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Research paper

Recovery of Copper by Using Flotation Techniques and Microbe- Mineral Surface Interaction

K.Prasad Babu [1*], K.S.K.Rao Patnaik [2], R.Shyam sunder [3]

[1] *Department of Chemical Engineering, Chaitanya Bharathi Institute of Technology, Hyderabad.*
[2,3] *University College of Technology, Osmania University, Hyderabad.*
**Corresponding Author E-mail: Prasad.ism@gmail.com*

Abstract

According to research paper, copper recovery from high grade copper was make an effort treating with a chemolithotrophic microorganism, and Acidithiobacillus ferrooxidans bacteria. The aim of the present study is to understand the changes in Copper ore beneficiation based on surface chemical properties of bacteria during adaptation to high grade copper minerals and the projected consequences in flotation and bio-flotation processes .The utility of bio processing in the beneficiation of Copper ore through bio-flotation is demonstrated in this work. An autotroph Thiobacillusferroxidansbacteria is adapted to high grade mixed copper ore sample, which was supplied from HCL Malanjkhand Copper Plant, Open cast mines. According to the procedure the collection and activation of the bacterial strains of Acidithiobacillus ferrooxidans.In 9K media Culture bacteria was developed, added sufficient amount of nutrients and agitated the culture to enhance the growth at room temperature. Copper sample was adapted by repeated subcultures of bacteria. The surface characteristics were studied Zeta Potential by analysis at different Ph values and different time intervals. After that the samples were analyzed by Chemical Analysis in the Laboratory for the percentage of the Copper recovered from each sample and also calculated rate constant (k) by using Flotation kinetics. From the studies it was observed that the mineral adapted cells became more hydrophobic as compared to un adapted cells during bio-flotation .It was also noticed that there was no significant changes in the surface charge of bacteria before and after adaption. If the adaption of bacteria is high then the recovery of Copper is more.

Keywords: *Recovery, Culture preparation, Bio processing, flotation, Bio-flotation, Zeta Potential studies.*

1. Introduction

Quick progress is being done in mineral processing based on biological principle. Microorganisms (Acidithiobacillus ferrooxidans) can be used beneficially in mineral processing, from mining to waste disposal and management. Low-Grade ore, small and complicated ore bodies, waste ores, tailings and ores that are uneconomical to be recovered by traditional methods can be economical recovered by bioleaching. Microbe process provides an economic substitute for the mineral industry, when high-grade mineral reserves are being decreased.

Rapid industrialization around the world has increased the demand for metals slowly but gradually, thus led to the depletion of high grade ore due to large-scale exploitation of the high-grade ores. Thus it has all come to processing of lean grade ores to meet the requirements of the industries. Bio processing techniques possess eye-catching characteristic for reacting with complex ores. Use of various microorganisms in beneficiation process like bio-leaching, bio-flotation and bio-flocculation has become a reality.

New resources for metals must be developed with aid of novel technologies. Improvement of already exist mining technologies can result in metal recovery from sources that have not been of economical interest until today. Metal-winning process based on activity of microorganisms offer a possibility to obtain metals from mineral resources not accessible by conventional methods. for example, its application could result in extraction of gold, copper, nickel and zinc from sulphide ore without emission of sulphide emission of sulfur dioxide as occurs with conventional smelting technologies. The mineral industry and the community will benefit enormously from a successful mineral biotechnology.

The main copper mineral in the copper ore is chalcopyrite. Researchers have been striving for decades to understand the reasons for slow dissolution of chalcopyrite in both chemical and biological leaching reactions. The main problem hindering commercial application of bio hydrometallurgy processing of chalcopyrite is the slow dissolution rate. The bioleaching rate of other copper sulphides such as covellite CuS and chalcocite Cu_2S are relatively high in the presence of iron oxidizing bacteria, since the mineral react favourable with ferric ion, the principle oxidant. However the solubilisation rate of chalcopyrite in an oxidizing medium is characteristically slow. Application of chalcopyrite bioleaching in heap and dump processes can potential result in lower cost and reduced environment impact of copper production, as well as a substantial increase in known-extractable resources of copper bearing minerals.

