# BIOLEACHING OF A COPPER SULPHIDE ORE BY IRON-OXIDISING BACTERIA

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## ABSTRACT

Bioleaching is now an established technology for the treatment of refractory gold ores and for the metal recovery from low-grade sulphide ores. Bioleaching of sulphide ores consists in the mobilisation of metal constituents through microbial oxidation of the metal sulphide. In the last years, indirect attack through the action of iron (III) was indicated as the most important mechanism of bioleaching. Bacterial function consists in the regeneration of the oxidant ferric ion. *Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* are capable of oxidising iron (II) but at different rate according to the pH and ferrous concentration. The ability of each microorganism to contribute to the bioleaching of a sulphide ore (Bajo La Alumbrera, Catamarca-Argentina) in different conditions is analysed in this paper.

## INTRODUCTION

In the last years, an increasing number of commercial bioleaching applications for processing ores have appeared in the world. The term bioleaching is used for the extraction of metal elements through the mediation of microorganisms; moreover, bioleaching is now an established technology for the treatment of refractory gold ores offering economic, environmental and technical advantages over pressure oxidation and roasting (Rawlings, 1997; Rawlings, 1998).

*Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans* and *Leptospirillum ferrooxidans* are the three most common chemolithotrophic bacteria frequently found in leaching operations and acid mine waters and they are responsible for oxidative leaching of sulphide minerals. Sulphur compounds are used both as electron donor and energy source by bacteria belonging to the genera *Thiobacillus*. *L. ferrooxidans* and also *T. ferrooxidans* oxidise inorganic ferrous iron to the ferric form. (Helle and Onken, 1988; Sand et al., 1992; Barrett et al., 1993; Donati et al., 1996; Rawlings, 1997; Breed and Hansford, 1999).

Almost since the discovery of *T. ferrooxidans* in acid mine drainage, two dissolution mechanisms are accepted: the direct one and the indirect one. The direct mechanism implies the sulphide oxidation by an enzyme system with oxygen to sulphate and metal cations while the indirect mechanism comprises the oxidising action of iron (III) ions dissolving the metal sulphide. In the last process, iron (II) ions and elemental sulphur are generated and then biologically oxidised to iron (III) and sulphate (Pogliani et al., 1990; Donati et al., 1996; Porro et al., 1997). Recently, a new integral model for bioleaching has been reported (Schippers et al., 1996; Schippers and Sand, 1999) indicating that metal sulphides are degraded by a chemical attack of iron (III) or protons on the crystal lattice. According to these mechanisms, iron (III) ions are exclusively the oxidising agents for the dissolution of some metal sulphides and consequently only iron (III) ion-oxidising bacteria are able to oxidise these sulphides. Since *T. ferrooxidans* and *L. ferrooxidans* present different ferrous-iron oxidation rate according to the pH values and iron (II) concentration, studies about metal recovery at different conditions using each microorganism could clarify its importance in the whole process of bioleaching.

In this paper, we present the results of copper recovery in the bioleaching of a low grade sulphide ore (Bajo La Alumbrera, Catamarca-Argentina) using pure cultures of *T. ferrooxidans* and *L. ferrooxidans* in media with different pH values and iron (II) concentrations.

## EXPERIMENTAL

A pure strain of *T. ferrooxidans* (DSM 11477) and another of *L. ferrooxidans* (ATCC 29047) were used in the bioleaching tests. Both bacteria were previously cultured in 9 K medium (Silverman and Lundgren, 1957) at pH 1.8.

When 90 % of iron (II) was oxidised, cultures were filtered through blue ribbon filter paper to retain

jarosite deposits. Culture suspensions were passed through a 0.22 μm, washed at least twice with iron-free 9 K (0 K) medium and suspended in 0 K medium at pH 1.5. These suspensions (with about $1.2x10^8$ cells/ml) were used as inocula in bioleaching tests.

In bioleaching test, three media with 9 or 3 g/l of iron (II) or without iron (named 9 K, 3 K and 0 K respectively) and at three initial pH values (1.1, 1.5 and 2.0) were used. Shake-flask bioleaching tests were carried out on an orbital shaker at 30°C and 180 r.p.m. Each flask contained 150 ml of the specific medium (at each iron (II) concentration and pH) with 10 % v/v inocula and 3.75 g of the ore.

