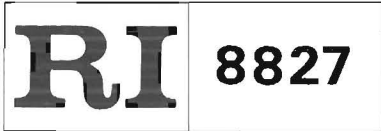


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Percolation Leaching of a Chalcopyrite-Bearing Ore at Ambient and Elevated Temperatures With Bacteria

By B. W. Madsen and R. D. Groves



UNITED STATES DEPARTMENT OF THE INTERIOR

Report of Investigations 8827

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

| | | | |
|-----|----------------|--------|------------------|
| °C | degree Celsius | L/min | liter per minute |
| cm | centimeter | m | meter |
| g | gram | mL | milliliter |
| g/L | gram per liter | mol/L | mole per liter |
| h | hour | pct | percent |
| kg | kilogram | t | metric ton |
| L | liter | wt pct | weight percent |

PERCOLATION LEACHING OF A CHALCOPYRITE-BEARING ORE AT AMBIENT AND ELEVATED TEMPERATURES WITH BACTERIA

By B. W. Madsen,¹ and R. D. Groves²

ABSTRACT

The Bureau of Mines conducted a large-scale (6.4 t), long-term (2,165 days) test to gain a better understanding of the leaching characteristics of chalcopyritic ores. An ore sample containing 0.77 pct Cu was leached in a fiberglass column by downward percolation of acidified ferric sulfate solutions. Three sets of leaching conditions were investigated: (1) ambient temperature leaching, (2) elevated temperature (50° to 60° C) leaching, and (3) elevated temperature leaching after inoculation with thermophilic bacteria.

Leaching at ambient temperature resulted in a copper extraction rate of 0.44 pct per 100 days. Increasing the temperature to 50° to 60° C resulted in decreased activity of natural mesophilic bacteria, and the leaching rate decreased to 0.22 pct per 100 days. The pH was lowered from 2.0 to 1.6, and nutrient solutions that contained thermophilic bacteria were added. This procedure resulted in an increase in the ferric-to-ferrous iron ratio and an increase in the copper leaching rate. However, the increased leaching rate was not sustained, and 120 days after inoculation the bacterial activity declined, the ferrous iron content increased, and the copper leaching rate decreased.

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INTRODUCTION

Dump or heap leaching of copper ores is an important supplement to open pit mine production of copper and provides about 11 pct of the total copper recovered in the United States (13).³ Chalcopyritic ores comprise the largest portion of these low-grade ores and are the most difficult to leach. Modern dump leaching of chalcopyrite is slow and inefficient, and much of the copper remains in the leached dump. Research to improve the leaching efficiency of chalcopyritic ores was initiated by the Bureau of Mines, and the results are reported herein.

Previous leaching studies have been conducted by the Bureau with 6- to 8-t samples of copper sulfide ore. These ores were leached at ambient temperature and pressure (15-20) and simulated a portion of a leaching dump or heap near the surface. These studies demonstrated that copper extraction could be improved by (1) removing the ore fines to enhance air accessibility, (2) injecting the ore column with gaseous oxygen, (3) using solvent extraction rather than cementation to avoid plugging of the ore bed with precipitated iron salts, and (4) injecting gaseous sulfur dioxide to dissolve and remove precipitated iron salts and provide better solution and air flow through the ore (16-19). Each of these techniques resulted in a higher partial pressure of oxygen in the interior of the column and stimulated the growth of bacteria. Iron-oxidizing bacteria (*Thiobacillus ferrooxidans*) and sulfur-oxidizing bacteria (*Thiobacillus thiooxidans*) continuously replenish the supply of ferric ions and acid necessary for leaching.

Although kinetic studies of sterile chalcopyrite minerals have shown that the leaching rate increases with increased temperature (12, 21), the rate has been found to decrease with increased temperature when *T. ferrooxidans* or other low-temperature bacteria are involved in

the leaching process (7, 21). Cathles and Schlitt (7) have shown that a large dump size can produce heat that lowers the reaction rate by reducing bacterial activity at temperatures exceeding the optimum for a particular species of bacteria. Recent incentives to develop high-temperature bacterial leaching regimes have been provided by the isolation of thermophilic bacteria. These bacteria oxidize ferrous iron and sulfide minerals (3, 5-6) and are capable of growing at temperatures of 45° to 80° C and at pH values of 1 to 6 (4). Thermophilic bacteria were found particularly useful in increasing the rate of chalcopyrite leaching in low-grade waste material containing pyrite (2) and were observed during leaching of a large experimental copper-bearing waste sample. A definite correlation between the leaching rate and thermophilic bacteria population could not be made because of the complexity of the test (22).

The additional research presented in this report involves the leaching of a chalcopyritic ore at both ambient and elevated temperatures. By conducting the test at variable temperatures, a portion of ore in an actual dump was closely simulated. In commercial practice, the ore is placed at the top of a heap or dump where it encounters near-ambient temperatures for a period of time. As new material is placed at the top of the heap, the original portion of ore is heated, owing to the thermal insulating effect of the ore and the exothermic reactions that occur in the ore bed. The leaching rate of copper in this study was found to be low at ambient temperature and even lower at elevated temperatures. These facts are supported by other studies (7, 22). It was decided to use the new technology of inoculating hot (55° to 60° C) ore beds with thermophilic bacteria in order to enhance the copper extraction rate. The leaching rate of copper was studied with respect to temperature, dissolved ferric ion concentration, and the presence or absence of low-temperature and thermophilic bacteria.

³Underlined numbers in parentheses refer to items in the list of references at the end of this report.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the contributions of Corale L. Brierley, President, Advanced Mineral Technologies Inc., Socorro, NM, to the currently reported research. She provided necessary bacterial assays of leach solution

samples, dense suspensions of thermophilic bacteria for ore inoculations, and continued advice and suggestions on the biological aspects of the research. These contributions were important and essential to the investigation.

