Physicochemical Problems of Mineral Processing, 38 (2004) 291-299
Fizykochemiczne Problemy Mineralurgii, 38 (2004) 291-299

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BIOLEACHING OF COBALT FROM MINERAL PRODUCTS

Received May 20, 2004; reviewed; accepted June 30, 2004

A kinetic approach to study cobalt, copper and arsenic bioleaching has been proposed and discussed. Two flotation by-products from the Lubin mine have been used. *Acidithiobacillus ferrooxidans* bacteria isolated from water from the "colour" lakes of Boguszow (Lower Silesia), was adopted to metal leaching. Semi-empirical model has been proposed to describe the metal extraction from collected samples. This model originated from the shrinking core and it was able to fit the experimental data. This model is an useful tool to investigate and compare ore bioleaching process for different size fractions.

Key words: bioleaching, cobalt, kinetic model, biomining

INTRODUCTION

Bioleaching of mineral products from KGHM Polska Miedz has been a subject of research for over three decades (Sadowski, 1998, 2002). This process has been used to extract metal from low-grade ores and more recently there in an increasing interest in metal leaching from cobalt-bearing products.

There are two mechanisms of bioleaching: one is indirect leaching, in which microbial (*A. ferrooxidans*) acts on iron(II) ions in solution producing iron(III) ions, and the other, direct mechanism, in which microbial cells interact directly with the solid surface. For both of the above mechanisms, the rate of leaching makes a biologically assisted process economically attractive to conventional roasting or pressure oxidation process.

Many authors have assumed that kinetic model of bioleaching is related to the kinetic of ferrous iron oxidation (Boon et al., 1999, Nemati et al., 1998). Veglio

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(Beolchini et al., 1999, Veglio et al., 2000), suggested that the pyrrothite ore leaching process kinetics is controlled by the chemical reaction. It was confirmed by the activation energy of the process equal to about 100 kJ/mol.

Small quantities of cobalt (101 ppm) occur in the copper ores, which are actually exploited by KGHM Polska Miedz S.A. The highest concentration of cobalt has been observed at the Lubin mine. The beneficiation of cobalt from copper ore is (70.8%). The copper flotation concentrate contains 1055 ppm of cobalt. In the smelting process, cobalt gos towards a converter slag. The conventional production of cobalt from copper deposits is uneconomic. For this reason alternative technology must be developed.

The objective of the present study was to examine the bioleaching process of two by-products from the Lubin copper mine. The bioleaching data will be fit to a simple bioleaching kinetic model, which will able to describe the cobalt extraction from cobalt bearing sulphide minerals.

The aim of the present work was to compare the bioleaching kinetics between two particle size groups and establish a correlation between the leaching kinetic and the particle size.

MATERIAL AND METHODS

CULTURE OF MICROORGANISM

A pure culture of microorganism, *Acidithiobacillus ferrooxidans* was used in this study. These acidiphilic bacteria were selected from water taken from "colour" lakes of Boguszow (Lower Silesia). The strain was routinely cultured in 2K liquid medium. An inoculum age of about 3 days was used in the experimental trials.

MINERALS

Two kinds of cobalt-bearing mineral samples were obtained from the flotation plant of ZWR Lubin mine (Poland). Before experiments these samples were sieved using a 0.315 mm sieve. Table 1 provides the chemical composition of the cobalt-bearing flotation samples used in these studies.

Table 1. The composition of the cobalt-bearing samples

Sample No	Sample	Weight [g]	Weight Recovery [%]	Element [mg/kg]		
				Cu	Co	As
1	ZWR Lubin I -0.315 mm	1630	52.67	12.25	0.126	0.347
2	ZWR Lubin I +0.315 mm	1465	47.33	20.45	0.191	0.812
3	ZWR Lubin II -0. 315 mm	2014	65.20	12.35	0.135	0.325
4	ZWR Lubin II +0.315	1075	34.80	22.35	0.121	0.81

BIOLEACHING BIOREACTOR

The biooxidation studies were carried out in a 12-dm^3 bioreactor at constant temperature (30^{o}C). Bioleaching experiments were performed with 1 kg sample. The pH of the solution in the bioreactor was maintained by addition of sulphuric acid. The pH was adjusted to 2.5 for mesophilic bacteria. A bioleaching run was started, when 2.5 dm^3 of an active culture of the microorganisms was added. Samples of solid particle were regularly analysed using BET method.

