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Mesophilic leaching of copper sulphide sludge

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Abstract: Copper was precipitated using a sodium sulphide solution as the precipitation agent from an acid solution containing 17 g/l copper and 350 g/l sulphuric acid. The particle size of nearly 1 µm in the sulphide sludge sample was detected by optical microscopy. Based on chemical and X-ray diffraction analyses, covellite was detected as the major sulphide mineral. The batch bioleach amenability test was performed at 32 °C on the Tk31 mine mesophilic mixed culture using a residence time of 28 days. The dissolution of copper sulphide by direct catalytic leaching of the sulphides with bacteria attached to the particles was found to be worthy, although a small quantity of ferrous ions had to be added to raise the activity of the bacteria and the redox potential of the culture medium. Throughout the 22-day period of the bioleach test, copper recovery based on residue analysis indicated a copper extraction of 95 %, with copper concentration in the bioleach solution of 15 g/l. The slope of the straight line tangential to the exponential part of the extraction curve gave a copper solubilisation rate of 1.1 g/l per day. This suggests that a copper extraction of 95 % for the period of bioleach test of 13.6 days may be attained in a three-stage bioreactor system.

Keywords: copper; acid solutions; hydrogen sulphide; sulphide sludge; bioleaching.

INTRODUCTION

The ecological hazards caused by uncontrolled release of the Bor mining and metallurgical effluent streams have not been addressed for a long time. Acidic effluent streams from industrial activities are traditionally treated by the process of lime neutralization. This treatment method is expensive, and produces a gypsum sludge which requires dewatering and disposal.[1]

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Over the course of time, the Bor Mining and Metallurgical Company has developed several projects for copper extraction and neutralization of the mine water and acid solutions, but not one of them gave a sufficiently good result. These processes were as follows: copper sulphate production from tank house bleed electrolyte, copper cementation from mine water, improvement of cementation on scrap iron,[2,3] neutralization of mine acid water in a tailing pond[4,5] and electrowinning of copper from acid solutions.[6–8]

The low recovery and the low grade of the copper produced in these plants meant that further smelting was required, which is often not economically justified. The present situation in the mining and metallurgical complex Bor is that copper losses with mine water are nearly 300 tons per year, with a concentration of copper from 0.3 to 1 g/l and a pH ranging from 1.8 to 3.5. Moreover, loses with metallurgical acid solutions are nearly 50 tons per year, with a concentration of Cu of 3 to 20 g/l with that of sulphuric acid ranging between 20 to 400 g/l.

Successful treatment of tank house acid solution was performed by the Cerro Copper Product, which includes solvent extraction, electrowinning, evaporation, crystallization and filtration processes for copper and nickel sulphate production.[9]

The object of this study was to attempt to solve the problem of copper recovery from acid effluent streams by new biohydrometallurgical processes and, at the same time, to decrease the environmental hazards in the area of East Serbia. It has already been demonstrated that the particle size distribution can dramatically affect the bioleaching efficiency when using extreme thermophilic bacteria.[10–12] The sulphide sludge was produced from metallurgical effluent streams (tank house, copper sulphate plant, copper powder plant and dore plant) by conventional hydrogen sulphide precipitation followed by mesophilic leaching, solvent extraction and electrowinning of the obtained leach solution.

EXPERIMENTAL

Bacterial inoculum

A mesophilic acidophiles culture provided by Mining and Smelting Company Bor was used as the inoculum. This culture (named Tk31) originates from the underground copper mine Tilva Ros. The bacterial strains were identified as a mixed culture of acidithiobacillus ferrooxidans and acidithiobacillus thiooxidans. Their optimum growth temperature was in the range between 30 and 35 °C, and their tolerance to copper and iron was attained naturally in the existing underground copper mine.[13]

Sulphide materials

The laboratory scale study was performed using copper sulphide sludge obtained by conventional hydrogen sulphide precipitation from an acid solution received from the copper sulphate plant.

A sodium sulphide solution was used as the precipitation agent from an acid solution with a copper content of 17 g/l and a concentration of sulphuric acid of 350 g/l.

Mineralogical analysis

The relative proportions of the minerals present in a sample were determined by the X-ray diffraction analysis.

Nutrient

The composition of the nutrition medium used during the test was (in g/l): $(NH_4)_2SO_4$, 3.0; KCl, 0.10; K_2HPO_4, 0.50; $MgSO_4 \cdot 7H_2O$, 0.50; $Ca(NO_3)_2$ $4H_2O$, 0.010 and ferrous irons, 2.2.

