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on Mining and Metallurgy**

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**Editors:
Ljubiša Balanović
Dejan Tanikić**



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Editors:

Prof. dr Ljubiša Balanović

Prof. dr Dejan Tanikić

University of Belgrade, Technical Faculty in Bor

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HYDROMETALLURGICAL TREATMENT OF MINING WASTE FROM BOR - SERBIA IN AIM OF COPPER RECOVERY

Ljiljana Avramović, Zoran Stevanović, Vanja Trifunović, Radmila Marković,
Dragana Božić, Daniela Urošević, Silvana Dimitrijević

Mining and Metallurgy Institute Bor, Zeleni bulevar 35, 19210 Bor, Serbia

Abstract

Flotation tailings deposited on the Old Flotation Tailing Dump in Bor contains 0.2-0.4% Cu and represents a significant resource for recovery of copper and other useful components. The results of experimental laboratory tests of the copper recovery process from the flotation tailings using the beaker leaching (BL) and high pressure leaching (HPL) are given in this paper. By the use of beaker leaching, the degree of copper recovery of 70% and iron of 12% at temperature of 60°C, time of 24 hours and concentration of sulfuric acid of 15 g/l was achieved. A high degree of copper recovery of 99% was achieved by the high pressure leaching using water as an leaching reagent at a temperature of 180°C and pressure of 1.5 MPa.

Keywords: flotation tailings, beaker leaching, high pressure leaching, copper recovery

1. INTRODUCTION

Pyrometallurgical process for copper production from sulphide minerals has existed in Bor for many years. During the processing of such type of ore, there is a formation of tailings generated during the flotation processes and containing the metal sulphides and under the effect of atmospheric conditions, the self-leaching process of tailings is developed resulting in a significant degradation the quality of surrounding water and soil [1,2].

It is estimated that more than 2000 ha of the most fertile coastal area of the Bor River, Bela River, and downstream Timok and Danube have been degraded by the flotation tailings. In addition to the physical contamination of the coastal area, the Bor River is constantly contaminated with wastewater generated by a drainage through the flotation tailing dumps and landfills.

This work presents the results of experimental laboratory test of copper recovery from the flotation tailings by the acid leaching process of tailings at the atmospheric pressure (BL) and high pressure leaching with the addition of oxidant (HPL). The highest level of copper leaching of 99% was achieved using the HPL method.

2. EXPERIMENTAL

For the experimental tests of the leaching process: BL and HPL, the flotation tailings from the Old Flotation Tailing Dump in Bor was used with a particle size of 72% -75 µm. The chemical composition of the initial flotation tailings sample is given in Table 1.

Table 1 - Chemical composition of flotation tailings

Element	Cu	Fe	S-total	S-sulphide	Ag	Au	As
Unit	%	%	%	%	g/t	g/t	%
Content	0.29	9.51	10.10	7.32	1.10	0.50	0.013

The BL experiments were carried out in order to investigate the effect of the following parameters: temperature (20-80°C), sulfuric acid concentration (2-40 g/l H₂SO₄) and process time (2-48 h). The pulp density of 25% and stirring rate of 700 rpm were constant in all experiments. After completion of the leaching process, the filtered leaching solutions were analyzed to determine the leaching degree of Cu and Fe.

The HPL experiments were carried out on the same samples of flotation tailings in the Nitto Koastu autoclave, Japan, with a volume of 2 L of reaction vessel. The effect of sulfuric acid concentration (0-50 g/l), pulp density in the range of 10-40% and temperature (140-180°C) with the oxygen introduction at total pressure of 0.8 to 2.0 MPa was tested. The reaction time in all experiments is 60 minutes and stirring rate is 700 rpm.

The ICP-OES Spectro Vision device was used to analyze the concentration of tested elements.

3. DISCUSSION OF RESULTS

3.1. Beaker Leaching

The leaching degrees of copper and iron, depending on the process temperature, concentration of H₂SO₄ in the leaching solution and leaching time are shown in Figures 1,2 and 3, respectively.

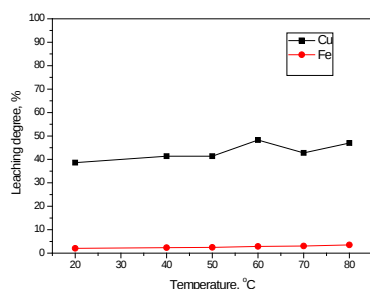


Figure 1 - The temperature effect on a leaching degree of Cu and Fe ($\tau=2$ h, 2g/l H₂SO₄)

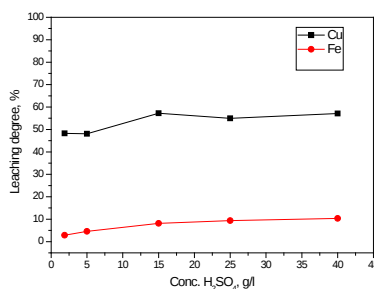


Figure 2 - The concentration effect of H₂SO₄ on a leaching degree of Cu and Fe ($\tau=2$ h, $t=60^\circ\text{C}$)

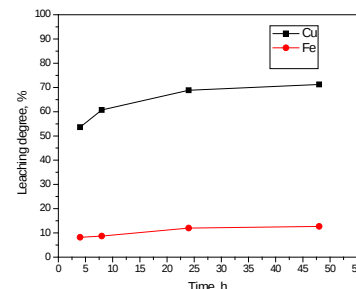


Figure 3 - The time effect on a leaching degree of Cu and Fe (15g/l H₂SO₄, $t=60^\circ\text{C}$)

Based on the obtained testing results of the temperature effect (Figure 1), the leaching degree of copper ranges from 38% (20°C) - 48% (80°C). Considering that the similar values for the leaching degree of copper were obtained at temperatures of 60°C and 80°C (48% and 47%, respectively), it was decided that the further tests of the flotation tailings leaching process should be carried out at 60°C. With an increase in H₂SO₄ concentration in the leaching solution (Figure 2), an increase in the leaching degree of copper to 15 g/l was observed. Further increase in the concentration of H₂SO₄ to 40 g/l did not have a significant effect on a leaching degree of Cu. Maximum copper leaching degree of 71% was achieved at a leaching time 48 hours, temperature 60°C and 15g/l H₂SO₄ (Figure 3).

