in the Flotation Plant Bor after crushing to the upper size class limit of 20 mm. One part of the sample was melted in furnace and then cooled with a jet of water when it was poured into a thin jet, whereby small – granulated pieces of amorphous glass structure of the upper size class limit of 6 mm were formed. Comparison of some properties of this sample was done with the sample in a form in which it was deposited in the depot.

Figure 1 present a view of sample before and after melting and cooling.

Figure 1 Sample of slag before melting (a) Sample of slag after cooling (b)

Figure 2 presents a photo of granulated slag taken with binocular with a magnification of 20 times.

Figure 2 Photo of sample of granulated slag taken with a binocular with a magnification of 20 times
Figure 2 shows the amorphous glass structure of the pieces. It is also noticed that many pieces have a proper spherical appearance.

Table 1 presents the chemical analysis of two slag samples that are differently cooled.

| Element, compound | Slag   | Granulated slag |
|-------------------|--------|-----------------|
| Cu, %             | 0.68   | 1.05            |
| Fe$_3$O$_4$, %    | 1.754  | 0.092           |
| CaO, %            | 17.26  | 15.50           |
| S, %              | 1.07   | 0.56            |
| Fe, %             | 25.69  | 26.25           |
| FeO, %            | 26.75  | 28.65           |
| SiO$_2$, %        | 43.76  | 36.28           |
| Al$_2$O$_3$, %    | 3.89   | 12.67           |

Differences in chemical analysis are not the result of the cooling method of slag, but are primarily the result of furnace operation mode. Melting was carried out in a Birlec electric arc furnace. When pouring the material from the furnace, a certain amount of material of higher density that cannot be discharged is retained at the bottom, thus there are differences in the chemical composition between two tested samples.

The mineral composition [3] is determined on the slag sample: fayalite, ferrite with sprayed pyrite, chalcopyrite, chalcocite, bornite, cuprite, magnetite, copper matte and native copper. Copper are pierced.

The following mineral composition was determined on the granulated slag sample [5]: Mainly fayalite and ferrite, on which basis the fine grains of magnetite, pyrite, chalcopyrite, chalcocite, bornite, copper matte and native copper are sprayed.

A photo of the taken starting sample by a scanning electron microscope is shown in Figure 3.
Table 2 presents the slag density, natural pH value, bulk density for two size classes and the Bond working index in the rod and ball mill.
Table 2 Some characteristic sizes of slag samples

| Size                              | Slag                      | Granulated slag                   |
|-----------------------------------|---------------------------|-----------------------------------|
| Density                           | 3410 kg/m³                | 3230 kg/m³                        |
| Natural pH                        | 6.58                      | 7.83                              |
| Bulk density at size class -12.7 mm | 2.090 t/m³               | 1.578 t/m³                        |
| Bulk density at size class -3.35 mm | 1.969 t/m³               | 1.544 t/m³                        |
| Bond's working index in a rod mill | 22.2 kWh/t                | 29.41 kWh/t                       |
| Bond's working index in a ball mill | 15.22 kWh/t               | 19.84 kWh/t                       |
| Upper size class limit of pieces after cooling | 150 mm                  | 6 mm                              |

SPECIFIC CONSUMPTION OF COMMINUTION ENERGY

In the processes of mineral processing, about 70% of energy is spent on crushing and grinding and depending on the raw material it can be up to 20 – 60 kWh/t [5].

In the mineral processing, the methodology of estimation the energy consumption on comminution, developed by F.C. Bond [6], is based on the studying the real processes of comminution. Bond also developed a laboratory methodology for calculation the Wi coefficient (the Bond working index) used in calculation the required energy for comminution of the mineral raw material by the equation:

\[ W = W_i \left( \frac{10}{\sqrt{P}} - \frac{10}{\sqrt{F}} \right) \text{ kWh/t} \]

where:

- \( W \) – specific energy consumption, kWh/t
- \( W_i \) – Bond’s working index, kWh/t.

