World Journal of Microbiology and Biotechnology, 8, 305–308

Bioleaching of metallic sulphides with *Thiobacillus ferrooxidans* in the absence of iron (II)

E. Donati, G. Curutchet, S. Porro and P. Tedesco*

Bioleaching of metallic sulphides with *Thiobacillus ferrooxidans* in the absence of iron (II) was studied using pure sulphides and mixtures. The direct mode of bacterial action was analysed with respect to sulphide solubility, exposed solid surfaces and bacterial attachment to the solids. Bioleaching of mixed sulphides showed enhancement of metal extraction in comparison with pure sulphides which suggests metal extractions would be better from polymetallic sulphide ores than from similar matrices with only one sulphide.

Key words: Bioleaching, metallic sulphides, *Thiobacillus ferrooxidans*

Thiobacillus ferrooxidans is an autotrophic bacterium able to catalyse oxidation of iron (II) and reduced sulphur compounds with O_2 as the terminal electron acceptor.

In the absence of iron (II) as soluble source of energy, *Thiobacillus ferrooxidans* satisfies its energy requirements through direct oxidation of metallic sulphides, according to the following overall mechanism:

$$MS \text{ (insoluble)} + 2O_2 \rightarrow MSO_4 \text{ (generally soluble)}$$

The importance of bacterial attachment to the solid sulphide for direct attack has been demonstrated (Pogliani *et al.* 1990) but this mechanism also occurs in solution. Obviously, in the latter case, the previous dissolution of the metallic sulphide is required.

In this paper, the direct oxidation of some pure metallic sulphides by *Thiobacillus ferrooxidans* in the absence of iron (II) is studied. Moreover, the possible effect of one sulphide on another, in mixtures, in the oxidation of each of them by the bacteria has been considered through bioleaching of mixtures of covellite (CuS) with other sulphides.

Materials and Methods

Bioleachings of the sulphides CoS, MoS_2, NiS, CdS, ZnS and CuS and of binary mixtures of Cus with each of the other sulphides were made. Each was used at 0.1% (w/v) including when in mixtures.

Specific surfaces of the sulphides were determined by the BET method (Brunauer *et al.* 1938).

Bioleachings were done in thermostatted 250-ml flasks containing 100 ml of 9 K culture medium without iron (II) (Silverman & Lundgren 1959) at 28°C and an initial pH of 2.3. For each system two flasks were used: one was inoculated with 5 ml of *Thiobacillus ferrooxidans* culture in mid-growth phase from which iron (III) had been stripped through repeated washing with sulphuric acid solutions at pH 2.3 and centrifugation. To the second flask (sterile), 5 ml of a 2% (w/v) thymol in methanol solution was added.

Metal ion concentrations were measured by atomic absorption spectrophotometry and the bacterial population was determined by counting under phase-contrast microscopy with a camera attachment. Occasionally, bacteria were counted using the most probable number method (Collins 1967). Differences between the methods were not greater than 10%.

Solid residues of bioleachings were analysed by X-ray diffractometry (Klug & Alexander 1970).

Results and Discussion

Table 1 shows the extraction of metal ions and ratios of extracted metal in the inoculated system to extracted metal in the sterile system. No quantitative data for MoS_2 are indicated because bacterial extraction is negligible.

In Table 2 extraction percentages corresponding to bioleaching of mixtures and extraction ratios for pure sulphides and mixtures can be seen.

E. Donati, G. Curutchet and S. Porro are with the Departamento de Quimica, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Argentina. P. Tedesco is with CETMIC, Cno. Centenario y 506, C.C. 49, M.B. Gonnet, (1897) Argentina. * Corresponding author.

Table 1. Extractions and volumetric productivities of metal ion extractions after 20 days leaching of pure sulphides.

Extractions and productivities	Metal ion				
	Cu	Co	Cd	Zn	Ni
E_{is}(M)	36.0	32.0	77.6	59.0	36.0
E_{ss}(M)	11.3	24.0	58.5	23.3	19.3
P_i	0.19	0.18	0.27	0.30	0.21
P_s	0.06	0.13	0.20	0.12	0.11
m_i	3.76	3.51	5.38	6.06	4.09
m_s	1.19	2.64	4.06	2.39	2.16
E_{is}/E_{ss}(M)	3.16	1.33	1.32	2.54	1.89

Productivity determinations had a precision of 0.003 (for Cu, Co, Ni and Cd) and 0.007 for Zn.
For definitions, see Appendix.

All extraction data in both tables correspond to 20 days of bioleaching.

Specific surfaces of the sulphides were as follows (in $m^2\ g^{-1}$): CuS, 0.9; CoS, 0.6; CdS, 14.7; ZnS, 5.1; NiS, 2.2; MoS_2, 3.7.

