Electrobioleaching of Base Metal Sulfides

K.A. NATARAJAN

Bioleaching of base metal sulfides, such as pyrite, chalcopyrite, and sphalerite, under the influence of applied direct current (DC) potentials is discussed. Contributions toward mineral dissolution from three effects, namely, galvanic, applied potential, and microbiological, are analyzed and compared. Sphalerite could be selectively bioleached in the presence of *Thiobacillus ferro-oxidans* under an applied potential of -500 mV (SCE) from mixed sulfides containing sphalerite, pyrite, and chalcopyrite. Bacterial activity and growth were found to be promoted under electrobioleaching conditions. Probable mechanisms involved in the bioleaching of different sulfides under positive and negative applied potentials are discussed.

I. INTRODUCTION

THIOBACILLUS ferrooxidans is the primary organism implicated in the leaching of several sulfides. Its commercial potential in the leaching of lean grade and refractory ores, desulfurization of coals, and in mineral beneficiation has been well established.^[1-7] In addition to the above applications, bioprocessing has also been found to be very promising in the leaching of copper, zinc, and pyrite concentrates, and substantial metal concentrations in the leach liquor could be built up using specially designed reactors.^[8-13] However, in many cases, slowness of the biooxidation reactions and practical difficulties associated with the harvesting of sufficient biomass of these organisms have limited the scope and wider commercial utilization of this biotechnology. Bacterial activity as well as cell biomass are two important parameters influencing bioleaching rates. Besides microbiological physicochemical, factors. several electrochemical, as well as mineralogical factors also influence biooxidation reactions. For example, the redox potential of the mineral and the medium, type of crystal structure and conductivity of the minerals, medium acidity, concentrations of ferrous, ferric, and other soluble anions and cations, temperature, availability of oxygen and carbon dioxide, solubility of products of oxidation, particle size, and pulp density of the leaching system are all parameters to be controlled.^[1-3,7]

Electrochemical principles could be used with advantage in bioleaching. Galvanic interactions among sulfide minerals in a bioleaching system would enhance the selective biooxidation of active minerals.^[14–17] Mineral dissolution in a leaching medium could also be controlled by application of direct current (DC) potentials. Some electrochemical aspects of pyrite and zinc sulfide oxidation in the presence of *Thiobacillus ferrooxidans* have been reported recently.^[18,19] Activity as well as cell biomass of *Thiobacillus ferrooxidans* could be enhanced through electrochemical means. Enhanced yields of iron oxidizing bacteria may be achieved by *in situ* electrolysis of the soluble iron in the growth medium.^[20–24] The role of applied DC potentials on the activity and growth of *Thiobacillus ferrooxidans* has also been recently studied.^[25] In this article, the role of electrochemical factors such as galvanic and applied potential effects on the dissolution behavior of base metal sulfides such as pyrite, chalcopyrite, and sphalerite in the presence and absence of *Thiobacillus ferrooxidans* is discussed. Mechanisms involved in the electrobioleaching of the above sulfides are outlined. Dissolution behavior of various sulfides when present alone or in different binary combinations is analyzed with respect to three contributing factors, namely, galvanic, applied potential, and microbiological.

II. EXPERIMENTAL

A strain of *Thiobacillus ferrooxidans*, ATCC 19859, was used in all the experiments. Iron-free cell suspensions were used in bioleaching experiments using different sulfide minerals. For this purpose, one liter of a four-day-old culture was first passed through Whatman No. 41 filter paper in order to remove the precipitates. The filtrate was centrifuged in a SORVALL* RC-5B re-

*SORVALL is a trademark of E.I. Du Pont de Nemours & Co., Inc., Wilmington, DE.

frigerated centrifuge at 15,000 rpm in a SS-34 rotor for 15 minutes. The pellet was suspended in a solution of pH 2.0 sulfuric acid and allowed to stand for 2 hours in a refrigerator to allow settling of all precipitates. The supernatant containing iron-free cells were again centrifuged in this manner and washed repeatedly with pH 2.0 sulfuric acid. The cell pellet was finally suspended in 100 ml of the acid and stored at 4 °C.