Batch bioleach test

The laboratory-scale unit consisted of 4-litre glass reactors with 2.9 l of culture media. The operating temperature was maintained at around 32 °C. The bioleach culture medium consisted of sulphide sludge with a low solids concentration, concentrated nutritive medium (1.5×) and Tk31 inoculum, which was stirred with a magnetic stirrer. The operating conditions were as follows: solids concentration 3 % (w/w), air flow 20 Nl/h, with a 21 % (v/v) oxygen content and a 0.03 % (v/v) carbon dioxide content, and a residence time of 28 days. Existence of free bacteria in leach solution was detected using sample of bioleach medium as inoculum in 9 K solution. The pH value was maintained at approximately 1.7 by adjusting the pH of the culture medium during the leach test.

At the end of the bioleach test, after centrifugation of the solution at 3000 rpm for 5 min, microscopic observations revealed a high amount of mesophilic acidophiles.

Analytical technique

The copper and total iron concentrations in the solution were measured by atomic absorption spectrophotometry, PE-403. The pH of the leach solution was measured with a combined glass electrode at ambient temperature. The copper dissolution rates and final copper recovery were calculated by material balance using the copper concentrations in the culture medium and in the sludge residue.

RESULTS AND DISCUSSION

The results of the chemical analysis of the sulphide sludge sample are given in Table I.

TABLE I. Chemical analyses of the sulphide sludge

Element	Content (w/w)
Cu	62.10
Fe	0.18
S^{tot}	24.00
Mg	0.02
Ca	0.03
Zn	0.01
Pb	0.02
Ni	0.02

A particle size of the sludge was ≈ 1 µm as detected by optical microscopy.

The result of X-ray analysis, presented in Fig. 1, shows covellite (CuS) as the major phase in the sample.

The sulphide mineral component of the sulphide sludge was ≈ 99 %. According to the chemical and X-ray analyses of the sample, the extent of copper sulphides was about 98 %, the rest were traces of other metal sulphides. It should be noted that the X-ray analysis could not distinguish between covellite and chalcocite (Cu_2S), due to their finely intergrown nature. Consequently, these two species are designated as Cu-sulphides in which, according to chemical analysis, due to lower content of sulphur, the amount of covellite and chalcocite was approximately 65 and 35 %, respectively. The fine material was used as the feed material in the test work programme.

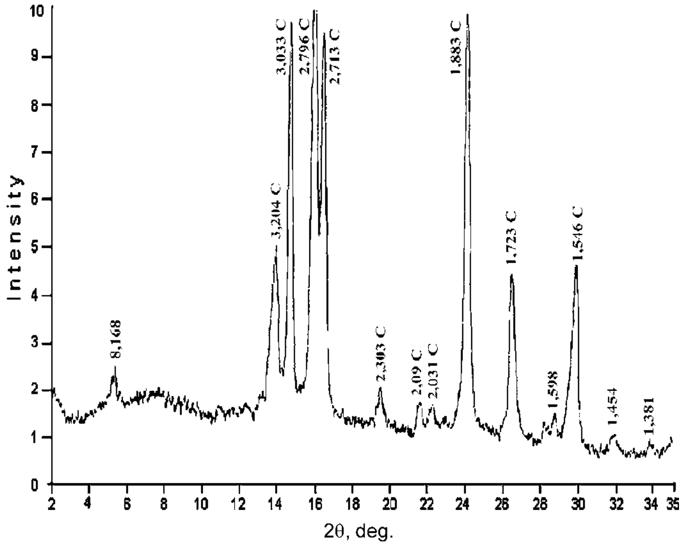

Fig. 1. X-Ray diffraction pattern of the sample (C – covellite).

The variation of pH monitored in the culture medium during the test is presented in Fig. 2. The pH, initially adjusted to 1.7 with sulphuric acid, always attained a value over 2 because of the neutralization of some quantity of sodium remaining in sample and the chemical dissolution of copper generated during the direct bioleaching of chalcocite.

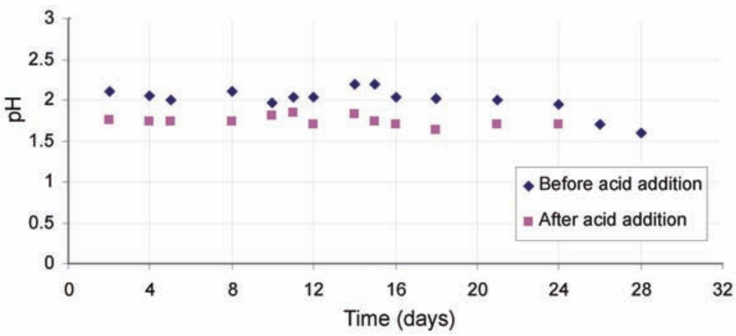

Fig. 2. pH Values as a function of time.

