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NON-FERROUS METALS BIOLEACHING FROM PYROMETALLURGY COPPER SLAG USING SPENT MEDIUM OF DIFFERENT FUNGAL SPECIES

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ABSTRACT – This study aimed to compare the recovery of non-ferrous metals from a pyrometallurgy copper slag containing 1.93 % Zn, 0.36 % Cu, and 0.09 % Co by spent medium bioleaching of fungi *Aspergillus niger* and *Penicillium ochrochloron*. The fungal species were cultivated for a week; microbial biomass was separated, and the shake-flask technique carried out the leaching. Factors such as temperature, pulp density, the organic acids ratio and the amount of added acidity strongly affected the extraction of the non-ferrous metals from copper slag.

Keywords: Raw Materials, Copper Slag, Fungi, Bioleaching.

INTRODUCTION

Pyrometallurgical copper slags are used nowadays for road construction and preparing different types of cement. However, these wastes, especially old slags, contain significant quantities of valuable components (copper, cobalt, zinc and nickel in some cases) and, for that reason, are subject to further processing. Their flotation processing usually resulted in a final recovery not higher than 50 % [1]. The efficiency of chemical/biological leaching of base metals is in the range of 85-95 % due to the combined action of several weathering processes such as acidolysis, oxidation, and complexolysis.

This study presents some results about the leaching of copper, zinc, and cobalt from old copper slags by the spent medium of fungi *A. niger* and *P. ochrochloron*.

EXPERIMENTAL

The copper slag sample was collected from the surface of the weathered zone of copper slag deposit Eliseyna, located in Northwestern Bulgaria. The sample was transported to the laboratory in a dust-free bucket and stored at a lower temperature for further use.

A representative sample of cooper slag was subjected to digestion with aqua regia, and the content of chemical elements in liquid obtained after that was analyzed by

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atomic absorption spectrometry and inductively coupled plasma. The mineralogical composition of copper slag was determined by X-ray Diffraction analysis EMPYREAN supplied with copper as anode material.

Table 1 Chemical content of copper slag used in this study

Index (in %)	Value
Al_2O_3	5.25
CaO	9.68
K_2O	1.16
MgO	3.07
MnO	1.10
Na_2O	1.70
P_2O_5	0.21
SiO_2	34.05
Fe	27.22
Cu	0.36
Co	0.09
Zn	1.93
S	0.91

Leaching experiments were carried out with grounded copper slags with dominant particle size – 75 µm to + 25 µm. The acid consumption of the slag was studied at 25 °C and 55 °C, respectively. It was determined by serial addition of sulfuric acid to pulp in a regime of agitation with an overhead mixer with a rate of 300 rpm. The acid addition stopped when the pulp's pH reached the targeted value (5.0, 4.0, 3.5, and 2.5) and remained constant for 6 hours.

The leaching abilities of fungal species *Aspergillus niger* and *Penicillium ochrochloron* to the mineral composition and non-ferrous metals in copper slag were compared. *Aspergillus niger* originated from the Microbial Culture Collection maintained at the Department of General and Industrial Microbiology, University of Sofia. *Penicillium ochrochloron CCM F-158* was obtained from the Czech Collection of Microorganisms to the Department of Experimental Biology at Masaryk University. The strains were maintained on Czapek Dox medium by sub-culturing at 25 °C and were preserved at 4 °C when needed. Each fungal species was cultivated in a medium consisting of sucrose (185 g/ L), KH_2PO_4 (3.0 g/ L), NH_4Cl (0.96 g/ L), $MgSO_4 \cdot 7H_2O$ (1.2 g/ L), and traces of $FeSO_4 \cdot 7H_2O$, $ZnSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 7H_2O$. The medium was inoculated with 10^6 spores/ ml and incubated for 7 days at 25 °C under continuous shaking (150 rpm). The spent medium for further experiments was obtained by separating the fungal biomass with vacuum filtration. The extracellular organic acids in the spent medium were determined by Water's 510 HPLC, equipped with an E18 column, at a flow rate of 1 ml/ min, and six mM H_3PO_4 as a solvent, and the peaks` detection following the method described in Bosshard et al., [2]. The alkaline consumption (0.2 N NaOH) of the spent medium up to pH 8.5 was determined by the Metrohm 718 STAT Titrino titrator.

The leaching experiments were performed by the shake-flask technique using an Erlenmeyer flask of 500 ml volume containing 150 ml spent medium and copper slag at a pulp density of 5 %, 10%, or 15 %, respectively. The pulp was homogenized by an orbital shaker (150 rpm) at temperatures of 25° or 55 °C, respectively. The effect of sulfuric acid extra addition (5 g, 10g, and 25 g/ L) was studied also. The total duration of the leaching experiments was 72 hours. The solid residues from the Erlenmeyer flasks were separated by filtration and washed with tap water until the pH reached 7.0. The chemical and mineral content of solid residues obtained from each experiment were determined after drying out to constant weight.

