THE EFFECT OF THE PULP DENSITY OF A COPPER SLAG ON THE EFFICIENCY OF ITS BIOLEACHING BY MEANS OF DIFFERENT MICROORGANISMS

P. Georgiev[1], M. Nikolova[1], I. Spasova[1], S. Groudev[1], V. Groudeva[2]

[1] *University of Mining and Geology "St. Ivan Rilski", Sofia 1700, Bulgaria*
[2] *Sofia University "St. Climent Ohridski", Sofia 1000, Bulgaria*

ABSTRACT. Copper slag containing 0.62% Cu, 1.07% Zn, 0.08% Co, and 32.5% Fe as the most essential components was subjected to leaching by means of different chemolithotrophic microorganisms at different temperatures (from 35 to 90°C). The bioleaching was carried out by the shake-flask technique at different pulp densities (from 5 to 30%) of slag crushed to minus 100 microns. The highest rates of extraction of the non-ferrous metals and iron were achieved by means of some extreme thermophilic archaea (of the genera *Sulfolobus, Thermoplasma, Acidianus*, and *Metallosphaera*) at relatively low pulp densities (5–8% at 90°C and 10–15% at 75°C). The highest extractions by the moderate thermophilic bacteria (of the genera *Sulfobacillus, Alicyclobacillus*, and *Acidimicrobium)* were achieved at 55°C with pulp densities of 15–20%. The mesophilic bacteria (from the genera *Acidithiobacillus* and *Leptospirillum*) were efficient at 35–37°C at relatively high pulp densities (of 15–25%).

Keywords: copper slag, chemolithotrophs, leaching, valuable metals

ВЛИЯНИЕ НА ПЛЪТНОСТТА НА ПУЛПА ВЪРХУ ЕФЕКТИВНОСТТА НА БИОЛОГИЧНОТО ИЗЛУГВАНЕ НА МЕДНА ШЛАКА ПРИ ИЗПОЛЗВАНЕ НА РАЗЛИЧНИ МИКРООРГАНИЗМИ

П. Георгиев[1], М. Николова[1], И. Спасова[1], С. Грудев[1], В Грудева[2]
[1] *Минно геоложки университет „Св. Иван Рилски", София 1700, България*
[2] *Софийски университет „Св. Климент Охридски", София 1000, България*

РЕЗЮМЕ. Медна шлака, съдържаща 0.62% Cu, 1.07% Zn, 0.08% Co и 32.5% Fe, като най-важни компоненти, беше подложена на излугване с помощта на различни хемолитотрофни микроорганизми при различни температури (от 35 до 90 °C). Биологичното излугване бе проведено в колби на шейкър при различна плътност на пулпа (от 5 до 30%) с шлаки с едрина до минус 100 микрона. Най-високите скористи на извличане на цветните метали и желязото бяха постигнати чрез екстремни термофилни археи (от родовете *Sulfolobus, Thermoplasma, Acidianus* и *Metallosphaera*) при относително ниска плътност на пулпа (5-8% при 90 °C и 10-15% при 75°C). Най-високо извличане от умерените термофилни бактерии (от родовете *Sulfobacillus, Alicyclobacillus* и *Acidimicrobium*) бе постигнато при 55°C и плътност на пулпа от 15-20%. Мезофилни бактерии (от родовете *Acidithiobacillus* и *Leptospirillum*) бяха ефикасни при 35-37°C и при относително високи плътности на пулпа (от 15-25%).

Ключови думи: медна шлака, хемолитотрофи, излугване, ценни метали

Introduction

The pyrometallurgical slags, mainly these from the copper recovery, are wastes containing considerable quantities of valuable components, mainly non-ferrous metals (especially copper, zinc, and cobalt) but also iron and manganese, aluminum and silicon. At present, the slags are used mainly in the construction of roads and for the preparation of cements of different types. However, the investigations on the possibilities to extract the different more valuable components of the slags, especially the non-ferrous metals, as real commercial-scale products, are steadily increasing in numbers. In this respect, special interest is paid to the possibility to use various chemolithotrophic microorganisms, both bacteria and archaea, to efficiently extract the various metal components of the slags by means of leaching in agitated bioreactors (Panda et al., 2015; Kaksonen et al., 2016; Potysz et al., 2016; Georgiev et al., 2017; Spasova et al., 2017). Such treatment is performed on finely ground slags present in the relevant optimum concentrations and treated at conditions optimum for the microorganisms (bacteria and archaea) used as the relevant leaching agents. The present paper contains data in this aspect.

