BIOLEACHING OF COPPER SLAGS BY MEANS OF DIFFERENT MICROBIAL CULTURES

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Abstract: *Copper final slags containing 0.62 % Cu, 1.07 % Zn, 0.08 % Co and 32.5 % Fe as the most essential components were subjected to chemical (by means of sulphuric acid and ferric ions) and biological leaching by means of chemolithotrophic microorganisms of three different types: mesophilic and moderate thermophilic bacteria and extreme thermophilic archaea, with temperature optimum at 37, 55 and 75 degrees Celsius, respectively. The leaching was carried out by the shake-flask technique and in agitated bioreactors. 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 %). The moderate thermophilic bacteria were the most efficient for the leaching at a higher pulp density (within 15 – 20 %).*

Keywords: COPPER SLAGS, CHEMICAL AND BIOLOGICAL LEACHING, NON-FERROUS METALS

1. Introduction

The pyrometallurgical slags, mainly from the copper recovery, 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 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 are subjected again to pyrometallurgical treatment for an economically attractive recovery of different valuable components. At the same time, a large number of investigations are connected with the chemical and/or the biological leaching of 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). It must be noted that the industrial processing of the slags is directly connected with the protection of environment due to the removal of different toxic components which during their storage 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 final copper slags by means of different microorganisms are shown in this paper.

2. Materials and Methods

The slag sample used in this study contained 0.62 % Cu, 1.07 % Zn, 0.08 % Co, 1.90 % S, 32.5 % Fe and 16.3 % Si as the most essential components of its chemical composition. The fayalite (Fe_2SiO_4) and diopside ($CaMgSi_2O_6$) were the main mineral phases in the slags 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, covellite and chalcopyrite but also in oxides. Zinc was present mainly as the relevant oxide but also in its own elemental form (Zn^o) 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. 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. These microorganisms were related to three different groups on the basis of the optimum temperature for their growth and activity: mesophilic bacteria, mainly of the species *Acidithiobacillus ferrooxidans*, *Leptospirillum ferrooxdians* and *Acidithiobacillus thiooxidans*, with a temperature optimum at 32 – 37 ^oC; moderate thermophilic bacteria, mainly of the species *Sulfobacillus thermosulphidooxidans* and *Acidithiobacillus caldus*, with a temperature optimum at 50 – 60 ^oC, and extremely thermophilic archaea, mainly of the species *Sulfobacillus metallicus* and some strains related to the genera *Acidianus* and *Metalosphaera* with a temperature optimum within the range of 65 – 86^{o}C. In these comparative experiments each of the different microbial species mentioned above was presented by 5 – 7 different strains, at least. The experiments of this type initially were performed by the shake-flask technique using Erlenmeyer flasks of 500 ml volume containing 100 ml of 9K nutrient medium with 10 g slag with a particle size minus 100 microns. The cultivation was carried out at 35, 55 or 70^{o}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 the more active strains as follows: pH within the values from 1.0 to 3.7, pulp density – 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 species was increased to different extents by means of consecutive cultivations in the medium 9K supplied by slags with a step-by-step increasing of the relevant pulp density.

In some experiments the combined chemico-biological leaching of the slags 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 slags was performed by adding sulphuric acid to the relevant pH levels which was the optimal for the growth and activity of the microorganisms acting in the second (bio)reactor.

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

3. Results and Discussion

It was found that some 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 slags (Table 1 and 2).

Very active strains from the three temperature groups mentioned above were established. 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 strains to the slags used in this study increased to some extend 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.

Table 1. *Leaching of non-ferrous metals from the slags by means of mesophilic bacteria*

Leaching agents	Cu	Zn	Co
	Extraction, %		
Acidithiobacillus ferrooxidans	71 – 88	75 – 90	70 – 92
Leptospirillum ferrooxidans	55 – 69	60 – 75	64 – 80
Acidithiobacillus thiooxidans	32 – 35	29 – 37	35 - 41
At. ferrooxidans + At. thiooxidans	73 – 92	77 – 91	73 - 95
L. ferrooxidans + At. Thiooxidans	68 - 84	64 - 80	68 - 88
Chemical leaching:			
H_2SO_4 (pH 2.0)	35	37	44
$H_2SO_4 + Fe^{3+}$ (10 g/l at pH 2.0)	51	59	62

The biological and chemical leaching were carried out in agitated reactors at 37°C and pH 2.0 maintained by addition of sulphuric acid. Pulp density 10% in 9K nutrient medium with slags with a particle size minus 100 microns. Duration of leaching 72 hours.

Table 2. *Leaching of non-ferrous metals from the slags by means of moderate thermopilic bacteria and extreme thermophilic arhaea*

Leaching agents	Cu	Zn	Co
	Extraction, %		
Sulfobacillus thermosulphidooxidans	75 - 91	79 – 93	71 – 95
Acidithiobacillus caldus	39 – 47	37 – 49	41 – 50
S.thermosulphidooxidans + At. caldus	77 – 91	76 – 95	73 – 95
Sulfobacillus metallicus	77 – 93	78 – 93	73 – 95
Acidianus sp.	71 - 91	75 - 88	70 - 91
Chemical leaching:			
H_2SO_4 (pH 2.0)	41	46	48
$H_2SO_4 + Fe^{3+}$ (10 g/l at pH 2.0)	57	62	66

The biological and chemical leaching were carried out in agitated reactors at 37°C and pH 2.0 with the moderate thermophilic bacteria (Sulfobacillus thermosulphidooxidans and At. caldus) and 75°C and pH 2.0 with the extreme thermophilic archaea Sulfobacillus metallicus and Acidianus sp.). Pulp density 10% in 9K nutrient medium with slags with a particle size minus 100 microns. Duration of leaching 48 hours.

The addition of yeast extract to the nutrient medium 9K used for the cultivation of archaea usually increased the growth rate, and to some extent, their oxidation rates but in most cases the level of the increase was different. A positive effect of this type was observed also with some strains of the moderate thermophilic bacteria. Some strains of these bacteria were the most efficient for the leaching of slags at higher pulp density (especially of 15 – 20%). However, leaching by some mesophiles at pH 3.0 – 3.5 was very attractive since it was connected with high extractions of the non-ferrous heavy metals, much lower acid consumption and low solubilization of fayalite which resulted in the production of pregnant solutions suitable for the recovery of the dissolved non-ferrous metals.

In any case, the efficient bioleaching of slags was possible only by microorganism possessing ferrous iron oxidizing ability. These microorganisms, such as *Acidithiobacillus ferrooxidans*, *Sulfobacillus thermosulphidooxidans* and *Sulfolobus metallicus*, oxidized the ferrous ions solubilized from the slags during the leaching to the ferric ions. The ferric ions are efficient oxidizers of the most sulphide minerals, including of these present in the slags. However, it is essential to be noted that the role of these microorganisms in the leaching of these slags is not connected only with the generation of ferric ions *in situ*. Some of these microorganisms, such as the three species mentioned above, possessed also sulphur-oxidizing ability and were able to oxidize the sulphide minerals in the slags directly, i.e. without the presence of soluble iron ions. This was demonstrated by the fact that strains of *At. ferrooxidans* possessing both ferrous and sulphur oxidizing abilities were able to leach the slags in the absence of iron ions introduced to the system from outside at much higher rate 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 strains of *At. ferrooxidans* possessing both ferrous and sulphur oxidizing abilities oxidized the slags at higher rates than strains of *L. ferrooxidans* which were able to oxidize the Fe^{2+} but not only any form of the sulphur in the absence of iron.

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