

## Low Grade Pyrites and their Possible Beneficiation by *Thiobacillus ferrooxidans*

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An iron-oxidizing chemoautotroph, *T. ferrooxidans* was found to be quite efficient in oxidation of pyrite from pyriteferous shales. The oxidation was negligible in the absence of essential nutrients. The bacterium in association with the shales showed a great potential to recover copper from a copper ore tailings sample. Five different rock phosphate samples were also made vulnerable to bacterial attack with the help of shales. The leached liquor from the shales was utilized for preparation of chemicals such as ammonium sulfate and iron oxide mass. The latter being useful as a desulfurizing agent. In addition, other possible exploitations of such unutilized low grade pyrites have been discussed.

**Key Words :** *Thiobacillus*, Pyrite, Low grade ores, Minerals, Leaching

### Introduction

The involvement of iron-oxidizing *Thiobacillus ferrooxidans* in most of the biohydrometallurgical extraction processes has been successfully encountered (Lundgren & Silver 1980, Torma & Bosecker 1982). However, this technique is confined mostly to reasonably high grade ore deposits and concentrates. High grade ore resources are fast depleting. The increased demand for metal, therefore, requires the development of new technology for exploration of existing low grade ores and waste materials. The possibility resides in utilizing low-sulfur-containing mineral ores due to the fact that, the bacterium has the capacity to oxidise both the reduced metal part and sulfur

moieties of the mineral (Silverman 1967, Lundgren & Silver 1980). Oxidation of pyrite by *T. ferrooxidans* which is present as a common contaminant in most of the sulfide ores, actually plays a pivotal role to regenerate the oxidant ferric iron as well as the solvent sulfuric acid which in turn is of extreme importance in leaching operations (Brierley 1978).

India possesses substantial amounts of low grade pyrites, which till now have remained unutilized. These could be of great commercial importance through bacterial treatment. In order to find out a feasible relief for exploration of these mineral ores, an attempt was made to leach

a low grade pyrite viz. pyriteferous shales by *T. ferrooxidans*. The applicability of bioleaching, on copper ore tailings and some minerals of rock phosphate was also done.

### Materials and Methods

Pyriteferous shales of Amjhore Mine (India) containing 13% total iron (11.43% pyritic iron) was used for pyrite oxidation studies. Copper ore tailings containing as low as 0.05% total copper were collected from Mossaboni group of Copper Mines (India). Five rock phosphate samples from various parts of India i.e. Mussoorie (MRP & RRP); Jhamarkotra (JRP) and Purulia (PRP<sub>I</sub> & PRP<sub>II</sub>) were used. The sample MRP contained 17.5%, RRP-26.2%, JRP-30.0%; PRP<sub>I</sub>-34.8% and PRP<sub>II</sub>-32.7% of total mineral phosphate. For leaching experiments each sample was ground to—240 BSS (<63 microns particle size).

A strain of *T. ferrooxidans* (NCIB-8455) was used. The cells were grown in modified 9K medium (Roy & Mishra 1981a) in the presence of pyriteferous shales at 10% pulp density and at pH 2.0. The same solid to liquid concentration ratio was maintained in case of mixed suspensions, where requisite amount of the shales were added with the sample.

For leaching studies, freshly growing cell suspensions ( $2 \times 10^9$  cells/ml) were prepared by harvesting pyrite grown cells on Millipore membrane filter (0.45  $\mu$ m, pore size) and resuspending the same in acidified water (0.01N H<sub>2</sub>SO<sub>4</sub>). Five milliliters of this cell suspension was inoculated in 100 ml fresh mineral ore suspended medium and incubated at 28°C under rotary shaking condition (150 rpm). Suspensions from the growing culture were taken periodically to estimate water soluble iron, copper, sulfate and phosphate (as the case may be) according to the standard procedures (Snell & Snell 1949).

