University of Belgrade
Technical Faculty in Bor

Chamber of Commerce
and Industry of Serbia

XV International Mineral Processing & Recycling Conference

IMPRC
INTERNATIONAL MINERAL PROCESSING & RECYCLING CONFERENCE

Proceedings

Editors:
Jovica Sokolović
Milan Trumić

17-19 May 2023

Belgrade
SERBIA

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TABLE OF CONTENTS

XV International Mineral Processing and Recycling Conference
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COPPER ORE BIOLEACHING FROM ECOLOGICAL POINT OF VIEW

V. Conić[#], I. Jovanović

Mining and Metallurgy Institute Bor, Bor, Serbia

ABSTRACT – Microorganisms in bioleaching processes are characterized by their oxidative effect on iron ions and forms of reduced sulfur species in acidic environments. To oxidize metal sulfides found in copper ores and concentrates using microorganisms, copper leachate is oxidized as copper sulfate. The bioleach solution is extracted through extraction technologies, after which the technology of electrodeposition of copper, obtaining the final product a copper cathode of high purity.

Keywords: Bioleaching, Eco Friendly Technology, Base Metal, Sulfide Ore, Concentrate.

INTRODUCTION

The mineral industry has suffered in recent year's two significant impacts: The raise on energy cost and more strict environmental regulations were in place for the metallurgical processing of sulfide ores and concentrates, mainly those containing arsenic. These impacts moved the mineral industry to develop alternative processes to roasting and smelting and searching for alternative processes to avoid the high energy consumption, grinding operation and flotation of sulphide minerals. Bioleaching must compete with alternative approaches for extracting metals from ores and concentrates. The main obstacle is the time required for metal extraction, which ranges from days, in the case of bioreactor leaching, to one or more years in the case of bio-piles and waste rock dumps. On the other hand, bioleaching is generally a much more ecological ("green") approach, requiring operation at much lower temperatures, thus energy costs are lower. Microorganisms in oxidation processes are autotrophs, i.e. they consume carbon dioxide like plants. Large amounts of CO_2 are emitted during melting. Bioprocessing also works at atmospheric pressure and at relatively low temperatures (20–80 °C). An external heat source is usually not needed because, like the oxidation of sulphide minerals, it is an exothermic process. Indeed, excess heat is generated where oxidation rates are intense (eg stirred tank operation) and systems need to be cooled to maintain the appropriate temperature. Bioprocessing also has advantages where, first of all, the ore or concentrate contains significant amounts of arsenic (which is released in gaseous emissions during smelting but remains in the liquid and solid phase in (bio)hydrometallurgical processing) and secondly, for the processing of low-quality and complex polymetallic ore.

In the Mining and Metallurgy Institute Bor (MMI Bor) Serbia Figure 1., two continuous facilities for the treatment of bioleaching raw materials were installed in

[#] corresponding author: vesna.conic@irmbor.co.rs

order to evaluate the techno-economic drivers that regulate the application of this technology. Topics covered include choosing between tank and pile bioleaching, microbiology and process operating temperature selection, influence of ore mineralogy on process options, environmental considerations, and metallurgical test design programs.

Bor lake MMI Bor Bor Serbia

City Bor

Figure 1 Conventional pyrometallurgical treatment of mineral raw materials in Bor

EXPERIMENTAL

Evolution of bioleaching technology

Microbes that play a very important role in the leaching processes of copper minerals are: *At. Thiooxidans*, which was isolated in 1922 by (Waksman and Joffre), then *At. Ferrooxidans* isolated in 1947 by (Colmer and Hinkler) and *Ferroobacilus Ferrooxidans* isolated in 1954 by (Leathen and Breley). Their ability is reflected in the ability to oxidize iron with the formation of ferric iron (the main oxidant of sulphide minerals) and the formation of sulfuric acid, which accelerates the dissolution of minerals.

The first forms of leaching in situ, dump leaching and heap leaching are replicated to the improved procedures of heap bioleaching arranged drained piles, for providing oxygen, carbon dioxide and microbes, universally adapted, such as plastic membranes covers, to capture heat and preventing water evaporation, drainage tubes to collect the solutions, network of drippers to irrigate the heap with solutions leaving behind the sprinklers, on/off irrigation system, and slowly adding more instrumentation to monitor the process [1].

