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## **Use of the GEOCOAT™ Process for the Recovery of Copper from Chalcopyrite**

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In this study, the GEOCOAT™ process was evaluated as a low cost alternative for chalcopyrite bioleaching. The effect of temperature, leach solution composition, silver addition, and type of microorganisms inoculated were investigated in laboratory tests. Experiments were carried out at moderate temperature (35-45°C) using a mixed mesophilic bacterial culture, and at elevated temperature (70°C) using thermophilic archaea (extreme thermophiles). Chalcopyrite concentrate was coated onto inert support for the moderate temperature experiments, and onto low-grade chalcopyrite ore for the elevated temperature experiment. The rates of copper leaching were determined by analysis of leach solutions from small temperature-controlled columns. The extent of total copper removal was determined by residual copper analysis. The use of thermophilic archaea at 70°C resulted in 94% extraction of the concentrate copper, and 86% of the total copper, in 90 days. The improved leaching at elevated temperatures supports the contention that chalcopyrite bioleaching at lower temperatures is limited by the formation of a heat labile passivation layer. The best result at moderate temperature was 97% copper removal achieved with the addition of 0.1% silver sulfate, compared to 19.2% without silver. This result agrees with previous reports which found that silver enhanced chalcopyrite bioleaching at moderate temperatures. The GEOCOAT™ process can be used to leach high yields of copper from chalcopyrite concentrates over a wide range of copper grades. In addition, substantial copper recoveries may be achieved in as little as 90 days.

### **1. INTRODUCTION**

Chalcopyrite is economically the most important source of copper. It is also notoriously slow to bioleach. Although chemical and biological processes have been used to successfully extract copper from secondary copper sulfides, such as chalcocite, none have achieved commercial success with chalcopyrite. Stirred tank and heap biooxidations with mesophiles, such as *Thiobacillus ferrooxidans*, have been largely unsuccessful. A stirred tank process utilizing moderate thermophiles and fine grinding for chalcopyrite oxidation has shown some promise [1]. This process is currently at the pilot testing stage. Stirred tank processes utilizing extreme thermophiles have resulted in faster bioleaching of chalcopyrite than those using mesophiles or moderate thermophiles, but they required very low pulp densities, possibly due to the low solubility of oxygen at high temperature [2]. A large scale column test using thermophiles and mesophiles to biooxidize chalcopyrite ore [3] resulted in recovery of only 10.9 percent of the copper in 2,165 days.

The slow leach kinetics and incomplete biooxidation of chalcopyrite are often attributed to the formation of an inhibiting layer on the surface of the chalcopyrite as it oxidizes. Any biohydrometallurgical process for treating chalcopyrite will have to address the problem of this surface layer. Several theories concerning the nature of the inhibiting layer have been proposed [4].

One theory is that a jarosite coating forms on the chalcopyrite surface as it is leached [5]. Jarosite is formed in the presence of sulfate and ferric iron, in environments in which the pH increases above about 1.8. However, high concentrations of jarosite constituents (sulfate, ferric iron, ammonium or potassium) may lead to jarosite formation at lower pH [6]. The presence of high levels of iron and sulfate in residues of bioleached chalcopyrite supports this theory. However, experiments at GeoBiotics in which slow leaching occurred at low pH with dilute sulfate and iron, as well as reports in the literature [7], contradict this theory.

Another theory is that elemental sulfur produced during bioleaching forms a thick blanket that excludes bacteria and chemical oxidants from the chalcopyrite surface. The detection of large amounts of sulfur in bioleached chalcopyrite supports this theory [8]. In addition, electron micrographs have shown



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a thick sulfur coating on leached chalcopyrite [9]. However, evidence also exists, both in the literature [10] and from experiments at GeoBiotics, that the inhibiting layer is not composed of elemental sulfur. For example, thermophilic chalcopyrite biooxidations performed at GeoBiotics resulted in the formation of 5 to 6 weight percent elemental sulfur while still producing over 90% copper extraction (data not shown).

A third theory proposes that the inhibition is caused by the formation of an intermediate sulfide passivation layer. This passivation layer is less reactive than the original sulfide, and may also inhibit the flow of electrons and oxidants to and from chalcopyrite [11]. The exact nature of this passivation layer is complex and is the subject of scientific debate. However, there is good agreement that it is unstable at high temperatures [4, 7].