The results of copper extraction obtained in terms of biochemical leaching of the sample are presented in Fig. 3 as a plot of the copper content *vs.* time. The plot shows a pronounced "S"-shaped curve. The section of this curve corresponds to the lag, exponential and asymptotic growth regions, respectively. Through a series of inoculations, the bacteria will adapt to the sulphide sludge, and the lag phase will be considerably decreased, and the bacterial growth and leaching rate increased.[14]

Throughout the 22-day bioleach test, the copper recovery based on residue analysis indicated a copper extraction of 95 %, with copper concentration in the bioleach solution of 15 g/l (corresponding to the maximum content of copper in Fig. 3, representing the highest value of copper in g/l). The bioleach solution obtained of 15 g/l and pH 1.7 is convenient for down stream processes, which includes three stages of extraction, two stages of stripping and electrowinning for cathodic copper production.

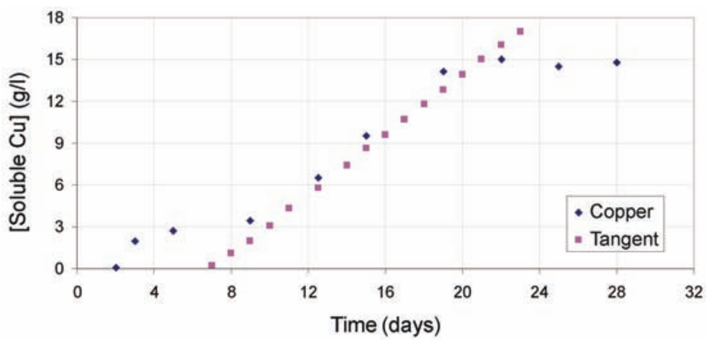

Fig. 3. Content of Cu as a function of time.

A summary of the extractions based on residue analysis is presented in Table II.

TABLE II. Summary of the results obtained from the batch bioleach test during 22 days

Element	Amount extracted, %
Cu	95
S^{2-}	96

Gericke[15] suggested that in a multi-stage reactor system, an acceptable copper solubilisation rate should be achievable in line with those demonstrated by the mesophilic batch bioleach test. The slope of the straight line tangential to the exponential part of the curve, which is a measure of the copper solubilisation rate, was 1.1 g/l per day. This indicates that at a high redox potential it is possible to achieve a copper extraction of 95 % for the period of bioleach test of 13.6 days in a three-stage bioreactor system.

The dissolution of a copper sulphide sludge by bacteria involves direct and indirect leaching. Recently, some authors[16] disregarded the difference between the direct and indirect leaching, combining these mechanisms into a single process. For the present purposes, the direct/indirect model is still useful for the introduction of the basic chemical reactions arising in the process.

It is supposed that the dissolution of covellite and chalcosite by bacteria was involved in the direct leaching; the bacteria attached to the particles catalyse the oxidation of the covellite and chalcosite crystals into soluble sulphates, thereby dissolving copper in the sulphuric acid solution.[17–19] Direct leaching includes the oxidation by *T. ferrooxidans* of covellite into copper sulphate ($CuSO_4$), and chalcosite (Cu_2S) into copper sulphate and copper. These processes are illustrated by the following chemical Reactions:

$$CuS + 2H^+ + 1/2O_2 \rightarrow \textit{T. ferrooxidans} \rightarrow Cu^{2+} + S + H_2O \quad (1)$$

$$Cu_2S + 2H^+ + 1/2O_2 \rightarrow \textit{T. ferrooxidans} \rightarrow Cu^{2+} + S + H_2O + Cu \quad (2)$$

Moreover, according to the electrochemical principle, it is necessary for the dissolution of a mineral that a distinct difference between the redox potential (E_h) of the medium solution and the electrostatic potential of the sulphide mineral condition should exist.[20]

In the present work, in order to improve the bioleaching process, a small quantity of 2.5 g/l of ferrous ions was added to the leach solution. A better optimization of the culture conditions by adding different oxidants, such as pure pyrite or a higher content of ferric ions, as well as nutrient requirements and carbon dioxide, would improve the overall bioleaching performances.

The variation of the iron content in the culture media is illustrated in Fig. 4. Initially, the added 2.5 g/l of ferrous iron was oxidized during the bioleaching process to ferric iron, increasing the Fe^{3+}/Fe^{2+} ratio, *i.e.*, the redox potential of the culture medium up to approximately 18 g/l.

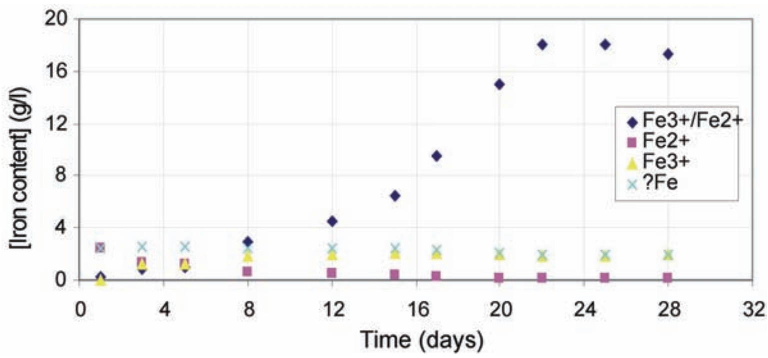

Fig. 4. Ferric/ferrous ratio as a function of time.

