The 55th International October Conference on Mining and Metallurgy
15 - 17 October 2024, Kladovo, Serbia
https://ioc.irmbor.co.rs

DOI: 10.5937/IOC24335M Original Scientific Paper-Technology

LEACHING OF FLOTATION TAILINGS WITH A SULFURIC ACID AND AN IONIC LIQUID IN THE PRESENCE OF HYDROGEN PEROXIDE

Dragana Marilović[1a], Grozdanka Bogdanović[1b]

[1]Technical Faculty Bor, University of Belgrade, V.J. 12, 19210 Bor, Serbia

[1a] dmarilovic@tfbor.bg.ac.rs, https://orcid.org/0000-0001-8301-750X;
[1b] gbogdanovic@tfbor.bg.ac.rs, https://orcid.org/0000-0002-1013-4075

Abstract

This study focuses on leaching of flotation tailings with sulphuric acid (H_2SO_4) and ionic liquid 1-butyl-3-methyl-imidazolium hydrogen sulfate ([bmim]HSO_4) in the presence of hydrogen peroxide (H_2O_2). Reagent concentrations of 0.01 mol/dm^3 and 0.05 mol/dm^3 in the present of 0.1 mol/dm^3 H_2O_2 were tested. When leaching with sulfuric acid in the presence of oxidants, the leaching degree of copper was 80.85% (for 0.01 mol/dm^3) and 82.24 (for 0.05 mol/dm^3). When flotation tailings were leached in an ionic liquid solution with the same concentrations in the present of oxidants, the leaching degree of copper was 72.56% and 83.14 % for 0.01 and 0.05 mol/dm^3, respectively. The results showed that the maximum dissolution of iron of 3.65% in the presence of hydrogen peroxide was attained with 0.05 mol/dm^3 H_2SO_4 after 120 min of the reaction and 1 % in the 0.05 mol/dm^3 solution of the ionic liquid [bmim]HSO_4 after 120 min of the reaction.

Keywords: *flotation tailings, copper, ionic liquid, sulphuric acid*

1. INTRODUCTION

Flotation tailings represent waste material generated during the flotation process, and their proper management and storage are crucial for minimizing negative environmental impacts. The flotation tailings pond of the Bor Copper Mine is a major ecological problem not only for the city of Bor, but also for the surrounding soils and rivers. Recent studies have shown that the mining industry produces around 10 billion tons of tailings every year, and this figure is expected to double by 2035. The biggest problem is the dissolution of toxic elements and the acid mine drainage waters that is produced. The recovery of precious metals and other metals from the tailings adds potential value to this raw material [1].

The application of hydrometallurgical operations is possible for raw materials that have a low metal content or a complex composition. The right choice of reagents is important for a successful process. Sulfuric acid is used as one of the most common reagents for leaching copper from flotation tailings [2]. On the other hand, ionic liquids are recognized as green reagents due to their characteristics such as viscosity, thermal stability, negligible volatility, non-toxicity and high conductivity [3].

This paper presents the comparative results of flotation tailings leaching with sulfuric acid (H_2SO_4) and the ionic liquid 1-butyl-3-methyl imidazolium hydrogen sulfate ([bmim]HSO_4) in the presence of hydrogen peroxide (H_2O_2).

2. EXPERIMENTAL

Main elements contained in flotation tailings are copper and iron. Samples with the following chemical composition were used for the experiments:

Table 1. *Chemical composition of the flotation tailings*

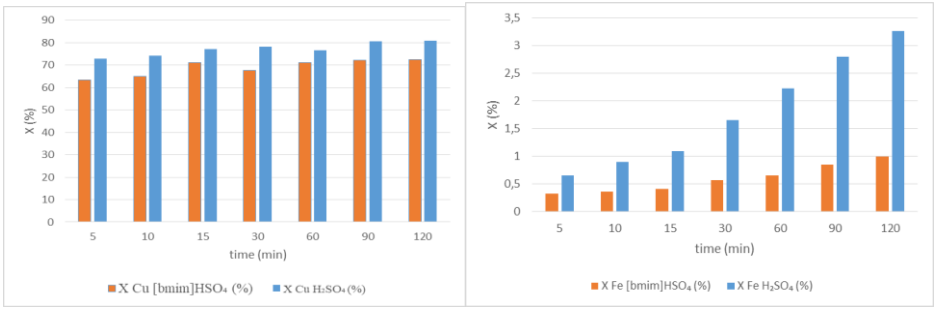
Element	Cu	Cu_{ox}	Fe	Zn	Pb	S	SiO_2	Fe_3O_4	MgO	CaO	As_{ppm}
%	0.13	0.09	4.22	0.01	0.01	4.70	60.02	0.03	0.48	3.50	13.24

The leaching experiments were done in a sulfuric acid solution (H_2SO_4) and an ionic liquid solution 1-butyl-3-methyl-imidazolium hydrogen sulfate ([bmim]HSO_4) in the presence of hydrogen peroxide (H_2O_2). A 600 cm^3 glass reactor with a magnetic stirrer was used. After setting the working parameters, 10 g of the tailings was added to 200 ml of a solution of a certain concentration. The stirring speed was 400 rpm. At regular time intervals (5, 10, 15, 30, 60, 90 and 120 minutes) 1 ml of the solution was taken and filtered. The diluted solution was analysed for copper and iron using an ICP-OES and multiparameter photometer.