The most influential parameters for the leaching degree of iron is the concentration of H₂SO₄ in leaching solution (Figure 2) and ranges from 2% (2 g/l H₂SO₄) to 10% (40 g/l H₂SO₄). With an increase in the leaching time of 48 h, an increase in the leaching degree of iron at 12.7% was observed (Figure 3).

Having in mind the fact that copper from the leaching solutions is recovered by the solvent extraction processes and electro-winning SX-EW, and that the increased iron concentration has a negative impact on the electrochemical copper extraction, in a selection the optimal parameter BL, the time was adopted of 24 h, temperature 60°C and concentration H₂SO₄ of 15 g/l.

3.2. High Pressure Leaching

The results of a high pressure leaching (HPL) are presented in Table 2.

Table 2 - Experimental conditions and results of the HPL process

Exp. No.	Pulp density (%)	Reagent	P _{total} (MPa)	Temperature (°C)	Time (h)	Stirring rate (rpm)	Leaching degree (%)	
							Cu	Fe
1	10	H ₂ O	2	180	1	700	95	24
2	20	H ₂ O	2	180	1	700	98	43
3	30	H ₂ O	2	180	1	700	92	60
4	40	H ₂ O	2	180	1	700	94	61
5	10	20 g/l H ₂ SO ₄	2	180	1	700	97	66
6	10	50 g/l H ₂ SO ₄	2	180	1	700	98	95
7	10	H ₂ O	0.8	180	1	700	21	2,35
8	10	H ₂ O	1.5	180	1	700	99	49
9	10	H ₂ O	2	140	1	700	89	40
10	10	H ₂ O	2	160	1	700	90	37

Water and sulfuric acid were used as a leaching reagent for the HPL process (Table 2). Leaching with water is based on the fact that the high content of pyrite (FeS₂) in the flotation tailings sample can be the source of H₂SO₄ (Equation 1) [3], which leads to a decrease in the pH (from 3.79 to 0.35) and thus increases copper dissolution (chalcopyrite as the main copper minerals).



By leaching with water, the realized degree of copper leaching was 99%, iron 49%, at 180°C, pressure of 2 MPa, pulp density 10%, time 1 h, stirring rate 700 rpm. With an increase in the H₂SO₄ concentration from 20 g/l to 50 g/l, the percentage of copper leaching has been slightly increased from 97% to 98%, while the degree of iron leaching increases from 67% to 95%. From an economic point of view, H₂O has been selected as a copper leaching medium from the flotation tailings.

The effect of total pressure on copper dissolution from the flotation tailings has been tested in the range of 0.8 to 2.0 MPa, with water as a dissolving medium, temperature of 180°C, pulp density of 10% and time of 60 min (Table 2). The degree of copper leaching was 21% and iron 2.35% at pressure of 0.8 MPa (without the introduction of oxygen). It can be concluded that after the initial dissolution of copper, a passive layer of elemental sulfur [4] was formed on chalcopyrite, which had a negative effect on kinetics of copper dissolution. With an increase in the pressure of 0.8 to 2.0 MPa with the oxygen supply, the degree of copper and iron leaching increased to 99%, i.e. 49%, respectively. The present oxygen allows oxidation and prevents the formation of passivation layer (Equation 2) [3,5].



With a temperature increase of 140 to 160°C, the degree of copper and iron leaching increased from 89 to 99% and from 37 to 49%, respectively. Based on the literature data [5], the chalcopyrite leaching controls the kinetics of chemical reaction on the grain surface with activation energy of about 70-90 kJ/mol. This implies that the leaching degree is highly dependent on temperature. An optimum condition for the next experiments was chosen to be the temperature of 180°C with a copper leaching degree of 99%.

As shown in Table 2, the first degree of copper leaching has not changed much with an increase of pulp density from 10 to 40%, i.e. no effect on the copper leaching degree [6,7]. As an optimal, the pulp density of 40% is chosen, since in this case the copper concentration in leaching solution is four times higher than the copper concentration in 10% pulp, which is a significant parameter for the copper extraction process from leaching solutions.

4. CONCLUSION

On the basis of the results obtained for the BL process of flotation tailings leaching, it can be concluded that the maximum degree of copper recovery is 71% and iron 12%, while in the HPL process, with the application of water as the leaching reagent, a significantly higher degree of copper recovery of 99% and iron recovery of 61% was realized.

A high concentration of iron in the solution after leaching in the HPL process is a serious problem in further copper recovery processes (SX-EW process) as a commercial product. Due to this reason, a consideration should be given to the possibility of introducing an additional phase of iron removal from the pregnant leaching solutions before the SX-EW process.

In order to select the method of copper leaching from the flotation tailings will largely be a decisive economic aspect of the tested BL and HPL processes what will be the subject of future research.

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