ANALYTICAL TECHNIQUE

Solution samples were collected at various times during the bioleaching experiment runs. The concentrations of copper, cobalt, and arsenic were measured by atomic-absorption spectrophotometry. Metal leaching recovery was expressed as the fraction of original metal extracted into solution.

RESULTS AND DISCUSSION

The chemical leaching of samples in the absence of microorganism was realised during the pH adjust procedure. Typical bioleaching process started when an inoculum was added. Bioleaching kinetic data are presented in Figures 1-4.

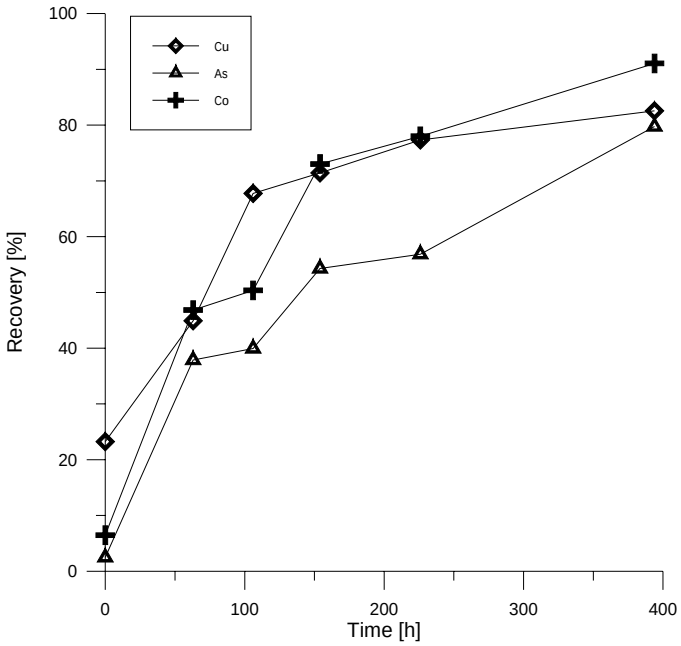

Fig. 1. Recovery of Cu, Co and As from sample I (-0.315mm)

Figure 1 presents the metal recovery evolution as a function of leaching time. As can be seen the solution concentration of Cu, As and Co obtained from the biooxidation of tested mineral sample systematically increased. Experimental cobalt, copper and arsenic recovery (R) is calculated following the standard formula:

$$R = \frac{Q_n}{Q_0} 100$$

where Q_n and Q_0 are masses of solids during and before leaching, respectively.

Bioleaching is a particulate process, which is dependent on the size distribution of leached particles. The microbiological profiles of Cu, Co and As for +0.315 mm fraction were presented at Fig. 2.

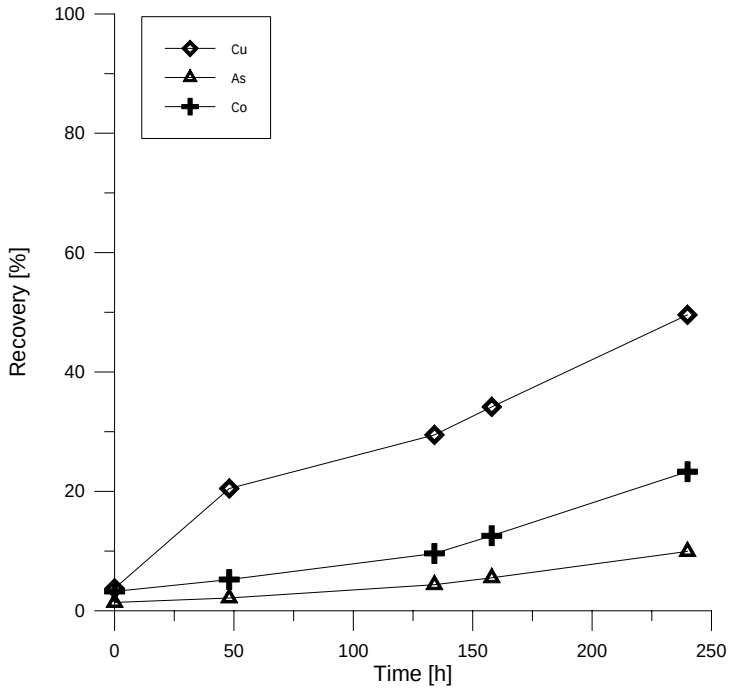

Fig. 2. Copper, cobalt and arsenic extraction in the bacterial leaching of sample I (+ 0.315 mm)

Figures 3 and 4 show the experimental kinetic curves for each size fraction of the second sample, respectively.