Highly mineralized samples of pyrite (97 pct pure), chalcopyrite (65 pct pure), and sphalerite (98 pct pure) were used in leaching tests, the particle size of all the mineral samples being $75/53 \ \mu m$.

Rest potentials of sulfide mineral suspensions in the bioleaching medium were measured using a platinumstandard calomel electrode (SCE) couple. For studying the role of galvanic effects in the bioleaching of pyrite, chalcopyrite, and sphalerite, they were mixed in a 1:1 ratio at 20 pct pulp density in different possible binary combinations. A 0.9K medium (containing 4.4 g/L of ferrous sulfate) adjusted to pH 2.0 to 2.3 was used for this purpose.^[26] Leaching tests were carried out in Erlenmeyer flasks incubated on a rotary shaker (240 rpm) at 30 °C \pm 2 °C. A 10 pct v/v inoculum was

K.A. NATARAJAN, Professor, is with the Department of Metallurgy, Indian Institute of Science, Bangalore 560 012, India. Manuscript submitted January 2, 1991.

used in bioleaching tests, while corresponding controls contained a 5 pct alcoholic thymol solution.

Electrobioleaching tests under an applied potential using different sulfide minerals were carried out using a PYREX* glass cell of cylindrical cross section with a

*PYREX is a trademark of Corning Glass Works, Corning, NY.

capacity of about 200 ml. Thermostated water was circulated through an outer glass jacket in the cell to maintain a constant temperature of 30 °C. Five grams of the mineral sample were taken in 100 ml of 0.9K medium. In some tests, various sulfide minerals were mixed in a 1:1 ratio by weight. A platinum mesh electrode submerged into the mineral slurry served as the working electrode. A platinum foil auxiliary electrode was introduced into the cell close to the working electrode but separated through a fritted tube compartment. A saturated calomel electrode connected through a Luggin capillary served as the reference electrode. The mineral slurry was agitated using a magnetic stirrer. Desired potentials were applied through a Wenking model ST-72 potentiostat. A 10 pct iron-free inoculum was used in all of the tests. In the sterile control tests (no bacterial inoculum), 5 pct alcoholic thymol equal to the inoculum volume was added to prevent bacterial growth.

Copper, zinc, and total iron in leach solutions were analyzed using an atomic absorption spectrophotometer, while ferrous and ferric ion concentrations were monitored using visible spectrophotometry. The Eh and pH of the medium were also frequently monitored.

III. RESULTS AND DISCUSSION

A. Galvanic Effects

Before discussing the role of applied DC potentials on the dissolution behavior of different basic sulfide minerals such as pyrite, chalcopyrite, and sphalerite in a bioleaching medium, it is essential to understand the open-circuit electrochemical characteristics of these base metal sulfides. The measured rest potentials (Eh) for the various sulfide minerals in a bioleaching medium of pH 2.3 are given below:

pyrite, 700 mV chalcopyrite, 560 mV sphalerite, 240 mV

Sphalerite is the most electrochemically active, while pyrite and chalcopyrite are relatively nobler. Thus, in any galvanic combinations involving these minerals, sphalerite will undergo selective anodic dissolution.

$$ZnS \rightarrow Zn^{++} + S^{\circ} + 2e \qquad [1]$$

On the other hand, while chalcopyrite will behave anodically with respect to pyrite, it would remain cathodic to active sphalerite. Thus, depending on the type of the mineral with which it is in contact, either anodic dissolution of chalcopyrite as

$$CuFeS_2 \rightarrow Cu^{++} + Fe^{++} + 2S^\circ + 4e \qquad [2]$$

would occur or cathodic reduction of oxygen will be promoted on its surface as

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O \qquad [3]$$

Only Reaction [3] as above can be expected on pyrite surfaces in any combinations involving the above three sulfides. Under the above circumstances, pyrite dissolution can be expected to be higher only if present alone.