The by-products were prepared from the solution of thiobacillus leached shale suspension. After complete cessation of bacterial growth, the leached liquor was made ammoniacal. Precipitated mass of ferric hydroxide and the filtrate, both were dried separately at room temperature. The residue obtained from filtrate was used for pyrite oxidation studies. Additional nitrogen and phosphorus sources, as usually present in the medium were omitted during requisite amount of residue supplementation.

### Results and Discussion

Figure 1a shows the oxidation of pyrite from pyriteferous shales at various shale concentrations. There was no lag period before exponential pyrite oxidation (studied up to 40% pulp density). The rate of leaching increased with increasing shale concentration up to 20% pulp density (31mg iron/1/hr), after which it gradually decreased (figure 1b), with maximum extraction being at 10% pulp density (74%). Iron release from pyrite increased steadily up to about 300 hr and, beyond this period up to 450 hr the total soluble iron leached remained constant (figure 1a). Control experiments showed negligible pyrite oxidation and not more than 5% pyrite was oxidised after 450 hr. These results suggest that for leaching experiment the optimum pulp density should be chosen at a point where both leach rate and percent extraction are optimum. Here the optimum pulp density was between 10% (w/v) to 20% (w/v) and, as such all further experiments were performed at 10% pulp density to attain maximum metal extraction. The bacterial growth was synonymous to iron leach profile and continued up to 300 hr of leaching, after which it almost ceased (unpublished data). Oxidation between 300 hr and 450 hr, where iron leach rate was considerably slow (figure 1a), occurred

probably due to chemical oxidation of bacterially regenerated oxidant ferric-ions as suggested by Silverman (1967). Presence of some toxic elements in the ore might also show similar effect of growth uncoupled iron oxidation by the bacterium (Roy & Mishra 1981b).

Significant recovery of copper from a copper ore tailings was observed within 30 days using *T. ferrooxidans* (figure 2). Copper leaching was enhanced with the addition of pyrite. The sample containing 0.05% copper showed not more than 58.0% solubilisation of copper at 5% pulp density, whereas with the addition of pyrite (5% w/v), almost complete solubilisation was achieved (98.3%). Copper solubilisation gradually decreased above 5% (w/v) of tailings but, the efficiency was nearly three times greater with the addition of pyrite as compared to

tailings samples with no pyrite at 20% pulp density. Only 4% copper was solubilised in controls during this period. It is clear, even low grade sulfide ore is amenable to attack by *T. ferrooxidans*. The optimum bacterial activity largely depends on the absolute amount of the substrate present in the sample which was probably not so in the case of tailings hence presence of pyrite increased the leaching rate.

During leaching the bacterial activity was found to decrease above 20% of total particle concentration (figure 1 & 2). Low grade sulfide ores are largely associated with several host rocks (Torma, 1977). The increase in total particle concentration in the medium, therefore, increases not only the total surface area for mineral particles to be oxidised, but also results into a larger surface area from the associated host rocks.