Some chemical additives have been shown to increase the dissolution of copper from chalcopyrite, presumably by disrupting the passivating layer. These additives include metals such as silver and bismuth [12], and nonmetals such as graphite [13]. Other methods that have shown promise include performing biooxidations at higher temperatures [14, 15], using chloride solutions rather than sulfate [16, 17], and enhancing galvanic reactions that occur between chalcopyrite and pyrite [18, 19]. Experiments investigating a number of these methods in combination with the GEOCOAT™ process were carried out at GeoBiotics.

The GEOCOAT™ process [20, 21] was developed to solve two major problems in heap bioprocessing: obstruction of liquid and air flow by fine particles of ore and other materials, and limited exposure of the sulfide to air, leach solution, and bacteria. In this process, sulfide concentrate is coated onto sized support rocks which are then stacked to form a heap. The heap is inoculated with suitable bacteria and bathed in a solution containing nutrients and other compounds, such as ferric iron. By removing fines and creating a sulfide-rich biooxidation environment, the GEOCOAT™ process ensures rapid biooxidation.

Initial attempts to biooxidize chalcopyrite using the GEOCOAT™ process with mesophiles were disappointing, resulting in copper extractions of less than 50% after several months of biooxidation. The slow leach rates supported the theory that some type of surface layer was inhibiting chalcopyrite bioleaching. Methods for circumventing this problem and obtaining high copper recoveries were explored. Promising results were obtained by combining the benefits of high temperature biooxidation with those of the GEOCOAT™ process. Chalcopyrite concentrates and ores were effectively bioleached in column tests at 60 to 70°C, resulting in 94% copper extraction in 90 days.

## **2. MATERIALS AND METHODS**

### **2.1 Moderate Temperature Columns (mesophiles)**

A series of bioleaching experiments (designated M1 through M3) were carried out in 8 cm diameter columns using the GEOCOAT™ process at moderate temperatures (35-45°C). These columns provided biooxidation rates for three different conditions: sulfate medium, chloride medium, and sulfate medium with silver sulfate. Each of these experiments contained 500g of chalcopyrite concentrate A (Table 1), coated on 3.5 kg of quartz rock support measuring 6.4 to 13.0 mm in diameter, as described in Kohr [20]. Another sulfate column (M4) was constructed as above, using chalcopyrite concentrate B. This column provided a direct comparison to the elevated temperature column (T1), which also contained concentrate B. The columns were wrapped with electrically resistive heating tape to control the temperature at 40 +/- 5°C.

**Table 1**  
**Composition and Origin of Ores and Concentrates**  
**Used in Column Experiments**

<b>Sample</b>	<b>Origin</b>	<b>Weight% Cu</b>	<b>Weight % Fe</b>
Concentrate A	Australia	22.40	32.50
Concentrate B	Arizona, U. S. A.	28.50	27.50
Low-grade ore	Arizona, U. S. A.	0.54	2.38

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The pH was controlled by adding a low pH nutrient solution to the column at a flow rate of approximately one liter per day. The pH of the effluent was recorded, readjusted and the solution was reapplied to the top of the column. Initially, pH was maintained between 1.5 and 2.3. As the experiment progressed the pH was lowered to between 1.1 and 1.5 to minimize obvious iron precipitation. Air was continuously added to ensure an adequate oxygen supply. The extent of copper and iron leaching were estimated by atomic absorption analysis of the effluent solution.

The columns were inoculated with 25 ml or more of a mixed culture containing approximately  $10^8$  bacteria per ml. The inoculum was dripped onto the top of the column after the pH of the effluent had dropped below 1.8. The mixed mesophilic culture consisted of *Thiobacillus ferrooxidans*, derived from ATCC strains #14119, #19859, #23270 and #33020, *Thiobacillus thiooxidans* derived from ATCC strains #8085 and #15494, and a *Leptospirillum ferrooxidans*-like organism which had been observed in the culture. *T. ferrooxidans* and the *Leptospirillum*-like bacteria were grown at 35 °C on 9K medium [21] supplemented with 20 g/l  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  at a pH of 1.6-1.8. *T. thiooxidans* were maintained at 35 °C on 9K medium supplemented with 10 g/l elemental sulfur.