As can be seen from Fig 3, copper, cobalt and arsenic extraction after 240 hours of bioleaching were 73.09, 79.20 and 59.01%, respectively. Copper, cobalt and arsenic extractions after 240 hours of bioleaching of + 0.315 mm fraction are shown at Fig. 4.

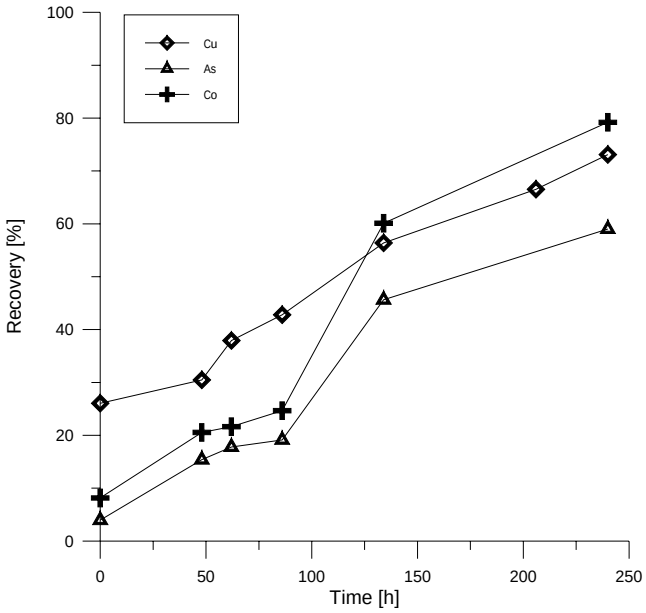

Fig. 3. Bioleaching of -0.315 mm fraction of cobalt bearing sample II

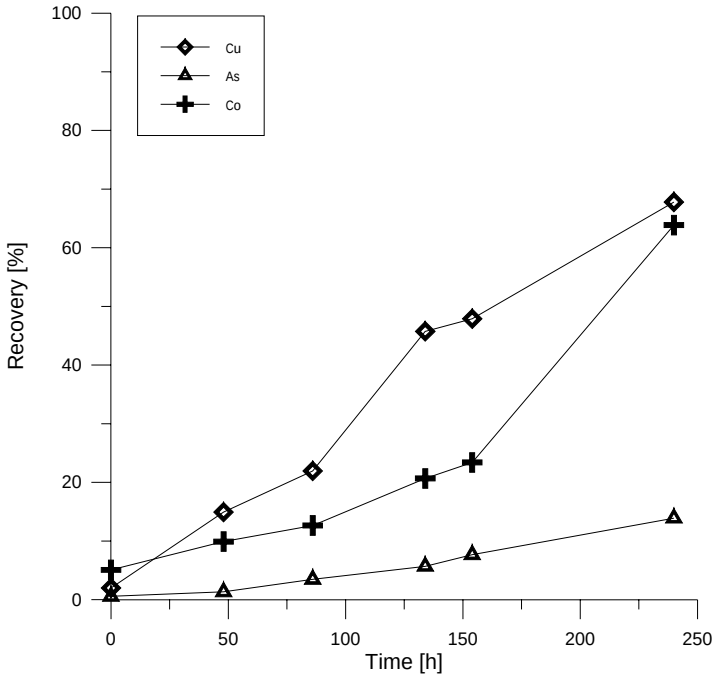

Fig. 4. Bioleaching of +0.315 mm fraction of cobalt bearing sample II

Final recovery of metals at the end of the bioleaching tests are summarised in Table 2.

Table 2. Summary of the metal recoveries obtained in these experiments

Sample	Recovery [%]		
	Cu	Co	As
Sample I -0.310 mm	82.2258	91.07	79.74
Sample I +0.310 mm	49.58	23.30	9.92
Sample II -0.310 mm	73.09	79.2	59.01
Sample II +0.310 mm	67.79	63.85	13.90

According to the shrinking core model (Lizama et al. 2003) the leaching kinetic involves a surface reaction and pore diffusion transport. The kinetics of leaching can be described by the equation:

$$1-\left(\frac{2}{3}\right)\alpha_{Co}-\left(1-\alpha_{Co}\right)^{\frac{2}{3}}=kt$$

where: α_{Co} is the cobalt recovery, k is the rate constant and, t is time (day) of bioleaching.