Materials and Methods

The slag used in this study contained 0.62% Cu, 1.07% Zn, 0.08% Co, 0.09% Mn, 2.91% Al, 32,5% Fe, 1.90% S, and 16.3% Si as the most essential components of the chemical composition. The fayalite (Fe_2SiO_4) and diopside ($CaMgSi_2O_6$) were the main mineral phases in the slag but some oxides, mainly of iron, such as hematite (Fe_2O_3) and magnetite (Fe_3O_4), were also present, as well as some plagioclases, quartz and calcite. The content of pyrite (FeS_2) was relatively low but considerable portions of the non-ferrous metals were present as the relevant sulphides. Copper was present mainly in sulphides (bornite, covellite, and chalcopyrite) but also in oxides and as its elemental form (Cu^0). Zinc was present as the relevant oxide (ZnO) but also in its own elemental form (Zn^0).

The bioleaching of the slags was performed by means of microorganisms related to three different groups on the basis of the optimum temperature for their growth and activity: mesophilic bacteria of the genera *Acidithiobacillus* and *Leptospirillum*, as well as an archaeon related to the genus *Ferroplasma*, all tested at their optimum temperatures of 30–37°C; moderate thermophilic bacteria, with temperature optimum within 50–60°C; and extreme thermophilic archaea, with temperature optimum of 65–80°C but able to grow and active even at higher temperatures.

The comparative experiments for the leaching of the slag were performed in 9K nutrient medium using some components of the slag (ferrous iron and sulphidic sulphur) as energy sources. However, in some experiments, Fe^{2+} (in the form of ferrous sulphate) and sulphur (in its elemental form) were also added as energy sources.

The bioleaching was performed in agitated Erlenmeyer flasks of 300 ml volume each containing 100 ml leach solution inoculated by microorganisms and slag with a particle size of minus 100 microns added in quantities to form pulp densities from 5 to 30%. Aeration by air enriched with CO_2 to 0.10–0.20% was used in some of the tests.

The activity of some microbial strains from the different taxonomic species was increased to some extent by means of consecutive cultivations in the nutrient medium 9K supplied by slag with a step-by-step increasing of the relevant pulp densities.

In some experiments, the leaching of the slag was performed in agitated bioreactors with a volume of 1 L each. Apart from the batch leaching, such bioreactors were also used for performing the continuous-flow leaching.

Elemental analysis of the liquid samples was performed by atomic absorption spectrometry (AAS) and inductively coupled plasma spectrometry (ICP). The isolation, identification, and enumeration of microorganisms were carried by the classical physiological and biochemical tests and by the molecular PCR methods (Karavaiko et al., 1988; Sanz and Köchling, 2007; Escobar et al., 2008).

Results and Discussion

The level of extraction (in % for 48 hours, i.e. until about the end of the logarithmic growth phase) of the non-ferrous metals from the slag by means of mesophilic bacteria at 37°C decreased with the increase of the pulp density from 10 to 25% (Table 1). At the same time, the rates of extraction of these most valuable components of the slag (present in mg.l/h) were increased to some extent. However, the residual contents of the non-ferrous metals in the slag after the leaching were still quite high, especially in the tests with the higher pulp densities.

The levels of extraction of the non-ferrous metals by means of moderate thermophilic bacteria at 55°C also decreased with the increase of the pulp density from 10 to 20% (Table 2). The best results were achieved by means of *Sulfobacillus thermosulphidooxidans* which possessed both ferrous- and sulphur-oxidizing abilities. However, some of the mixed cultures of moderate thermophilic bacteria, especially such consisting of *S. thermosulphidooxidans* and a strain of *Acidithiobacillus caldus* (not able to oxidize Fe^{2+} but possessing sulphur-oxidizing ability), were very efficient, especially at pulp densities of 10 and 15%.

Table 1.
Bioleaching of slag by means of mesophilic bacteria at 37°C

Pulp density	Components	Extraction, % for 24 h	Rate of extraction, mg/l.h
10%	Cu	82	10.59
	Zn	70	15.60
	Co	87	1.14
15%	Cu	73	14.14
	Zn	62	20.73
	Co	80	1.19
20%	Cu	68	17.56
	Zn	55	24.52
	Co	77	1.71
25%	Cu	60	19.36
	Zn	48	26.74
	Co	71	1.97

Note: The results in the table are obtained by means of a mixed culture consisting of *At. ferrooxidans, L. ferrooxidans*, and *At. thiooxidans.*

Table 2.
Bioleaching of slag by means of moderate thermophilic bacteria at 55°C

Microorganisms	Components	Pulp density, %		
		10	15	20
		Extraction, % for 48 h		
Sulfobacillus thermosulphidooxidans	Cu	88	77	71
	Zn	75	68	60
	Co	91	84	78
Alicyclobacillus tolerans	Cu	84	73	70
	Zn	71	64	59
	Co	88	80	75
Sulfobacillus acidiphilus	Cu	82	70	65
	Zn	73	62	56
	Co	85	80	77
Mixed cultures	Cu	80-88	71-79	71-75
	Zn	71-77	62-68	59-62
	Co	82-90	79-84	73-80

