BACTERIAL LEACHING OF COMPLEX SULPHIDES FROM MINE TAILINGS ALTERED BY ACID DRAINAGE

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ABSTRACT

The laid down tailings accumulated during more than 40 year operation of the Gecamine's concentrator at Kipushi, Democratic Republic of Congo present nowadays a reprocessing challenge with both economic and environmental implications. An experimental study aimed at re-flotation of this material to bring sulphide concentrate suitable for further processing by hydrometallurgical means has been realized. The results from a bioleaching route chosen to accomplish the later task by use of moderate thermophilic and mesophilic microorganisms are reported. It has been found that due to the complexity of the treated material, the leaching pattern of the two principal metals of interest, copper and zinc vary. Whilst the copper bearing minerals have been leached relatively fast by direct mechanism, the leaching kinetics for the zinc minerals has been moderate involving predominantly an indirect mechanism. The effects of pH and temperature variations and ferrous ions addition upon the extent of copper and zinc dissolution have been examined. The presence of ferrous ions has been found beneficial for the leaching of sphalerite, however the concomitant formation of jarosite precipitates has led to copper leaching hindrance. Similarly, the rapid zinc solubilisation has been counterbalanced by decrease in rate of copper dissolution. It has been found that the increased leach temperatures associated with use of moderately thermophilic microorganisms, have limited the passivation phenomena and have brought better extraction especially for zinc.

INTRODUCTION

It is acknowledged fact that nowadays some concentrators are opting for re-processing of their stocked tailings with the aim to recover certain metals of interest. This is due both to the high prices of metal commodities and to the increased environmental concern. The Kipushi concentrator in the Democratic Republic of Congo is one such plant having deposited about 37 million tonnes of sulphide tailings during its 40 year operation. It is estimated that about 127,000 tones of copper and 880000 tones of zinc, an amount quite appreciable to be neglected, are contained in the already ground tailings material [Kitobo *et al.*, 2007]. Mineralogical studies have revealed that large proportion of the copper and zinc bearing minerals are found as fine inclusions and intergrowths with pyrite and as associations with the dolomitic gangue. Fine re-grinding followed by selective flotation is not a justifiable option for this material due to the high associated costs. Hence the challenge is to efficiently recover zinc and copper without significant added capital cost.

Bioleaching effectively competes with the classical hydro and pyro metallurgical techniques at certain instances when treatment sulphide bearing mineral ores and tailings is concerned [1, 5; 6; 12, 15, 19, Pina *et al.*, 2004;, Ndlovu; 2007,]. The generic principles of the bioleaching have been outlined in several excellent reviews [4, 8, 14, 17] and although there are still gaps in knowledge regarding the intrinsic mechanisms involved, it is believed that there are two principal routes under which metals are dissolved by bacterial systems. The first one, known as indirect route is based on the capacity of certain strain (under the generic name *ferrooxydans*) to oxidize and regenerate the ferrous to ferric iron according to reaction 1 bellow. The metal sulphides are subsequently chemically leached by the ferric sulphate following the pattern of reaction (2).

$$2FeSO_4 + H_2SO_4 + \frac{1}{2} O_2 \rightarrow Fe_2 (SO_4)_3 + H_2O \quad (1)$$
$$MS + Fe_2 (SO_4)_3 \rightarrow MSO_4 + FeSO_4 + S^0 \quad (2)$$

The second mechanism supposes a catalytic oxidation of the sulphides through direct bacterial contact in the presence of sulphuric acid, in a manner shown by reactions 3 and 4.

$$MS + \frac{1}{2} O_2 + H_2SO_4 \rightarrow MSO_4 + H_2O + S^0 \quad (3)$$
$$S + 3/2O_2 + H_20 \rightarrow H_2SO_4 \quad (4)$$

It is also accepted that leaching is often controlled by the products from the reactions such as elemental sulphur, which when deposited on the mineral surfaces could form coatings or layers restricting the access of the ferric ions onto mineral surfaces.