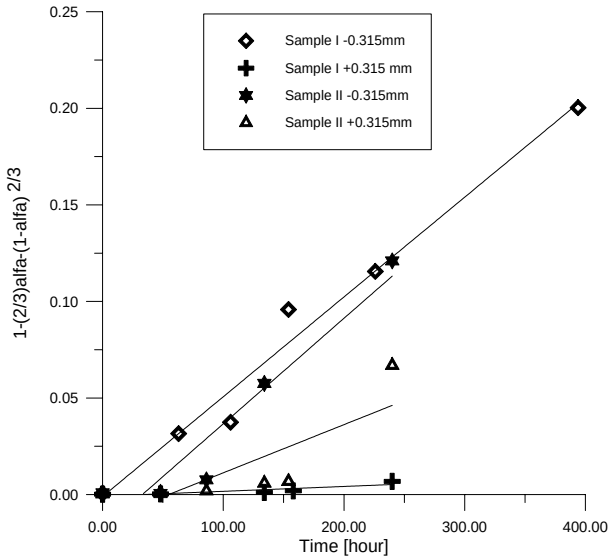

Fig. 5. Experimental data for cobalt according to the shrinking core model

The shrinking core rate constant "k" is related to the surface area of leaching samples and should be constant over time. If the particle shrinks at a uniform rate, the leaching rate is proportional to the surface area of the mineral particle. The bioleaching process has been controlled by the change of the surface area. Table 3 presents the initial and final surface areas of bioleached samples.

Table 3. Surface areas of samples before and after bioleaching

Sample	Surface area [m^2/g]	
	before bioleaching	after bioleaching
Sample I (+0.315mm)	3.88	7.35
Sample I (-0.315 mm)	5.50	8.21
Sample II (+0.315 mm)	3.36	6.64
Sample II (-0.315 mm)	4.89	7.44

The kinetics of dissolution of single particles can be expressed by the following equation:

$$\frac{dM}{t} = 3\alpha\rho D_P^2 \frac{d\left(dD_P\right)}{dt}$$

where M is the mass particle and dD_P is the diameter of the particle (Haddadin et al., 1995). This model can predict the evolution of particle size as a function of leaching time:

$$\frac{dD_P}{dD_{P0}} = \left(1 - \frac{at^b}{f_c c_0}\right)^{\frac{1}{3}}$$

where: a and b are constants.

Based on the evolution of cobalt concentration in solution for each particles size treated, the evolution of cobalt recovery (and other metals) has been calculated and fitted using a first order kinetic function (Brochot et al., 2004, d'Hugues at al.,1997):

$$R = R_{\max}\left(1 - e^{kt}\right)$$

where: R recovery at time t; R_{max} maximum recovery; k, kinetic constant.

It was observed that kinetic constant k linearly depends on 1/D, the inverse of the particle diameter (Brochot et al., 2003). The particle diameter is decreasing during the bioleaching process with a constant rate. According to the shrinking core model, the quantity of material reacting is proportional to the available surface of unreacted core. At the shrinking core model, the diameter of leaching particle decreases during the

bioleaching process. If this happens, for a population of particles, the size fraction must be a function of an initial size distribution and leaching time.

The leaching phenomenon is governed by the particle surface developed. The reduction of particle size is realised with a constant rate $dx/dt = -k^*$. Where, x is the particle diameter (m) and k^* is the kinetic constant expressed as the diameter decrease rate (m/s). Table 4 shows a comparison between the parameter k (shrinking core rate constant) and the surface area increase (Δs) during bioleaching process.

Table 4. Comparison between estimated kinetic parameter and surface area increase

Sample	Size [mm]	k 10^{-4}	Δs	Sample	Size [mm]	k 10^{-4}	Δs
I	- 0.315	5.16	2.71	I	+ 0.315	2.54	3.47
II	- 0.315	5.46	2.55	II	+0.315	2.49	3.28

It is evident, as can be expected, an increase of surface area is inversely proportional to the bioleaching rate constant. However, we must remember that, the overall leaching kinetics is a result of a multiplicity of elementary processes, of which three are the most important:

i. Adhesion of microbial cells to the mineral surface and their detachment
ii. Direct oxidation of the mineral by the attached bacteria
iii. Chemical oxidation of the sulphide mineral with iron(III)
iv. For these reasons, the shrinking core model should be rebuilt for both bacterial growth and colonisation kinetics.