The medium for the sulfate columns (M1 and M4) consisted of 1g/l  $(\text{NH}_4)_2\text{SO}_4$ , 0.17g/l  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.02g/l  $\text{K}_2\text{HPO}_4$ , and 0.03g/l KCl. This is a one-fifth strength solution of the standard 9K medium [21], designated 0.2X 9K, which has been found to perform as well as full-strength 9K in tests at GeoBiotics. The initial solution also contained 2g/l iron as  $\text{Fe}_2(\text{SO}_4)_3$ . The medium for the chloride column consisted of 0.8g/l  $\text{NH}_4\text{Cl}$ , 0.14g/l  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , 0.02 g/l  $\text{K}_2\text{HPO}_4$ , and 0.03g/l KCl, representing the chloride equivalent of 0.2X 9K. The initial solution also contained 2g/l iron as  $\text{FeCl}_3$ . Bacteria were not pre-adapted to this medium since the chloride levels were below those found to be inhibitory in tests at GeoBiotics. The medium for the silver sulfate column (M3) was identical to that of M1 and M4, without additional iron. For this column, 0.45 g silver as silver sulfate was added to the chalcopyrite concentrate during coating of the support rocks.

## **2.2 High Temperature Column (thermophiles)**

The high temperature experiment was performed at 70°C in an 8 cm internal diameter glass column which was wrapped in electrically resistive tape to control temperature. The temperature was monitored by thermocouples taped to the outside of the glass tube and by a glass thermometer in the top of the sample charge in the column. Air was applied to the top of the column through a heated stainless steel tube after being heated by bubbling through 90°C water. Effluent collected from the column was kept at 65°C. The flow rate was about 5 liters per day and the pH was maintained between 1.1 and 1.3. Solution was removed if the copper concentration exceeded 2 g/l; the volume was made up with the appropriate medium. The extent of copper leaching was estimated by the determination of copper in solution using atomic absorption spectroscopy.

The thermophilic column (T1) contained 486.8 g of chalcopyrite concentrate B coated on 5 kg of sized low-grade copper ore (Table 1), half at 3.2 mm to 6.4 mm and half at 6.4 mm to 12.7 mm. The concentrate was coated by applying the dry powder to wet support as described in Kohr [20]. An additional 100 g of uncoated ore was placed on top of the coated material, forming a 5 cm thick layer which provided insulation to lessen heat losses.

The temperature was maintained at 35°C for the first 3 days, while 2 liters of 5% sulfuric acid were circulated through the coated material in order to reduce the pH to less than 1. Following this pH adjustment, the temperature of the column was increased to 70°C and a low-chloride nutrient solution containing 0.16g/l  $\text{NH}_4\text{Cl}$ , 0.33 g/l  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , 0.1g/l  $\text{K}_2\text{HPO}_4$  and 0.1 g/l KCl, plus trace minerals, was circulated through the column. The nutrient salts solution is the chloride equivalent of that used by LeRoux and Wakerley [15] and others. The trace mineral solution is that used in DSMZ Medium 88 [22]. The pH of the nutrient solution was maintained at 1.1 to 1.3. Following equilibration of the column with nutrient solution, a mixed culture containing the extreme thermophiles *Acidianus brierleyi* (DSM #1651 and #6334), *Acidianus infernus* (DSM #3191), *Sulfolobus acidocaldarius* (ATCC #49426), and *Sulfolobus metallicus* (DSM #6482) was added to the column. This mixed culture was routinely maintained on DSMZ Medium 88 [22] at 70-75 °C.

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Seven days later, Column T1 was inoculated with thermophilic microorganisms recovered from a completed biooxidation column that had contained the same concentrate (Concentrate B) and low grade ore support as Column T1. This previous column, which had been inoculated with the same species of thermophiles that Column T1 received, resulted in a recovery of 86% total copper in 93 days (data not shown).