EXPERIMENTAL PROCEDURE

SAMPLE DESCRIPTION

A sample containing about 9 t of a granitic copper ore was obtained from an Arizona copper mine. A portion of the sample was used for the leach test. The sample contained 0.77 pct Cu, which was entirely in the form of chalcopyrite. The pyrite content was 2.6 pct. Although ore for dump leaching may contain boulders larger than 2 m in diameter, the maximum diameter of particles in the as-received sample was near 15 cm. A 2.1-t portion of the ore was used for a screen analysis, and a smaller sample was taken from each size fraction for chemical analysis. The screen and chemical analyses are presented in table 1 and show a nearly uniform distribution of copper among the particle sizes. A concentration of iron and sulfur (probably pyrite) in the finer ore fragments is noted in the table.

LEACHING AND COPPER RECOVERY

A portion of the ore sample weighing 6.43 t was leached in a fiberglass column 1.37 m in diameter by 3.04 m high. Figure 1 shows the side view of two

leaching columns as used at ambient temperature. The column on the right contained the chalcopyrite ore described in this report. For tests conducted at elevated temperatures, the column was covered with 9 cm of fiberglass insulation to provide a uniform temperature in the column and reservoir. A covered fiberglass reservoir tank below the leaching column and a lid at the top of the ore column were used to minimize evaporation. Figure 2 shows the solution distribution system, which consisted of a rotating perforated arm. When the lid was used, the solution distribution system was changed to a perforated hose that sprayed solution evenly over the ore. The solution was collected in a reservoir at the bottom of the column and continuously recirculated to the top at a rate of 0.85 L/min. Water at pH 7 was initially used to wet the ore. As a result of recirculating the water for 36 days, the solution pH remained at 7 and no copper was extracted. The volume of the leach solution was 280 L in the ore column and 200 L in the reservoirs, giving a total of 480 L in the leaching system during circulation.

TABLE 1. - Head analyses of copper sulfide ore

| Size fraction, cm | wt pct | Chemical analysis, pct | | |
|------------------------|--------|------------------------|------|------|
| | | Cu | Fe | S |
| Plus 15.24..... | 2.4 | 0.85 | 3.00 | 1.95 |
| Minus 15.24 plus 10.16 | 27.5 | .78 | 3.00 | 1.99 |
| Minus 10.16 plus 7.62. | 23.4 | .80 | 3.35 | 2.31 |
| Minus 7.62 plus 5.08.. | 19.7 | .74 | 3.20 | 2.24 |
| Minus 5.08 plus 2.54.. | 15.6 | .73 | 3.25 | 2.14 |
| Minus 2.54 plus 1.27.. | 3.1 | .75 | 3.30 | 2.18 |
| Minus 1.27 plus 0.635. | 1.5 | .73 | 3.10 | 2.12 |
| Minus 0.635..... | 6.8 | .76 | 4.20 | 3.09 |
| Composite..... | 100.0 | .77 | 3.25 | 2.22 |

