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TECHNOLOGICAL INVESTIGATIONS OF SULPHIDE OXIDATION FROM FLOTATION TAILINGS IN ORDER TO INCREASE THE DEGREE OF COPPER LEACHING[***]

Abstract

The off-balance resources present the environmental problem and potential resource for copper extraction. 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. Using the $Fe_2(SO_4)_3$ as an oxidant, the achieved copper leaching degree was 76.8%. 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 are suitable for the SX-EW process of obtaining the copper.

Keywords: *flotation tailings, oxidation, leaching, copper*

INTRODUCTION

The most commonly used method in the world for copper valorization from off-balance mine resources is the hydrometallurgical process. The method consists of the following stages: comminuting, leaching, solvent extraction and electrolytic copper extraction. Hydrometallurgical treatment is applied in the countries (USA, Chile, Australia, and Peru), which have readily available off-balance deposits with low content of copper and with more oxide forms of [1.2]. Copper, present in the off-balance resources in the municipality of Bor, created during centuries of mining and processing of copper ore, presents an important economic resource if it is valorized in an appropriate way with affordable and sustainable technology. Otherwise, it presents the major generator of contaminated mine water that directly flow into the basin of the Bor River, with a significant impact on the quality of water downstream of the river Timok, and further to the Danube River [3-8].

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. In this mine, there was the flotation tailing dump that were deposited in about 34 million tons of tailings with the average copper content of 0.33%, out of which oxide

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copper is around 50%. Flotation tailings was treated by the conventional method of agitation acid leaching at pH = 1.5 with the processing capacity of about 450 t/h of tailings. Total copper leaching for leaching time of about 26 h was 57%. Total costs, from mining tailings to electrolysis to produce one ton of cathode copper from flotation tailings in this mine, amounted to 740 $/t of copper cathodes [9].

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 [10], around $27x10^6$ 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. Based on this, with the quantitative and qualitative point of view, the flotation tailings deposited in the old Bor flotation tailing dump, present an exceptional raw material for further revaluation 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 [11] implemented by Mitsui Mineral Development Engineering Co., Ltd (MINDECO). Within these studies, the exploration drilling of flotation tailings was done and the new representative sample was formed from extracted nuclei on which further laboratory testing was carried out. Investigations have included leaching experiments wherein the grade of copper leaching reached 60% [12] which indicates that only oxide coper ore reacts in the leaching solution without addition of oxidant. From leaching solution, copper was extracted by the method of solvent extraction and electrolysis, therefore the complete L-SX-EW method.

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. Testing was carried out on a sample formed from the cores of drill holes from depths of 14 from surface of tailing dump. The physicochemical characterization of a sample of tailings was carried out. The effect of the following oxidants was carried out on the leaching degree of copper: iron(III) sulfate and concentrated sulphuric acid. Copper sulfides are transferred into the forms soluble in acidic aqueous solutions under the oxidative conditions.

EXPERIMENTAL TESTING WITH DISCUSSION OF THE RESULTS

The samples of tailings from depth of 14 m 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 14 m*

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 testing results are shown in Table 2.

Table 2 *Results of carried out leaching test and TCLP test on a sample of flotation tailings from depth of 14 m*

Element	Unit measure	Content		
		Leaching test	TCLP test	MDK of water for III and IV class*
Cu	mg/l	196	89	0.1
Fe	mg/l	256	105	1.0
Pb	mg/l	<0.1	<0.1	0.1
Zn	mg/l	12	5,8	1.0
Mn	mg/l	2,7	1,4	/
Ag	mg/l	<0.02	<0.02	/
As	mg/l	<0.1	<0.1	0.05
Hg	mg/l	<1	<1	0.001

**Regulations on Hazardous Substances in Water (Official Gazette of SRS, No.31/82)*

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.