Selective dissolution of sphalerite will be promoted if it is coupled to either pyrite and chalcopyrite, while preferential oxidation of chalcopyrite would be enhanced if contacted with pyrite. The presence of *Thiobacillus ferrooxidans* would further enhance the above types of galvanic dissolution.^[17,27]

Results presented in Figures 1 and 2 illustrate the dissolution behavior of sphalerite and chalcopyrite when present alone and in galvanic combinations, in the presence and absence of Thiobacillus ferrooxidans. Significant enhancement in active mineral dissolution due to galvanic effect, as discussed above, is clearly evident. For example, in the presence of the bacteria, zinc extraction from sphalerite was found to be enhanced almost 2.5 and 3.5 times when coupled to chalcopyrite and pyrite, respectively, after about 75 days of leaching compared to that in the absence of any galvanic contact. Similarly, copper recovery from chalcopyrite when coupled to pyrite increased about threefold when compared to that for chalcopyrite alone after bioleaching for about 75 days. In the absence of bacteria, such galvanic contacts brought about only marginal increases in the selective dissolution of zinc and copper. The presence of Thiobacillus ferrooxidans further accelerates the galvanic dissolution process. The extent of active mineral dissolution in the presence of noble minerals follows the electrochemical trend with respect to their rest potentials in the leaching medium.

B. Effect of Applied DC Potentials on the Dissolution of Sulfide Minerals

The dissolution behavior of the above three sulfides in a bioleaching medium as a function of applied potentials is discussed below.

The applied potentials were impressed for a period of 4 hours in all of the cases. Zinc dissolution from sphalerite in the presence and absence of Thiobacillus ferrooxidans under applied potentials in the range of -600to +600 mV (SCE) is illustrated in Figure 3. The polarization currents corresponding to applied potentials are also indicated in the same figure. Sphalerite exhibited two characteristic peaks (one each at the cathodic and anodic sides of the polarization diagram) at about -450to -500 mV and +400 mV. The above peaks corresponded to current and zinc dissolution maxima, implying higher leaching rates for sphalerite at two specific applied potentials. The presence of the bacteria significantly enhanced zinc dissolution, though their influence on the magnitude of polarization currents was not very high. The presence of bacteria thus promotes sphalerite dissolution under applied potentials.

Current-potential relationships for pyrite and chalcopyrite are illustrated in Figures 4 and 5. In the ranges of applied potentials used in this study, pyrite exhibited a dissolution and current maximum corresponding to +400 mV. On the other hand, chalcopyrite exhibited a current/dissolution maximum at a positive applied potential of about +600 mV. Iron dissolution from



Fig. 1—Role of galvanic effect in the dissolution of sphalerite in the presence (I) and absence (B) of *Thiobacillus ferrooxidans*. Py = Pyrite, Cp = Chalcopyrite, and Sp = sphalerite.

chalcopyrite showed a maximum value at about +650 mV. The presence of the bacteria significantly enhanced iron dissolution from chalcopyrite, while its influence on copper dissolution was only marginal at positive potentials in the range of 530 to 650 mV for the duration of the present study. It may be emphasized, however,



Fig. 2—Copper recovery from chalcopyrite in the presence and absence of galvanic contacts. I = Inoculated and B = Blank.



Fig. 3—Variation of current and dissolved zinc from sphalerite as a function of applied potentials in the presence and absence of *Thiobacillus ferrooxidans*.

that with increasing periods of impression of the potentials, the dissolution rates of these sulfides can be expected to increase with a corresponding increase in dissolved metal ion concentrations.

Comparing the results presented in Figures 3 through 5 brings out the following significant facts of practical importance:

(a) Among the three sulfides used in this study, only sphalerite exhibits maximum dissolution in the negative potential range of about -500 mV (SCE), at which potential chalcopyrite and pyrite exhibit minimum solubility in the bioleaching medium.

(b) The presence of *Thiobacillus ferrooxidans* further promotes such electrochemical dissolution.

(c) It further becomes evident that in a mixture of the above three sulfide minerals, selective bioleaching of sphalerite without significant dissolution of copper and iron would be possible under an applied potential of about -500 mV.