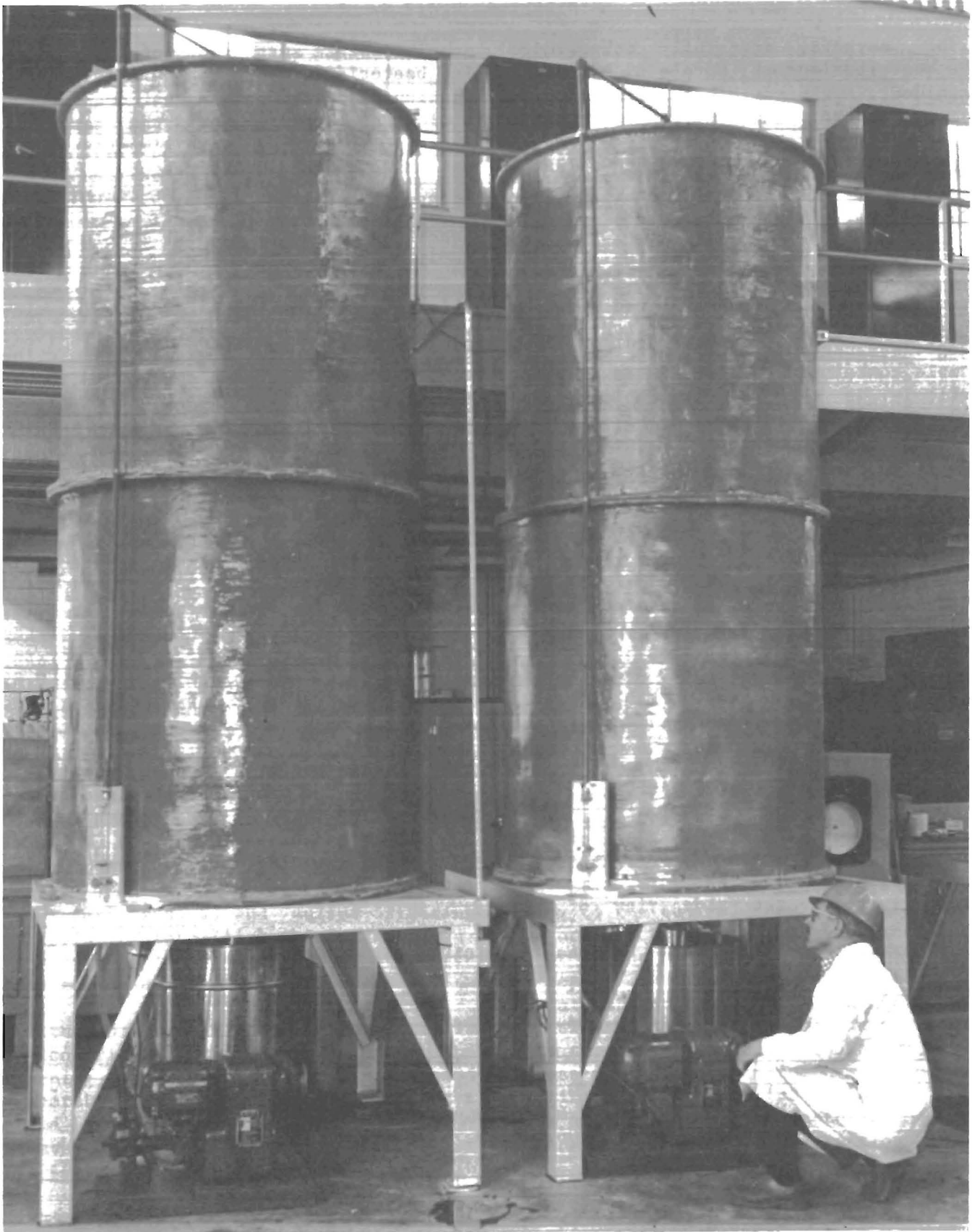


FIGURE 1. - Side view of leaching columns showing solution pumps and surge tanks.

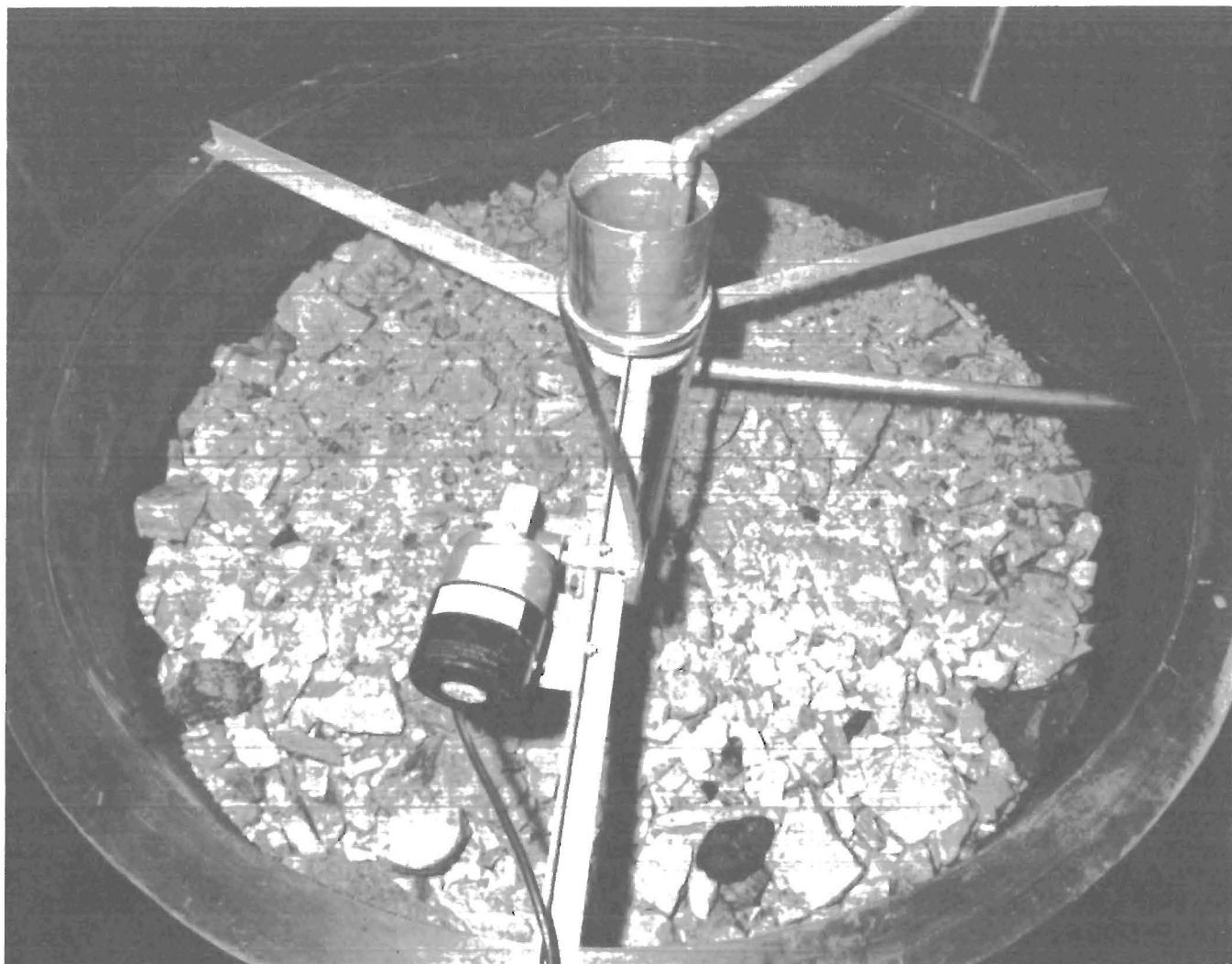


FIGURE 2. - Top view of leaching column showing solution distribution system.

The leaching of the ore was initiated by the addition of sulfuric acid, which lowered the solution pH to 2. As a result, both the ferric iron and copper concentrations in the solution increased. Acid was added as needed to keep the pH between 2 and 2.1. When the copper content of the leach solution increased to between 0.5 and 1.0 g/L, the circulation was temporarily discontinued and the column allowed to drain. Copper was removed from the solution by solvent extraction with LIX-64.⁴ After a drying or resting period of 2 days, leaching was continued

with barren solution from the solvent extraction stage. This procedure simulated dump leaching operations in that periodic leaching and resting periods were used. Murr (22) states that there are some very important consequences of intermittent solution cycles. When the solution flow is stopped, the lixiviant film surrounding individual ore particles tends to concentrate bacteria, ferric ions, and oxygen at the ore surface. This condition promotes oxidation reactions if aeration is sufficient.