The sulphide ore was procured from Bajo La Alumbrera (Catamarca, Argentina) with particle size smaller than 60 mesh. The mineralogical composition shows magnetite, hematite, pyrite and covellite. The last was the mayor copper source although chalcopyrite and chalcosite were also found. The ore contained 78.30 % Si (as $SiO_2$), 10.0 % Fe (as $Fe_2O_3$), 2.85 % S, 1.12 % Cu, 0.035 % Zn and 0.08 % Mn (as $MnO_2$).

Samples were periodically withdrawn for measurements of pH and redox potential (Eh) and chemical analyses. Ferrous iron concentrations were determined titrimetrically with $KMnO_4$. Total iron and copper in solution were analysed using atomic absorption spectrophotometry.

## RESULTS

Figures 1 and 2 show rates of ferrous iron oxidation by *L. ferrooxidans* and *T. ferrooxidans* respectively as affected by culture pH and initial ferrous concentration. Data for cultures poised initially at pH 1.1 and inoculated with *T. ferrooxidans* do not appear since, at this pH, iron oxidation was negligible.

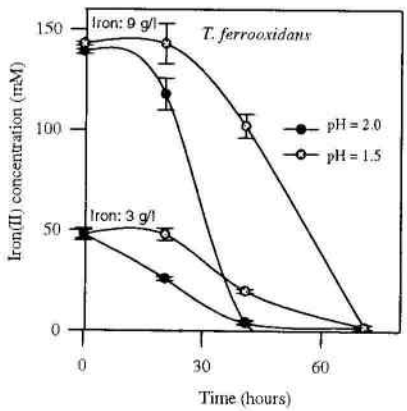


Figure 1: Iron (II) oxidation by *L. ferrooxidans*

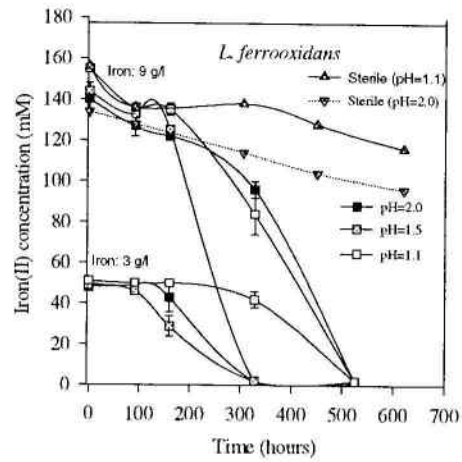


Figure 2: Iron (II) oxidation by *T. ferrooxidans*

In the cultures, iron (II) oxidation produced an initial increase of pH (oxygen reduction consumes protons) but finally there was a decrease of pH (due to ferric hydrolysis). Figure 3 shows the highest pH value and the final pH value in each culture.

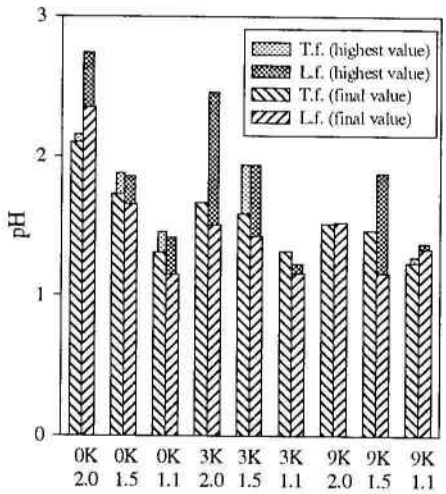


Figure 3: Highest and final pH values

Outer graphics in figure 4 (a: *L. ferrooxidans* and b: *T. ferrooxidans*) depict the kinetics of iron solubilisation in cultures without supplemented iron. Inner graphics show soluble iron in cultures supplemented with iron after 26 days.