In the experiments with pure sulphides (Table 1), extractions of metal ions in the sterile flasks (chemical extractions) are generally proportional to the specific surfaces of the sulphides. Exceptions are due to differences in solubility (CuS, the most insoluble sulphide, shows the lowest extraction).

Since sterile experiments show very different chemical attack for each sulphide, extractions due only to bacterial action have been calculated for each sulphide as the difference between values corresponding to the inoculated and sterile flasks, assuming that chemical action proceeds at the same speed in both flasks, which is an acceptable approximation. According to this, the increasing order of bacterial action is:

$$MoS_2 \ll CoS < CdS < NiS < CuS < ZnS$$

Moreover bacterial populations (see Figure 1) are in the order:

$$MoS_2 \ll CdS,\ CoS < CuS < NiS < ZnS$$

In spite of previous studies (Pogliani *et al.* 1990) in which the need for bacterial attachment to the solid surface for the direct oxidation of covellite was shown, an analysis made as a function of bacterial attachment was not possible in the present study because the differences in bacterial populations were too large. This means that the expected order for the attached bacterial fraction (Donati *et al.* 1991) is only significant with similar bacterial populations and with insignificant oxidation of sulphide ions in solution. This difference in bacterial populations may be related to a greater importance of the oxidation mechanism of sulphide ions in solution due to a greater chemical dissolution.

However, a direct contribution of the solid could be present because CdS, which shows a considerable chemical dissolution, does not support good bacterial growth. Furthermore, increasing bacterial growth does not correspond with greater bacterial extraction.

Regarding bacterial action on the surfaces, two conclusions can be drawn.

(1) Apparently, no important bacterial attack is produced on CoS and CdS. A comparison between them is

Table 2. Extraction of metal ions from binary mixtures of CuS with ZnS, CoS, CdS, NiS and MoS_2 after 20 days leaching.

	Metal ion				
	Zn	Co	Cd	Ni	Mo
E_{im}(Cu)(%)	35.2	62.8	51.1	44.2	45.5
E_{sm}(Cu)(%)	8.0	8.2	<0.1	7.3	10.6
E_{im}(M)(%)	68.4	36.7	95.3	28.1	—
E_{sm}(M)(%)	4.2	14.3	22.3	13.1	—
E_{im}/E_{is}(Cu)	1.0	1.8	1.4	1.2	1.3
E_{sm}/E_{ss}(Cu)	0.7	1.0	<0.1	0.6	0.9
E_{im}/E_{is}(M)	1.2	1.2	1.2	0.8	—
E_{sm}/E_{ss}(M)	0.2	0.6	0.4	0.7	—
E_{im}/E_{sm}(Cu)	4.4	5.7	>100	6.1	4.3
E_{im}/E_{sm}(M)	16.0	2.6	4.2	2.1	—

M—metal other than Cu.
For definitions, see Appendix.

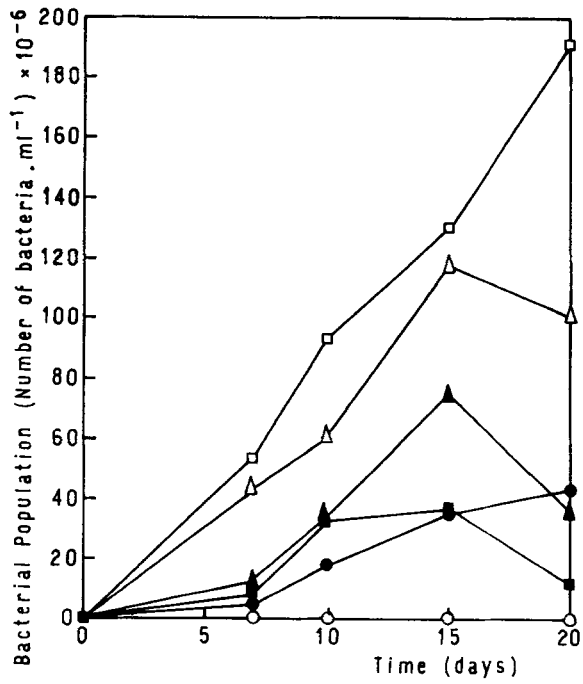

Figure 1. Bacterial population in the liquid medium during bioleaching of pure sulphides in agitated flasks using *Thiobacillus ferrooxidans* in a culture medium without iron (II). △—NiS; ▲—CuS; □—ZnS; ■—CdS; ●—CoS; ○—MoS_2.

meaningless because of their very different specific surfaces.

(2) CuS, NiS and ZnS show bacterial populations in line with their dissolutions in sterile solutions. It is reasonable to expect similar bacterial action on the three sulphides although somewhat greater for CuS than for NiS.

No toxicity effects have been considered because, at the pulp densities used, even a total dissolution would not give products at toxic concentrations, except for MoS_2 (Tedesco *et al.* 1990).