The copper was not continuously removed from the pregnant leach solution, as in commercial leaching operations, because the increase in copper content in the

⁴Reference to specific brand names is made for identification only and does not imply endorsement by the Bureau of Mines.

solution was very small for each pass through the column. However, the copper was removed from solution when its concentration reached near 1 g/L, approximately the level attained in commercial operations.

Analysis of the solutions before and after solvent extraction allowed calculation of the copper extraction. Other metallic ions, including Fe^{3+} , Mg^{2+} , Al^{3+} , Ca^{+} , Mn^{4+} , and Zn^{2+} , were present in the leach solutions but were not removed from the solution in the solvent extraction step. Natural buffering of the solution by jarosite formation generally maintained the solution pH near 2. The initial part of the experiment lasted for 1,135 days and typified surface conditions of a leaching dump where ambient temperatures are most likely to occur.

Pyrite leaching is exothermic and provides the heat necessary for the elevated temperatures found in the leach dumps. The experimental leach was heated to 50° C to simulate conditions within the interior of a leaching dump. An immersion heater was used to heat the solution, and the circulating solution heated the ore. During a 32-h heat-up period, the reservoir temperature was maintained at 50° C and the column temperature slowly increased. At day 1,600, the column temperature was raised further, to 60° C, and beginning on day 1,880 the leach column was aerated to provide optimum conditions for the growth of the aerobic thermophilic bacteria. Air was forced through a perforated plastic pipe that was embedded in the center of the ore bed to a depth of 2 m. This simulated the natural convection that occurs in a commercial leaching operation.

BACTERIAL INOCULATION

During the ambient-temperature phase of the experiment the ore was not inoculated with bacteria because natural mesophilic bacteria, T. thiooxidans and T. ferrooxidans, were initially present in the ore. Their presence in leach solutions was verified by a most probable number

(MPN) analysis technique (9). This technique involves dilution, culturing, and microscopic examination to determine the number of active bacteria, and identifying bacteria by morphology and growth conditions.

When the temperature of the leaching environment was raised to 50° C, the low-temperature bacteria were rendered less active and it was necessary to inoculate with thermophilic bacteria. On days 1,305 and 1,334, the ore was inoculated with a culture containing two thermophilic microbe species, Sulfolobus acidocaldarius and Sulfolobus brierleyi. The inoculation procedure consisted of sprinkling a small amount (0.023 L) of a dense suspension of bacteria on the top of the ore. The dense suspensions were prepared by incubating bacteria in 9K solution at 60° C for 10 to 15 days and then concentrating the bacteria by centrifuging. Table 2 lists the components of the 9K nutrient solution.

TABLE 2. - Composition of modified 9K nutrient solution

| Component | Weight added to 1.0 L of distilled water, ¹ g |
|---|--|
| $(\text{NH}_4)_2\text{SO}_4$ | 3.0 |
| KCl..... | .1 |
| K_2HPO_4 | .5 |
| $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ | .5 |
| $\text{Ca}(\text{NO}_3)_2$ | .01 |
| Yeast extract.... | .20 |
| $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ | 10.0 |

¹The pH was adjusted to 1.6 with H_2SO_4 .

After the ore column was heated to 60° C, a different procedure was used to inoculate the ore with thermophilic bacteria, which involved pumping 50 to 85 L of freshly prepared dilute suspensions of bacteria to the top of the ore. The dilute suspensions of thermophilic bacteria were prepared by inoculating 85 L of 9K solution, incubating for 10 to 15 days at 60° C in an incubator separate from the ore column, and then pumping about 90 pct of the culture to the ore. The remaining 10 pct was used to inoculate another

batch of 9K nutrient solution. This procedure was used on four separate occasions: days 1,957, 1,971, 1,983, and 2,002. The pH of this solution was 1.6, to avoid precipitation of iron salts to which bacteria may attach. Attachment of bacteria to the salts would make them unavailable for distribution to the ore column as a suspension in a liquid.

At a point 27 days prior to the addition of the nutrient solutions, the pH of

the leach solution in the ore column was lowered from 2.0 to 1.6 by adding sulfuric acid. The lower pH was needed to keep the bacteria in suspension in the nutrient solution so that they could be evenly distributed to all parts of the ore column before attaching to mineral particles. Because the pH in the large column was the same as the pH in the incubating tank, the transition for the bacteria to a new environment was easier.

RESULTS AND DISCUSSION

AMBIENT TEMPERATURE LEACHING

The copper extraction for the ambient temperature leaching period is shown in figure 3. The extraction rate was very slow. Only 5.0 pct of the copper was leached from the ore in 1,135 days. This amounts to a leaching rate of 0.12 kg Cu per metric ton ore per year and compares with rates of 0.21 and 0.09 kg Cu per metric ton ore per year established for two other chalcopyritic ores previously leached at ambient temperature (20).

The following chemical equation has been reported to represent the stoichiometry for the acid ferric sulfate leaching of chalcopyrite (12, 20):

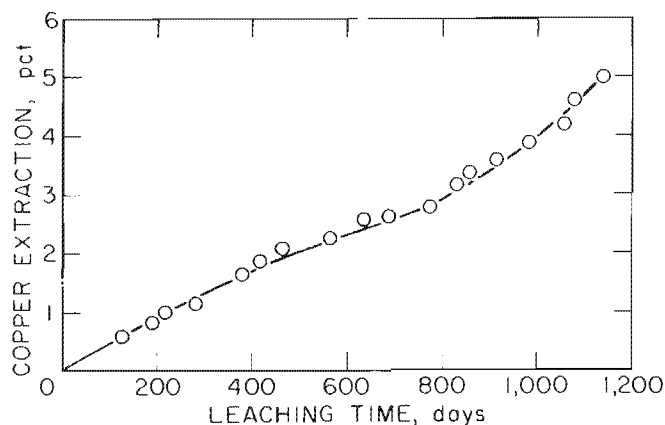
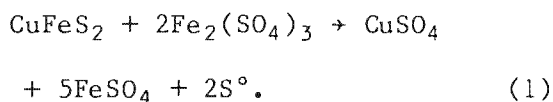
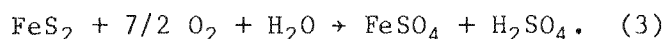
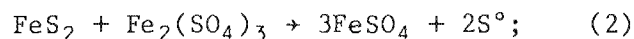


FIGURE 3. - Copper extraction from ore at ambient temperature.

