LEACHING OF VALUABLE METALS FROM COPPER SLAG BY MEANS OF CHEMOLITHOTROPHIC ARCHAEA AND BACTERIA

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ABSTRACT. Copper slag containing 0.62% Cu, 1.07% Zn, 0.08% Co, 32.5% Fe, 1.90% S and 16.3% Si as basic components was subjected to leaching by means of chemolithotrophic microorganisms (bacteria and archaea) in flasks on shaker and agitated reactors. Chemolithotrophs of three different groups based on their optimum temperatures for growth and activity were used: mesophilic bacteria and archaeon Ferroplasma acidiphilium at temperature of 35° C; moderate thermophilic bacteria at 55° C, and the extreme thermophilic archaea at 75° C. The optimum conditions for the leaching (temperature, composition of the leaching solution, particle size, pulp density) were determined. It was found that the archaea leach the slag with higher rates than the bacteria but at relatively lower pulp density (up to 6 – 8 %) and the moderate thermophilic bacteria were more efficient at the higher pulp densities (from 10 – to 20 %).

Key words: copper slag, chemolithotrophs, leaching, valuable metals

ИЗЛУГВАНЕ НА ЦЕННИ МЕТАЛИ ОТ МЕДНА ШЛАКА ЧРЕЗ ХЕМОЛИТОТРОФНИ АРХЕИ И БАКТЕРИИ

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РЕЗЮМЕ. Медна шлака, съдържаща 0.62 % Cu, 1.07 % Zn, 0.08 % Co, 32,5 % Fe, 1.90 % S и 16.3 % Si като основни компонети беше подложена на излугване чрез хемолитотрофни микроорганизми (бактерии и археи) в колби на шейкър и в реактори с механично разбъркване. Хемолитотрофи от три различни групи, основани на техните оптимални температури за растеж и активност бяха използвани: мезофилни бактерии и археона *Ferroplasma acidiphilum* при температура в границите 35 °C; умерено термофилни бактерии при 55 °C, и екстремално термофилни археи при 75 °C. Оптималните условия за излугването (температура, състав на излугващия разтвор, размер на частиците, плътност на пулпа) бяха определени. Установено бе, че археите излугват шлаката с по-високи скорости от бактериите, но при сравнително по-ниска плътност на пулпа (до 6 – 8 %) и умерено термофилните бактерии бяха по-ефикасни при по-високи плътности на пулпа (от 10 до 20 %).

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

Introduction

The pyrometallurgical slags are wastes containing significant quantities of valuable components, mainly non-ferrous metals (such as copper, zinc, cobalt and nickel) but also iron and silicon. At present, the slags are used mainly in the construction of roads and for the preparation of cements of different types. In some cases old slags rich-in-valuable metals are mixed with some other rich-in-metals raw materials and wastes and then subjected again to pyrometallurgical treatments for an economically efficient recovery of different valuable components. At the same time, a large number of investigations are connected with the chemical and/or biological leaching of the slags for extraction of some of their residual valuable components (Genchev and Groudev, 1981; Arslan C. and Arslan F., 2002; Banza et al., 2002; Kaksonen et al., 2011, 2016; Panda et al., 2015). It must be pointed that industrial processing of the slags is directly connected with the environment protection due to removal of different toxic components which during the storage of slags as wastes are subjected to the natural processes of solubilization and migration. Some data about the possibility to leach some valuable and, at the same time, toxic metals from a final copper slag by means of different microorganisms are shown in this paper.

Materials and Methods

The slag used in this study contains 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 bornite (Cu_5FeS_4), covellite (CuS) and chalcopyrite ($CuFeS_2$) 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) and as the sphalerite (ZnS).

A large number of microorganisms were tested in the experiments for microbial leaching of the non-ferrous metals from the slag (Table 1).

Table 1.
Ferrous and sulphur oxidizing abilities of different chemolithotrophic microorganisms used in this study

Microorganisms	Fe^{2+}	S^0
	Maximum oxidation rate, mg/L.h[x]	
Mesophilic bacteria		
Acidithiobacillus ferrooxidans	215 – 464	14 – 53
Acidithiobacillus ferrivorans	231 – 435	12 – 46
Acidithiobacillus thiooxidans	–	18 – 62
Leptospirillum ferrooxidans	190 – 394	–
Ferroplasma acidiphilum[x]	203 – 372	–
Moderate thermophilic bacteria		
Sulfobacillus thermosulphidooxidans	275 – 509	44 – 73
Sulfobacillus acidiphilus	246 – 471	46 – 62
Alicyclobacillus sp.	280 – 495	48 – 73
Alicyclobacillus tolerans	302 – 507	53 – 77
Acidithiobacillus caldus	–	47 – 73
Leptospirillum ferriphilum	305 – 503	–
Acidimicrobium ferrooxidans	291 – 495	–
Acidianus sp.	277 – 401	41 – 60
Extreme thermophilic archaea		
Sulfolobus metallicus	415 – 518	51 – 79
Sulfolobus acidocaldarius	–	59 – 84
Sulfolobus solfataricus	–	77 – 86
Metallosphaera sedula	246 – 471	55 – 77
Acidianus infernus	280 – 495	48 – 71
Thermoplasma acidophilum	321 – 460	51 – 64