All experiments were repeated in triplicate, and the results represent the mean value.

RESULTS AND DISCUSSION

Results of the chemical content revealed the presence of copper, zinc, and cobalt as raw materials in the higher amount in the copper slag (Table 1).

X-ray diffraction study showed that the main silicate mineral in the studied copper slag was fayalite (Fe_2O_4Si) (Figure 1). The higher content of protomangano-ferro-anthophyllite ($H_2Fe_{4.48}Mg_{1.08}Mn_{1.44}O_{24}Si_8$) revealed that the weathering process had carried out intensively near the surface of the copper slag deposit. The copper slag's chemical and mineralogical content determined the higher value of acid consumption, especially when the target pH was lower than 4.0 (Table 2). It was determined by the preferential leaching of iron oxides and the gradual increase of ferrous iron concentration in the pregnant solution. That process was combined with stepwise leaching of non-ferrous metals, as at pH 3.5, the copper, zinc, and cobalt leaching reached 38.5 %, 58.0 %, and 40.0 %, respectively. These results revealed that the non-ferrous metals` stock in pyrometallurgical copper slags could be unlocked and recovered using acidolysis as a leading process in their hydrometallurgical processing.

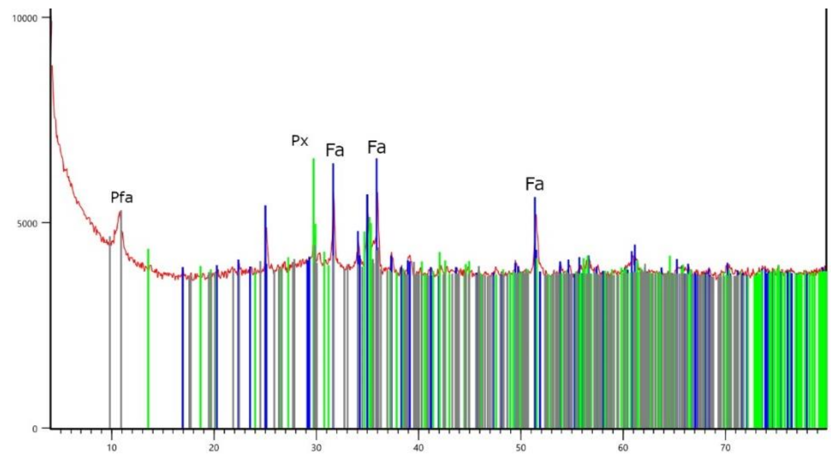

Figure 1 X-ray diffraction pattern of the copper slag sample showing the presence of Fa -Fayalite, Px-Clinopyroxene and Pfa-protomangano-ferro-anthophyllite (Minerals abbreviation according to [3])

There are twoapproaches to putting it into practice: slag leaching with strong inorganic or polycarboxylic acids (4). Sulfuric acid is an example of a strong inorganic acid that could be added to the slag's pulp or generated due to the activity of acidophilic chemolithotrophic bacteria growing on S° as a source of donors and energy. In that case, the main drawbacks are the considerable lowering of the pulp pH and substantial iron co-leaching, as its concentration could reach up to 30 g/ L. It turns the processing of laden leach solution into a challenging task [5]. Polycarboxylic acids contain more than one carboxylic group, which donates hydrogen ions in a wide pH range. Fungi produce a dozen such metabolites, and with higher concentrations are citric and oxalic acid (6). For example, oxalic acid is a diprotonic strong acid with lower pKa values of the carboxylic groups (1.25 and 4.14, respectively). In contrast, citric acid is a weak triprotonic acid with pKa values of 3.13, 4.76, and 6.39, respectively. The main advantage of citric acid is the excellent complexing properties of citrate anions towards already leached cations and complexes formation with a net negative charge, which enables their migration even at slightly acidic-alkaline pH. The peak concentration of citric acid in the spent medium of A. niger and P. ochrochloron was measured after seven days of cultivation. The spent medium of A. niger contained a higher amount of citric acid, had a higher value of citric: oxalic acid ratio (3:1), and the total amount of protons available for acidolysis reached almost 1.0 g H+/ L compared to the values measured in the spent medium of other fungal species (Table 3). It resulted in 22.5 %, 25.1 %, and 44.4 % of copper, zinc, and cobalt leaching, respectively, at an equilibrium pH of 4.39 on the third day of the leaching test (Table 4). Therefore, all further experiments were carried out with a spent medium of A. niger.

