Available online at www.sciencedirect.com
SCIENCE DIRECT®
Minerals Engineering 18 (2005) 549–551
MINERALS ENGINEERING
This article is also available online at:
www.elsevier.com/locate/mineng

The effect of ferrous and ferric iron on sphalerite bioleaching with *Acidithiobacillus sp.*

P.S. Pina [a], V.A. Leão [a,*], C.A. Silva [a], D. Daman [a], J. Frenay [b]

[a] *Universidade Federal de Ouro Preto—Praça Tiradentes 20, Ouro Preto, MG, 35400-000, Brazil.*
[b] *Université de Liège—Chemain des Chevreuils, 1—Bât. 52, Liège 4000, Belgique.*

Received 12 May 2004; accepted 13 August 2004

Abstract

Bioleaching has gained increased interest as an alternative for processing zinc sulfide ores without the generation of SO_2. The bioleaching of sphalerite with mesophile microorganisms at 1% pulp density has been studied. Batch experiments were carried out at 34 °C and 200 rpm. The effects of pH, concentration of Fe(II), as well as the presence of Fe(III) in the zinc extraction were assessed. Fast zinc dissolution can be achieved working with *Acidithiobacillus sp*. The best pH for bioleaching is in the 1.75–2.00 range and the presence of Fe(III) has a strong influence in zinc extraction, increasing the rate of dissolution and does not adversely affect the growth of the *Acidithiobacillus* population.

Keywords: Bioleaching; Biooxidation; Sulphide ores

1. Introduction

Bioleaching may be applied as an alternative to increase zinc production without the consequent production of SO_2. In the process, acidophilic microorganisms oxidize ferrous iron, elemental and reduced forms of sulfur. This technique has been successfully applied in the treatment of refractory gold ores, in copper production from tailings and low grade ores, in uranium production and also in the processing of other sulfide ores (Nemati et al., 1998).

Since Fe(III) is available from the processing of zinc during the "acid" leaching of ZnO, this work studies the effect of ferric iron in the bioleaching of ZnS. High concentrations of Fe(III) are considered detrimental to the development of *Acidithiobacillus sp*. (Kawabe et al., 2003). It has been also proposed that Fe(III) contents over 1 g/L results in the reduction of zinc extraction. This was credited to the formation of jarosite on the mineral surface which caused a negative effect on both bacterial growth and zinc sulfide leaching (Konishi et al., 1992).

This work presents the results of the bioleaching of ZnS with mesophile microorganisms at 1% pulp density. The results show that fast zinc dissolution can be achieved working with *Acidithiobacillus sp*. The presence of Fe(III) has a strong effect in the initial zinc bioleaching, increasing the rate of dissolution and not adversely affecting the growth of the *Acidithiobacillus* population, as it has been previously stated.

2. Experimental

The microorganism studied was isolated from a brazilian zinc sulfide mine (Daman et al., 2002). A sterilized medium was used as a substrate for bacterial growth. Its composition: $(NH_4)_2SO_4$: 0.2 g/L; $MgSO_4{\cdot}7H_2O$: 0.4 g/L,

* Corresponding author. Tel./fax: +55 31 3559 1596.
E-mail address: versiane@demet.em.ufop.br (V.A. Leão).

0892-6875/$ - see front matter
doi:10.1016/j.mineng.2004.08.011

K_2HPO_4: 0.1 g/L, iron (II) ($FeSO_4 \cdot 7H_2O$, *Synth*) and distilled water, at pH 1.8–2.0. The microorganism population was assessed by direct counting in a Neubauer chamber placed in a phase contrast microscopy.

The sphalerite concentrate studied has a particle size 100% minus 45 μm. Its main elements are: Zn (48.13%), S (31.02%) and Fe (12.12%). X-rays diffraction indicated the presence of mainly sphalerite in the sample.

Bioleaching experiments were carried out in 250 mL erlenmeyers, containing 100 mL of solution and 1 g of sphalerite, using an orbital shaker at 200 rpm and 34 °C. The systems were inoculated with a 10 mL suspension containing cells previously cultured in sphalerite. In all experiments, the initial bacterial population was 40×10^6 cell/mL. The pH was kept constant during the experiments by addition of concentrated sulfuric acid (1 mol/L) or sodium hydroxide (6 mol/L). Evaporation losses were compensated by the addition of distilled water. Sterile controls were also run in a thymol solution.

Total iron (Fe_T) and zinc concentration in suspension were analyzed by atomic absorption spectrofotometry. Fe(II) solution concentrations were determined regularly by titration with potassium dichromate. Eh's, against an Ag/AgCl electrode, and pH were measured on a daily basis.