2. Materials and Methods

2.1. Materials

The high grade copper ore sample supplied from Hindustan Copper Limited ,Malanjkhand About 25kg from supplied sample was taken for processing .The high grade copper ore is subjected for size analysis ,the result are given in table. Further and the ore was subjected for grinding to produce 65%-75µm particle sizes. The chemical analysis of the sample indicated 1.7%Cu and 2.8% Fe in the ore samples. Mineral samples of -75µm fractions were also subjected to Zeta potential meter for its surface study.

2.2 Culture Preparation

Microbial culture was developed from the tailings of Hindustan Copper Limited and recultured.The growth was carried out in 250 ml conical flasks containing 90 ml of the 9-K Media with 10 ml of inoculums (old culture), i.e.10% V/V inoculums without ore. The flasks were incubated at room temperature on a rotary shaker at 120 rpm. After 10 days the culture was ready for bioleaching tests.

Fig.1: Full Growned culture

Chemical used	Amount Required
$FeSO_4.7H_2O$	44.2 gm
$(NH_4)_2SO_4$	3 gm
10N H_2SO_4	1ml
$MgSO_4.7H_2O$	0.5 gm
KCl	0.1 gm
pH-2.9,Temperature30ºC	

2.3 Flotation

Flotation is a process of separation and concentration based on differences in the physicochemical properties of interfaces. Flotation can take place either at a liquid–gas, a liquid–liquid, a liquid–solid or a solid–gas interface. In froth flotation, the flotation takes place on a gas–liquid interface. Hydrophobic particles, which may be molecular, colloidal, or macro-particulate in size, are selectively adsorbed or attached to and remain on the surface of gas bubbles rising through suspension, and are thereby concentrated or separated from the suspension in the form of froth. This ability to modify the floatability of minerals has made possible many otherwise difficult separations that are now common practice in modern mills. Flotation is widely used to concentrate copper, lead, and zinc minerals, which commonly accompany one another in their ores. Many complex ore mixtures formerly of little value have become major sources of certain metals by means of the flotation process.

2.4 Bio-Flotation

The bio flotation process concern the mineral response to the bacterium presence, which is essentially considered as interplay between microorganism and physico-chemical separation process.