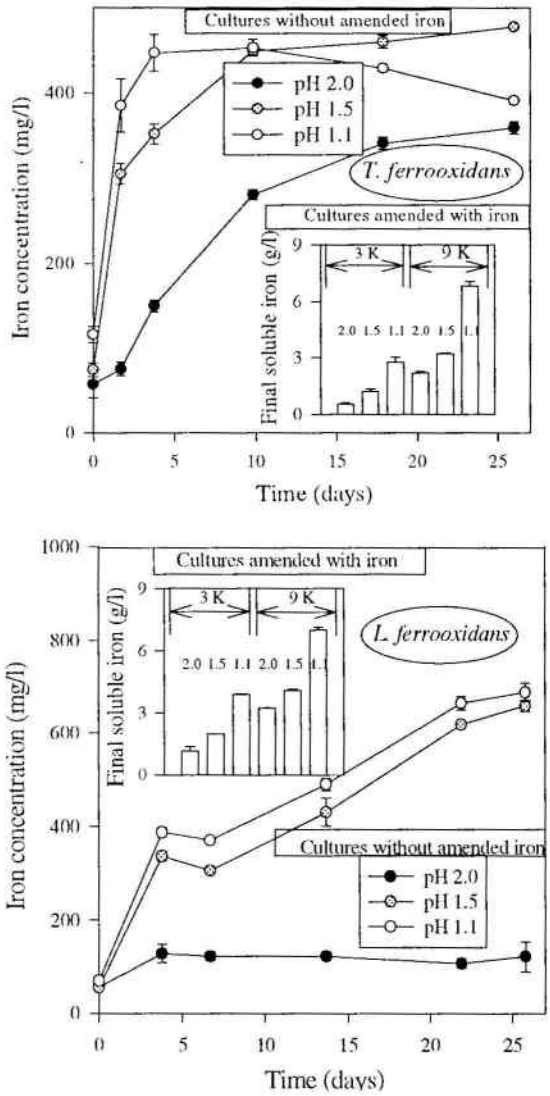


Figure 4: Iron solubilisation kinetics (cultures without initial iron) and soluble iron concentration (cultures with initial iron) a: *L. ferrooxidans*; b: *T. ferrooxidans*

Copper solubilisation is shown in figure 5. In order to clarify the figure, only cultures at extreme pH (1.1 and 2.0) without iron and with 9 g/l of iron, have been included.

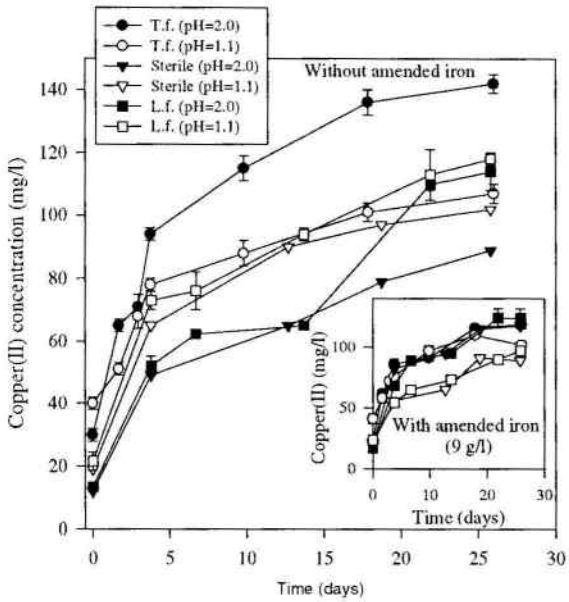


Figure 5: Copper solubilisation in cultures without (outer graphic) and with amended iron (inner graph). T.f.: *T. ferrooxidans*. L.f.: *L. ferrooxidans*

## DISCUSSION

As it has been reported, the mean generation time recorded for *L. ferrooxidans* was considerably greater than that of *T. ferrooxidans*. From 300 to 500 hours (according to the pH and ferrous iron concentration) were required for ferrous iron to be totally oxidised while the same process required between 40-70 hours for *T. ferrooxidans*. On the other hand, *L. ferrooxidans* displayed greater tolerance to acidity than *T. ferrooxidans*. Thus, this microorganism shows more activity in cultures at higher pH values and there was no bacterial activity in culture at pH 1.1. The evolution of Eh (data not shown) is in agreement with iron (II) oxidation.

Iron (II) iron oxidation with oxygen as the last electron acceptor produces an increase of pH as it was observed in all cultures. Further pH decrease (as indicated in figure 3) suggests the following processes: iron precipitation as jarosite (basic ferric sulphate) and sulphur oxidation by *T. ferrooxidans*. The sulphur could have been formed during the sulphide oxidation by ferric iron. The absence of the last process in *L. ferrooxidans* cultures, justify that the pH in this case was higher than that in *T. ferrooxidans* cultures.