According to their operational temperatures, the cultures employed in mineral biotechnology have been grouped as follows:

- Mesophylic bacteria operating at low to moderate temperatures (30 – 45°C) from the species *Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans, Leptospirillum ferrooxidans* (thermo tolerant up to 50°C) and *Acidithiobacillus caldus;*
- Moderate thermophilic bacteria that thrive at 50 – 55°C, from the species *Thiobacillus caldus, Sulfobacillus* (strains known to resists up to 63°C), *Sulfobacillus thermosulfidooxydans, Sulfobacillus acidophilus* and *Acidimicrobium;*
- Extreme thermophilic archaea operating in the range 60 - 85°C from the species *Sulfolobus* (*sulfolobus metallicus, Sulfolobus acidocaldarius*) and *Acidianus brierleyi.*

Among the above noted groups, the mesophilic bacteria have been the strains with the dominating industrial significance [3]. Nevertheless recent work with higher temperature systems have suggested improved leaching kinetics, one such development being the BIOCOP™ process [2; 10]. Some bioleach technology companies claim to poses improved strains in the face of consortium of micro organisms that are best suited for specific applications. Apart from knowledge of microbiology, the technical knowledge of important operational aspects such as pH, temperature and control over goethite or jarosite formation is required for maintaining optimal technological conditions for the bioleaching [2; 9].

The objective of the present study is to determine the most important parameters for the bio-solubilisation of copper and zinc sulphides (bornite, chalcocite, chalcopyrite and sphalerite) from the tailings of Kipushi, comparing for this task the leaching ability of mesophilic and thermophilic bacterial cultures. Moreover, since the surfaces of the studied minerals are partly altered due to effects in tailings pond similar to these of acid drainage, one should expect significant mineralogical changes leading to different leaching behaviour to that known for non-altered sulphides.

MATERIALS AND METHODS

Sulphide Flotation Concentrate

The concentrate which has been subjected to bioleaching has been obtained by bulk collective flotation of the tailings using a classical flotation flow-sheet with potassium amyl xanthogenate (dosage 150-175 g/t) as collector and Dowfroth 200 (30-40 g/t) as frother. The objective of the re-flotation has been to concentrate the economically extractable metals and to reduce the amount of carbonates in the material prior to leaching in a way to prevent high consumption of lixiviant. The chemical composition of the flotation concentrate and the principle minerals as indicated by XRD analysis are presented in Table 1.

Table 1: Chemical and mineralogical characteristics of the bulk flotation concentrate subjected to bio-leaching

Element	**Content (%)**	**Principal minerals**
Zn	19	Sphalerite, smithsonite,
Fe	11	Pyrite, arsenopyrite, chalcopyrite, goethite
Cu	3.3	Chalcopyrite, chalcocite, bornite, covelite
Pb	0.35	Galena
Ga	1.5	Gallite
Ag	0.016	Tenantite, tetrahedrite
As	2.4	Arsenopyrite, tenantite
S	16	-
SiO2	5.4	Quartz
MgO	10.8	Dolomite
CaO	1.8	Dolomite

The particle size distribution analysis of the material has suggested an extremely fine granulometry, with 87% of material below 38 μm, 72% below 20μm and 61% below 10 μm. The examination of several polished sections from the flotation concentrate (fraction +20 μm) has indicated that copper minerals are more associated with pyrite and dolomite – a micrograph illustrating this aspect being shown in Figure 1. It could be noted that intergrowths are very limited in distribution and the largest number of minerals especially the sphalerite are well liberated.

Figure 1: General view of a sector with normal distribution of ore particles in bulk flotation concentrate (fraction +20 μm). Pyrite (white), chalcopyrite (pale yellow), covellite (blue), bornite (brown) and sphalerite (grey). *Refl. Light (x 50)*