Results presented in Figure 6 illustrate the dissolution behavior of sphalerite under different conditions. An applied potential of -500 mV promotes zinc dissolution, the presence of the bacteria further enhancing the electrochemical dissolution process. For example, under applied potential conditions, the presence of the bacteria enhanced zinc dissolution almost twofold after about 3 days of leaching compared to sterile conditions. Bioleaching in the absence of applied potential resulted in zinc dissolution which was only about one third of that attained under impressed potential.

The results of bioleaching of pyrite and chalcopyrite under applied potential conditions are illustrated in



Fig. 4—Variation of current and pyrite dissolution as a function of applied potential in the presence and absence of *Thiobacillus ferrooxidans*.

Figures 7 and 8. Potentials corresponding to dissolution maxima observed earlier were used. Bioleaching of pyrite was observed to be enhanced under an applied potential of +400 mV, while that of chalcopyrite at an applied potential of +600 mV. Copper dissolution from chalcopyrite after 3 days increased fourfold if the bioleaching was carried out under an impressed potential of +600 mV. Pyrite oxidation increased 2.5-fold after bioleaching for a period of 3 days under an impressed potential of +400 mV.

The above applied potentials did not inhibit bacterial activity in the presence of sulfides, which supplied the energy requirements for the bacteria in the form of ferrous iron, sulfide, sulfur, and other reduced sulfur compounds.

C. Electrochemical Bioleaching of Mixed Sulfides under Impressed Potentials

It also becomes evident that only at a negative applied potential of -500 mV can the dissolution of pyrite and chalcopyrite be minimized while that of sphalerite alone promoted. Positive potentials of the order of 400 to 600 mV may lead to random bulk dissolution of all three sulfides with no selectivity. The results presented in



Fig. 5—Variation of current and chalcopyrite dissolution as a function of applied potential in the presence and absence of *Thiobacillus ferrooxidans*.



Fig. 6—Bioleaching of sphalerite in the presence and absence of an applied potential of -500 mV.



Fig. 7—Bioleaching of pyrite in the presence and absence of an applied potential of +400 mV.

Figure 9 illustrate selective dissolution behavior of active sphalerite from binary mixtures containing pyrite or chalcopyrite under different applied potentials in the presence of *Thiobacillus ferrooxidans*. The role of the following factors simultaneously contributing toward selection dissolution of the desired mineral phase from a mixed sulfide system need to be considered in this context:



Fig. 8—Bioleaching of chalcopyrite in the presence and absence of an applied potential of +600 mV.



Fig. 9—Bioleaching of sphalerite (Sp) in contact with pyrite (Py) or chalcopyrite (Cp) under different applied potentials.

(a) Galvanic effect — promoting preferential dissolution of an active mineral only in contact with a nobler mineral.
(b) Applied potential effect — promoting the rate and selectivity of dissolution of a mineral at a specific impressed potential in the absence and presence of galvanic contacts.

(c) Biological effect — promoting the role of *Thiobacillus ferrooxidans* in enhancing both the above electrochemical effects.

An appropriate combination of the above three influential parameters would result in higher leaching rates than those encountered under conditions where only one or two of them are present.

Zinc dissolution from binary mixtures containing either pyrite or chalcopyrite in addition to sphalerite was found to be the highest at an applied potential of -500 mV, unlike at +400 and +600 mV in the presence of bacteria (Figure 9). Compared to the dissolution of zinc from sphalerite alone under an applied potential of -500 mV in the presence of bacteria, coupling it with nobler materials such as pyrite and chalcopyrite further enhances zinc dissolution under the same experimental conditions, due presumably to the added influence of the galvanic effect. For example, after about 100 hours of leaching in the presence of Thiobacillus ferrooxidans and an applied potential of -500 mV, zinc dissolution from binary mixtures containing pyrite or chalcopyrite in addition to sphalerite was almost five times higher than that observed with sphalerite alone under similar conditions.

