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THE METHODS OF OXIDATION OF SULPHIDE FORM OF COPPER FROM FLOTATION TAILINGS

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ABSTRACT
This paper presents the results obtained using different reagents for the process of sulphide form oxidation of copper from flotation tailings. For the investigation in this paper work, the samples of flotation tailings were taken from the Old Flotation Tailing Dump of the Mining and Smelting Complex Bor in Eastern Serbia. Experimental testing was carried out in order to increase the leaching degree of copper with addition of oxidants during leaching. During the leaching process of flotation tailings, the followings were used as oxidant hydrogen peroxide H_2O_2. The achieved copper leaching degree was 91.83% in the presence of hydrogen peroxide as an oxidant.. .The effect of thermal destruction of sulfide copper from flotation tailings in the presence of concentrated sulfuric acid was also investigated. After leaching of calcine with water, the degree of copper leaching was attained of 92%. Solutions after leaching contain about 2 g/l of Cu and less than 1 g/l of Fe, and they are suitable for the SX-EW process of obtaining the commercial quality copper.
Keywords: flotation tailings, oxidation, leaching, copper

1. INTRODUCTION
The world experiences show that copper can be cost-effectively valorized from flotation tailings. One example is the old flotation tailing dump of the Miami mine in Arizona [1].
The old Bor flotation tailing dump is located on the border of urban and industrial part of town, and beneath it a collector of municipal waste water is situated. Due to the immediate close of the town center, it is also one of the sources of negative environmental impact that is reflected in dissemination of fine dust into the environment during windy periods and acidified water runoff.
Disposal of tailings in the Bor Flotation Plant from 1933 to 1987 was done in the valley of the Bor River. According to data [2], around 27x106 t of tailings was deposited in the tailing dump with the average copper content of about 0.2%, which means that this waste material contains about 54,000 t of copper. The laboratory tests of acid agitation leaching of copper were carried out from the old Bor flotation tailings during 2007 in the Mining and Metallurgy Institute Bor [3] implemented by Mitsui Mineral Development Engineering Co.., Ltd (MINDECO). Investigations have included leaching experiments wherein the grade of copper leaching reached 60% [4] which indicates that only oxide coper ore reacts in the leaching solution without addition of oxide. In order to increase the degree of

copper extraction from flotation tailings, technological testing of sulphide oxidation from flotation tailings was carried out in order to increase the degree of copper leaching.

2. EXPERIMENTAL TESTING WITH THE DISCUSSION OF THE RESULTS

The samples of tailings from depth of 14m were used for testing with four different locations marked with B-1, B-2, B-3 and B-4, whose chemical characterization is shown in Table 1.

Table 1. Chemical characterization of the samples of flotation tailing from depth of 14m

Content , mass %	Samples			
	B-1	B-2	B-3	B-4
Cu, total	0.46	0.44	0.39	0.58
Cu, ox	0.27	0.27	0.27	0.27
Fe	10.18	10.94	6.37	17.28
S	9.7	11.08	7.50	18.58

The leaching test and TCLP (Toxicity Characteristic Leaching Procedure) test were carried out on a composite sample of flotation tailings from depth of 14 m.

Based on the results of leaching test (conducted according to the standard procedure SRPS EN 12457-2) and the TCLP test (conducted according to the standard procedure of EPA Test Method 1311), where the concentrations of heavy metals are several hundred times higher than the legally prescribed MDK values, it can be concluded that the tailing dump present the major environmental problem for the surrounding waterways. The stage content of flotation tailings is present in Figure 1.

