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MICROBIAL LEACHING

COPPER MINERALS

by JOSEPH A. SUTTON and JOHN D. CORRICK

The continuing depletion of high-grade ore deposits in this country has created a need to develop more effective methods for recovering valuable metals from low-grade ores. The use of microorganisms for their biochemical reactions is one possible way to solve certain phases of this problem.^{10,3} Bacteria have been used successfully by many diversified industries. Until recently, however, little attention has been focused on the use of bacteria in mining and metallurgical processes.

This report summarizes one phase of the microbial studies being conducted at the U.S. Bureau of Mines, College Park Metallurgy Research Center. The two-fold objective of this study was, first, to determine if pure strains of the bacteria *Ferrobacillus ferrooxidans*, *Thiobacillus* concretivorus and *Thiobacillus ferrooxidans* could utilize the iron and sulfur occurring in sulfide minerals to produce appreciable quantities of ferric sulfate and sulfuric acid for dissolving copper and, second, to develop the chemistry involved in the microbial oxidation of sulfide minerals. These are of particular interest as they relate directly to the feasibility of employing microorganisms in leaching operations.

The three strains of bacteria investigated are known to be present in the effluent waters of several copper mines in southwestern United States.⁴ The presence of these bacteria in ore deposits testifies to their ability to withstand highly acidic environments and to derive necessary food for survival from their immediate surroundings.

Acid-ferric-sulfate, a solvent for extracting copper from low-grade ores, is formed within leaching areas by what has previously been considered atmospheric oxidation of sulfuritic materials associated with the copper deposits. Recent discoveries, however, provide conclusive evidence that certain

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JUNE 1963, MINING ENGINEERING-37

5.8

10.4

Fig. 1—Dark field photomicrograph of Thiobacillus sp. (X728).

MINING ENGINEERS

oxygen consumed in chemical and microbial reactions.

naicopyrit

Chalcocite

29.1 26.7

38-MINING ENGINEERING, JUNE 1963



Fig. 3—Warburg constant volume respirometer.

brought about the oxidation of substantial quantities of ferrous iron.

However, it was not known how the bacteria accomplished the dissolution of iron-bearing minerals. The basic question underlying the microbial oxidation of iron sulfide minerals has been whether the organisms directly attack the iron compounded with iron sulfide minerals or if they attack the ferrous sulfate released into solution as a result of the atmospheric oxidation of the iron sulfide minerals. Volger' has reported that the sulfur-oxidizing bacterium T. thiooxidans must make physical contact with sulfur in order to oxidize it. Our manometric tests with T. thiooxidans supported Volger's conclusions. The results of these tests (Table I) show that an increased oscillation rate which caused shorter contact time between the sulfur particles and the organisms, resulted in a drop in the $Q_{0_2}(N)$. This expression is a means of indicating the oxygen uptake by the organisms. Results of parallel tests with F. ferrooxidans and pyrite show that increased oscillation rate increased the up-take of oxygen. Apparently, microbial oxidation of the pyrite can be enhanced by the same mechanisms that effect

reaction rates in all ordinary agitated chemical reactors. These data support the conclusion that this bacterium does not require contact with pyrite in order to oxidize it; instead, it oxidizes the ferrous iron released into solution as a result of chemical oxidation.

'The acid-ferric-sulfate solutions formed as a result of microbial oxidation of iron-bearing minerals should serve as effective metal solvents and bring about the dissolution of copper from copper minerals. Although a majority of copper minerals do not contain ferrous iron, they are commonly associated in their natural environments with the minerals pyrite and chalcopyrite. The data from a series of percolator tests involving F, ferrooxidans reacting on ferrous sulfate show that, after 56 days of percolation, 23.7% of the copper was extracted from chalcocite, 56.3% from covellite and 29.8% from bornite. The organisms extracted 3.4 times more copper from the chalcocite than was extracted in the uninoculated control (Fig. 7).