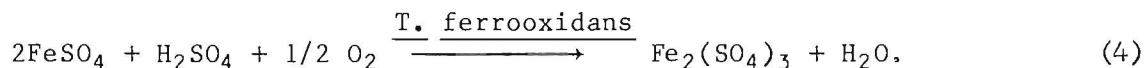
This reaction produces a dense, tenacious layer of sulfur that covers the unreacted chalcopyrite and severely retards the leaching rate. As reported by Munoz (21), the transfer of electrons through this sulfur layer is probably the rate-limiting factor in chalcopyrite leaching. Removal of this sulfur layer or changing the environment to aid in electron transport through the sulfur layer accelerates the leaching kinetics.

The original leach solution did not contain iron. However, after acid addition and a few weeks of leaching, the iron content increased because of the small amount of acid-soluble iron that leached from the ore. This dissolved iron was oxidized by bacterial activity and was then used to leach more iron from the ore according to the reactions:



It may be noted that reaction 3 is exothermic and produces acid.

The concentration of the ferric iron in the leach solution during the ambient temperature leaching period is plotted in figure 4. The ferric iron content gradually increased during this leaching period. T. ferrooxidans activity within the ore column promoted oxidation of the ferrous iron (produced primarily by reaction 2) according to the following reaction:



Because the kinetics of reaction 4 are rapid compared with the kinetics of reaction 2, the dissolved ferrous iron concentration remained less than 0.01 g/L during leaching. Increased ferric ion concentration increases the rate of diffusion of ferric ions through ore fragments. Figures 3 and 4 show an increase in copper extraction rate and dissolved ferric iron concentration, respectively. However, the copper leaching rate did not increase in the same proportion as the dissolved ferric iron concentration did.

Mesophilic bacteria were present and active during the initial 1,135 days of leaching at ambient temperature. The low ferrous and high ferric iron content of the leach solution during this period gave indirect evidence of this bacterial activity. To support this indirect evidence, it has been shown that the rate of reaction for equation 3 is roughly 10^6 times faster with these bacteria than without (14). In addition, leach solution samples collected on day 601 were subjected to an MPN bacteria analysis and found to contain 10^6 cells of *T. ferrooxidans* and 10^5 cells of *T. thiooxidans* per milliliter of solution.

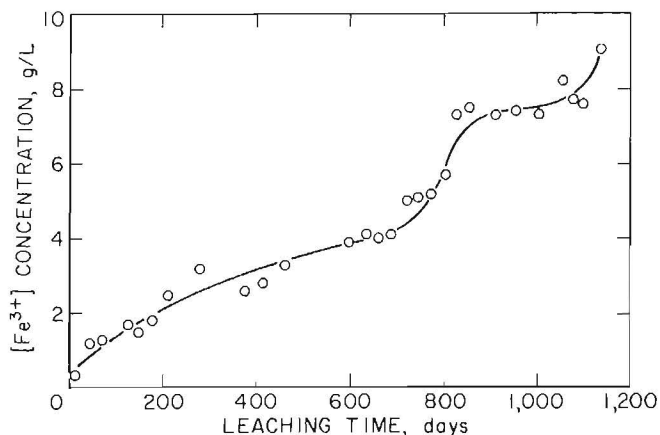


FIGURE 4. - Ferric iron concentration in leach solution during ambient temperature leaching.

ELEVATED TEMPERATURE LEACHING WITHOUT ACTIVE THERMOPHILIC BACTERIA

Increasing the temperature of the ore column and solution to 50° C resulted in a decrease in the copper extraction rate, as shown in figure 5. During this period the copper leaching rate was very low. Raising the temperature further to 60° C at day 1,600 resulted in a slight increase in the copper extraction rate, followed by a very slow extraction rate.

Increasing the temperature caused the iron concentration of the solution to decrease as shown in figure 6. This decrease was primarily a result of the decreased solubility of ferric iron compounds at the elevated temperatures. Figure 6 shows that the ferric concentration decreased from a maximum of 8.8 g/L at day 1,126 to 0.1 g/L at day 1,210. The ratio of ferric to total iron dropped from about 1.0 to 0.01 during this leaching period. Murr (22) states that too much heat retards or stops the bacterial catalysis of the mesophilic microbes that are present during the ambient temperature leaching. Since the bacteria provide the principal catalyst for iron oxidation, it follows that the decrease in the ferric-to-total iron ratio was the

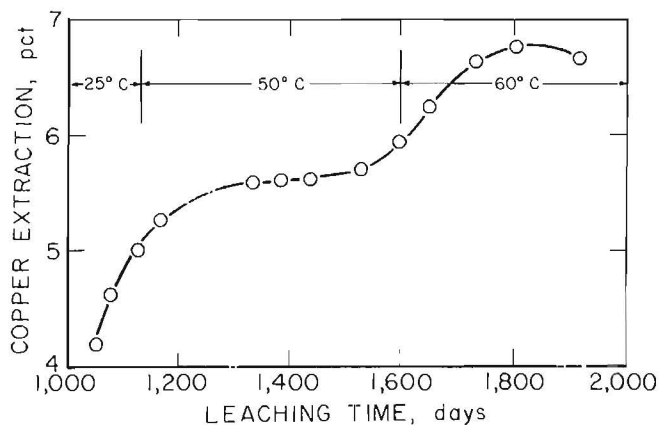


FIGURE 5. - Copper extraction after increasing temperature to 50° and 60° C.