According to the definition [6], Bond’s working index is the energy that is required for one short ton of an infinitely large class size of raw material to be comminuted to a size class where 80% of the raw material passes through a sieve with the square holes in the size of 100 μm. (Through the methodology of laboratory determination the Bond index, a short ton was transformed into a metric).

\( F, P \) – dimensions of the square openings of the sieve through which 80% of the raw material passes before \( (F) \) and after \( (P) \) comminution, μm

If the required energy is calculated for comminution the samples from the size class after cooling to the size class in which 80% of the material passes through a sieve of 212 μm, according to the Bond form where the size \( F \) for slag of 42300 μm, and the same size for granulated slag of 2967 μm, and the value of \( P \) for both samples of 212 μm, the following values are obtained:

\[ W_i = 9.713 \text{ kWh/t} \]
\[ W_{gs} = 9.984 \text{ kWh/t} \]

GRINDING OF SAMPLES

After grinding to the size class of -3.35 mm, the samples were ground in a laboratory mill. Table 3 and 4 show the content of the class -75 μm depending on the grinding time of the slag and the granulated slag and Figures 7 and 8 show the kinetics of slag grinding and granulated slag.

Table 3 Class content -75 μm in slag for different grinding times

| Grinding time, min | 5   | 10  | 15  | 30  |
|--------------------|-----|-----|-----|-----|
| Class content -75 μm % | 31.20 | 64.80 | 80.00 | 96.00 |
Figure 7 Dependence of the class content -75 µm on the grinding time of slag

Table 4 Class content -0.075 mm in granulated slag for different grinding times

| Grinding time, min | 5    | 10   | 15   | 30   | 40   |
|-------------------|------|------|------|------|------|
| Class content -75 µm % | 24.80 | 49.00 | 63.60 | 91.20 | 96.80 |

Figure 8 Dependence of the class content -75 µm on the grinding time of granulated slag
FLOTATION CONCENTRATION

Experiments on flotation concentrations were carried out on slag and granulated clay in order to examine the influence of grinding fineness on technological results. All flotation concentration experiments were carried out under the same conditions with 920 g of slag, a dose of KAX collector of 200 g/t, different grinding fineness. Tables 5 and 6 and Figures 9 and 10 present the test results.

Table 5 Slag starting sample

| Grinding fineness | m, % | Cu, % | Cu recovery, % |
|-------------------|------|-------|---------------|
| 60 % -75 μm       | 9.55 | 3.02  | 58.08         |
| 65 % -75 μm       | 11.73| 2.7   | 61.35         |
| 70 % -75 μm       | 10.32| 3.0   | 61.16         |
| 75 % -75 μm       | 11.12| 3.08  | 63.15         |
| 80 % -75 μm       | 12.25| 2.8   | 64.08         |
| 85 % -75 μm       | 12.99| 2.64  | 64.40         |
| 90 % -75 μm       | 14.93| 2.44  | 66.99         |
| 95 % -75 μm       | 14.80| 2.38  | 66.96         |

There is a clear trend of increasing the copper recovery in the basic slag concentrate, depending on the grinding fineness. The copper recovery in the basic concentrate ranged from 58.08 to 66.96% with an increase in grinding fineness of 60-95% -75 μm.

Figure 9 Dependence of the copper recovery in the concentrate on the class content -75 μm in slag
Table 6 Granulated slag

| Grinding fineness | m, % | Cu, % | Cu recovery, % |
|-------------------|------|-------|---------------|
| 60 % -75 µm       | 14.48| 5.5   | 82.91         |
| 65 % -75 µm       | 17.72| 4.95  | 84.73         |
| 70 % -75 µm       | 17.80| 4.95  | 84.67         |
| 75 % -75 µm       | 20.40| 4.78  | 86.39         |
| 80 % -75 µm       | 22.05| 4.1   | 85.80         |
| 85 % -75 µm       | 24.30| 3.6   | 85.88         |
| 90 % -75 µm       | 28.00| 3.34  | 87.00         |
| 95 % -75 µm       | 30.39| 2.9   | 86.42         |

Figure 10 Dependence of the copper recovery in the concentrate on the class content -75 µm in granulated slag

In the granulated slag, the copper recovery in the basic concentrate is also increased with an increase in grinding fineness from 82.91 to 87.0% for grinding fineness of 60-95% -75 µm. In comparison with the results on the slag samples, the higher copper recoveries were obtained by 19.46 - 24.83%.

