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Note

Leaching Mechanism of Manganese Dioxide by *Thiobacillus ferrooxidans*

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Thiobacillus ferrooxidans leached manganese from manganese dioxide in the presence of sulfide ores of copper (chalcocite-Cu_2S and covellite-CuS) as the sole source of energy. The amount of copper leached from the copper sulfides decreased with increasing concentrations of manganese dioxide while that of manganese leached increased with increasing manganese dioxide concentrations. The X-ray diffractometric analysis of the sediments obtained after the leaching process indicated the formation of $Cu(OH)_2$ from Cu_2S and $Cu_4SO_4(OH)_6$ from CuS during manganese leaching, while CuS was the only compound detected in the absence of manganese dioxide. Possible leaching mechanisms of manganese dioxide coexisting with copper sulfides are discussed.

The phenomena of copper leaching from different sulfide ores have been well studied by several investigators.[1-9] The most important ore is chalcopyrite ($CuFeS_2$) which is abundant and is the common source for extraction of copper. Since, this ore has iron in the ferrous state and sulfur as sulfide, it is degraded by the iron oxidizing *Thiobacillus ferrooxidans* and the leaching mechanism has been well elucidated.[3]

The leaching of other types of sulfide ores of copper like covellite (CuS) and chalcocite (Cu_2S) have also been studied; these could be leached by autotrophs other than *Thiobacillus ferrooxidans*.[1,2,4] It was quite recently proved that *Thiobacillus ferrooxidans* also could leach covellite and chalcocite by a direct mechanism, along with the indirect way wherein ferric ions act as a lixiviant.[5]

In this study we show that the acid-insoluble tetravalent manganese-MnO_2 can be reduced and solubilized as $MnSO_4$ during the oxidative leaching of chalcocite and covellite coexisting with MnO_2. However, we observed that there was a decrease in the concentration of copper in the leachate with an increase in the concentration of MnO_2 in the leaching systems.

This observation then led to further investigation into the mechanism of the leaching of copper from these 2 types of ores, and the most probable role of MnO_2 has been elucidated.

Materials and Methods

The strain of *Thiobacillus ferrooxidans* AP-19 was obtained from this laboratory and was grown in the 9 K medium of Silverman and Lundgren.[10] After 7 days of incubation at 30°C on a reciprocating shaker (140 rpm), the cells were harvested by centrifugation (10,000 rpm for 10 min), washed with sterile 9 K medium (without $FeSO_4$) and resuspended in an equal volume of the same medium. This was used as the inoculum for the leaching experiments.

The manganese dioxide (more than 90% in purity) was ground to −400 mesh size. Cuprous sulfide and cupric sulfide were all of the same purity as MnO_2 and ground to −100 mesh size, (MnO_2 and Cu_2S were obtained from Ishizu Pharmaceuticals, Japan, and CuS

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was obtained from Mitsuwa Chemicals, Japan).

All experiments were done in 9 K medium (without $FeSO_4$; pH 2.5) with manganese dioxide and either cuprous sulfide or cupric sulfide added, and cultured for 5 days at 30°C with shaking (140 rpm). Although the concentration of manganese dioxide was varied in the experiments as indicated further, cuprous sulfide or cupric sulfide was added at the 1% level in all experiments unless otherwise specified.

The solubilized manganese and copper were detected by atomic absorption spectrophotometry (Atomic Absorption Spectrophotometer Model AA 625-01 of Shimadzu, Japan). The sediments after leaching were examined by X-ray diffractometry[11] (X-ray Diffractometer, Model XD-3A of Shimadzu, Japan) with a X-ray source of copper.

Results and Discussion

It is clear from Fig. 1 and 2 that tetravalent manganese is reduced and solubilized during the leaching of copper from chalcocite and covellite (in coexistence with MnO_2) by *T. ferrooxidans*. However, the amount of copper in the leachate decreased with increasing concentrations of manganese dioxide, but the amount of solubilized manganese increased with increasing concentration of manganese dioxide.