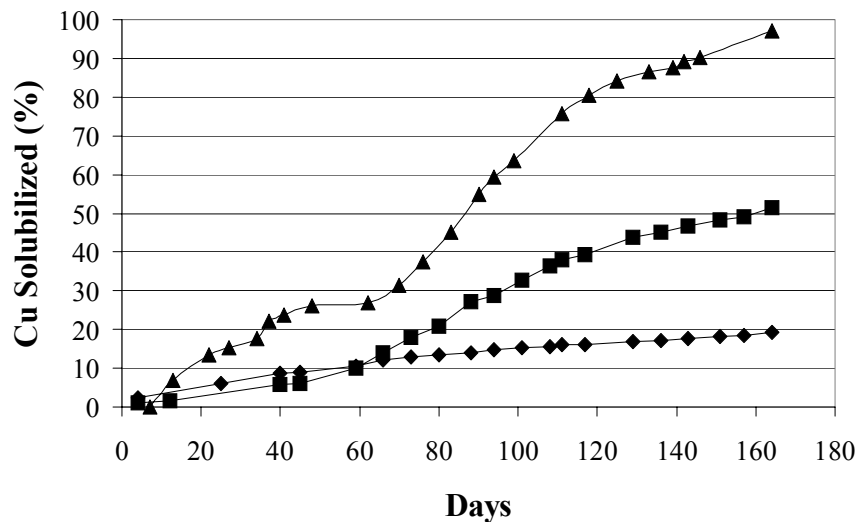
### 3. RESULTS AND DISCUSSION

#### 3.1 Mesophilic Test Results

As can be seen in Figure 1 and Table 2, the rate and extent of copper leaching were greatest in the column containing silver (M3): 97% of the copper was leached in 160 days. Only 19.2% of the copper was recovered from the sulfate column (M1) and 51.5% of the copper was recovered from the chloride column (M2) in the same time period.

Column	Conditions	Inoculum	Percent
M1	35-45 °C, sulfate, Conc. A	Mixed mesophiles	19.2%
M2	35-45 °C, chloride, Conc. A	Mixed mesophiles	51.5%
M3	35-45 °C, sulfate, Ag, Conc. A	Mixed mesophiles	97.0%
M4	35-45 °C, sulfate, Conc. B	Mixed mesophiles	25.2%
T1	60-70 °C, chloride, Conc. B	Mixed thermophiles	93.8% (86.0%*)

\* Copper leached from combined concentrate and whole ore support rock.



**Figure 1 - Copper solubilization from Concentrate A in three mesophilic columns under different chemical conditions.**

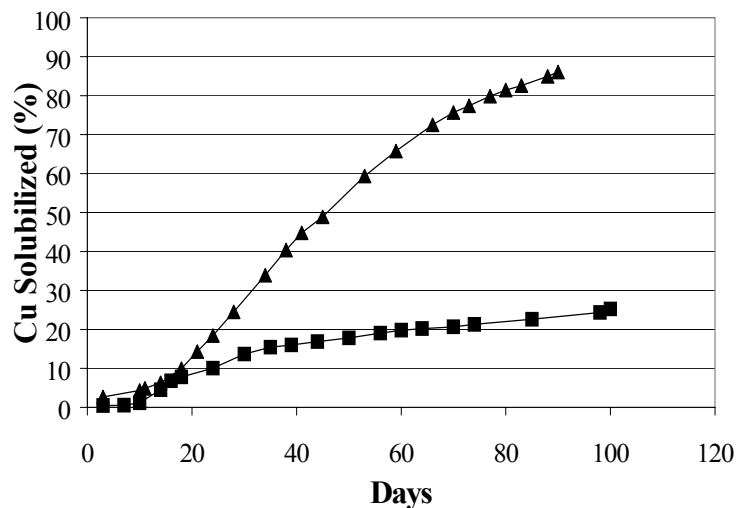
◆ M1, sulfate; ■ M2, chloride; ▲ M3 sulfate, Ag

The use of silver to accelerate chalcopyrite leaching has been extensively studied since it was patented in 1976 [23]. However, use of this method has been limited by the high cost of adding silver at 0.1% or 1 kg/ton. Lesser amounts of silver have a reduced effect on leaching.

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The catalytic mechanism appears to involve the precipitation of the silver, in the form of silver sulfide, on the surface of the chalcopyrite [24]. These sites create cathodic areas that promote galvanic coupling, resulting in faster and more complete dissolution of the chalcopyrite [13]. In fact, although the residue of the mesophilic column containing silver (M3) contained 22 weight percent elemental sulfur (data not shown), the catalytic effect of the silver was still able to occur. Despite the excellent recoveries obtained with the use of silver [25], it is of limited utility due to its high cost.

Chalcopyrite bioleaching utilizing a low concentration of chloride (~3 g/l) in combination with chemolithotrophic microorganisms appears promising. Research has shown that chemical leaching of chalcopyrite proceeds more rapidly in chloride than in sulfate solution [7, 26]. Both ferric chloride and cupric chloride at various concentrations have been used as lixiviants in chalcopyrite oxidations [4, 16,



17, 26, 27].