3. Results and discussion

Initially, the effect of pH over the sphalerite leaching was studied in a medium containing 4 g/L as initial Fe(II) concentration. Fig. 1 shows that the best pH for ZnS dissolution is on the 1.75–2.00 range. Zinc extraction in solution is lower in the experiments carried out at pH 1.50, 2.25 and 2.50 than those observed at pH 1.75 and 2.00. At pH 1.50, the low zinc extraction can be credited to the difficulty of *Acidithiobacillus sp.* to thrive at this condition. The bacterial population (at this pH) is the lowest compared with those determined at higher pH's (data not shown here).

In the experiments carried out at pH 2.25 and higher, the reduction of zinc extraction can be credited to iron (III) precipitation which probably took place under the jarosite form. Jarosite starts to precipitate at pH 2.0, thus reducing the oxidant (Fe(III)) concentration. There is also a reduction in the cell population in solution for the experiments carried out at pH 2.25 and 2.50, after approximately 90 h (data not shown here). As the bacteria have a high affinity for jarosite, they tend to sorb in the solid particles and the bacterial population in solution tends to decrease (Pogliani and Donati, 2000). Besides, the substrate concentration also drops which results in reduction of the growth rate. However, the zinc leaching is only marginally affected. This is because the E_h of the medium changes slightly by the drop in the Fe_T concentration. At pH 2.25 and 2.50, the E_h is around 500 mV close to those values observed at pH 1.75 and 2.00, which are around 530 mV. The fastest leaching rates (approximately 0.050 g $Zn\,L^{-1}\,h^{-1}$) are achieved in experiments carried out at both pH 1.75 and 2.00. These rates are similar to those observed by other authors, i.e. in the 0.025–0.040 g $Zn\,L^{-1}\,h^{-1}$ range (Torma et al., 1970; Daman et al., 2002).

Fig. 2 depicts zinc dissolution for different initial Fe(II) concentrations. Zinc extraction is very low in the absence of microorganism as compared with the experiments carried out with *Acidithiobacillus sp.* In the presence of 2 g/L Fe(II), there is a substrate concentration suitable for bacterial growth at pH 1.75. Above 2 g Fe(II)/L, zinc extraction (Fig. 2) and bacterial population (data not shown here) are independent of the ferrous iron concentration: zinc extraction is always higher than 70% and bacterial population is above 1.2×10^8 cell/mL. Lower concentrations lead to lower bacterial populations.

In the experiments without Fe(II), zinc extraction and bacterial population are much lower than those where Fe(II) was added. This is because there is a lack of substrate for bacterial growth and consequently of oxidant (ferric iron) for the sulfide oxidation. In this case, all iron present in solution (there is around 12% Fe in the

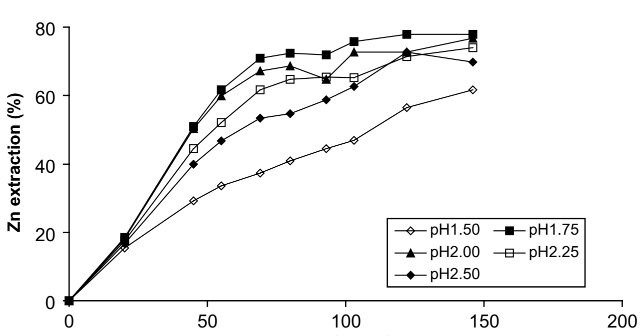

Fig. 1. Effect of pH on zinc extraction from sphalerite with *Acidithiobacillus sp*. 1% solids, 34 °C.

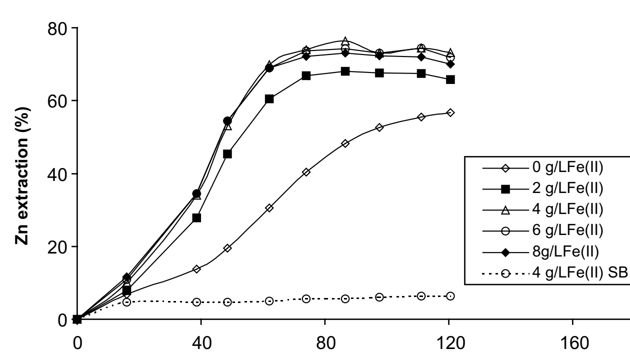

Fig. 2. Zinc extraction in the presence of *Acidithiobacillus sp.* as a function of time. SB: sterilized test 1% solids, 34 °C, pH = 1.75.