It is not possible to change the exposed area without changing other factors such as bioleaching on the surface due to change of the attached bacteria, change in chemical leaching and, as a consequence, change in chemical action in solution.

It has been stated (Torma 1978) that differences in the bioleaching rate of metallic sulphides are caused by their different solubilities. Although some of the reported results seem to support this point of view, comparisons appear to be unreliable due to the large differences in both exposed areas and chemical attacks.

Other researchers (Tributsch & Bennet 1981a,b) tried to relate bacterial action to crystalline structure and/or electrical conductance of each sulphide. However, in their papers, several deviations from the suggested relationships are observed and, additionally, some factors such as porosity, crystalline defects and interfacial deposits between solids and liquids have not been considered. These factors, not controlled in bioleaching processes, probably have a more important influence than crystalline structure. Perhaps MoS_2 is the exception because its layer structure is very different to that of the other sulphides.

More copper is generally extracted in bioleaching of the mixtures than with CuS alone (Table 2). Similarly, more of the other metals (except Mo, which is never extracted, and Ni) are extracted in sulphide mixtures. In the sterile experiments exactly the opposite situation is observed: all metals are better extracted as pure sulphides than in mixtures. This is reasonable because total solid mass and total exposed area are greater in mixtures and consequently a lesser chemical attack is directed to each sulphide. The presence of CdS, in particular, leads to a great decrease in CuS extraction, possibly due to the fact that the specific surface of CdS is 16 times greater than that of CuS.

Bacterial populations in all the mixtures (see Figure 2) are similar, except in experiments where CdS or MoS_2 are present. In general, bacterial populations in flasks of sulphide mixtures lie within the ranges of those from flasks of single sulphides.

The greater metal extraction by bioleaching from mixtures than from pure sulphides may be explained by the greater area of available substratum in the mixtures and, as a consequence, greater bacterial growth and bacterial activity.

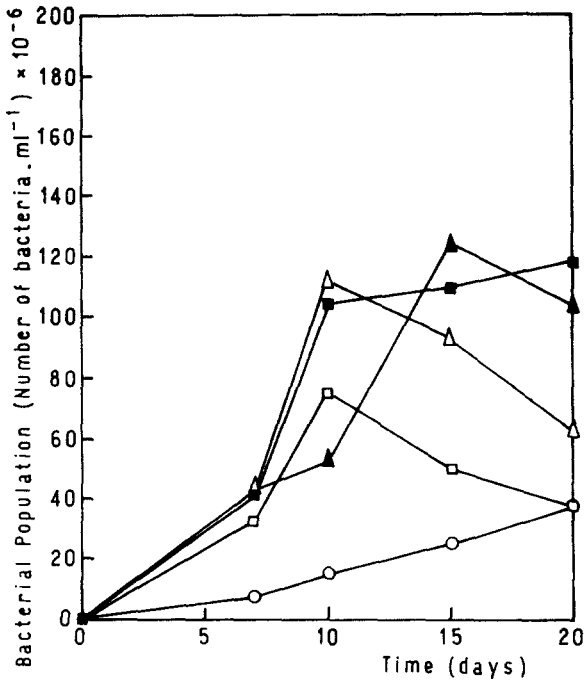

Figure 2. Bacterial population in the liquid medium during bioleaching of binary mixtures of CuS with another metallic sulphide in agitated flasks using *Thiobacillus ferrooxidans* in a culture medium without iron (II). △—CuS/ZnS; ▲—CuS/CoS; ■—CuS/CdS; ■—CuS/NiS; ○—CuS/MoS_2.

Conclusions

Results of bioleaching of pure sulphides show the great importance of chemical action and exposed area in bioleaching studies. Any comparison of the behaviour of different sulphides in bioleaching which fails to take into account these factors is useless. However, it is not possible to change any one factor without introducing changes in the other factors, and this makes any study particularly difficult to rationalize.

Results of bioleaching sulphide mixtures indicate that there is more bacterial activity on each constituent sulphide when these are in mixtures than when used alone. This explains why there is a greater productivity and percentage of extraction in bioleaching experiments using polymetallic sulphide ores than expected from extractions in a similar matrix with only one sulphide.

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(Received in revised form 6 January 1992; accepted 17 January 1992)

Appendix

E_{is}(M)—percentage of metal M extraction in inoculated medium with single sulphide.

E_{ss}(M)—percentage of metal M extraction in sterile medium with single sulphide.

E_{im}(M)—percentage of metal M extraction in inoculated medium with mixed sulphides.

E_{sm}(M)—percentage of metal M extraction in sterile medium with mixed sulphides.

P_i—volumetric productivity of metallic ion in inoculated medium (millimol litre^{-1} day^{-1}).

P_s—volumetric productivity of metallic ion in sterile medium (millimol litre^{-1} day^{-1}).

m_i—metal extraction (millimol) in inoculated medium.

m_s—metal extraction (millimol) in sterile medium.