The effect of galvanic combination on the dissolution tendency of a mineral could also be viewed from the angle of decreased solubility of the nobler mineral in the added presence of an active one. Thus, the rate of dissolution of a mineral could either be increased or decreased by inducing appropriate galvanic effects. As discussed earlier, the rate of dissolution of an active mineral in a mixed mineral system could be controlled by controlling the relative surface area ratio (which, in turn, is proportional to the weights at which they are mixed) of the minerals as well as by promoting contacts among them for as long a period as possible.^[17] In shake flask and reactor leaching systems involving finer mineral particles, creation and destruction of different types of galvanic contacts would be occurring on a continuous basis. Also, while maintaining an impressed potential, a larger submerged area for the working (contact) electrode needs to be ensured so that the majority of the suspended mineral particles could assume the impressed potential at a given time.

Copper dissolution from chalcopyrite in the presence and absence of an active mineral such as sphalerite under an impressed potential of +600 and -500 mV in the presence of Thiobacillus ferrooxidans is illustrated in Figure 10. In the absence of applied potentials, mere galvanic contact of chalcopyrite, a nobler mineral, with sphalerite, a very active sulfide, will not promote copper dissolution as mentioned before. However, at an applied potential of +600 mV, relatively higher amounts of copper were found to be dissolved than that observed at -500 mV from a chalcopyrite-sphalerite combination. The reason behind such an observation can be found with respect to the results presented in Figures 3 and 5, from which it becomes evident that at an impressed potential of about +600 mV, both chalcopyrite and sphalerite could dissolve in significant quantities, whereas at -500 mV, copper dissolution will not be favorable. Compared to a chalcopyrite-sphalerite combination, dissolution of chalcopyrite would be higher at an applied potential of +600 mV if present alone, since the additional presence of an active mineral would tend to impede the dissolution of the nobler mineral. Higher amounts of copper were observed to be dissolved under an applied potential of +600 mV from chalcopyrite alone than from its combination with active sphalerite. As could be seen from the results presented in Figure 11, bioleaching of nobler pyrite would be significantly decreased if coupled to active sphalerite, even under an applied potential (+400 and -500 mV). In the absence of such galvanic contact, biooxidation of pyrite would be promoted under an impressed potential of +400 mV (as maximum dissolution of pyrite corresponds to this applied potential, as given in Figure 4).

D. Probable Mechanisms

The effect of applied DC potentials, both in the positive and negative range, on the activity and growth of *Thiobacillus ferrooxidans* has been discussed elsewhere.^[25] It has been observed that application of positive potentials of the order of 500 to 1000 mV (SCE) is detrimental to bacterial activity and growth in the absence of ferrous iron yielding substrates. However, in the presence of sulfide minerals (even in the absence of



Fig. 10—Bioleaching of chalcopyrite (Cp) in the presence and absence of sphalerite (Sp) under different applied potentials.



Fig. 11—Bioleaching of pyrite (Py) in the presence and absence of sphalerite (Sp) under different applied potentials.

ferrous iron in the liquid medium), bacterial activity will not be inhibited as the microorganisms attach themselves to the minerals to derive energy. On the other hand, at negative applied potentials, electrolytic reduction of biochemically generated ferric iron takes place, providing a continuous *in situ* supply of the energy source for the bacteria, with the generation time of the bacteria found to be decreased with a corresponding increase in cell biomass.^[16,25,27] One should thus expect application of negative potentials to be relatively more beneficial.

Probable mechanisms involved in electrochemical bioleaching of sulfide minerals are outlined below.

1. Electrobiochemical dissolution of sphalerite at - 500 mV

Reductive dissolution of sphalerite under negative potential can be represented as follows:

$$ZnS + 2H^+ \rightarrow Zn^{++} + H_2S \qquad [4]$$

$$Zn + 2H^+ \rightarrow Zn^{++} + H_2$$
 [5]

$$S^{\circ} + 2H^{+} + 2e \rightarrow H_2S$$
 [6]

Reducing conditions favor ferrous ion generation with a corresponding lowering in solution Eh.