Microorganisms

Two different bacterial strains have been tested. The first group has been those of the mesophilic bacteria representing different species from (the genus *Bacillus)* (*Acidithiobacillus ferrooxidans, Leptospirillum ferrooxidans, Acidithiobacillus thiooxidans.)*. The cultivation for that consortium has been carried out in 250 cm^3 Erlenmeyer flasks containing 80 cm^3 9K nutrient medium and 20 cm^3 late-log-phase bacterial inoculum. The flasks have been agitated on an orbital shaker at 120 rpm at 35°C for 72 hours. The cultures have been continuously adapted on metal bearing mineral materials and have shown to be well tolerant in presence of high concentrations of copper and zinc. Moderate thermophilic species from the genus *Sulfobacillus thermosulfidooxydans* have been studied as a second group. These bacteria have been grown on a nutrient media with the following composition (g/L): ($FeSO_4$ x $7H_2O$) – 44.2, $(NH_4)_2SO_4$ – 0.4, $MgSO_4$ x $7H_2O$ – 0.4, K_2HPO_4 – 0.4, pH 2. The flasks have been agitated on an orbital shaker at 120 rpm and 50° C for one week.

Leaching

The bacterial leaching experiments have been carried out in a batch wise manner utilising 250 cm^3 Erlenmeyer flasks containing 95 cm^3 of inoculated culture and nutrient media plus a pre-determined mass of concentrate added to reach 1% pulp density. In order to stabilise the pH during the leaching stage, the gangue and the oxidized matter have been neutralised at the beginning by acid washing using H_2SO_4 4M. The leaching temperature when moderate thermophiles were used has been maintained at 55 ± 2°C and at 33 ± 2°C respectively for the leaching with mesophilic bacteria. The flasks have been placed on an orbital shaker and agitated at 120 rpm. Distilled water has been added to compensate for the evaporation losses and for the samples taken for analysis. Control experiments of acid leach without bacteria but with addition of thymol at 5% V instead have been done for comparative purposes. The effect of pH variation between 1.5 and 1.9 has been investigated upon the degree of copper and zinc extraction for the both thermophilic and mesophilic leaching systems, while the effect of Fe^{2+} ions addition has been examined for the case of mesophilic microorganisms only. The latter is based on the assumption that the higher temperatures do stimulate the provision of soluble iron by preventing the generation of jarosite-type precipitates.

Chemical Analysis

Copper and zinc in the leach solutions have been analyzed by atomic adsorption spectrometer (AAS Perkin Elmer) following filtration of the samples. Total iron and K^+ have been also determined using AAS in order to get idea about the degree of jarosite precipitation in solution [2, 13]. The later aspects however have not been discussed in the course of present paper.

RESULTS AND DISCUSIONS

Effect of pH

The results concerning the effect of pH on the recovery of zinc and copper as function of the leaching time are depicted in Figures 2 and 3 for the mesophilic and for the moderate thermophilic bacteria respectively. It could be noted that variation of pH within the range studied does not have profound influence upon the degree of metals extraction in the pregnant leach solutions (PLS). The studied pH zone between 1.5 and 1.9 seems to be an optimal one for our system, a fact which is in line with findings of other authors having observed reduced sulphur oxidation by bacteria when pH was dropped below 1.4 [2; 13]. On the other hand, at pH higher than 2, ferric (III) precipitates start to form leading ultimately to grains passivation and inhibition of mineral dissolution. In our case, owing to the fact that leaching is carried out in sulphate media and that calcite and dolomite are present in the concentrate, precipitation of gypsum ($CaSO_4 x2H_2O$) could be expected. This effect should however not be viewed as a technological obstacle since gypsum possesses porous structure and hence should not block the leaching reactions [18]. Data in Figure 2 is showing that when mesophilic bacteria were used, the leaching kinetics for copper attains its maximum within 10 – 15 days and that copper kinetics is better than that for zinc. Similar behaviour could be postulated when moderate thermophilic strains have been used. It should be noted however, that whilst copper recovery has been nearly similar for the both type of bacterial cultures (80 – 83%), the use of high temperature system has brought almost 96% zinc recovery. Possible explanation of this phenomenon could be the accelerated kinetics of the principal biolixiviation reaction for the ZnS at higher temperatures, as shown below:

$$ZnS + Fe^{3+} \rightarrow Zn^{2+} + Fe^{2+} + S^0 \quad (5)$$

For the both studied systems the best extractions have been noted at pH 1.7. When comparing the control systems (i.e., pure chemical leaching) with the bacterial ones, it could be seen that some part of the metals has been leached very fast, within the first 24 hours. That amount could be estimated as 30 - 35% of the total copper and about 12 – 15% of the zinc. Since the concentrate under study is a mixed one, the chemically leached metals reporting in the solution could be part either of the oxidized minerals or of the altered sulphides. At closer look at the results shown in Figure 2 slight diminution of copper recovery in the PLS after certain time could be seen, accompanied by concomitant rise in zinc solubilisation. This could be explained by galvanic interaction effects between dissolved copper and ZnS similar to those known from the practice of sphalerite activation in flotation.