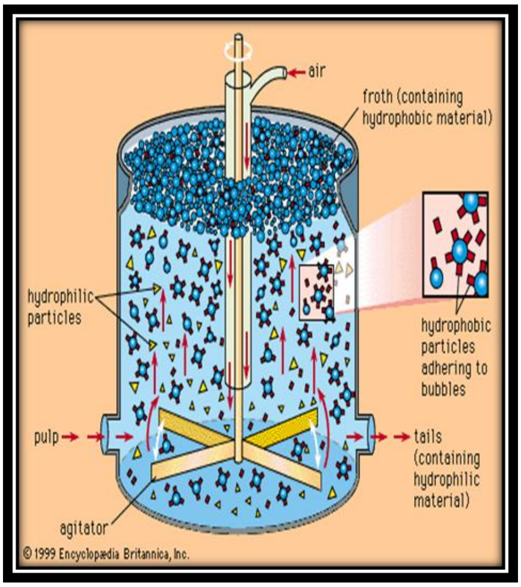


Fig.2: Flotation Mechanism

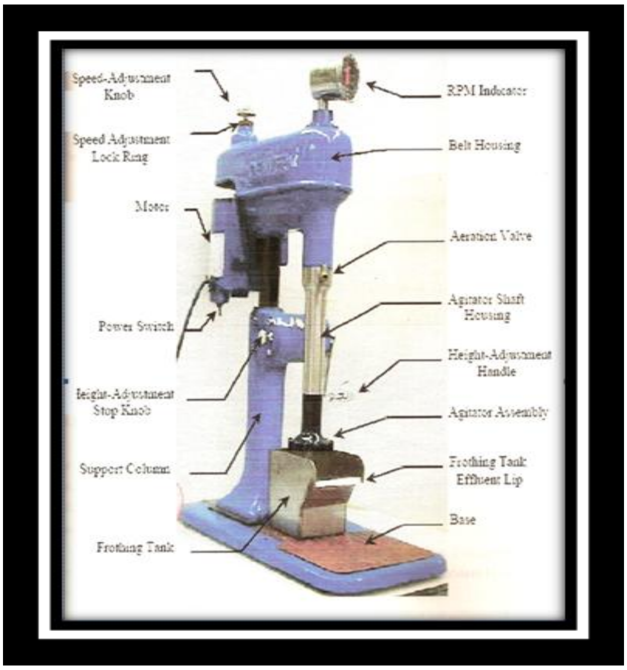


Fig.3: Denver Flotation Cell

The process of material being recovered by flotation from the pulp consists of three mechanisms:

- Selective attachment to air bubbles (or "true flotation").
- Entrainment in the water which passes through the froth.
- Physical entrapment between particles in the froth attached to air bubbles (often referred to as "aggregation").
- Minerals are classified into two types i.e. polar and non-polar. Polar minerals are those with strong covalent bond. These minerals react effectively with water and also having hydrophobicity in nature. Non-polar minerals characterized by weak molecular bond. These minerals are establishing the covalent bond together by Vander Waals forces. Non-polar surface not attached to the water molecules and then they are water repellent. Examples are graphite, sulphur; diamond and coal have natural floatability with a contact angle of 60 and 90 degree.

Formulation used for calculating recovery is:
Recovery = (Cc/Ff)*100
Where
C-Weight of final copper concentrate

c-% copper in concentrate
F-Weight of copper sample taken for flotation
f-% of copper in copper sample taken for flotation
2.5 Flotation reagents:
The mineral particles can only attach to the air bubbles if they are to some extent water-repellent, or hydrophobic. Having reached the surface, the air bubbles can only continue to support the mineral particles if they can form a stable froth, otherwise they will burst and drop the mineral particles. To achieve these conditions it is necessary to use the numerous chemical compounds known as flotation reagents. The classifications of different reagents are
Collectors :Minerals have to be hydrophobic so that they can float. To achieve this, collectors are added to the pulp and time is allowed for adsorption during agitation in what is known as conditioning period. Collectors are organic compound which make the minerals hydrophobic by making a layer on the surface, thus making the bubble to attach on the surface easily and thus float. Collectors are of two types non- ionizing and ionizing. Ionizing is of two types anionic and cationic. Cationic are water repellent. Anionic are divided into Oxyhydryl and Sulphydryl. Examples of oxyhydryl are carboxylic, sulphates and sulphonates. Sulphydryl consists of Xanthates and dithiophosphate. Apart from these bacterial proteins can also be used as collectors in flotation.

2.6 Frothers

They are added to stabilize the bubble formation in the pulp phase, to create a reasonable stable froth, to selectively drain the mineral and to increase the flotation kinetics. It should be able to act in water and air phase only. They should be able to create enough bubble strength. Widely used Frothers are crysylic acid, pine oil, Methyl iso butyl carbonyl (MIBC).

2.7 Regulators

This is used to reduce the action of collectors either by modifying the hydrophobocity on the surface of mineral. Thus then the reaction of the collectors most effective towards the minerals.
Types of regulators

- Activators
- Depressants
- pH regulators

Activators are reagents which enhance the chemical nature of the mineral surface thus changing to hydrophobic. E.g.: Copper Sulphate Depressants are reagents which render the mineral particle to hydrophilic by formation of hydrophilic coating at the surface. E.g.: Sodium Cyanide. pH regulators essentially regulate pH. They increase the selectivity by providing the stable condition for collectors. Xanthate is the most widely used collectors which has working range of 4-12.

2.8 Bacteria as Collector in Flotation

Same procedure is followed except that in the place of NaCN, a bacterium is used as Collector in flotation. The bacterium used is Thiobacillus Ferrooxidans which is given various interaction time of 20, 40 and 60 min with the ore before the experiment was started. The amount of bacteria (100,200,300 and 400ml) used for interaction with the ore was also changed. The Bacterium Thiobacillus Ferrooxidans was grown using 9K media for about 5 days at 350 C.
The result of the studies indicates an increase in the recovery in the percentage of Copper from 65% to 98.5%.