In situ leaching

This process allows the extraction of metals from a porous ore body without the need for conventional mining involving drill and blast, open cut or underground mining.

Microorganisms may be induced to release the metals into solution without any mechanical mining of the metal-bearing rocks. If the ore is not porous, holes are drilled in the ore deposit. Explosives are also used for easier penetration of the solution. The leaching solution is pumped into the deposit where it comes into contact with the ore. The leach solution is then pumped to the surface and processed, Figure 2.

Figure 2 In situ leaching

Dump leaching

The leaching of landfills begins with the leaching of tailings from large surface mines, the leaching time of which is measured in years. The ore is crushed and piled, then subjected to a continuous spray of water containing biomining microbes. The leaching solution is collected from the bottom and after metal extraction is used again for washing, Figure 3.

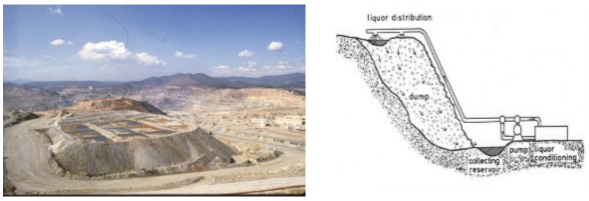

Figure 3 Dump leaching

Heap leaching

The ore is placed in orderly heaps on a water impermeable membrane. The leaching solution is pumped to the top of the pile and the leachate is collected and processed for metal recovery, Figure 4.

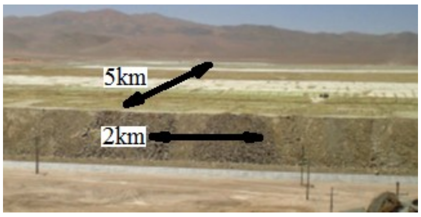

Figure 4 Heap leaching

Mechanism of bioleaching

Bioleaching of the ore body of copper ore is presented in Figure 5. Acidic iron-rich fluid is injected through the borehole into the fractured ore body, where it oxidizes the copper sulfide minerals. A liquid rich in copper and iron is pumped to the surface, the copper is extracted by the SX-EW process. The barren solution is regenerated in a bioreactor containing acidophilic cultures that oxidize iron Fe^{2+} to Fe^{3+}.

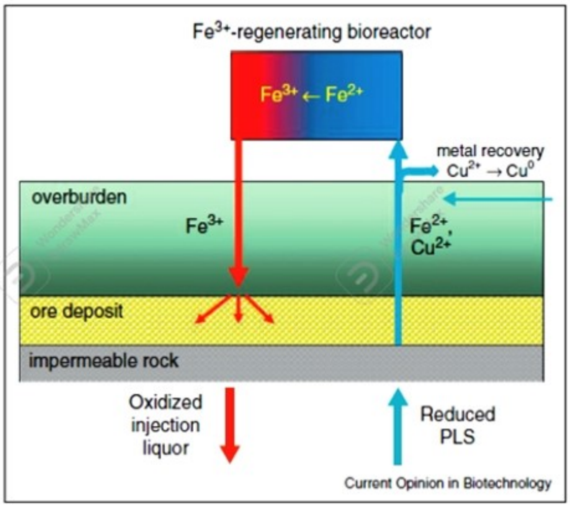

Figure 5 Indirect bioleaching mechanism ore body

Factors affecting the extraction of metals from minerals

Particle size

Ores and concentrates during the leaching process serve as substrates, so that the leaching activity is proportional to the available surface. Reducing the particle size means increasing the total surface area of the particles so that a higher metal yield can be achieved. This means that the surface area plays an important role. The particle size used in bioleaching processes of 20-75µm of about 42µm is considered optimal for bioreactor leaching, while the particle size is different from minerals in heap and landfill leaching in inches.

To carry out the bioleaching operation, it is necessary that the raw material be ground as finely as possible so that it does not destroy the microbes and that the microbes overcome it as easily as possible. On the other hand, research shows that 5% of the world's total energy production is spent on mining ore bodies and grinding ore.