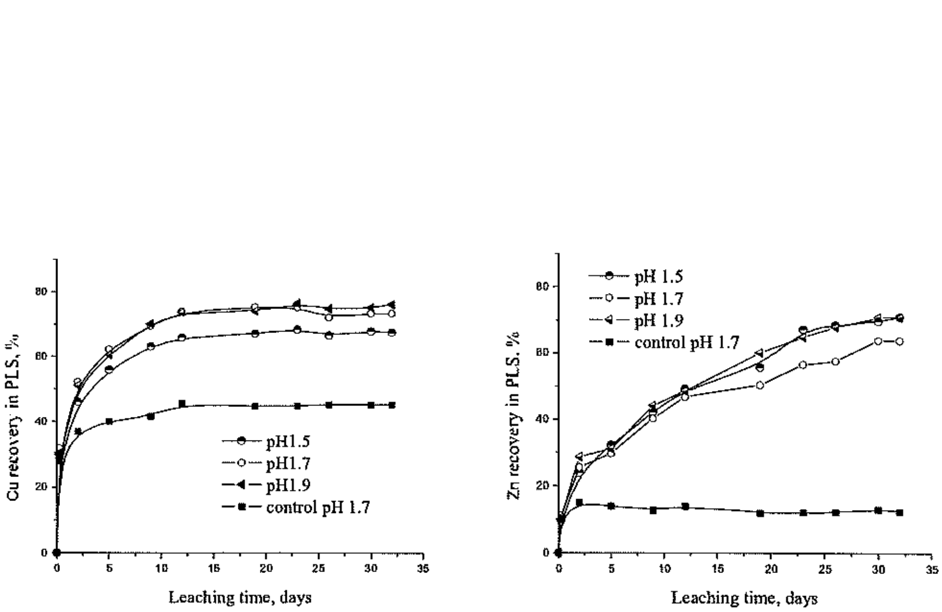

Figure 2: Influence of pH upon copper (left) and zinc (right) extraction in pregnant leach solution (mesophilic bacteria, 33°C)

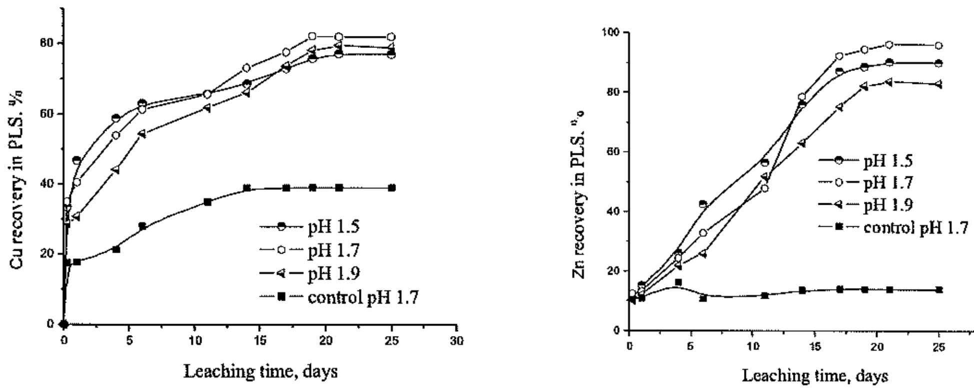

Figure 3: Influence of pH upon copper (left) and zinc (right) extraction in pregnant leach solution (moderate thermophilic bacteria, 55°C)