3. RESULTS AND DISCUSSION

Reagent concentrations of 0.01 mol/dm^3 and 0.05 mol/dm^3 without hydrogen peroxide were tested and the results are presented in previous studies [4]. At a reagent concentration of 0.01 mol/dm^3, the copper leaching degree was 71.05 and 72.57% for sulfuric acid and ionic liquid, respectively. At the higher tested concentration of 0.05 mol/dm^3, the copper leaching degree was 76.59% for the sulfuric acid solution and 77.10% for the ionic liquid solution.

Figure 1 shows the results of the flotation tailings leaching at a concentration of 0.01 mol/dm^3 sulfuric acid and the ionic liquid [bmim]HSO_4 as reagents in the presence of 0.1 mol/dm^3 hydrogen peroxide.



a) b)

Figure 1. *Leaching degree of copper (a) and iron (b) in 0.01 mol/dm^3 solution of sulfuric acid H_2SO_4 and 0.01 mol/dm^3 solution of the ionic liquid [bmim]HSO_4 in the presence of 0.1 mol/dm^3 H_2O_2*

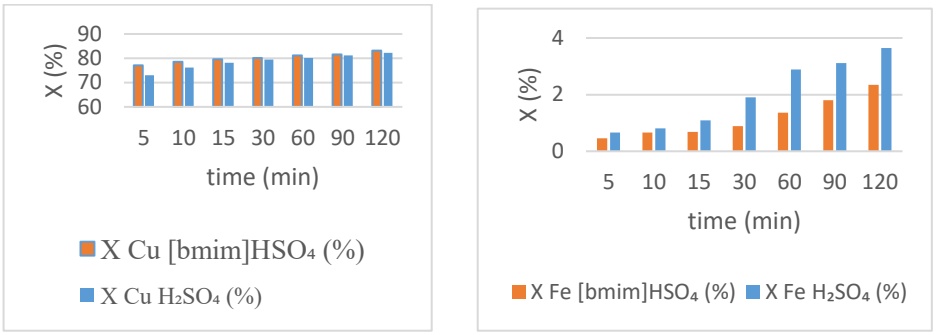
The results show that when leaching with sulfuric acid and in the presence of H_2O_2, the copper leaching degree was 80.85%, while the iron leaching degree was 3.27%. Compared to the results without hydrogen peroxide, the copper leaching degree increased for 9.8% and iron leaching increased for 2.5 % in the presence of H_2O_2.

When flotation tailings were leached in [bmim]HSO_4 solution of the same concentration, in the presence of oxidant the copper leaching degree was 72.56 as in the experiments performed without hydrogen peroxide, while the iron leaching was 1%. Under these conditions, hydrogen peroxide had a negligible effect in both tested systems. At lower

initial concentrations of sulphuric acid, it is first consumed in the leaching of calcium, magnesium and other alkali metals [5].

With increasing reagent concentration (0.05 mol/dm^3), the copper leaching degree in the sulphuric acid solution was 82.24% and the leaching of iron was 3.65%. When flotation tailings was leached with an ionic liquid solution with the same concentrations and in the presence of 0.1 mol/dm^3 H_2O_2, the copper leaching degree was 83.14% and iron 1%. It can be observed that with an increase in the concentration of the reagent, the copper leaching degree in the sulfuric acid solution increased by 2%, while it was about 10% higher in the ionic liquid solution. It can also be concluded that with the addition of peroxide, the copper leaching degree increased in both tested systems at a higher concentration. Since the solubility of oxygen in [bmim]HSO_4 is similar to that in water, a higher concentration of the ionic liquid can lead to a higher degree of oxidation and better dissolution of the metal [6].