2.9 Zeta Potential Study

In this study the surface charge of the particles are measured by Zeta potential equipment the zeta potential is measured for the ore or Copper concentrate which is interacted with or without bacteria for different interval of time at different pH. The solution is poured into the cell. A charge of 200 volts is applied through the solution. The measured zeta potential is noted down for all the sample accordingly In order to study chemical changes, resulting from microbe mineral surface interaction, zeta potential measurements have been carried out by using full grown culture of Thiobacillus ferrooxidans. Initially, the studies were carried out on the Copper ore. For this purpose the ore was ground to -75 µm size fraction and subjected for zeta potential studies in the absence of Thiobacillus Ferrooxidans. From the figure we observe that the mineral possess negative zeta potential all over the pH range. We also observe increase in the potential of the particle as the pH decreases.
Analytical Method: Chemical Analysis:
After size analysis, quantitative analysis was carried out by volumetric analysis to analyze the percentage of Copper in the given sample.

3. Results & Discussion:

The results obtained from the experimental work are described and discussed below:

- Analyzing the variation of pH and Microscopic studies
- Flotation &Bio flotation studies
- Zeta Potential studies.
- Equilibrium and kinetic studies

3.1 Results of Flotation Studies

These results are drawn from the froth flotation:

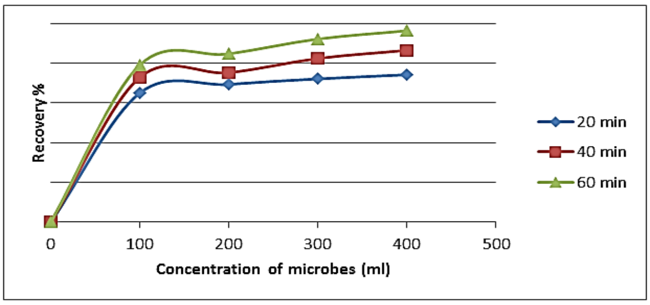
S.No.	Sample	Weight(gm)	Initial reading	Final reading	Difference	% of Copper	Recovery %
1	Froth	54.15	0ml	21.25ml	21.25ml	13.5	86
2	Tailing	445.84	21.25ml	22.75ml	1.5ml	0.95	49.7

3.2 Bacteria as Collector in Flotation

Same procedure is followed except that in the place of NaCN, a bacterium is used as collector in flotation. The bacterium used is Thiobacillus Ferrooxidans which is given various interaction time of 1hr, 4hr and 24hr with the ore before the experiment was started. The amount of bacteria (100,200,300 and 400ml) used for interaction with the ore was also changed. The Bacterium Thiobacillus Ferrooxidans was grown using 9K media for about 5 days at 350 C.

S.No.	Culture(ml)	Incubation Time(hr)	%Recovery
1.	100	24	82.82
2.	200	24	92
3.	300	24	98
4.	400	24	98.5

We can conclude from this comparison that the recovery of Copper has increased with the increase in the interaction time. The Copper recovery increased from 65 to 98.5 %. Thus we can conclude that interaction time of bacteria and
concentration of bacteria used are important factors in bio flotation. This is because these parameters changed the surface properties of the particle to hydrophobic.



Increase in Copper % in copper concentrate with increase in interaction time

3.3 Result of Zeta Potential Studies

In order to study chemical changes, resulting from microbe mineral surface interaction, zeta potential measurements have been carried out by using full grown culture of Thiobacillusferrooxidans. Initially, the studies were carried out on the ChalcoPyrite ore. For this purpose the ore was ground to -75 µm size fraction and subjected for zeta potential studies in the absence of ThiobacillusFerrooxidans. The results of the studies are given in figure. From the figure we observe that the mineral possess negative zeta potential all over the pH range. We also observe increase in the potential of the particle as the pH decreases.