Direct bacterial oxidation of ferrous iron (Fe^{2+}) compounds present in the leach solution to ferric iron (Fe^{3+}) may be described by the following chemical Reaction:

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow \textit{T. ferrooxidans} \rightarrow 4Fe^{3+} + 2H_2O \qquad (3)$$

In the indirect leaching, the oxidation of the metal sulphide crystals is mediated by ferric iron (Fe^{3+}) originating from the direct bacterial oxidation of ferrous iron (Fe^{2+}) compounds present in the culture medium, as shown in Eq. (3). Thus, the ferric iron produced in Eq. (3) can leach copper as copper sulphate from covellite and copper and copper sulphide (covellite) from chalcocite, as shown below:

$$CuS + 2Fe^{3+} \rightarrow \text{chemical oxidation} \rightarrow Cu^{2+} + S + 2Fe^{2+} \qquad (4)$$

$$Cu_2S + 2Fe^{3+} \rightarrow \text{chemical oxidation} \rightarrow Cu + 2Fe^{2+} + CuS \qquad (5)$$

$$Cu + 1/2O_2 + 2H^+ \rightarrow \text{chemical oxidation} \rightarrow Cu^{2+} + 2H_2O \qquad (6)$$

The sulphur resulting from Eq. (4) can, in turn, be recycled by *T. thiooxidans* into sulphuric acid, Eq. (7), where sulphuric acid is used as a reactant in Eq. (3) when only ferrous sulphate is available in the process for the generation of ferric sulphate:

$$2S + 3O_2 + 2H_2O \rightarrow \textit{T. thiooxidans} \rightarrow 2H_2SO_4 \qquad (7)$$

The Cu extraction data (based on the residue analyses) presented in Table II indicates that the amounts of copper and sulphur extracted from the copper sulphide sludge over a period of 22 days were 95 of 96 %, respectively.

An ongoing batch amenability ferric leach test at 70 °C that a 95 % copper recovery was attained with a 3-day residence time, *i.e.*, the result attainable in tests with thermophilic bacteria.

CONCLUSIONS

The starting point of this study was to provide appropriate operating parameters for the industrial application and to increase the copper recovery from secondary raw materials and improve environmental protection. The result achieved during the mesophilic bioleaching of sulphide sludge that the dissolution of sulphide copper from the sulphide sludge with mesophilic mixed culture is technically feasible. Over the period of the batch bioleach amenability test of 22 days, copper recovery (based on residue analysis) indicated a copper extraction of 95 %, with a copper concentration in the leach solution of 15 g/l. In a three-stage reactor system, an acceptable copper solubilisation rate should be achievable in line with those demonstrated by the mesophilic batch bioleach test. The slope of the straight line tangential to the exponential part of the curve, which is a measure of the copper solubilisation rate of 1.1 g/l per day, indicates a copper extraction of 95 % over the period of 13.6 days in the three-stage bioreactor system. Better optimization of the culture conditions by the addition of different oxidants, such as pure pyrite or higher amounts of ferric ions, as well as nutrient requirements and carbon dioxide, would improve the overall bioleaching performances.

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И З В О Д

ЛУЖЕЊЕ БАКАР-СУЛФИДНОГ МУЉА МЕЗОФИЛНИМ БАКТЕРИЈАМА

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Преципитација бакра остварена је употребом воденог раствора натријум-сулфида реагенса за преципитацију бакра из раствора који садржи 17 g/l бакра и 350 g/l сумпорне киселине. Величина честица у узорку, која се кретала око 1 µm, одређена је оптичком микроскопијом. Хемијском и рендгено дифракционом анализом установљено је присуство ковелина као главног сулфидног минерала. Лабораторијски биолужни тест је остварен на температури од 32 °C коришћењем Тк31 рударске мезофилне културе. Растварање сулфида бакра је остварено директним каталитичким растварањем сулфида са бактеријама на површини честица, али је незнатна количина феро-јона додата у раствор у циљу развоја бактерија и редокс потенцијала. У лабораторијском биолужном експерименту у периоду од 22 дана, растворено је 95 % бакра, и при томе остварен садржај бакра у лужном раствору 15 g/l. На основу нагиба праве линије, тј. тангенте на експоненцијални део криве растварања бакра, која представља брзину растварања бакра од 1,1 g/l на дан, одређено је растварање 95 % бакра у биолужном експерименту за време од 13,6 дана у систему континуалног рада три биореатора у серији.

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