The bioleaching of the slag by means of extreme thermophilic archaea at 75 and even at 86°C (Tables 3 and 4), specifically by means of pure cultures of *Sulfolobus metallicus* and of *Metallosphaera sedula*, as well as by means of some mixed cultures of these two species, was the most efficient during this study. It must be noted, however, that similar results were also achieved by means of mixed cultures of these two species but containing representatives of two additional species (*Thermoplasma acidophilum* and *Acidianus infernus*), especially at pulp densities of 10–12%. However, mixed cultures consisting only of *T. acidophilum* and *Ac. infernus* were not so active.

The economic evaluation of the whole treatment process, starting from the grinding of the slag intended for bioleaching to the optimum particle size (usually minus 100 microns), and the selection and adaptation of the most suitable microbial cultures intended for leaching of the real slag under the real optimum conditions, are all essential steps in the development of an efficient industrial-scale process of this type.

Table 3.
Bioleaching of slag by means of moderate thermophilic bacteria at 75°C

Microorganisms	Components	Pulp density, %		
		10	15	20
		Extraction, % for 48 h		
Sulfolobus metalicus	Cu	91	90	82
	Zn	80	79	68
	Co	93	91	87
Metallosphaera sedula	Cu	90	89	80
	Zn	80	77	65
	Co	91	89	86
Acidianus infernus	Cu	86	84	77
	Zn	77	73	64
	Co	88	86	82
Mixed cultures	Cu	87-91	86-92	79-84
	Zn	77-82	78-82	68-71
	Co	87-93	88-91	84-88

Table 4.
Bioleaching of slag by means of extreme thermophilic archaea at 86°C

Microorganisms	Components	Pulp density, %	
		5	10
		Extraction, % for 48 h	
Sulfolobus metalicus	Cu	93	91
	Zn	82	80
	Co	95	91
Metallosphaera sedula	Cu	91	89
	Zn	82	80
	Co	93	90
Thermoplasma acidophilium	Cu	93	90
	Zn	84	81
	Co	93	90
Mixed cultures	Cu	88-95	86-91
	Zn	80-86	78-84
	Co	88-93	90-93

References

Escobar, B., Bustos K., Morales, G., Salazar, O., Rapid and specific detection of *Acidithiobacillus ferrooxidans* and *Leptospirrilim ferrooxidans* by PCR, Hydrometallurgy, 92, 2008. - 102–106.

Georgiev, P. S., Spasova, I. I., Groudeva, V. I., Nikolova, M. V., Lazarova, A. I., Iliev, M., Ilieva, R., Groudev, S. N., Bioleaching of valuable components from a pyrometallurgical final slag, In: Solid State Phenomena, Trans Tech Publications, Swithzerland, vol., 262, 2017. - 696–699.

Kaksonen, A. H., Särkijärvi, S., Puhakka, J. A., Peuraniemi, J., Junnikkala, S., Tuovinen, O. H., Chemical and bacterial leaching of metals from a smelter slag in acid solutions, Hydrometallurgy, 159, 2016. - 46–53.

Karavaiko, G. I., Rossi, G., Agate, A. D., Groudev, S. N., Avakyan, Z. A. (eds.), Biogeotechnology of Metals. Mannual, GKNT Center for International Projects, Moscow, 1988.

Panda, S., Mishra, S., Rao, D. S. Pradhan, N., Mohapatsa, U. B., Angadi, S. K., Mishra B. K., Extraction of copper from copper slag: Mineralogical; insights, physical beneficiation and bioleaching studies, Korean J. Chem. Eng., 32 (4), 2015. - 667–676.

Potysz, A., Kiezczak, J., Fuchs, Y., Grybos, M., Guiband G., Lens, P. N. L., van Hullebush, E. D., Bacterially-mediated weathering of crystalline and amorphous Cu-slags, Applied Geochemistry, 64, 2016. - 92–106.

Sanz, J. L., Köchling, T., Molecular biology techniques used in wastewater treatment: An overview. Process Biochem.42, 2007. - 119–133.

Spasova, I. I., Groudev, S. N., Georgiev, P. S., Nikolova, M. V., Lazarova, A. I., Bioleaching of copper slags by means of different microbial cultures, In: XIV Int. Congress "Machines, Technologies, Materials", Borovetz, Bulgaria, March 15 – 18, 2017. - 57–58.