From such leaching characteristics, it was thought that the sulfide moiety of the copper compounds were being oxidized and the copper was being reprecipitated in some form other than the sulfide form. To investigate these phenomena, the sediments obtained after completion of the leaching process were dried in a lyophilizer (Virtis Co., U.S.A.) and examined by X-ray diffractometry (Fig. 3 and 4). Figure 5 shows the analysis of the sediments of leaching of Cu_2S and CuS in the absence of MnO_2. It was noted from these diffractograms that in the presence of manganese dioxide in a system containing Cu_2S as the substrate, the compound $Cu(OH)_2$ was detected and in the system containing CuS as the substrate the compound $Cu_4SO_4(OH)_6$ was detected. From these observations the possible leaching mechanisms of manganese dioxide, in the presence of Cu_2S and CuS, are postulated below:

A. Postulated reactions occuring during manganese leaching in the presence of Cu_2S:

$$Cu_2S + MnO_2 + H_2SO_4 \longrightarrow CuS + Cu(OH)_2 + MnSO_4 \quad (1)$$

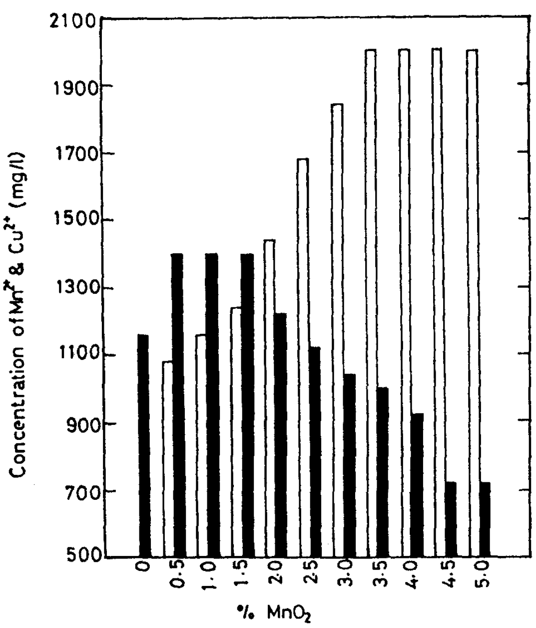

Fig. 1. Yield of soluble manganese and copper formed from MnO_2 and Cu_2S respectively.
▭ shows Mn^{++} and ■ shows Cu^{++}.

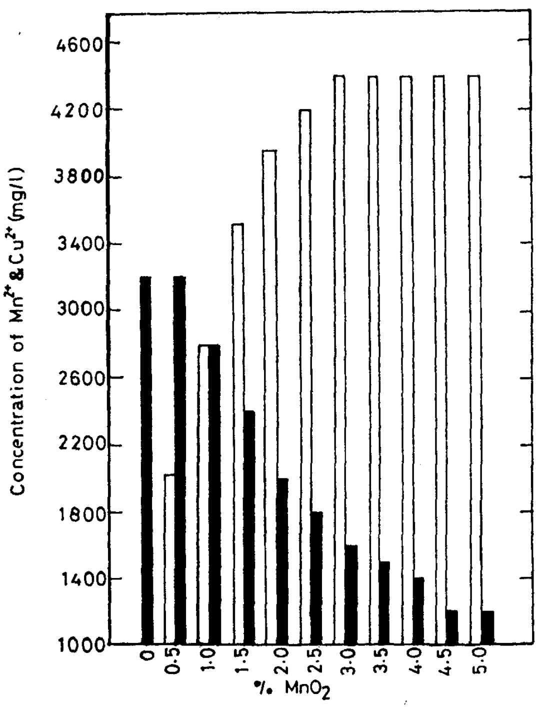

Fig. 2. Yield of soluble manganese and copper formed from MnO_2 and CuS respectively.
▭ shows Mn^{++} and ■ shows Cu^{++}.

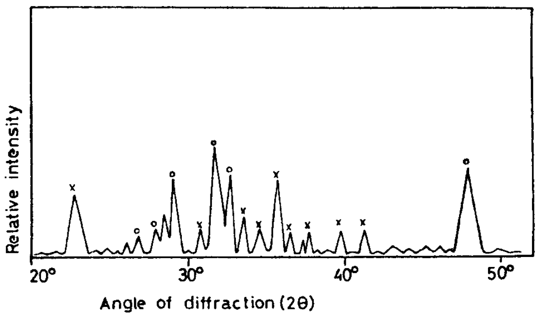

Fig. 3. X-ray diffractogram of sediment after leaching of MnO_2 in the presence of Cu_2S. (○) shows the peaks of CuS and (×) shows those of $Cu(OH)_2$; for the sake of clarity the peaks of CuS_2 are not shown.

$$2Cu_2S+MnO_2+\frac{1}{2}O_2+H_2O+H_2SO_4 \longrightarrow 2CuS+2Cu(OH)_2+MnSO_4 \quad (2)$$