CONCLUSION

The bacterial leaching tests of two cobalt-bearing samples showed a cobalt leaching ability of these samples. The most important parameter affecting the cobalt, copper and arsenic extraction from investigated samples is the initial mineral particle size. Decreasing the initial mineral particle size gives rise to an increase in copper, cobalt and arsenic recovery.

The results of preliminary leaching experiments reveal that the shrinking core model can represent the bioleaching process of cobalt-bearing samples.

REFERENCES

BEOLCHINI F., VEGLIO F., 1999, *Kinetic modeling of pyrrothite ore leaching by ferric iron and related statistical analysis*, Ind. Eng. Chem. Res., 38, pp. 3296-3299.

BOON M., BRASSER J.H., HANSFORD S.G., HEIJNEN J.J., 1999, *Comparison of the oxidation kinetics of different pyrites in the presence of Thiobacillus ferrooxidans or Leptospirillum ferrooxidans*, Hydrometallurgy, 53, pp. 57-72.

BROCHOT S., DURANCE MV.M., VILLENEUVE J., d'HUGUES P., MUGABI M., 2004, *Modelling of the bioleaching of sulphide ores: application for the simulation of bioleaching/gravity section of the Kasese Cobalt Company Ltd process plant*, Minerals Engineering, 17, pp. 253-260.

d'HUGUES P., CEZAC P., CABRAL T., BATTAGLIA F., TRUONG-MEYER X.M., MORIN D., 1997, *Bioleaching of cobaltiferous pyrite: a continuous laboratory-scale study at high solids concentration*, Minerals Engineering, 10 (5), pp. 507-527.

HADDADIN J., DAGOT Ch., FICK M., 1995, *Models of bacterial leaching*, Enzymes Microbial Technology, 17, pp. 290-305.

LIZAMA M.H., FAIRWEATHER J.M., DAI Z., ALLEGRETTO D.T., 2003, *How does bioleaching start?*, Hydrometallurgy, 69, pp.109-116.

NEMATI M., HARRISON L.T.S., HANSFORD S.G., WEBB C., 1998, *Biological oxidation of ferrous sulphate by Thibacillus ferrooxidans: a review on the kinetic aspects*, Biochemical Engineering J., 1, pp.171-190.

SADOWSKI Z., 1998, *Wstępna analiza możliwości wykorzystania procesów obróbki biologicznej surowców mineralnych dla potrzeb KGHM Polska Miedź S.A.*, Opracowanie na zlecenie KGHM Polska Miedź S.A.

SADOWSKI Z., 2002, *Analiza możliwości zastosowania procesów bioługowania w przeróbce produktów zbogacania rud miedzi*, Opracowanie na zlecenie KGHM Polska Miedź S.A.

VEGLIO F., BEOLCHINI F., NARDINI A., TORO L., 2000, *Bioleaching of a pyrrhotite ore by a sulfooxidans strain: kinetic analysis*, Chemical Engineering Sci., 55, pp.783-795.

Uryga A., Sadowski Z., Grotowski A., *Bioługowanie kobaltu z produktów mineralnych,* Physico-chemical Problems of Mineral Processing, 38 (2004) 291-299 (w jęz. ang.).

Badania kinetyki procesu bioługowania kobaltu, miedzi i arsenu zostały przeprowadzone w warunkach laboratoryjnych. Do badań użyto dwa półprodukty otrzymane z procesu flotacji z ZWR Lubin. Bakterie *Acidithiobacillus ferrooxidans*, które zostały wykorzystane w tych badaniach, były wyizolowane z kwaśnych wód pobranych z "kolorowych" jeziorek w okolicy Boguszowa (Dolny Śląsk). Do opisu procesu ekstrakcji badanych próbek został zastosowany półempiryczny model. Model ten zakłada istnienie warstwy półprzepuszczalnej nad ługowaną powierzchnią mineralną. Zastosowanie tego modelu okazało się odpowiednie dla opisu procesu bioługowania ziaren o różnych wymiarach.