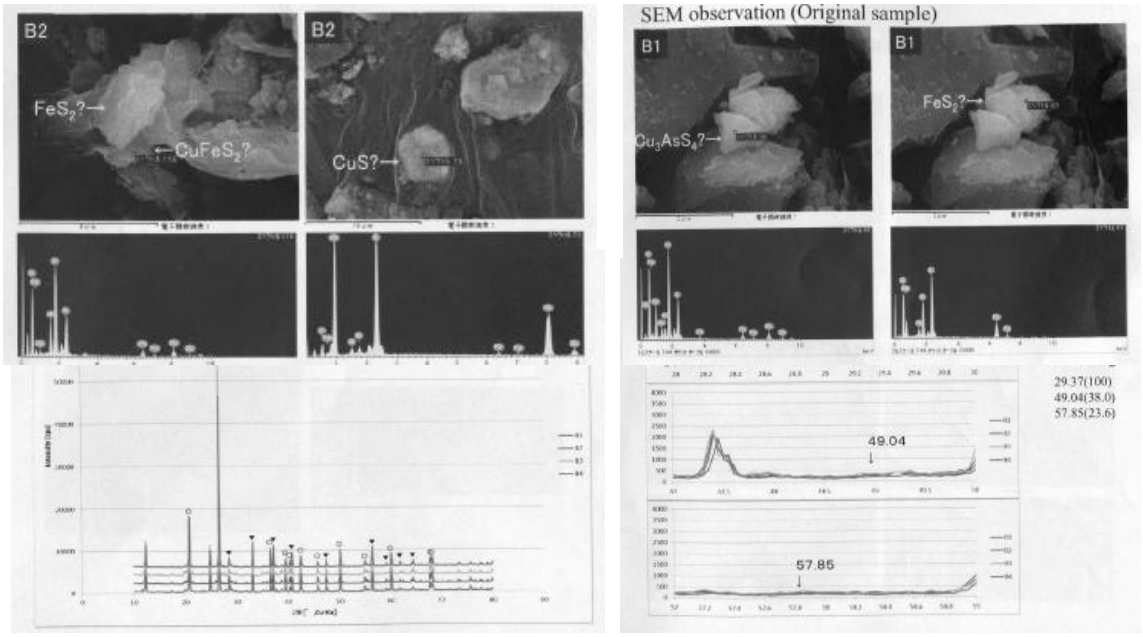

Figure 1. Stage composition of flotation tailings in leaching (High power XRD, 30 kV 200mA) recorded at the Akita University, Japan

Experimental testing the leaching process of flotation tailings in order to determine the optimal parameters of copper extraction were performed on a laboratory scale. Samples from flotation tailing dump were treated by the agitation leaching method. The mine water from the accumulation Robule (mine waste water) was used as leaching solution. The content of metals in mine water from the accumulation Robule is above the legally prescribed maximum allowed values, and the measured pH value of 3.5 indicates the acidic character of waste water. Before leaching, pH value of mine waste water was corrected to pH = 1 with concentrated sulphuric acid. The leaching process of copper was analyzed from flotation tailings with mine waste water in the following conditions: time: 4 h, temperature: 80°C, the ratio of solid: liquid = 1:2.5, pH of leaching solution = 1, degree of copper leaching was attained of about 60% as it is exactly the participation of copper oxide forms regarding to the total copper content [5].

Sulphide and other copper compounds (CuS, Cu_3AsS_4, $CuFeS_2$ - Stage composition of flotation tailings after leaching (High power XRD,30kV 200mA) recorded at the Akita University Japan), present in the flotation tailings in the given conditions of leaching stay in the unchanged form, i.e. there is no their chemical degradation.
The next series of experiments was aimed at increasing the degree of copper leaching that would be achieved by degradation of sulphide compounds of copper in tailings with addition of oxidants during leaching or thermal destruction of sulphide from tailings in the presence of an oxidant (sulphatization roasting) and subsequent leaching of the obtained calcine.

Leaching of flotation tailings with addition of H_2O_2 as oxidant

A series of experiments was aimed to determine the conditions for exctraction of metals (copper and iron) and sulfur from the mechano-chemically activated the Bor flotation tailings.Experiments were carried out with untreated and mechano-chemically treated samples of the Bor flotation tailings, whose chemical composition is shown in Table 1.
Two series of experiments were carried out: In the I series of experiments for leaching, 0.8 M H_2SO_4 was used with addition of 30 % H_2O_2 as oxidanrt. In the II series of experiments for leaching, 0.8 M H_2SO_4 was used with addition of 30 % H_2O_2 as oxidantr and in presence of chloride ions which were added into solution in the form of NaCl. Both series of experiments were carried out at temperature of 90±5^{o}C, with stirring for 600 o x min^{-1}, in the relation S:L = 1:20, for a period of 8 h. In the second series of experiments, the initial NaCl concentration was suitable to 1M of solution, and all other parameters were identical as in the first series of experiments.
Comparative results of Cu leaching are shown in Tables 2 respectively.

Table 2. Degree of copper leaching

Description	I serie of experiments	II serie of experiments
	% Cu leaching	
Untreated flotation tailings	59.08	62.15
Flotation tailings 1 MF*	67.32	74.32
Flotation tailings 1 NMF*	94.04	85.98
Flotation tailings 2 MF**	75.98	77.87
Flotation tailings 2 NMF**	66.95	72.64

Note:

- *Untreated* flotation tailings – *starting sample*
- Flotation tailings*1 MF* - magnetic fraction of mechano-chemically activated tailings without addition of reagents*
- Flotation tailings *1 NMF* - non-magnetic fraction of mechano-chemically activated tailings without addition of reagents*
- Flotation tailings *2 MF** - magnetic fraction of mechano-chemically activated tailings with addition of NaOH*
- Flotation tailings *2 NMF** - non-magnetic fraction of mechano-chemically activated with addition of NaOH*

Results indicate that the highest degree of copper leaching was achieved in the sample of flotation tailings 1 NMF* obtained by mechano-chemical activation without additions of reagents. The results are quite identical for degree of iron leaching.