Fig.4: Zeta Meter

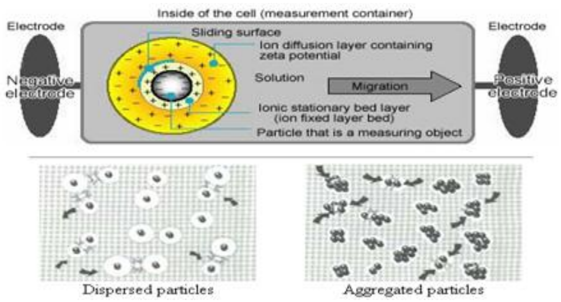
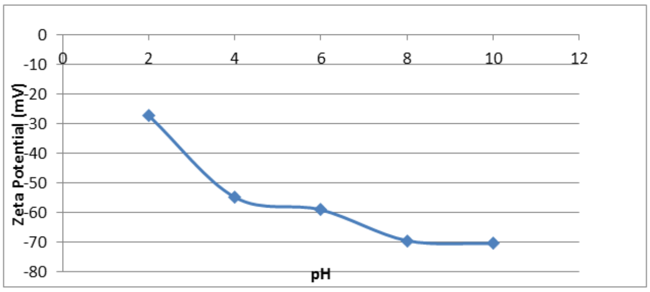


Fig.5: Zeta potential studies

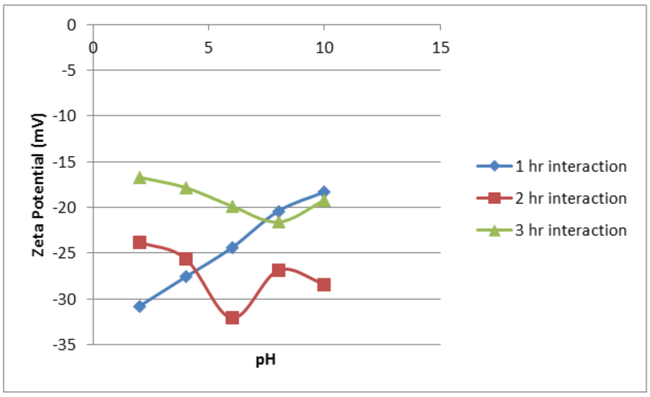
Zeta potential of microbe mineral Interaction at pH 2

Conditioning time (min)	Zeta Potential (Ore)	Zeta Potential (with microbial interaction)
30	-36.7	-26.5
60	-37.2	-23.7
90	-34.5	-20.2
120	-35.6	-10.4



Potential of ore without bacterial interaction at different pH

Further, in order to study the microbe mineral interactions studies were carried out on the copper ore .



Potential of ore with bacterial interaction at different pH

The result indicates changes in zeta potential due to surface chemical changes. From the figure it may also be observed that concentrates of copper possess negative potential throughout the pH range. From the studies it is interesting to note that the variation in zeta potential was higher in zinc concentrate – microbe mineral interaction than that of lead concentrate microbe interaction. This variation may be due to the increased adsorption of microbes to galena than sphalerite. Hence, critical observation of the results indicate that variation in zeta potential may be exploited in selective flotation of lead zinc complex sulphide ores.

4. Conclusion

From the studies the following conclusion can be drawn:

1. The bacterium Thiobacillus ferrooxidans takes at least 4 to 5 days to grow into a fully grown culture.
2. Using bioflotation i.e. by using Thiobacillus ferrooxidans as collector, there is an increase in the recovery of Copper.
3. The maximum recovery was found to be 98.5% for copper. This recovery was achieved using 400 ml microbial culture at 24hr interaction time.
4. From the Zeta potential studies it was found that maximum interaction between the ore and the bacteria takes place between pH 2-2.5.
5. Bio flotation is environment friendly process, were the use of microbe can used both as collector and can also used in water

treatment plant. From the studies carried out it may be observed that the bacterial culture can be used in flotation of high grade copper ore as a substitute for xanthate with appreciable recovery and grade.

6. From the studies carried out it may be observed that the Thiobacillus ferrooxidanscan be effectively used in floatation for valuable metals from lean grade and high grade ores.

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