Noble minerals such as pyrite and chalcopyrite do not undergo such reductive dissolution at this potential. The presence of *Thiobacillus ferrooxidans* further enhances the mineral dissolution process by oxidizing Fe⁺⁺, H₂S, and S° generated electrolytically. Further, the generation time of bacteria could be reduced and cell biomass significantly enhanced under the influence of the negative potential. For example, it was observed that under an impressed potential of -500 mV, bacterial generation time was reduced from 16 hours to 10 hours with a tenfold increase in biomass.^[25]

2. Electrobiochemical dissolution of sphalerite,

chalcopyrite, and pyrite at positive potentials

Dissolution of pyrite under a positive potential of $\pm 400 \text{ mV}$ (SCE) would take place as

$$\operatorname{FeS}_2 \to \operatorname{Fe}^{++} + 2\operatorname{S}^\circ + 2\operatorname{e}$$
 [7]

while that of sphalerite and chalcopyrite would take place in the same manner as given in Eqs. [1] and [2]. The presence of bacteria further enhances such a dissolution process by the oxidation of ferrous iron and elemental sulfur, which are the products of oxidation. Besides the above reactions, biooxidation through direct and indirect mechanisms would also contribute toward mineral dissolution. Under positive applied potentials, electrolytic oxidation of ferrous ions generated from mineral dissolution would take place, and thus, an increase in ferric iron concentration could result due to combined electrochemical and biological oxidation. This would result in higher oxidation potentials favoring mineral dissolution. As mentioned earlier, contribution from galvanic effects would also come into the picture in the case of mixed sulfides.

IV. CONCLUSIONS

The following major conclusions could be made based on this work. Sulfide minerals such as pyrite, chalcopyrite, and sphalerite exhibit different electrochemical activities in a bioleaching medium. Their dissolution behavior, when present individually and in galvanic combinations, could be predicted based on the rest potentials measured in the leaching medium. All of the above sulfides exhibit dissolution maxima corresponding to specific applied DC potentials in a bioleaching medium. Sphalerite could be selectively bioleached in the presence of Thiobacillus ferrooxidans from mixed sulfides containing pyrite and chalcopyrite besides the zinc sulfide if an applied potential of -500 mV (SCE) could be maintained. While only sphalerite dissolution is promoted at a negative potential of -500 mV, dissolution of all the sulfides, namely, pyrite, chalcopyrite, and sphalerite, is enhanced at a positive applied potential in the range of 400 to 650 mV. Activity and growth of Thiobacillus ferrooxidans were observed to be promoted under applied potential conditions in the presence of sulfide minerals. Electrobioleaching enables faster and selective dissolution of the desired mineral phase from complex sulfides, unlike the case with only bioleaching.

ACKNOWLEDGMENTS

Financial support to this work from the Department of Science and Technology, Government of India, under the Indo-US Science and Technology Initiative (STI) program is gratefully acknowledged. Thanks are due to Ms. K.N. Sudha for carrying out several electrochemical experiments.