Iron precipitation was greater at high pH and high initial ferrous iron concentration. Jarosite precipitation was higher in *T. ferrooxidans* cultures; this is consistent

with the higher iron (II) oxidation rate by the cells attached to the support, allowing higher iron (III) concentrations and higher pH values nearer the ore. In *L. ferrooxidans* cultures, there was also an important iron (III) precipitation except in the culture with 3 g/l iron at pH 1.1 where the final soluble iron concentration was higher than the initial. Under sterile conditions, jarosite precipitation was also found but the highest percentage of iron precipitation was 28 % in the system with 9 g/l at pH 2.0.

In cultures not supplemented with iron, iron appeared by dissolution of mineral. Except in the *T. ferrooxidans* culture at pH 1.1, iron from the ore was found as iron (III) probably for further bacterial oxidation. In *L. ferrooxidans* cultures iron (III) solubilisation was very high except at pH 2.0. *T. ferroxidans* cultures were less efficient in extracting iron (except at pH 2.0) than was *L. ferrooxidans* cultures but the extraction was similar at the three pH values. *ferrooxidans*.

Iron solubilisation in sterile systems were 138 mg/l at pH 2 (similar to that obtained in *L. ferrooxidans* culture) and 417 mg/l at pH 1.1(slightly more that in *T. ferrooxidans* culture). This result suggests that there was not *T. ferrooxidans* action at the pH value where iron (II) oxidation process was inhibited. On the other hand, at high pH values, no significant *L. ferrooxidans* action occurred.

As not expected, copper solubilisation in cultures was slightly more than in sterile systems. It could be explained by the large amount of jarosite covering the mineral surface and preventing dissolution. Additionally, cells did not easily attack some copper constituents of the ore. Thus, sterile controls with 9 g/l iron (III) did not leach more than 94 mg/l of copper; moreover, there was an important iron precipitation (about of 30 %).

The highest copper extraction (51 %) was reached by *T. ferrooxidans* culture not supplemented with iron at pH 2.0. This extraction was higher than that obtained by *L. ferrooxidans* culture (41 %) and that corresponding to the sterile system (32 %) in the same conditions. At pH 1.5, the efficiency of copper solubilisation (43 %) was similar for both bacteria. Finally, at pH 1.1, *L. ferrooxidans* culture was more efficient in extracting copper than was *T. ferrooxidans* culture and this slightly better than the sterile control.

In cultures supplemented with iron, copper extraction increases with the pH although the highest percentages were only 44 % and 42 % for *L. ferrooxidans* and *T. ferrooxidans* cultures respectively in 9 K medium at pH 2.0. These extractions were slightly higher than those in sterile controls except in 9 K medium at pH 1.1; in the last case, sterile controls showed the same extraction than the cultures.

These results confirm that the direct mechanism using *T. ferrooxidans* (at least, at pH values where ferrous iron oxidation is inhibited) is negligible. On the other hand, indirect mechanism using *L. ferrooxidans* is almost independent of pH value or of the initial addition of iron. At pH 2.0, results for *T. ferrooxidans* cultures show an enhancement of copper dissolution. This fact could be associated to the mentioned direct mechanism or another mechanism might have taken place. The last mechanism would consist in the dissolution by bacterial action of the sulphur layer deposited on the sulphide during the oxidation by ferric iron (Pogliani and Donati, 1999). However, any of these mechanisms should be greatly affected by culture pH value in agreement with the fact that the enhancement of copper dissolution was not observed at pH 1.5. Moreover, copper dissolution at pH 1.5 was similar to that obtained using *L. ferrooxidans* and this last bacterium is not able to do the mechanisms proposed above.

On the other hand, cultures supplemented with iron could not improve copper dissolution due to the greater iron precipitation.

Summarising, bioleaching of this copper sulphide ore was particularly successful in *T. ferrooxidans* cultures without amended iron and at high pH while *L. ferrooxidans* only shows higher extraction in cultures at pH 1.1.

## ACKNOWLEDGEMENTS

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