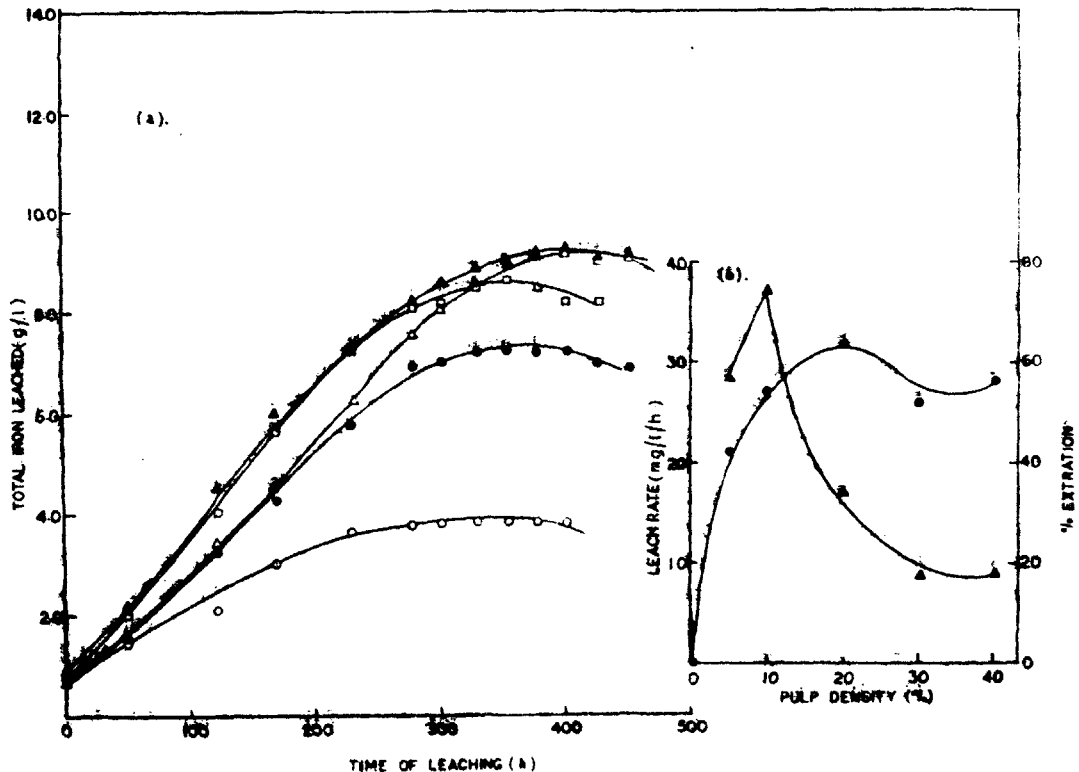
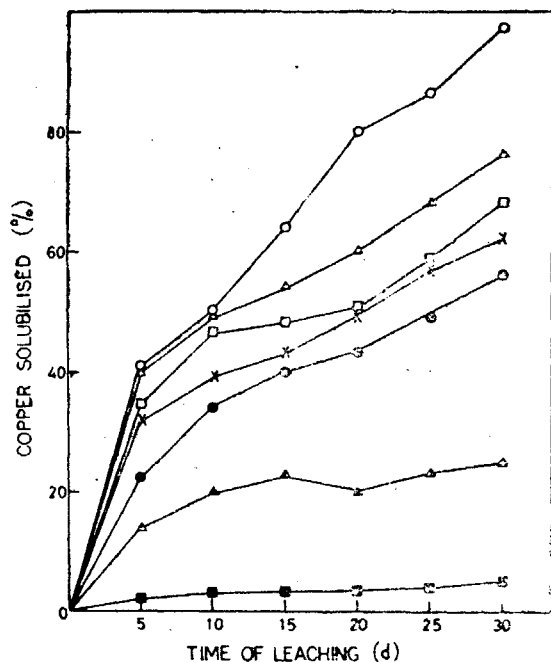


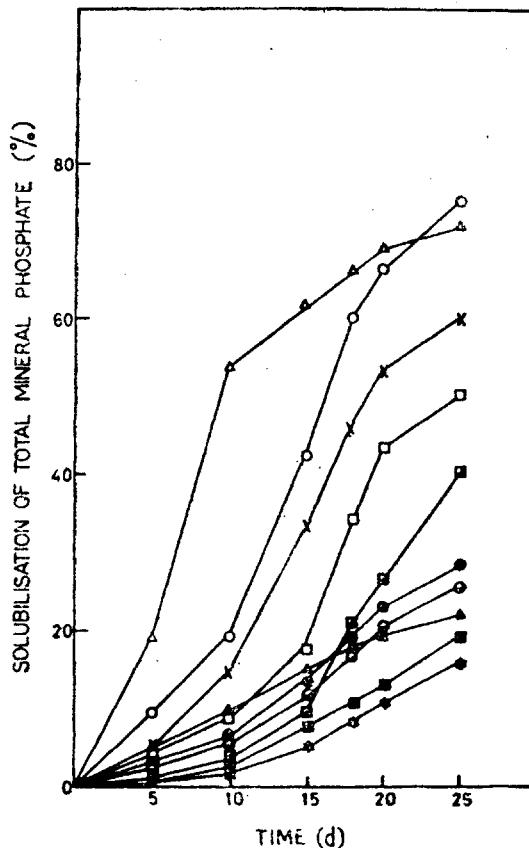
Figure 1 Oxidation of pyriteferous shales by *T. ferrooxidans* at various pulp densities  
 (a) Production of soluble iron at shale concentration (% w/v): 5 (O); 10 (Δ); 20 (□); 30 (●); 40 (▲).  
 (b) Iron leach rate (●) and % Extraction (▲) at 450 hr.