Note: The maximum oxidation rate is measured at the end of the exponential growth phase on the relevant substrate (Fe^{2+} or S^0).
The oxidation rate of the mesophilic microorganisms was measured at 35° C; of the moderate thermophilic bacteria at 55° C, and of the extreme thermophilic archaea at 75° C. These temperatures are not the real optimum of each of the microorganisms tested in this study but are close to this optimum for all microorganisms of the relevant group.
[x] – the *Ferroplasma* is a mesophilic archaeon.

Most of these microorganisms were acidophilic chemolithotrophs possessing the ability to oxidize the ferrous iron and/or the low-valence form of sulphur (the sulphidic) and its zero-valence elemental form (S^0). These microorganisms were related to three different groups on the basis of the optimum temperature for their growth and activity: mesophilic bacteria, with temperature optimum at 30 – 37° C; moderate thermophilic bacteria, with a temperature optimum at 50 – 60° C, and extremely thermophilic archaea, with a temperature optimum within the range of about 65 – 86° C. In these comparative experiments each of the different microbial species was present by 3 – 7 different strains, at least. The experiments of this type were performed by the shake-flask technique using Erlenmeyer flasks of 300 ml volume containing 100 ml of 9K nutrient medium (Silverman and Lundgren, 1959) with different quantities of slag. Fe^{2+} (added as ferrous sulphate) and/or elemental sulphur (S^0) were used as potential sources of energy for the chemolithotrophs. For the cultivation of archaea, yeast extract (0.5 g in 100 ml nutrient 9K medium) was added.

The comparative experiments for the ability of the different microorganisms to leach the slag were carried out at 35, 55 and 75° C for the mesophilic, moderate thermophilic and extreme thermophilic species, respectively. The effect of the most essential environmental factors, apart from the temperature, was studied with more active strains as follows: pH within the values from 1.0 to 3.7, particle size of the slag - minus 100 and minus 200 microns, pulp density of the slag in the leach solution - from 5 to 20 %, aeration by air enriched with CO_2 to 0.10 – 0.20 %.

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

In some experiments the combined chemico-biological leaching of the slag was performed in agitated bioreactors with a volume of 1 L each. Apart from the batch leaching, such bioreactors were used also for performing the continuous-flow leaching. Such leaching was performed not only in a single bioreactor but also in a two-step system consisting of two connected reactors. In the first reactor the initial acidification of the slag was performed by adding sulphuric acid to the relevant pH levels which were optimal for the growth and activity of the microorganisms acting in the second bioreactor.

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

It was found that many of the microbial strains used in this study, even some related to one and the same taxonomic species, differed considerably from each other with respect to their ability to leach the heavy metals from the slag (Table 2).

Very active strains from the three temperature groups mentioned above were found. It must be noted, however, that the most efficient extractions of the non-ferrous metals and iron from the slag were achieved by means of microorganisms possessing both ferrous and sulphur oxidizing abilities (Table 1 and 2).

Table 2.
Batch leaching of non-ferrous metals from the slag by means of different microorganisms [x]

Microorganisms	Cu	Zn	Co
	Extraction, %		
Mesophiles at 35 °C			
At. ferrooxidans	82	86	90
At. ferrivorans	77	80	86
At. thiooxidans	37	41	46

L. ferrooxidans	68	73	80
F. acidophilum[x]	64	68	71
Mixed cultures	80 – 84	82 – 89	84 – 92
Moderate themophilic bacteria at 55 °C			
S. thermosulphidooxidans	88	86	93
S. acidophilus	84	81	88
Alicyclobacillus sp.	88	83	91
At. caldus	47	53	56
L. ferriphilum	80	84	88
Ac. ferrooxidans	78	84	86
Acidianus sp.	50	62	68
Mixed cultures	82 – 88	84 – 91	88 – 94
Extreme thermophilic archaea at 75 °C			
S. metallicus	89	87	93
S. acidocaldarius	53	60	64
M. sedula	88	87	93
Ac. infernus	80	85	87
T. acidophilium	77	82	85
Mixed cultures	84 – 93	84 – 90	87 – 95

Note: The most active strains from each species were used in these experiments.