Table 2 Acid consumption of copper slag and its effect on the leaching of raw materials

pH	g H_2SO_4/ kg slag	Leached raw materials, mg/kg				
		Cu	Zn	Co	Fe	Si
4.9	12.0	220	3950	125	1190	18550
4.0	71.5	945	5350	255	49530	21880
3.5	292	1385	11190	360	138420	25990
2.5	505	2220	14450	490	210150	71280

Table 3 Characteristic of spent medium generated due to the growth of the tested fungal species

Index	*Aspergillus niger*	*Penicillium ochrochloron CCM F-158*
pH	2.58	3.24
Oxalic acid, g/L	8.1	10.9
Citric acid, g/ L	24.8	18.9
g H^+/ 1 L	0.94	0.65

The protomangano-ferro-anthophyllite was the mineral with the highest content and most reactive in the copper slag, and it consumed a substantial portion of protons in the spent medium instead of the non-ferrous metals` leaching; the experiments at a pulp density higher than 5 % revealed its negative effect on the recovery of non-ferrous metals (Table 5). For example, copper, zinc, and cobalt recovery at 15 % pulp density dropped by 16.7 %, 24.9 %, and 15.5 %, respectively. Therefore, all further experiments were carried out at 5 % pulp density.

Table 4 Effect of using the spent medium on the non-ferrous leaching from copper slag at 5 % pulp density and 25 °C

Index	*Aspergillus niger*	*Penicillium ochrochloron CCM F-158*
pH	4.39	5.27
$Cu_{leached}$, mg/ kg	810	715
$Zn_{leached}$, mg/ kg	4850	4490
$Co_{leached}$, mg/ kg	400	345
$Fe_{leached}$, mg/ kg	35500	23200

Table 5 Effect of pulp density on the non-ferrous leaching from copper slag with the spent medium of *Aspergillus niger* at 25 °C

Index	Pulp density, %		
	5	10	15
pH	4.39	5.07	5.34
$Cu_{leached}$, mg/ kg	810	725	680
$Zn_{leached}$, mg/ kg	4850	4370	3640
$Co_{leached}$, mg/ kg	400	385	335

Two crucial factors limited the non-ferrous leaching from copper slag - the temperature at which the processing was carried out and the available concentration of protons. The main advantage of indirect leaching compared to raw materials leaching in the presence of microbial cells is that both factors can be manipulated efficiently. For example, the gradual increase of the temperature from 25° to 55° C led to a higher rate of processes, which resulted in better leaching of non-ferrous metals - 26.6 %, 26.5 %, and 48.3 % for copper, zinc, and cobalt, respectively. The extra addition of sulfuric acid at the beginning of the test further improved the non-ferrous metals recovery, as in the case with 25 g H_2SO_4/ L and 55° C, it reached 78.9 %, 54.7 %, and 69.4 %, respectively, for the above-mentioned non-ferrous metals (Table 7).

Table 6 Effect of temperature on the non-ferrous leaching from copper slag with the spent medium of *A. niger*

Index	Temperature, °C		
	25	40	55
pH	4.39	4.77	5.16
$Cu_{leached}$, mg/ kg	810	875	960
$Zn_{leached}$, mg/ kg	4850	5040	5110
$Co_{leached}$, mg/ kg	400	420	435

Table 7 Effect of sulfuric acid addition to the spent medium of *A. niger* on the non-ferrous leaching from copper slag at 55 °C

Index	Added sulfuric acid, g/ L			
	0	5	10	25
pH	5.16	3.83	3.16	2.27
$Cu_{leached}$, mg/ kg	960	1770	2310	2840
$Zn_{leached}$, mg/ kg	5110	7970	9840	10560
$Co_{leached}$, mg/ kg	435	560	570	625

CONCLUSION

The higher content of citric acid in the spent medium of *A. niger*, compared to that of *P. ochrochloron,* determined it as a better leaching agent towards copper, zinc, and cobalt contained in pyrometallurgical copper slag. However, the concentration of hydrogen ions in the fungal spent medium was the main limiting factor on the leaching of non-ferrous metals due to the copper slag's mineral composition and a value of acid consumption higher than 200 g H_2SO_4/ kg slag.

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REFERENCES

1. Panda, S., Mishra, S., Rao, D.S., Pradhan, N., Mohapatra, U., Angadi, S., Mishra, B.K. (2015). Extraction of copper from copper slag: Mineralogical insights, physical beneficiation and bioleaching studies. Korean Journal of Chemical Engineering 32, 667-676.
2. Bosshard, P.P., Bachofen, R., Brandl, H. (1996). Metal leaching of fly ash from municipal waste incineration by *Aspergillus niger*. Environmental Science and Technology, 30, 3066-3070.
3. Kretz, R. (1983). Symbols of rock-forming minerals. American Mineralogist, 68, 277-279.
4. Srichandan, H., Mohapatra, R.K., Parhi, P.K., Mishra, S. (2019). Bioleaching approach for extraction of metal values from secondary solid wastes: A critical review. Hydrometallurgy 189, 105122.
5. Georgiev, P., Nicolova, M., Spasova, I., Groudev, S. (2023). Iron removal from laden leach solution by processes of solvent extraction and magnetite synthesis. Sustainable Extraction and Processing of Raw Materials, 4, 37-42.
6. Gadd, G.M. (1999). Fungal production of citric and oxalic acid: Importance in metal speciation, physiology and biogeochemical processes. Advances in Microbial Physiology, 41, 47-92.