**Figure 2 - Comparison of copper solubilized during thermophilic (T1) and mesophilic (M4) biooxidations of Concentrate B.**

▲ T1, ■ M4

### 3.2 Thermophilic Test Results

The fastest leaching of copper from chalcopyrite was observed at 70°C in chloride medium inoculated with extreme thermophiles (Column T1): 94% of the concentrate copper, and 86% of the total copper (concentrate and support ore, combined) were solubilized in 90 days (Figure 2). The effect of the higher temperature on chalcopyrite leaching was so pronounced that copper leached faster from the chalcopyrite ore used as support rock at 70°C than from the chalcopyrite concentrate at 35°C (data not shown).

Rapid leaching of chalcopyrite with thermophiles has been obtained in stirred reactors [15, 28, 29], but only at low pulp densities. Boon [2] has suggested that the pulp density limitation is due to insufficient gas-liquid mass transfer at higher temperatures. A large scale column study investigating the ability of thermophiles to bioleach chalcopyrite ore concluded that heap-based biooxidation of chalcopyrite by these organisms was ineffective, due to the rapid exhaustion of the easily-accessible sulfides [3].

Because they are capable of thriving on mineral sulfides in high temperature environments, thermophiles are ideal for use in bioleaching processes which require high temperatures or produce excess heat. In addition to biooxidizing mineral sulfides, many thermophiles also oxidize elemental sulfur



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and ferrous iron [22, 30]. By oxidizing elemental sulfur that may be formed during chalcopyrite biooxidation, thermophiles increase the chalcopyrite leach rate two-fold: they remove sulfur which may be obstructing the chalcopyrite surface and they produce heat which helps to maintain the heap temperature. Oxidation of ferrous iron by thermophiles results in a high redox potential and provides ferric for indirect leaching of the chalcopyrite. In addition, some thermophilic species are able to grow in extensions containing up to 4% NaCl [31, 32], allowing them to survive in chloride leach solutions.

Rapid biooxidation of chalcopyrite at high temperature provides some insight into the nature of the passivating surface layer. If the passivating layer is composed of jarosite, then one would expect more extensive formation of the layer at higher temperatures. The presence of high levels of sulfate and iron in the biooxidized residue from the thermophilic column suggests that jarosite formed during biooxidation (data not shown). However, its presence did not inhibit the rate and extent of biooxidation. If the surface layer is composed solely of elemental sulfur, then it would not be expected to break down at the temperatures used in these experiments. If the inhibiting layer is composed of a thermally-unstable combination of sulfide and elemental sulfur, as suggested by Ammou-Chokroum [4], Parker [7], and others, it could be degraded by both heat and thermophilic chemolithotrophs at 70°C, as was seen in experiments carried out at GeoBiotics.

#### **4. CONCLUSIONS**

Copper extraction of 94% was achieved from a recalcitrant chalcopyrite in 90 days using the GEOCOAT™ process at high temperature (70°C) in combination with thermophilic microorganisms and a low chloride salt medium. In this same column, copper was also leached from the low-grade chalcopyrite ore support rocks, resulting in an overall copper recovery of 86%. A copper recovery of 97% was also achieved from a different chalcopyrite concentrate in 160 days at moderate temperature using silver as a catalyst, compared to a recovery of 19.2% in the absence of silver. Of these two alternatives, the use of thermophilic archaea in a high temperature heap process is more economically promising. A well-designed heap process for thermophilic chalcopyrite bioleaching could circumvent some of the hindrances to thermophilic stirred tank bioprocesses, namely high operating costs and the requirement for low pulp density. In such a heap process, the exposed chalcopyrite concentrate will leach extensively at the optimum temperatures for growth and activity of the thermophilic microorganisms.

The rapid rate of chalcopyrite leaching at temperatures above 60°C, compared to that at 35°C, supports the theory of a heat-labile inhibiting layer. Because neither jarosite nor elemental sulfur, two theorized constituents of such a passivation layer, would be expected to decompose at this temperature, the layer may be composed of an intermediate sulfide which decomposes at high temperature as proposed by Ammou-Chokroum [4], Parker [7], and others [11, 33].

The heap leaching of refractory chalcopyrite at 60 to 80°C with extreme thermophiles has not yet been demonstrated at large scale. However, the possibility exists that it could prove to be a low cost method of treating even the most recalcitrant chalcopyrite ore. The heat generated from the biooxidation process itself may significantly reduce or eliminate the energy cost of maintaining the heap within the required temperature range.



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