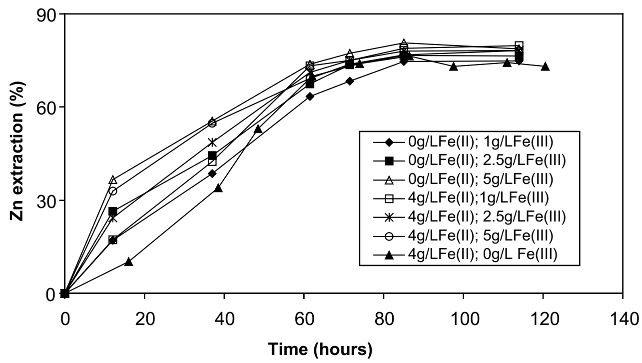

Fig. 3. Effect of iron (III) concentration over zinc extraction. 1% solids, 34 °C, pH 1.75.

concentrate) is provided by ZnS and its concentration in the reactor is not enough to allow bacterial growth under the same conditions as those observed where the substrate was intentionally added.

Fig. 3 depicts zinc dissolution in experiments carried out with different Fe(II) and Fe(III) concentrations. The zinc extraction confirms the results observed in other studies (Driessens et al., 1999; Daman et al., 2002). It can be seen that the presence of iron (III) in the beginning of the experiments accelerates sphalerite leaching since the oxidation occurs by a chemical mechanism and the rate of bacterial oxidation of ferrous ion is low in the initial stage of experiments. In the first 12 h, the zinc extraction (around 33%) observed in the experiment with 5 g Fe(III)/L is three times higher than that achieved when there was no Fe(III) addition. Besides it was observed no major effect on the bacterial population in the presence of 1 to 5 g Fe(III)/L, at pH 1.75. High Fe(III) concentrations may affect *Acidithiobacillus sp.* activity. Actually, the inhibitory effect of iron (III) on bacterial growth depends on the type of strain studied, but the smallest value reported in which the oxidation is completely inhibited is 0.3 mol Fe(III)/L (16.75 g Fe(III)/L) (Kawabe et al., 2003), well above the values studied in this work.

4. Conclusions

In this work, zinc extraction over 80% could be achieved in less than 100 h, proving the usefulness of the zinc sulfide bioleaching. The best pH for leaching are in the 1.75–2.00 range. pH's below 1.50 are not recommend due to the slowing effect on the microorganism metabolism. Values above 2.0 are not suggested either due to the precipitation of Fe(III) compounds such as jarosite.

Provided an appropriate pH is chosen, the presence of ferric iron in the initial step of leaching has a great impact on the leaching rate. Its presence creates a chemical contribution to the dissolution of sphalerite while the concentration of biologically generated Fe(III) is still low. Concentrations of Fe(III) up to 5 g/L do not affect the bacterial population in the batch reactor.

Acknowledgment

This work was supported by "Financiadora de Estudos e Projetos - FINEP" and the Université Liège.

References

Daman, D., Leão, V.A., Silva, C.A., Gomes, F.J., 2002. Bioxidação de esfalerita brasileira por *Acidithiobacills* sp. In: Baltar, C.A.M., Oliveira, J.C.S., Barbosa, J.P. (Eds.), XIX Encontro Nacional de Tratamento de Minérios e Metalurgia Extrativa. Recife, Brazil, pp. 76–82, In Portuguese.

Driessens, Y.P.M., Fowler, T.A., Crundwell, K.K., 1999. A comparison of the bacterial and chemical dissolution of sphalerite at the same solution conditions. In: Amils, R., Ballester, A. (Eds.), Biohydrometallurgy and environmental towards the mine of the 21st Century. Elsevier, Madrid, Spain, pp. 201–208.

Kawabe, Y., Inoue, C., Suto, K., Chida, T., 2003. Inhibitory effect of high concentrations of ferric ions on the activity of *Acidithiobacillus ferrooxidans*. Journal of Bioscience and Bioengineering 96 (4), 375–379.

Konishi, Y., Kubo, H., Asai, S., 1992. Bioleaching of zinc sulfide concentrate by *Thiobacillus ferrooxidans*. Biotechnology and Bioengineering 39, 66–74.

Nemati, M., Harrison, S.T.L., Hansford, G.S., Webb, C., 1998. Biological oxidation of ferrous sulphate by *Thiobacillus ferrooxidans*: a review on the kinetic aspects. Biochemical Engineering Journal 1 (1), 171–190.

Pogliani, C., Donati, E., 2000. Immobilisation of *Thiobacillus ferrooxidans*: importance of jarosite precipitation. Process Biochemistry 35, 997–1004.

Torma, A.E., Walden, C.C., Branion, R.M.R., 1970. Microbiological leaching of a zinc sulfide concentrate. Biotechnology and Bioengineering 12, 501–517.