REFERENCES

- 1. A.E. Torma: Adv. Biochem. Eng., 1977, vol. 6, pp. 1-37.
- G.I. Karavaiko, S.I. Kuznetsov, and A.I. Golomzik: *The Bacterial Leaching of Metals from Ores*, Technicopy Ltd., Stonehouse Glos, United Kingdom, 1977, pp. 1-183.
- C.L. Brierley: CRC Crit. Rev. Microbiol., 1978, vol. 6, pp. 207-62.
- 4. L.E. Murr: Miner. Sci. Eng., 1980, vol. 12, pp. 121-89.
- 5. C.L. Brierley: Sci. Am., 1982, vol. 247, pp. 44-53.
- B.J. Ralph: in *Comprehensive Biotechnology*, Murray Moo-Young, ed., Pergamon Press, Oxford, United Kingdom, 1985, vol. 4, pp. 201-34.
- A.E. Torma: in *Biotechnology, A Comprehensive Treatise in 8 Volumes*, H.J. Rehm and G. Reed, eds., VCH Verlagsgesellschaft, Weinheim, Federal Republic of Germany, 1988, vol. 6B, pp. 367-99.
- R.C. McElroy and A. Bruynesteyn: in *Metallurgical Applications* of Bacterial Leaching and Related Microbiological Phenomena, L.E. Murr, A.E. Torma, and J.A. Brierley, eds., Academic Press, New York, NY, 1978, pp. 441-62.
- 9. A.E. Torma, C.C. Walden, and R.M.R. Branion: Biotech. BioEng., 1970, vol. 12, pp. 501-17.
- A. Bruynesteyn, R.W. Lawrence, A. Vizsolyi, and R. Hackl: in *Progress in Biohydrometallurgy*, G. Rossi and A.E. Torma, eds., Associzione Mineraria Sarda, Iglesias, Italy, 1983, pp. 151-68.
- 11. A.E. Torma, C.C. Walden, D.W. Duncan, and R.M.R. Branion: Biotech. BioEng., 1972, vol. 14, pp. 777-86.
- V. Sanmugasundaram, R.M.R. Branion, and D.W. Duncan: in Fundamental and Applied Biohydrometallurgy, R.W. Lawrence, R.M.R. Branion, and H.G. Ebner, eds., Elsevier, Amsterdam, The Netherlands, 1986, pp. 263-75.
- L.S. Gormely and R.M.R. Branion: in *Biohydrometallurgy*, J. Salley, R.G.L. McCready, and P.L. Wichlacz, eds., CANMET, Ottawa, ON, Canada, 1989, pp. 499-515.
- 14. A.P. Mehta and L.E. Murr: Hydrometallurgy, 1983, vol. 9, pp. 235-56.
- 15. K.A. Natarajan: Miner. Metall. Proc., 1988, vol. 5, pp. 61-65.
- N. Jyothi, K.N. Sudha, G.P. Brahmaprakash, K.A. Natarajan, and G. Ramananda Rao: in *Biotechnology in Minerals and Metal Processing*, B.J. Scheiner, F.M. Doyle, and S.K. Kawatra, eds., SME (AIME), Littleton, CO, 1989, pp. 9-16.
- N. Jyothi, K.N. Sudha, and K.A. Natarajan: Int. J. Miner. Proc., 1989, vol. 27, pp. 189-203.
- W.K. Choi and A.E. Torma: in *Biotechnology in Minerals and Metal Processing*, B.J. Scheiner, F.M. Doyle, and S.K. Kawatra, eds., SME (AIME), Littleton, CO, 1989, pp. 17-24.
- L.M. Chia, W.K. Choi, R. Guay, and A.E. Torma: in Biohydrometallurgy, J. Salley, R.G.L. McCready, and P.L. Wichlacz, eds., CANMET, Ottawa, ON, Canada, 1989, pp. 35-47.
- 20. N.A. Kinsel and W.W. Umbreit: J. Bacteriol., 1964, vol. 87, pp. 1243-46.
- 21. B.G. Kovrov, G.V. Denisov, and L.G. Sekacheva: Microbiol., 1978, vol. 47, pp. 324-26.
- G.V. Denisov, B.G. Kovrov, I.N. Trubachev, I.V. Gribovskaya, A.E. Stephen, and O.I. Novoselova: *Microbiol.*, 1980, vol. 49, pp. 341-45.
- 23. S.B. Yunker and J.M. Radovich: *Biotech. BioEng.*, 1986, vol. 28, pp. 1867-75.
- R.C. Blake II, E.A. Shute, and K.J. White: in *Biohydrometallurgy*, J. Salley, R.G.L. McCready, and P.L. Wichlacz, eds., CANMET, Ottawa, ON, Canada, 1989, pp. 391-401.
- 25. K.A. Natarajan: Effect of Applied Potentials on the Activity and Growth of Thiobacillus ferrooxidans with Respect to Bioleaching, Indian Institute of Science, Bangalore, India, unpublished research, 1990.
- M.P. Silverman and D.G. Lundgren: J. Bacteriol., 1959, vol. 77, pp. 642-47.
- 27. K.A. Natarajan: in *Microbial. Mineral Recovery*, H.L. Ehrlich, C.L. Brierley, and J.A. Brierley, eds., McGraw Hill, New York, NY, 1990, pp. 79-106.