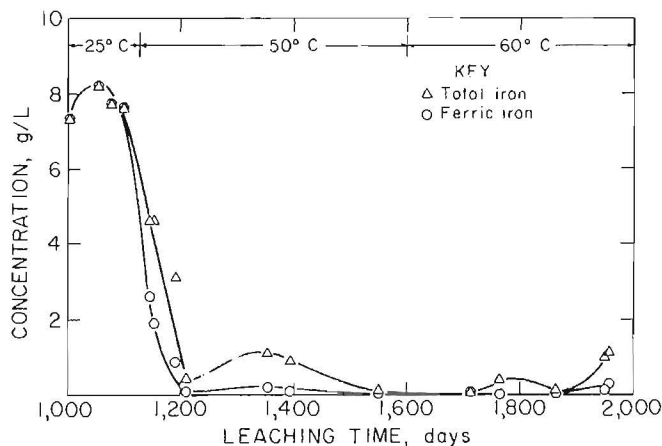


FIGURE 6. - Total and ferric iron concentration in solution after increasing temperature to 50° and 60° C.

direct result of decreased bacterial activity after the temperature of the ore was increased. Thus, there were insufficient ferric ions present to sustain the copper leaching rate attained at ambient temperature.

As stated before, during the period when the column was maintained at 50° C, an attempt was made to inoculate the column with the thermophilic microbe species, *S. acidocaldarius* and *S. brierleyi*. Dense suspensions of these bacteria were sprinkled on the ore on days 1,305 and 1,334. Then, on days 1,334, 1,343, and 1,366, leach solution samples were collected and bacterial analyses made by an MPN counting technique. The data show a complete absence of thermophilic bacteria, but the last sample did contain a very small number (25 cells per milliliter) of *T. ferrooxidans*. The failure to inoculate the ore was probably due to the change in environment or the lack of nutrients in the leach column.

The temperature of the column was increased to 60° C on day 1,600, and leaching continued for an additional 357 days without further attempts to inoculate with thermophilic bacteria. As a result, the ratio of ferric to total iron remained at about 0.1 and the copper leaching rate increased slightly between 1,600 and 1,800 days. Air injection was

started at 1,800 days and was continued until termination of the test. The air was injected into the leach column through a perforated pipe embedded in the ore bed. No increase of copper extraction was experienced immediately after air injection started. Brierley (3) found that air injection did not appreciably increase the copper extraction rate either from ore columns inoculated with thermophilic bacteria or from uninoculated columns.

ELEVATED TEMPERATURE LEACHING WITH ACTIVE THERMOPHILIC BACTERIA

The ore column was inoculated on four occasions between days 1,957 and 2,002 at 60° C. A volume of 50 to 85 L of solution containing active thermophilic bacteria was used for each inoculation, for a total of 295 L. The copper extraction rate increased dramatically (fig. 7) to a rate that was 6.64 times that of the average ambient temperature (25° C) leaching rate. This result agrees with Chakraborti and Murr (8), who found that the oxidation of chalcopyrite was much more effective with thermophilic bacteria than with mesophilic bacteria. They stated that the rate of reaction should increase 1.93 times for each 10° C temperature rise or 6.76 times for the temperature rise (from 25° C to 60° C) encountered in the present study. Figure 8 shows the copper extraction for the entire leaching test so that a comparison

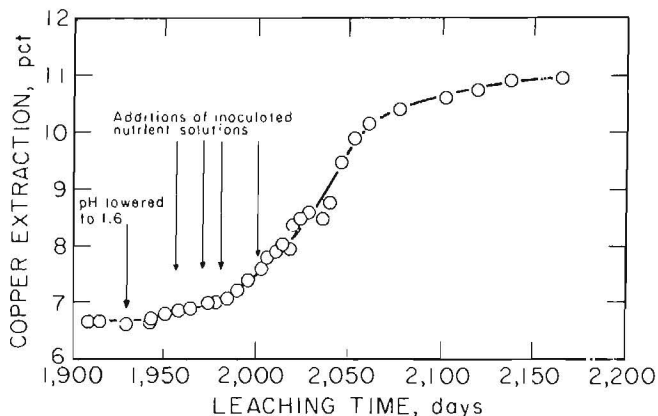


FIGURE 7. - Copper extraction after inoculation of ore with thermophilic bacteria.

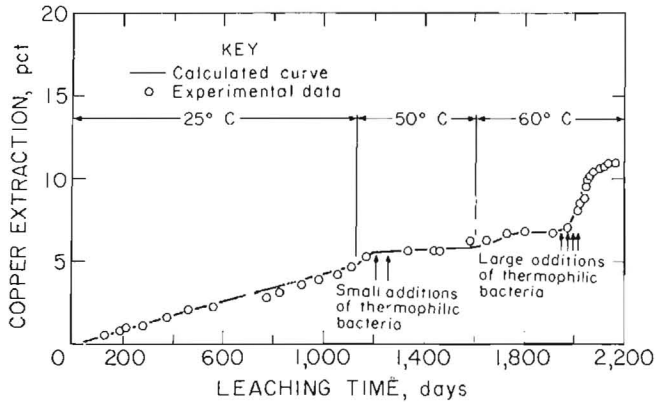


FIGURE 8. - Effect of heating and inoculating an experimental leach column of chalcopyrite-bearing ore.

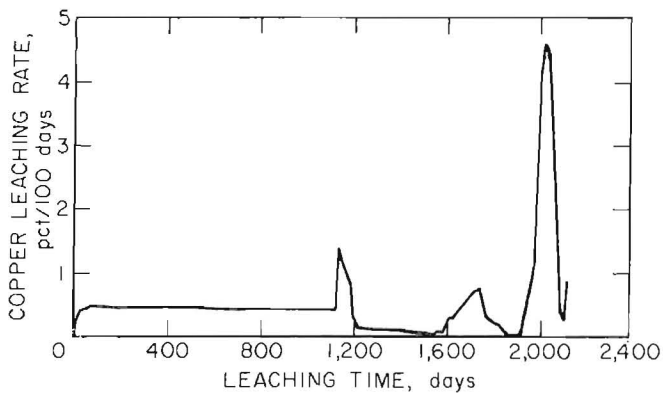


FIGURE 9. - Leaching rate as a function of time.

can be made of the different leaching conditions encountered.