CONCLUSION

Comparison of sample characteristics of different cooled slag was performed in this paper. One is the slag sample from the "Slag Depot 1". It is a slag that is left from the metallurgical melting process of the copper concentrate. This slag was poured on the depot and it was cooled down. The slag sample was excluded from the technological
process of flotation processing after crushing to -20 mm. The second sample is a sample of granulated slag obtained by melting one part of the slag sample of the deposit "Slag Depo 1" and then by rapidly cooling with the water jet during pouring.

Tests were carried out on the slag and granulated slag samples to determine the properties. The differences in the physical properties of sample are very noticeable. The size class of the "Slag Depot 1" in the deposit is -150 mm, while the class size of granulated slag is -6 mm. The granulated slag has a glass amorphous black structure with a lot of regular spherical grains, and slag has an irregular shape with a shell-like fracture and is gray in color.

The difference in the Bond working index is significant on tested samples both in the rod mill and ball mill. A sample of granulated slag has about 30% higher Bond index.

The required energy is calculated for comminution the samples from the size class after cooling to the size class in which 80% of the material passes through a sieve of 212 μm.

The obtained value for slag sample is 9.713 kWh/t and for granulated slag sample is 9.984 kWh/t, which is very similar to the granulated slag sample, although the calculated energy is for comminution of -150 mm, and granulated slag of -6 mm.

The density of these two slags is slightly different, but this is not the result of the cooling method, but the way of experiment performance. When pouring material from the Birlech furnace, it is not possible to empty the furnace to the end, but at the bottom there is a certain amount of material that is "washed" with the inert substance after the experiment. The retained material has a slightly higher density. For the same reason, the slag and granulated slag have a different chemical composition, and this is not the result of cooling.

A very significant difference in the two tested samples was observed in the flotation concentration experiments depending on the grinding fineness. Copper recoveries in the base concentrate from 58.08 to 66.99% were obtained on the slag sample, and on the granulated slag sample from 82.91-87.00%. The differences are from 19.46 to 24.83% in favor of the granulated slag. The highest recoveries in both samples were obtained with a grinding fineness of 90%.

The slag properties are largely dependent on the cooling mode of slag. Particularly large, variable, flotation results. When considering further use of the slag, this knowledge should be taken into account and the cooling mode should be selected accordingly.

REFERENCES

[1] Bipra Gorai, R.K. Jana, Premchand: Characteristics and Utilisation of Copper Slag - A Review Resources, Conservation and Recycling 39 (2003) 299 – 313, Elsevier;

[2] Nikolić K. et al., Project Study on Reserves of Technogenic Copper Deposit "Depo of Slag 1"- Bor, the State of 31th December 2005 to the text part. Fond of Technical Documentation of the Bureau of Geology MMI Bor, Bor, 2007 (in Serbian);

[3] V. Ljubojev, J. Petrović, S. Krstić, 2011. Mineralogical Characteristics of Smelting Slag in the Technogenic Deposit »Depo 1« (Bor, Serbia). The Geology in Digital Age: Proceedings of the 17-th Meeting of the Association of European Geological Societies (MAEGS 17), Belgrade; 14-18 September, 2011, pp. 237-240;
[4] V. Ljubojev, V. Marjanović, D. Milanović, S. Stanković; Mineralogical Characteristics of Slag (from the Flotation Plant of RTB Bor) Granulated in the Laboratory Conditions Mining and Metallurgy Institute Bor, 2 (2015), 1-6, Mining and Metallurgy Institute Bor;

[5] Chanturiya V. A. Innovations in a Comprehensive and Profound Mineral Processing in Russia, Bulletin of Mines, No 1-2, Vol. CXIII, 2016, Belgrade;

[6] Magdalinović N. Comminution and classification, Nauka, Belgrade, 1999 (in Serbian)