Results from a similar series of percolator tests indicate that the sulfur-oxidizing bacterium *T. concretivorus* was not able to utilize the sulfide sulfur occurring in the minerals chalcopyrite, chalcocite, covellite and bornite. Manometric studies show that this bacterium registered a mild response to the minerals chalcopyrite, chalcocite and pyrite (Table II). However, because these minerals contained minor quantities of elemental sulfur, it was concluded that bacterial activity was governed by the availability of this sulfur and that the organisms ceased to function after the sulfur was consumed.

The chemical reactions involved in the microbial dissolution of iron and copper from sulfide minerals can be described by reference to a series of chemical equations. Pyrite in the presence of oxygen and water is slowly oxidized to ferrous sulfate and sulfuric acid according to Equation 1,

$2\text{FeS}_2 + 7\text{O}_3 + 2\text{H}_2\text{O} \rightarrow 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4.$ [1]

The iron-oxidizing bacteria in the presence of oxy-



Fig. 4—Ferric iron from pyrite produced by iron-oxidizing bacteria.



Fig. 5—Effect of F. ferrooxidans and T. ferroxidans on the oxidation of iron in chalcopyrite.



Fig. 6—Effect of pH upon the ability of F. ferrooxidans to oxidize iron in chalcopyrite.

gen and sulfuric acid then oxidizes the available ferrous sulfate and, acting as a catalytic agent, accelerates the formation of ferric sulfate as shown in Equation 2,

$$4\text{FeSO}_{*} + 2\text{H}_{2}\text{SO}_{*} + \text{O}_{2} \xrightarrow{\text{Bacteria}} 2\text{Fe}_{2}(\text{SO}_{*})_{*} + 2\text{H}_{2}\text{O}_{*} \text{[2]}$$

The ferric sulfate that is formed can react with pyrite to form H₂SO, and ferrous sulfate according to Equation 3,

$$7Fe_2(SO_4)_3 + FeS_2 + 8H_2O \rightarrow 15FeSO_4 + 8H_2SO_4$$
 [3]

or it can react with a copper sulfide mineral, such as chalcocite, to form copper sulfate, ferrous sulfate and elemental sulfur as shown in Equation 4,

$$Cu_{2}S + 2Fe_{3}(SO_{4})_{3} \rightarrow 2CuSO_{4} + 4FeSO_{4} + S.$$
 [4]

The ferrous sulfate is then re-oxidized by the ironoxidizing bacteria to form more ferric sulfate and the cycle is repeated. The elemental sulfur set free (Equation 4) is oxidized by the sulfur-oxidizing

40-MINING ENGINEERING, JUNE 1963



Fig. 7—Copper extracted from chalcocite by F. ferrooxidans.... Sec. Carl ----

bacterium T. concretivorus in the presence of oxygen and water to sulfuric acid, as shown in Equation 5.

$$2S + 3O_{2} + 2H_{2}O \xrightarrow{\text{Bacteria}} 2H_{2}SO_{1}$$
 [5]

CONCLUSIONS

The conclusions drawn from this study are as follows:

1) The iron-oxidizing bacteria F. ferrooxidans and T. ferrooxidans are able to greatly accelerate the dissolution of the iron compounded with the minerals pyrite and chalcopyrite.

2) The bacterium F. ferrooxidans is capable of producing sufficient quantities of acid-ferric-sulfate from ferrous iron to bring about the dissolution of significant quantities of copper from chalcocite, covellite and bornite.

3) The bacterium F. ferrooxidans acts as a catalyst to the chemical oxidation of pyrite. The organism does not directly attack the iron in the mineral but rather oxidizes the ferrous iron released into solution as a result of atmospheric oxidation.

4) The sulfur-oxidizing bacterium T. concretivorus is not able to oxidize the sulfide sulfur occurring in the minerals pyrite, chalcopyrite, chalcocite, covellite and bornite.

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