After the pH of the column was lowered by adding sulfuric acid, the leaching

rate increased slightly (fig. 7), but no dramatic effect was experienced. This fact is supported by other studies that show no effect of acid concentration on the leaching rate of chalcopyrite for acid concentrations less than 1 mol/L (1, 10-11). Copper leaching did not accelerate greatly until after day 1,990. The time lag between inoculation and increased copper extraction rates was due to the incubation period required in the leach column. Chakraborti and Murr (8) found a similar time lag of about 20 to 30 days. This time period allowed for the bacterial population to increase to a level where rapid oxidation of ferrous iron was possible.

Table 3 shows the rate of copper leaching for the different time periods of leaching, and figure 9 is a plot of the leaching rate as a function of time. The leaching rate is the first derivative of the solid copper extraction curve (fig. 8) with respect to time. This analysis shows that the maximum leaching rate occurred at 2,014 days.

The leaching rate decreased after a period of about 120 days of accelerated copper leaching. This decrease was apparently the result of the consumption of the chalcopyrite mineral particles that were readily accessible. The depletion of accessible minerals may have caused lower bacterial activity since these minerals are an energy source for the

TABLE 3. - Leaching rates of copper from chalcopyrite ore under different conditions

| Conditions | Leaching time | | Copper extraction | | Relative extraction rate, ambient = 1.0 ¹ |
|--|---------------|------------|-------------------|---------------------------------|--|
| | Days included | Total days | For period, pct | Rate, pct/100 days ¹ | |
| Ambient temperature with active Thiobacilli..... | 0-1,135 | 1,135 | 5.0 | 0.44 | 1.00 |
| 50° C with low bacterial activity..... | 1,135-1,600 | 465 | 1.2 | .26 | .59 |
| 60° C with low bacterial activity..... | 1,600-1,957 | 357 | .7 | .20 | .45 |
| 60° C with active thermophilic bacteria..... | 1,957-2,077 | 120 | 3.5 | 2.92 | 6.64 |
| 60° C with lower bacterial activity..... | 2,077-2,165 | 88 | .5 | .57 | 1.30 |

¹These values reflect the averages for the corresponding time periods even though the extraction rate may be changing rapidly.

thermophilic bacteria. The exhaustion of nutrients in the leach solution may also have contributed to the decrease in bacteria activity. Brierley (3), however, found that elements leached from typical ore provide enough nutrients to sustain bacterial growth. Furthermore, Chakraborti and Murr (8) report data showing that leaching of an ore containing chalcopyrite and covellite with thermophilic bacteria (at 50° C) ceased after only 4.3 pct copper extraction. They used 10 g of ore (0.53 pct Cu) in 100 mL of inoculated nutrient solution, thus providing 10 mL of nutrient solution for every gram of ore. This nutrient solution-to-ore ratio is 218 times the ratio used in the present column leach study. Their results support the theory that the depletion of accessible minerals and not the depletion of nutrients was responsible for the decreased copper leaching rates.

Brierley (3) leached chalcopyrite ores with ferric iron and thermophilic bacteria and found that the copper leaching rate diminished appreciably after an initial high leaching rate. She speculated that copper leached more slowly after the minerals on the surface of the ore particles were leached, and that the coating of ore particles with precipitated iron salts may have contributed to the decreased leaching rate.

The thermophilic bacteria may have removed sulfur from chalcopyrite minerals, thus making the mineral surfaces more accessible to the solution. This is a possible explanation for the initial increased copper extraction rate. The bacteria also may have aided in the transport of electrons through the sulfur layer. Munoz (21) has reported electronic transport as the most probable rate-controlling factor in the leaching of chalcopyrite.

The ferric iron content and the ratio of ferric to total iron in the solution increased after the lowering of the pH to 1.6 and addition of the first two large volumes of solution containing thermophilic bacteria. The lower pH allows

greater ferric iron salt solubility, and high bacterial activity maintains a high ferric-to-total iron ratio in solution. Supporting data are shown in figures 10 and 11.

The increase in ferric iron concentration was a result of the increased reaction rate of reaction 3, the lower solution pH, and the iron added with the nutrient solutions. The total amount of ferric iron added with the nutrient solutions was 570 g, which is insufficient to leach the 1,980 g of copper extracted between day 1,957 and the end of the test. Calculations according to equation 1 show that 6,970 g of ferric iron are needed to leach 1,980 g of copper from chalcopyrite.

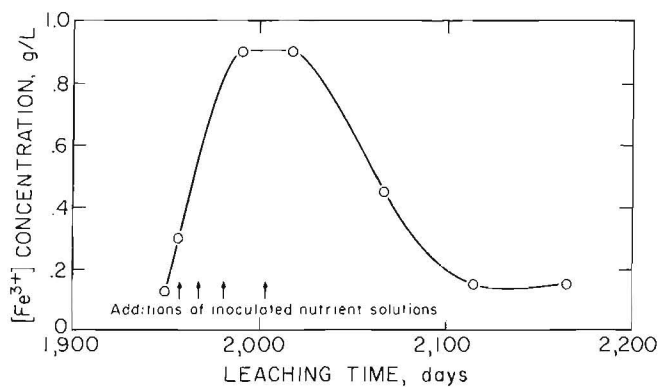


FIGURE 10. - Ferric iron concentration in leach solution after inoculation with thermophilic bacteria.