B. Postulated reactions occuring during manganese leaching in the presence of CuS:

$$4CuS+4MnO_2+6O_2+2H_2O+H_2SO_4 \longrightarrow Cu_4SO_4(OH)_6+4MnSO_4 \quad (3)$$

$$4CuS+6MnO_2+5O_2+3H_2SO_4 \longrightarrow Cu_4SO_4(OH)_6+6MnSO_4 \quad (4)$$

It is predicted that either reactions 1 or 2, occurring separately or simultaneously, in case of (A) and reactions 3 or 4, occurring separately or simultaneously, in case of (B), would be the most probable leaching mechanisms of manganese leaching in the presence of Cu_2S and CuS respectively. Since $Cu(OH)_2$ and $Cu_4SO_4(OH)_6$ were not detected and manganese was not solubilized in uninoculated controls, these reactions were thought to be catalyzed by *T. ferrooxidans*.

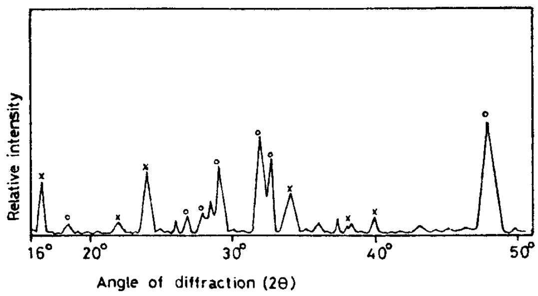

Fig. 4. X-ray diffractogram of sediment after MnO_2 leaching in the presence of CuS. (○) shows the peaks of CuS and (×) shows those of $Cu_4SO_4(OH)_6$.

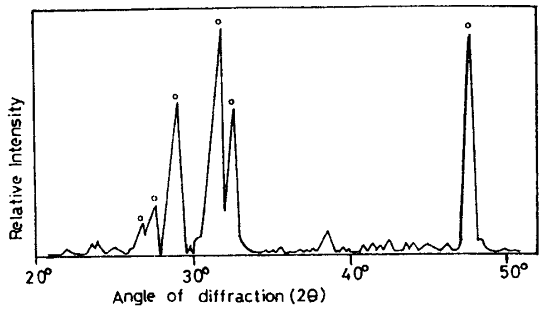

Fig. 5. X-ray diffractogram of copper leaching sediment (in the absence of MnO_2), in the presence of either Cu_2S or CuS. (○) shows the peaks of CuS.

However, it is predicted that with increasing concentrations of MnO_2 these reactions get preference over the other reactions (by which copper would be leached in the absence of MnO_2) and hence the concentration of soluble copper decreases with increases in the MnO_2 concentration.

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References

1) Rickard, P. A. D., Vanselow, D. G.: *Can. J. Microbiol.*, **24**, 998 (1978).
2) Fox, S. I.: Ph. D. Thesis, Rensselaer Polytechnic Institute, Troy, N.Y. (1967).
3) Duncan, D. W., Landesman, J., Walden, C. C.: *Can. J. Microbiol.*, **13**, 397 (1967).
4) Nielson, A. M., Beck, J. V.: *Science*, **175**, 1124 (1972).
5) Imai, K., Sakaguchi, H., Sugio, T., Tano, T.: *J. Ferment. Technol.*, **51**, 865 (1973).
6) Groudev, S. N., Genchev, F. N., Gadarjiev, S. S.: *Metallurgical Applications of Bacterial Leaching and Related Microbiological Phenomena*, (Murr, L. E., Torma, A. E., Brierley, J. A.) 253, Academic Press, N.Y. (1978).

7) McElroy, R. O., Bruynesteyn, A.: *Metallurgical Applications of Bacterial Leaching and Related Microbiological Phenomena*, (Murr, L. E., Torma, A. E., Brierley, J. A.), 441, Academic Press, N.Y. (1978).
8) LeRoux, N. W., Mehta, K. B.: *Metallurgical Applications of Bacterial Leaching and Related Microbiological Phenomena*, (Murr, L. E., Torma, A. E., Brierley, J. A.), 463, Academic Press, N.Y. (1978).
9) Brierley, J. A., Brierley, C. L.: *Metallurgical Applications of Bacterial Leaching and Related Microbiological Phenomena*, (Murr, L. E., Torma, A. E., Brierley, J. A.), 477, Academic Press, N.Y. (1978).
10) Silverman, M. P., Lundgren, D. G.: *J. Bacteriol.*, **77**, 642 (1959).
11) KWIC Guide To The (Inorganic Patterns of the) Powder Diffraction File: (Smith, J. V.), 74, American Society for Testing and Materials, Pa, U.S.A. (1968).

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