**Figure 2** Solubilisation of copper from copper ore tailings by *T. ferrooxidans* in the presence or absence of pyrite. Production of soluble copper at pulp density of tailings (% w/v): 5 (●); 5 with pyrite (○); 10 with pyrite (△); 15 with pyrite (□); 20 (▲); 20 with pyrite (×); sterilised control (■).

Thus the hindrance of bacterial activity by such increased surface area seems critical beyond 20% pulp density.

During solubilisation of mineral phosphate from five rock phosphate samples (figure 3), it is evident that *T. ferrooxidans* has an efficient role in solubilising rock phosphate in a medium containing only 0.1% ammonium sulfate. This shows that other mineral nutrients are possibly provided from the carried over minerals present in rock phosphate. Solubilisation was quite effective with 8% (w/v) pyrite supplementation which implies that the solubilisation of rock phosphate is mainly due to the chemical activity of acidic ferric sulfate solution produced during bacterial pyrite oxidation. The total phosphate extraction by this process was found to increase steadily up



**Figure 3** Solubilisation of phosphate from various rock phosphate samples by *T. ferrooxidans* under inoculated and uninoculated conditions

$P_3$  (MRP)—Sterilised, inoculated (△) & Unsterilised, Uninoculated (▲);  $P_4$  (JRP)—Sterilised, inoculated (○) & Unsterilised, Uninoculated (●);  $P_1$  (MRP)—Sterilised inoculated (□) & Unsterilised, Uninoculated (■);  $P_5$  (PRP)—Sterilised, inoculated (▲) & Unsterilised, Uninoculated (★);  $P_6$  (PRP)—Sterilised, inoculated (×) & Unsterilised, Uninoculated (■).

to 20 days, although it continued up to 25 days (figure 3). The samples (RRP & JRP) containing 26.2% and 30.0% total phosphate showed 72.3% to 76.4% solubilisation of phosphate respectively, whereas, not more than 40% of the same could be leached from the PRP<sub>I</sub> sample containing as high as 34.8% total phosphate. Low phosphate release was also evident in MRP and PRP<sub>II</sub>

samples. As such, rock phosphate solubilisation is not entirely dependent on the absolute concentration of phosphate present in the sample. The low solubility of some rock phosphates could arise due to the presence of basic carbonates of calcium and magnesium which are usually embedded over rock phosphate minerals. Besides the deleterious effect of carbonate on bacterial activity (Chandra et al. 1980), the presence of toxic elements in rock phosphate might also show similar effect as discussed earlier. In case of unsterilised, uninoculated samples significant phosphate solubilisation occurred (figure 3), although in sterilized, uninoculated samples the soluble phosphate concentrations were almost negligible (average of 2% to 3%). This indicates the presence of acidophilic phosphate solubilisers or iron oxidizers in rock phosphate or the pyrite. As these group of microbes are universally abundant in most of the sulfide bearing ores and minerals (Mishra et al. 1983), their enrichment thus could be made under natural environment to compensate the cost of applying any standard strain for leaching operation.