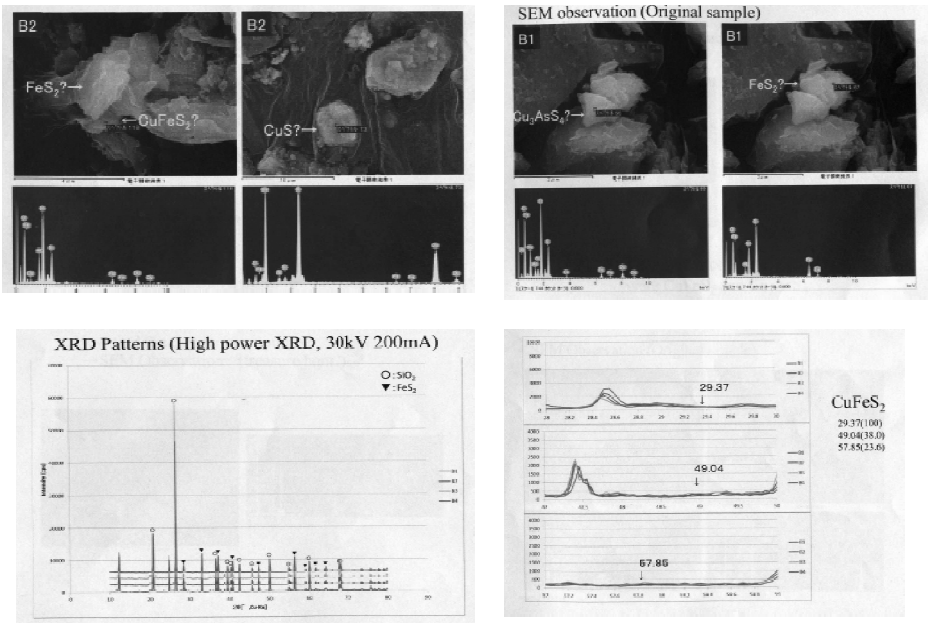

Figure 1 *Stage composition of flotation tailings (High power XRD, 30 kV 200 mA) recorded at the Akita University, Japan*

Experimental testing the leaching process composite sample 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 with the following chemical composition: Cu-69,10 mg/dm^3; Pb<0.05 mg/dm^3; Zn-26.30 mg/dm^3; Cd-0.12 mg/dm^3; Ni-0.34 mg/dm^3; Cr <0.02 mg/dm^3; Se<0.020 mg/dm^3; As<0.010 mg/dm^3; Fe-739.00 mg/dm^3; suspended matters - 12.00 mg/dm^3; SO_4^{2-} - 8243,10 mg/dm^3.

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 [13,14]. The experiments were carried out in a laboratory glass reactor with mechanical stirring.

Sulphide and other copper compounds (CuS, Cu_3AsS_4, $CuFeS_2$), present in the flotation tailings in the given conditions of leaching stay in the unchanged form, i.e. there is no their chemical degradation, what is shown in Figure 2.

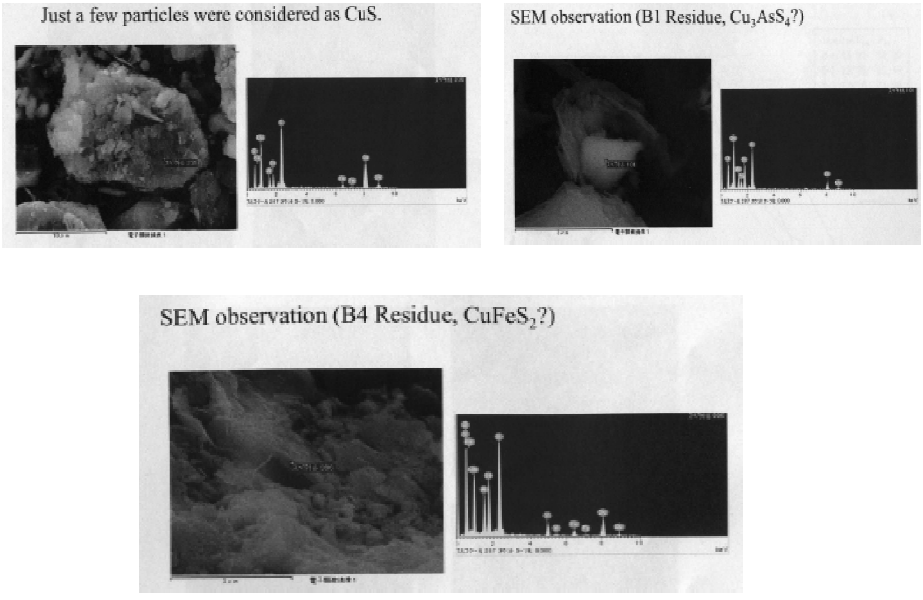

Figure 2 *Stage composition of flotation tailings after leaching (High power XRD, 30 kV 200 mA) recorded at the Akita University Japan*