The small amount of leached Fe can be attributed to reprecipitation, as $Fe(OH)_3$ is precipitated below a pH value of 2 [7]. As most of the iron is present in the form of pyrite, this could be one of the reasons for the low leaching degree under the conditions investigated.



a) b)

Figure 2. *Leaching degree of copper (a) and iron (b) in 0.05 mol/dm^3 solution of sulfuric acid H_2SO_4 and 0.05 mol/dm^3 solution of the ionic liquid [bmim]HSO_4 in presence of 0.1 mol/dm^3 H_2O_2*

These results indicate that hydrogen peroxide has a slight effect for the leaching process of flotation tailings under these conditions. A greater influence of hydrogen peroxide can also be observed at the higher acid ionic liquid concentration tested. Considering the copper oxide content in the initial sample, it can be assumed that all copper was dissolved in the form of easily leachable oxides and the part of the copper sulphide form. The strong influence of hydrogen peroxide on sulfide oxidation by increasing the ore's dissolution was reported by Habashi [8]. He explained that in H_2O_2 solution the sulphide partially converts into elemental sulphur and subsequently to sulfate, which other authors also proved [9-11]. Elementar sulfur at the particle surfaces reducing the leaching rate in the final stage of the reaction [12].

4. CONCLUSION

In the paper, the leaching of copper and iron in aqueous solutions of sulfuric acid and the ionic liquid [bmim]HSO_4 in the presence of oxidant was studied. The results showed that at reagent concentration of 0.01 mol/dm^3 in the presence of oxidising agents, the leaching degree of was 80.85 % and 72.56 % for sulfuric acid and ionic liquid, respectively. At the

higher tested concentration of 0.05 mol/dm^3 the copper leaching degree was 82.24 % for the sulfuric acid solution and 83.14 % for the ionic liquid solution. When used as a leaching agent in aqueous solution, ionic liquids provide better results than leaching with sulphuric acid at the higher reagents concentration tested. For both investigated systems, the copper leaching degree was less than 90% after 120 min of leaching. Further studies with higher concentrations of hydrogen peroxide are required.

ACKNOWLEDGEMENTS

The research presented in this paper was done with the financial support of the Ministry of Science, Technological Development and Innovation of the Republic of Serbia, within the funding of the scientific research work at the University of Belgrade, Technical Faculty in Bor, Grant No. 451-03-65/2024-03/200131.

REFERENCES

[1] Ruiz -Sánchez, A. Julio C. Juárez Tapia, G.T. Lapidus, Evaluation of acid mine drainage (AMD) from tailings and their valorization by copper recovery, Minerals Engineering, Volume 191, 2023.
[2] Jarosikova A., Ettler V., Mihaljevic M., Kribek B., Mapani B., Journal of Environmental Management, 2017, 187, 178 – 186.
[3] Li F., Chen M., 2017, Copper recovery from waste printed circuit boards and the correlation of Cu, Pb, Zn by ionic liquid. Environ. Prot. Eng. 43, 55 – 66.
[4] D. Marilovic, G. Bogdanovic, S. Petrovic, The 54th International October Conference on Mining and Metallurgy 18-21 October 2023, Bor Lake, Serbia, 456-459.
[5] Wang, Y.; Wen, S.; Feng, Q.; Xian, Y.; Liu, D. Leaching Characteristics and Mechanism of Copper Flotation Tailings in Sulfuric Acid Solution. Russian journal of nonferrous metals, 2015, 56, 127–133.
[6] Kilicarslan A., Nezihi Saridede M., Stopic S., Friedrich B., Use of ionic liquid in leaching process of brass wastes for copper and zinc recovery, International Journal of Minerals, Metallurgy and Materials, Volume 21, Number 2, February 2014, 138.
[7] Chen T., Lei C., Yan B., Xiao X., Metal recovery from the copper sulfide tailing with leaching and fractional precipitation technology, Hydrometallurgy 147–148 (2014) 178–182.
[8] Habashi, F.A., Textbook of Hydrometallurgy, Quebec: Metallurgie Extractive Quebec, 1999.
[9] Lin, H.K., Luong, H.V., Column leaching for simultaneous heap and in-situ soil remediation with metallic Fenton reaction, J. Miner. Mater. Charact. Eng., 2004, 3(1), 33–39.
[10] Misra, M., Fuerstenau, M.C., Chalcopyrite leaching at moderate temperature and ambient pressure in the presence of nanosize silica, Miner. Eng., 2005, 18, 3, 293–297.
[11] Turan, M.D., Altundogan, H.S., Leaching of chalcopyrite concentrate with hydrogen peroxide and sulfuric acid in an autoclave system, Metall. Mater. Trans. B, 2013, 44, 809–819.
[12] Sokic M., Stojanovic J., Markovic B., Kamberovic Z., Gajic N., Radosavljevic-Mihajlovic A., Milojkov D., Modification of Structural-Textural Properties of Sulfide Minerals at Polymetallic Concentrate Leaching with Sulfuric Acid and Hydrogen Peroxide Solutions, Russian Journal of Non-Ferrous Metals, 2022, 63 (5) 457–472.