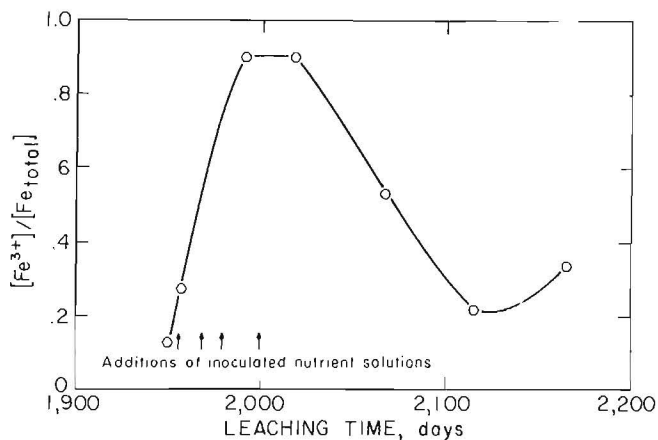


FIGURE 11. - Ratio of ferric to total iron in leach solution after inoculation with thermophilic bacteria.

The repeated oxidation of ferrous iron to ferric was needed to sustain leaching; otherwise, all of the ferric iron would convert to ferrous iron because of chemical reactions, and leaching would cease (7, 22). The bacterial activity provided the necessary catalyst for iron oxidation needed for leaching and lowered the ferrous iron concentration, as shown by Brierley (3). Dutrizac (9) showed that even small amounts of ferrous iron lower the initial leaching rate of chalcopyrite by ferric ions. The bacterial activity decreased the ferrous iron concentration from 0.87 g/L at 1,950 days to 0.10 g/L at 1,991 days and thus aided the leaching of chalcopyrite. Brierley (3) found that the bacteria were beneficial when smaller columns of chalcopyritic ore were leached because they kept dissolved iron in the oxidized state.

After about 2,050 days of leaching, a decrease was noted in the ferric ion concentration, the ratio of ferric to total iron (the bacterial activity indicator), and the copper extraction rate. It is believed that a depletion of chalcopyrite and pyrite minerals accessible to thermophilic bacteria was responsible for the change in these parameters.

Bacteria were microscopically observed in the leach solution during the high-temperature leaching period, but the solution samples were not cultured to obtain a quantitative analysis of the thermophilic bacteria. The number of bacteria present in the solution is not indicative of the total number of

bacteria present in both the solution and ore because there are generally more organisms attached to the ore particles than there are in the leach solution (3). The ferric-to-total iron ratio was used as an indication of bacterial activity in the ore column.

EXAMINATION OF THE LEACH RESIDUE

After leaching was stopped, the ore column was dismantled, and screen and chemical analyses were performed on the residue. Table 4 shows these analyses. The decrease in copper content and the increase in elemental sulfur (which adheres to the partially leached minerals) in the finer size fractions indicate that more leaching occurred in the finer size particles. A stoichiometric analysis of the principal chemical reactions and the chemical analyses (tables 1 and 4) showed that reaction 3 was the principal leaching reaction. Rapid leaching probably occurred where bacterial and ferric iron activity were greatest. The decrease in bacterial activity was probably due to a depletion of their energy sources, which were sulfide minerals or the nutrients in the solution.

The ore particles were covered with fine iron precipitates, thus making it difficult to quantify the amount of unleached sulfide minerals at the surface of the ore particles. An attempt was made in an earlier study (20) to determine the amount of sulfides as a function of radial position. But because of the

TABLE 4. - Residue analysis of leached ore

| Size fraction, cm | wt pct | Chemical analysis, pct | | | |
|------------------------|--------|------------------------|------|--------------------|----------------|
| | | Cu | Fe | S _{total} | S ^o |
| Plus 15.24..... | 4.0 | 0.87 | 3.56 | 1.64 | 0.11 |
| Minus 15.24 plus 10.16 | 28.3 | .77 | 3.55 | 1.01 | .11 |
| Minus 10.16 plus 7.62. | 22.6 | .71 | 3.70 | 1.17 | .11 |
| Minus 7.62 plus 5.08.. | 22.9 | .72 | 3.69 | 1.20 | .09 |
| Minus 5.08 plus 2.54.. | 10.7 | .62 | 4.07 | 1.17 | .14 |
| Minus 2.54 plus 1.27.. | 3.6 | .43 | 3.26 | .93 | .21 |
| Minus 1.27..... | 7.9 | .37 | 5.37 | 1.43 | .36 |
| Composite..... | 100.0 | .69 | 3.81 | 1.13 | .13 |

many cracks throughout the ore particles, the analysis did not provide useful data. Only a relatively few ore fragments can

can be analyzed in this manner, thus making data from such an analysis statistically meaningless.

SUMMARY AND CONCLUSIONS

A 2,165-day leaching test was performed on a chalcopyritic ore at both ambient and elevated temperatures. The rate of copper extraction decreased after the temperature was raised to 50° and 60° C, until the solution pH was lowered to 1.6 and the column inoculated with massive doses of thermophilic bacteria and nutrient solution. This resulted in an increase in the dissolved ferric iron concentration, a decrease in the dissolved ferrous iron concentration, and an accelerated copper leaching rate. However, the accelerated copper leaching lasted 120 days and then lowered to a slower rate. It is believed that the decreased leaching rate was caused by the depletion of exposed chalcopyrite minerals in the

fine ore fraction and on the outermost portion of the larger ore fragments. The remaining minerals were not accessible to the bacteria.

The rate of copper extraction is slow at ambient temperature with low-temperature bacteria and slower at elevated temperature with low bacterial activity. Lowering of the solution pH causes an increase in the amount of dissolved ferric iron at elevated temperatures. Active thermophilic bacteria can oxidize ferrous iron to ferric iron at 60° C and maintain a high ferric-to-ferrous ratio and thereby increase the copper leaching rate of exposed chalcopyrite minerals.

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