However, even microorganisms possessing the ability to oxidize only the Fe^{2+} (such as the species related to the genera *Leptospirillum, Acidimicrobium* and *Ferroplasma*), as well as microorganisms able to oxidize only the sulphur but not the ferrous iron (such as *Acidithiobacillus thiooxidans* and some species of the genera *Sulfolobus*, such as *S. acidocaldarius* and *S. solfataricus*) were able to leach the slag. It must be noted, however, that the leaching by these microorganisms was not so efficient and the extractions of the non-ferrous metals were similar to these obtained by means of the chemical leaching of the slag with sulphuric acid and ferric ions (Table 3).

Table 3.
Chemical batch leaching of the slag

Leaching system	Cu	Zn	Co
	Extraction, %		
H_2SO_4 (pH 2.0) at 35° C	35	32	44
H_2SO_4 (pH 2.0) at 55° C	42	40	48
H_2SO_4 (pH 2.0) at 75° C	46	44	57
H_2SO_4 + Fe^{3+} (10 g/l); pH 2.0, 35° C	48	46	55
H_2SO_4 + Fe^{3+} (10 g/l); pH 2.0, 55° C	53	50	64
H_2SO_4 + Fe^{3+} (10 g/l); pH 2.0, 75° C	61	59	68

Note: The leaching was performed at initial pulp density of 10 % and Fe^{3+} concentration of 10 g/l; pH was maintained at 2.0 by addition of H_2SO_4. The total concentration of dissolved iron increased during the leaching but the concentration of Fe^{3+} decreased. Duration of leaching 48 hours.

The highest rates of extraction of the non-ferrous metals and iron were achieved by means of some archaea but at relatively low pulp densities (5 – 10 %). It must be noted that the preliminary adaptation of most microbial strains to the slag used in this study increased to some extent the rates and efficiency of leaching. However, in most cases the increase was different at the different strains, even at such related to one and the same taxonomic species.

In any case, the most efficient bioleaching of slag was possible only by means of microorganisms possessing ferrous iron oxidizing ability. These microorganisms oxidized the ferrous ions solubilized from the slag during the leaching to the ferric ions. The ferric ions are efficient oxidizers of most sulphide minerals, including those present in the slag. However, it is essential to be noted that the role of these microorganisms in the leaching of slag was not connected only with the generation of ferric ions *in situ*. Some of these microorganisms, more especially the ones possessing also sulphur-oxidizing ability, were able to oxidize the sulphide minerals in the slag directly, i.e. without the presence of soluble iron ions. This was demonstrated by the fact that the strains of *At. ferrooxidans* possessing both ferrous and sulphur oxidizing abilities were able to leach the slag in the absence of iron ions introduced to the system from outer source at much higher rates than strains of *Leptospirillum ferrooxidans* possessing higher ferrous oxidizing ability but not able to oxidize sulphur in different forms (elemental or sulphidic in some iron-free sulphides such as covellite and chalcocite). This was also demonstrated by the fact that the strains of *At. ferrooxidans* possessing both ferrous and sulphur oxidizing abilities oxidized the slag at higher rates than strains of *L. ferrooxidans* which were able to oxidize the Fe^{2+} at higher rates than *At. ferrooxidans* but not any form of the sulphur in the absence of iron.

The bioleaching of slag under continuous-flow conditions was also very efficient (Table 4 and 5).

Table 4.
Continuous-flow leaching of the slag by means of moderate thermophilic bacteria

Component	Pulp density, %			
	5	10	15	20
	Extraction, %			
Cu	90.7	88.2	84.0	82.4
Zn	88.4	86.0	82.4	80.8
Co	95.0	90.7	88.4	86.8
Fe	52.1	50.5	48.8	47.0
Mn	92.9	90.1	89.4	88.0
Al	58.1	56.5	55.0	53.8

Table 5.
Continuous-flow leaching of the slag by means of archaea

Component	Pulp density, %			
	5	10	15	20
	Extraction, %			
Cu	91.4	87.5	79.0	70.1
Zn	89.4	84.0	76.1	68.0
Co	97.0	89.4	80.2	73.0
Fe	53.0	49.8	44.0	40.4
Mn	93.7	87.3	82.0	77.0
Al	59.0	56.0	51.9	49.5

The pH was maintained at about 1.8 – 2.0 by addition of sulphuric acid. It must be noted, however, that the leaching by some mesophiles and by some moderate thermophilic bacteria at pH 3.0 – 3.5 was also very promising since it was connected with high extractions of the non-ferrous metals but at much lower acid consumption (about 576 g H_2SO_4/kg slag for pH 3.50 versus about 800 g H_2SO_4/kg slag for pH 1.80 – 1.90.

Furthermore, the solubilization of fayalite at pH 3.0 – 3.5 was much lower which resulted in the production of pregnant solutions suitable for processing and recovery of the dissolved non-ferrous metals.

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This article was reviewed by Assoc. Prof. Dr. Dimitar Mochev and Assist. Prof. Dr. Mihail Iliev.