Pulp density

An increase in mineral surface area can be accompanied by an increase in pulp density. Usually, the content of the solid phase in the pulp used in bioleaching processes is up to 20% (w/v). An uncontrolled increase in pulp density has a negative effect on the diffusion of gases, mixing and therefore on the activity of the organism.

It can also lead to the dissolution of certain compounds that have an inhibitory or even toxic effect on the growth of bacteria.

Temperature

The optimal temperature growth and development mesophilic microorganisms *At. ferrooxidans* and *At. thiooxidans* is between 28-30 °C. The required temperature for the growth and development of moderate thermophiles such as *Sulfolobus, Acidiphilum, Thiobacillus caldus* is 45-55 °C. Extreme thermophiles have the greatest activity at temperature 60-90 °C.

pH

Necessary condition for the growth of acidophilic bacteria is the pH value, which ranges from pH 1.8 to 2.2. Adjusting the pH value in leaching processes is also one of the important factors for metal solubility.

Eh

The Eh-redox potential in bioleaching processes ranges from 350-700 mV. With the dissolution of iron and the increase in the concentration of Fe^{3+} ions, the redox potential increases. It is very important to maintain the redox potential to optimize metal dissolution and control iron deposition.

O_2 and CO_2

The concentration of carbon dioxide in the air is not sufficient for the growth of microbes, so it is necessary to add it. As bacteria are aerobic in nature, an adequate supply of oxygen is a prerequisite for a high degree of leaching.

Nutrients

Microbes need inorganic compounds for growth and development, which they otherwise acquire from nature, such as ammonium sulfate, dipotassium hydrogen phosphate, potassium chloride, magnesium sulfate, and calcium nitrate.

RESULTS AND DISCUSSION

Types of microbes and isolation

Mesophilic microorganisms *At. ferrooxidans* and *At. Thiooxidans*, Figure 6., can be isolated from open pit water presented in Figure 7., underground water that is collected in pits and from ore in Bor, Serbia and these are their natural habitats. Moderate thermophiles can be isolated from the warmer habitats of South Africa. Extremely thermophiles bacteria can be isolated example from hot springs [5].

The increase in the number of bacteria is achieved in a standard nutrient solution of mineral inorganic salts (KCl, $(NH_4)_2SO_4$, K_2HPO_4, $MgSO_4x7H_2O$) in an incubator at the required temperature for the growth of the selected bacterial culture, Figure 8.

After the development of microorganisms, it is very important that the microorganisms first adapt to the leaching conditions in the shaker, Figure 9., for the later successful management of the bioleaching process.

Mesophiles 28-32 °C	Moderate thermophiles 45-55 °C	Extreme thermophiles 60-90 °C

Figure 6 Spaces of microbes that participate in bioleaching processes

Figure 7 Inoculum isolation from open pit

Figure 8 Incubator

Figure 9 Shaker

With the help of adapted microbiological culture, bioleaching tests are performed in bioreactors with CO_2 gas and air supply. Monitoring of the bioleaching process is carried out by daily sampling, in order to control the pH value, redox potential and concentration of leached metals.

The intensity of the oxidation process during bioleaching increases due to the increase in the number of bacteria, the concentration of iron ions, the increase in the acidity of the solution and the redox potential of the solution Eh.

Intensive bioleaching occurs when the basic parameters of the process (pH, Eh, pulp density, concentration of metal ions in the solution, as well as the activity and number of microorganisms) are stabilized.

Bioleaching is a slow process, but by adapting microbes to mineral raw materials and establishing continuous bioleaching in a series of bioreactors after determining the residence time it is possible to continuously obtain leached pulp every day.

Small scale continuous bioleach reactors

Mintek believes that for tank bioleaching, much more value can be derived from continuous testing, as opposed to batch testing [3]. This is simply because batch tests do not provide the reliable kinetic data that can be obtained from continuous test work. The retention time in the continuous bioleaching process is usually six days. Taking into account the start-up time and residence time for the process to achieve stable operation, it takes about three weeks to complete the test. One of the biggest problems with this is that the amount of sample required to conduct such testing becomes very large.