Destruction of sulphide from flotation tailings at increased temperature with addition of H_2SO_4 as oxidant

The experimental testing of sulphatization process of flotation tailings were carried out. For thermal treatment of destructive sulphide in the presence of sulphuric acid,a tubular furnace with temperature control was used as an oxidant. Prior to the sulphatization roasting, the sample of tailings was mixed with addition of concentrated sulphuric acid in the ratio: 1: 0.5 by weight. The impurities are present in the The process of sulphatization roasting was carried out on the sample of 100 g of flotation tailings at two degrees: I degree: at temperature of 250^{o}C in time of 2 h and II degree: at temperature of 630^{o}C in time of 2 h. By XRD analysis on device EXPLORER GNR, the following mineralogical composition of a calcine sample was determined: quartz SiO_2 – 94.6 % and hematite Fe_2O_3 – 15.4 %.

After sulphatization roasting, the obtained calcine was leached with water for disolving the formed copper sulphates. The attained percentage of copper leaching was **92 %.** After process of sulphatization roasting and calcine leaching with water, the solid residue was obtained with chemical chatacterization given in Table 3.

Table 3. Chemical composition of solid residue obtained after thermal treatment and leaching process with water

Element	Content,%	Element	Content,%
Cu	0.034	Ag	<0.002
SiO_2	66.74	Hg, g/t	<0.1
Fe	10.89	Pb	<0.01
As	<0.003	Zn	0.0006
Mn	<0.0005		

Solid residure, obtaiend after leaching of calcine with water was undergone to the TCLP (Toxicity Characteristic Leaching Procedure) test. The results of TCLP test indicate that the metal concentrations are below MDK values, what points aout a fact that the solid residue, formed after copper extraction, is possible to store without a negative impact on the human environment because it belngs to the category of non-hazardous waste.

3. CONCLUSION

Based on the obtained results, it can be said that the leaching of flotation tailings with sulhuric acid solution in the presence of an oxidant significantly increases the degree of copper leaching compared . By the use of hydrogen peroxide as an oxidant, the best results were achieved with the nonmagnetic fraction of the sample of flotation tailings. The attained degree of copper leaching was 92.03%. The process of sulphide destruction and copper leaching from flotation tailings sample with concentrated sulphuric acid at 630°C and leaching of calcine with water has resulted into copper leaching degree of 92%. Solutions, after leaching, contain about 2 g/l Cu and less than 1 g/l and Fe and they are suitable for SX-EW process for obtaining the commercial quality copper. The additional effect of the sulphatization process of tailings is the complete destruction of sulphide what realizes the embedded precious metals in pyrite: gold and silver and provides the possibility of their valorization from tailings. The advantage of use the sulphatization procedure is the possibility of solid residue storage resulting from the process of thermal treatment and leaching of tailings with no risk of harm the human environment.

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4. REFERENCES

[1] Antonijević, M., Dimitrijević, M., Stevanović, Z., Šerbula, S., Bogdanović: G. Investigation of the Possibility of Copper recovery from flotation tailings by acid leaching. J.Hazard Mater.158, 2008, 23-34.
[2] Nikolić: K. Report on Quantities of Dumped Raw Materials for Hydrometallurgical treatment, Bor, 2001, 8–12.
[3] Stevanović, Z., Bugarin: M. Final Report - MMI Services in scope of Master Plan for Promotion of Mining Industry in Republic of Serbia, MMI Bor, Bor, 2010.
[4] Z. Stevanović, M. Antonijević, R. Jonović, Lj. Avramović, R. Marković, M.Bugarin: Leach-Sx-Ew Copper Revalorization from Overburden of Abandoned Copper Mine Cerovo, Eastern Serbia, Journal of Mining and Metallurgy 45 B (1), 2009, 45-57.
[5] Stevanović, Z., Antonijević, M., Bogdanović, G, Bugarin, M., Trujić, V., Marković, R., Nedeljković, D: The Effect of Oxidants Through a Tailing Dump Depth and the Leaching of Copper, Carpathian Journal of Earth and Environmental Sciences, 8 (1), 2013, 29-38.