Effect of Ferrous (II) Ions Addition

The presence of ferrous ions is an indispensable factor when bioleaching of sulphides via indirect route is concerned. Normally this amount is supplied through the leaching of pyrite, but in the material under study large proportion of pyrite has already being leached by acid drainage. The acid leach tests (controls) have shown that the dissolution of goethite alone could bring about 0.3 – 0.5 g/L of ferrous ions in the leach system. This concentration seems fairly insufficient for guarantying complete zinc solubilization owing to the concentration of zinc in the concentrate. Hence with the aim of improved leaching kinetics of zinc when mesophilic bacteria were used, ferrous ions have been added in concentrations of 2.5 and 5 g/L. The pulp pH has not been adjusted but pH values have been found to vary between 1.45 and 1.9 at the different tests. The results of these experimental trials are depicted in Figure 4. The immediate impression is that the addition of ferrous ions does favour zinc dissolution but this is accomplished on the expense of copper dissolution which decreases.

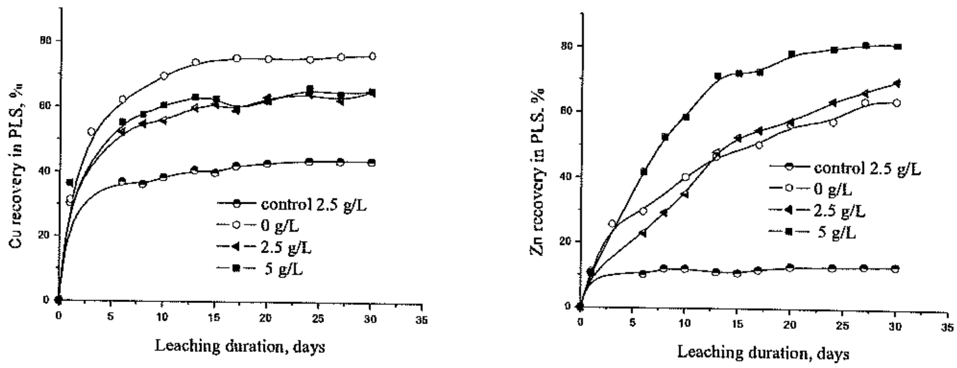

Figure 4: Influence of Fe (II) addition upon copper (left) and zinc (right) extraction in pregnant leach solution (mesophilic bacteria, 33°C, pH 1.7)

These observations confirm the results obtained by other authors [Rodriguez *et al.,* 2004; 10] who have postulated that the bioleaching of sphalerite is realized predominately via an indirect mechanism under the action of Fe^{3+} coming from the bacterial regeneration of Fe^{2+} ions. The diffusion of Fe^{3+} ions towards the mineral surface is determined according to Fick's law, by their concentration in solution. The exact patterns of sphalerite leaching are still uncertain but it is sure that the intermediate products which are formed at the surface also play role. On the other hand, there are evidences that the secondary copper sulphides (CuS, Cu_2S, etc.) are easily oxidized by direct bacterial action. It is logically to assume that, the addition of Fe^{2+} ions in the leach system has favourable effect on the indirect leaching route, but do inhibit the direct one.

CONCLUSIONS

Based on the results obtained from the performed study the following conclusions could be summarized.

The oxides and the altered sulphides are the mineral components to be firstly leached possibly via pure chemical way in the course of bioleaching of concentrate coming from re-flotation of laid sulphide tailings with complex mineralogy. Pulp pH variation between 1.5 and 2 does not influence significantly the rate of extraction of copper and zinc in the pregnant leach solution. It could be argued, that copper minerals are leached via direct mechanism characterised by fast kinetics, while an indirect route could be assumed for the sphalerite being the main zinc bearing mineral.

The use of moderate thermophilic bacteria at 55°C is limiting the passivation effects and as consequence, recoveries of about 80% for copper and 96% for zinc have been reached – Figure 3. At ambient temperatures (the case of mesophilic bacteria); the addition of ferrous ions has a favourable effect on the efficiency of zinc dissolution but has a negative one on copper extraction.

Being preliminary the study does not permit conclusions of universal character. A detailed experimental program is underway at present to reveal some of the hypothesis presented. A focus upon kinetic aspects at higher pulp densities and on characterisation of jarosite precipitates is envisaged.

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