In order to avoid this, at MMI Bor (Institute for Mining and Metallurgy in Bor) a set of reactors for continuous bioleaching of small scales, with a total process volume of up to 6 L per reactor, was designed and established, which enable continuous tests to be carried out without consumption of large quantities of (usually scarce) concentrate samples. This is particularly useful in the early stages of a metallurgical testing work program and increases the value of the data that can be provided to the client at scope study or pre-feasibility study level. The bioreactor continuous system is shown in Figure 10.

Figure 10 Small scale continuous bioleach reactors of ore with a capacity of 1L pulp/day

Integrated bioleach Pilot plant

For larger-scale piloting, usually conducted to provide data for a feasibility study, an integrated pilot plant incorporating several downstream process unit operations was developed with the help of Mintek Company from Johannesburg (South Africa) at the Institute of Mining and Metallurgy Bor, as shown in Figure 11. This plant can provide detailed design information for the bioleaching process, as well as solid-liquid separation, iron removal and solution purification, SX -EW, and metal hydroxide precipitation.

In South Africa is initially processed 14 tons concentrate/day, while now being produced 55 t/day. In Kazakhstan on Suzdal BIOX plant are produce 192 t gold concentrate/day in sub-zero temperatures, Figure 12.

Figure 11 Integrated bioleach Pilot plant facility, capacity 20L pulp/day

a) b)

Figure 12 Bioleaching tanks of refractory gold in a) South Africa, b) Kazakhstan

Solvent extraction

Extraction of copper by solvent extraction, Figure 13, is based on the interphase transfer of copper from the aqueous phase to the organic phase. The transfer takes place at the interphase boundary, where the kinetics of the process depends on the intensity of agitation of the two phases (flow of phases through the agitator-precipitator). The process then continues with phase separation, whereby agitators-settlers are used in hydrometallurgy. During the interphase transfer, cupric ions move to the organic phase and hydrogen ions to the aqueous phase, and copper forms an organometallic complex with the extractant according to the reaction:

$$2RH + Cu^{2+} = CuR_2 + 2H^+ \quad (1)$$

in which two moles of oxime (active component) in the organic phase and one mole of copper release two moles of hydrogen ions in the pH range of 0.5 - 3.5.

Extractants based on 5-nonyl-salicylic-aldoxes are capable of reacting with the stoichiometric amount of copper from alkaline solutions up to 35 g/L Cu^{2+} and a minimum acidity of pH 1.4. The extractant itself forms a very strong organometallic complex from which copper is difficult to extract using the output electrolyte with a composition of 30 g/L Cu and 190 g/L H_2SO_4. This problem is solved by adding a suitable modifier to the extractant. Specific modifiers for certain extracts are nonyl phenol, tridecanol and ester modifier.

Figure 13 Laboratory plant for leaching, solvent extraction and electrowinning
A1 - reactor for leaching, B1 - feed tank for bioleach solution, C1 - tank for organic solution, D1 - mixer - settlers, E1 – electrowinning cell, F1 - control panel

For copper extraction, organic reagent M.5640 is used. Reagent M.5640 from Acorga is an ideal extractant for extracting copper from solution due to the high selectivity of copper extraction compared to iron. The laboratory solvent extraction system for copper extraction is composed of 5 identical mixer-settlers there of 3 in extraction and 2 in stripping. The process of solvent extraction is followed by the process of electrolytic extraction.

Electrolytic extraction of copper

Electrolytic extraction of copper using insoluble anodes can be described as the deposition of copper from a copper-bearing electrolyte due to the passage of a direct current. The overall reaction is represented as follows:

$$CuSO_4 + H_2O \rightarrow Cu^o + H_2SO_4 + 0.5O_2 \quad (2)$$

according to which copper is deposited on the cathode and oxygen is released on the anode. PVC electrolytic cell equipped with Ti cathodes and Pb/Sn/Ca anodes.

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CONCLUSION

By applying biotechnology in the metal extraction process, energy consumption is reduced, almost any risk of air pollution is eliminated, and the extracted metals of interest as well as potential pollutants are translated into an aqueous solution that can be easily further treated. Compared to pyrometallurgical processes, biotechnology is better for the environment and human health.

New technologies and scada software that are installed in reactor systems enable all information about the operation of the instruments and the monitoring of the technological parameters of the process to be sent wirelessly to the operator. At the same time, precise correction of process parameters can lead to a reduction in process management costs and an increase in recovery.

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