In most of the experiments, the initial acidity (pH 2.0) was found to increase to a final pH value of 1.3 to 1.4. The diverse oxidizing ability of the bacterium *T. ferrooxidans* on several metal sulfides leads to the production of soluble metal sulfates. The pyrite in pyriteferous shales has both reduced iron and sulfur moiety, which on oxidation yield acid ferric sulfate. The increased production of sulfate ions whose requirement is less in the ferrous part oxidation leads to lowering of medium pH, and as such the leaching of metals is an acid generating phenomenon.

The effect of residue obtained after ammonia treatment of the leached liquor on oxidation of pyriteferous shales shows that the same could be used as a good nitrogen source ranging from 0.01% to 0.20%

concentrations (figure 4). These concentrations gave similar oxidation kinetics as for complete medium. The residue supplemented as a source of phosphate carried over, if any, in the medium containing the usual amount of nitrogen source (0.1%) resulted in 45% less oxidation than complete medium and, the absence of regular phosphate source in the medium also gave similar results. Absence of nitrogen in the medium showed negligible oxidation rate and only 6% pyrite could be oxidised after 200 hr, whereas 77% oxidation occurred in the complete medium. These results imply that supply of mineral nutrients, especially nitrogen and phosphorus are essential during leaching of low grade sulfide ores. This finding is in agreement with Lundgren and Silver (1980), Roy and Mishra (1981a) but in disagreement with Tuovinen et al. (1971) who did not observe any deterioration of iron oxidation rate in

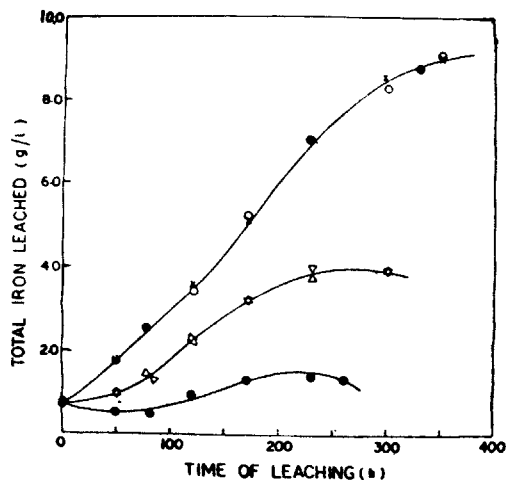


Figure 4 Oxidation of pyriteferous shales by *T. ferrooxidans* in the absence of mineral nutrients and the effect of residue obtained as filtrate from ammonia treated leached solution.

Production of soluble iron in absence of nitrogen (●); Phosphorus (▽); complete medium (O); medium having residue as nitrogen source double, half and one tenth of the complete medium (×); (Δ) medium with the residue as a source of phosphorus in the complete medium

the absence of nitrogen while absence of phosphorus reduced the rate. These variable observations could either possibly be due to certain dissimilarities of the sulfide samples or strain variation. The residue obtained as ammonium sulfate has been shown to be free of phosphate source (figure 4) and its percent conversion with respect to pyrite-ferrous shales was found to be nearly 48.0%. The residue, a good source of nitrogen could be used along with phosphate source and thus may prove to be quite effective in exploiting low grade pyrites. The ferric hydroxide also a by product of this process upon weathering could be utilized for coal desulfurization. Supply of ammonia for such purpose could be made easily and economically from any blasting or milling operation as suggested by Lundgren and Silver (1980).

*T. ferrooxidans* is unique in aqueous processing of metals from low grade ores

and waste materials. Use of low grade pyrite for efficient production of ferric ions as oxidant to solubilise copper or phosphate (figures 2 & 3) might also show a way to solubilise uranium or other minerals by the process of ferric ion dependent chemical oxidation. The pyrite associated rock phosphate solubilisation as developed here could also prove useful under different soil conditions for enhancing soil ecosystem metabolism.

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