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 $Fe_2(SO_4)_3$ as oxidant

Testing the effect of $Fe_2(SO_4)_3$ as an oxidant in the leaching process a composite sample of flotation tailings was carried out at room temperature with the concentration of sulfuric acid in leach solution of 0.1 M (pH=1) in the ratio S:L=1:2.5. Leaching experiments were carried out with different concentrations of Fe^{3+} ions in the sulfur-acidic solution ranged from 1 g/dm^3 to 10 g/dm^3.

Dependence of copper leaching degree on concentration of iron (III) sulfate at different leaching times (2-120 min) is given in Table 5.

Table 5 *Effect of iron (III) sulfate concentration on copper leaching*

Time (min)	1 g/dm^3 Fe^{3+}	2 g/dm^3 Fe^{3+}	7 g/dm^3 Fe^{3+}	10 g/ dm^3 Fe^{3+}
	Leaching degree of copper, %			
2	52	52	56	52
5	56	60	60	56
10	60	64	64	60
30	64	66	68	60
60	64	66	68	60
120	64	66	68	60

It can be concluded from the obtained results that the effect of concentration Fe^{3+} ions in sulfur-acidic leaching solution, or more precisely, has very little impact on copper leaching degree. The achieved results of copper leaching have approximate values and differ only by ± 4%. Leaching solution with concentration of oxidants of 7 g/l Fe^{3+} was used for further testing, where some better copper leaching results were achieved. The effect of temperature on copper leaching degree was tested at the following conditions: time: 120 min; temperature: room, 50^{o}C and 80^{o}C; S:L = 1:2.5; leaching solution: 0.1M H_2SO_4 (pH=1); concentration oxidant: 7 g/dm^3 Fe^{3+}. Testing results of the effect of temperature on copper leaching degree in the presence of oxidants are given in Table 6.

Table 6 *Temperature effect on copper leaching degree*

Temperature	Leaching degree of copper, %
Room	68.0
50^{o}C	70.7
80^{o}C	76.8

Based on the obtained results, it can be concluded that the highest degree of copper leaching was achieved at temperature of 80^{o}C with addition of $Fe_2(SO4)_3$ as the oxidant in concentration of 7 g/dm^3 Fe^{3+} in the leaching time of 120 min.

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 Bor flotation tailings that affect that dissociation of copper sulphate to the oxide forms beginning at lower temperature. Experimental studies of sulphatization process of the Bor flotation tailings at temperature of 700°C have shown that copper sulphate dissociates to a large extent to the oxides insoluble in water. After a series of experiments, the optimum roasting temperature of sulphatization roasting of flotation tailings was determined at 630°C. 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°C for a period of 2 h and II degree: at temperature of 630°C for a period 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 7.

Table 7 *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.

Table 8 *Results of carried out TCLP test on a sample of solid residue obtained after leaching of calcine with water*

Element	Unit measure	Results of analyses	MDK of water for III and IV class*
Cu	mg/l	<0.1	0.1
Fe	mg/l	<0.2	1.0
Pb	mg/l	<0.1	0.1
Zn	mg/l	0.18	1.0
As	mg/l	<0.1	0.05
Hg	mg/l	<0.001	0.001

**Regulations on Hazardous Substances in Water (Official Gazette of SRS, No.31/82)*

The results of TCLP test, given in Tabeli 8, 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.

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 $Fe_2(SO_4)_3$ as an oxidant in concentration of 7 g/dm^3 Fe^{3+} at leaching temperature of 80^{o}C and leaching time of 120 min, the attained degree of copper leaching was 76.8 %. 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/dm^3 Cu and less than 1 g/dm^3 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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