DIRECT AND INDIRECT MECHANISMS IN THE BACTERIAL LEACHING OF COVELLITE

E.R.Donati,S.Porro[1] and P.H.Tedesco[2]

Facultad de Ciencias Exactas de la Universidad Nacional de La Plata
47 y 115,1900,La Plata,Argentina.
1 Under a scholarship granted by CIC(Comisión de Investigaciones
 Científicas de la Provincia de Buenos Aires).
2 Principal Researcher of CIC

SUMMARY

   Bacterial leachings of sample of covellite using a strain of Thiobacillus
ferrooxidans in 9 K medium with and without iron were made at several pulp
densities.Rates of solubilization with and without iron correspond to total
and to direct mechanism respectively.Orders of reaction(at each pulp density)
for each mechanism at two temperatures were calculated.

INTRODUCTION

   In the last twenty years many authors(Duncan et al.,1964;Sakaguchi et al.,
1978;Brierley,1978;Kelly,1976;Lundgren et al.,1980;Torma et al.,1984)have
studied the bioleaching of low grade sulphide minerals,which can be
represented by the equation:

$$MS_{(s)} + 2\ O_{2(g)} \longrightarrow MSO_{4(aq)} \qquad (1)$$
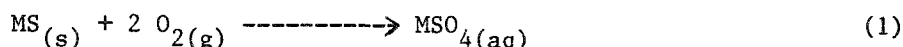
   This represents the conversion of an insoluble compound MS into a soluble
product MSO_4(with the exception of $PbSO_4$).The process is catalyzed by the
microorganism Thiobacillus ferrooxidans(T.f.), which has been characterised
in numerous papers(Colmer et al.,1947;Silverman et al.,1964;Holt et al.,1974;
Tuovinen et al.,1972).This bacteria is able to obtain energy from the
oxidation of Fe^{2+} and reduced sulphur compounds mainly S^{2-}.
Metallic sulphides in ores are frequently together with reduced iron as
pyrite or chalcopyrite and two bioleaching mechanisms have been proposed:
1)direct attack of metallic sulphide with bacterial catalysis,which is
   represented by equation (1).
2)indirect attack represented by these equations:

$$Fe^{2+} \longrightarrow Fe^{3+} + e^{-} \qquad (2)$$

$$MS + 2\ Fe^{3+} \longrightarrow 2\ Fe^{2+} + S^{\circ} + M^{2+} \qquad (3)$$
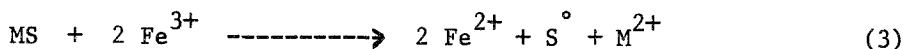
which means that the microorganisms catalyze the oxidation of Fe^{2+} to Fe^{3+}
and this ion oxidizes the S^{2-} to S°.Bacteria are able to catalyze the
oxidation of S°:

$$S^{\circ} + O_2 + H_2O \longrightarrow H_2SO_4 \qquad (4)$$
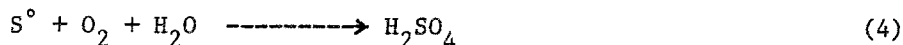
   There is no agreement on the way by which these mechanisms occur:some
authors claim that it requires the previous dissolution of the sulphide
according to the equation:

$$MS_{(s)} \longrightarrow M^{2+}_{(aq)} + S^{2-}_{(aq)} \qquad (5)$$
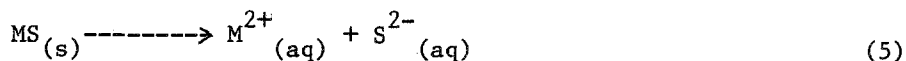
and then the dissolved S^{2-} is captured and oxidized by bacterial action,
shifting the equilibrium of the equation(5) to the right(Torma et al.,1978;
Torma,1982).Others propose models which imply a direct action on the
substrate surface(Bruynesteyn,1980;Tributsch et al.,1981;Tributsch et al.,
1981).

In this paper we try to arrive to a better understanding of these mechanisms by studying the bioleaching of a simple system as covellite (CuS) with and without Fe^{2+} in the medium.Rates of bioleaching and its variation with the temperature were measured and analysed.

MATERIALS AND METHODS

The used substrate was pure CuS Fluka A.G.

Strains of Thiobacillus ferrooxidans identified as T.f. 18 isolated at the University of Cayetano Heredia(Perú)and provided by Dr.Carlos Aguirre,were used.The bacteria were initially adapted to the substrate in modified 9 K medium(Silverman et. al.,1959)in which CuS was used as energy source instead of $FeSO_4$.Final cultures were prepared using pulp densities(grams of solid in 100 ml solution)between 0.5 and 2.5(%w/v) in 95 ml of 9 K medium with and without Fe^{2+} (iron concentration,when used,was 0.16 M)and adding inocule with the bacteria in the log-phase to 100 ml.Sterile samples were prepared using 5 ml of a 2% solution of thymol in methanol instead of the inoculum.

Erlenmeyers flasks with the cultures were agitated at 200 rpm at 31 or 35°C, adjusting the pH to 2.3.These were the optimum reported conditions(Torma et al.,1970;Sakaguchi et al.,1976).

Periodically samples were taken for analysis of the Cu^{2+} by atomic absortion spectrophotometry and the volume replaced by 9 K medium.

RESULTS AND DISCUSSION

In figure 1 the curves correspond to pulp density 0.5 %.Similar curves were obtained for other pulp densities(not shown in the figure).From the slopes of the curves concentration vs. time(in the zone of rapid increasing of the metallic ion concentration corresponding to the first six hours)the rates of disolution were determined for three different times.These rates were plotted against time and extrapolated to zero time and the obtained rate was used in the following calculations.When the 9 K medium was used with Fe^{2+} the obtained rate was considered as the total rate(both mechanisms included)and when Fe^{2+} was not added the direct rate was obtained(which corresponds to direct mechanism).These data are shown in table 1.

In a first and rough approach the indirect rate(corresponding to indirect mechanism)was calculated as the difference between the total and the direct rate.

From the relationship $V= K.d^n$ (Torma et al.,1977),where V is the rate of solubilization(% w/v .h^{-1}),d the pulp density(% w/v),K the specific rate and n the order of the reaction,K and n were calculated from the intercept and the slope respectively of the plot log V vs. log d.The data at two temperatures are shown in table 2.

The influence of temperature on each mechanism and-for each pulp density-on the relationships of rates between the two different mechanisms are shown in tables 3 and 4 ,respectively.

Moreover the activation energy for each mechanism was calculated using the Arrhenius equation;values are indicated in table 5.

The orders of reaction can be considered as the exponents which show the dependence of rates of reaction and surface of the substratum,using pulp densities.These orders of reaction at both temperatures shown in the tables are lower for the total mechanism than the observed orders when Fe^{2+} is not present,i.e.,when only the direct mechanism operates.This means that the surface is more important in this last case.The reasons supporting this point of view are:
1)the direct process occurs predominantly at the surface and the indirect process probably in solution.
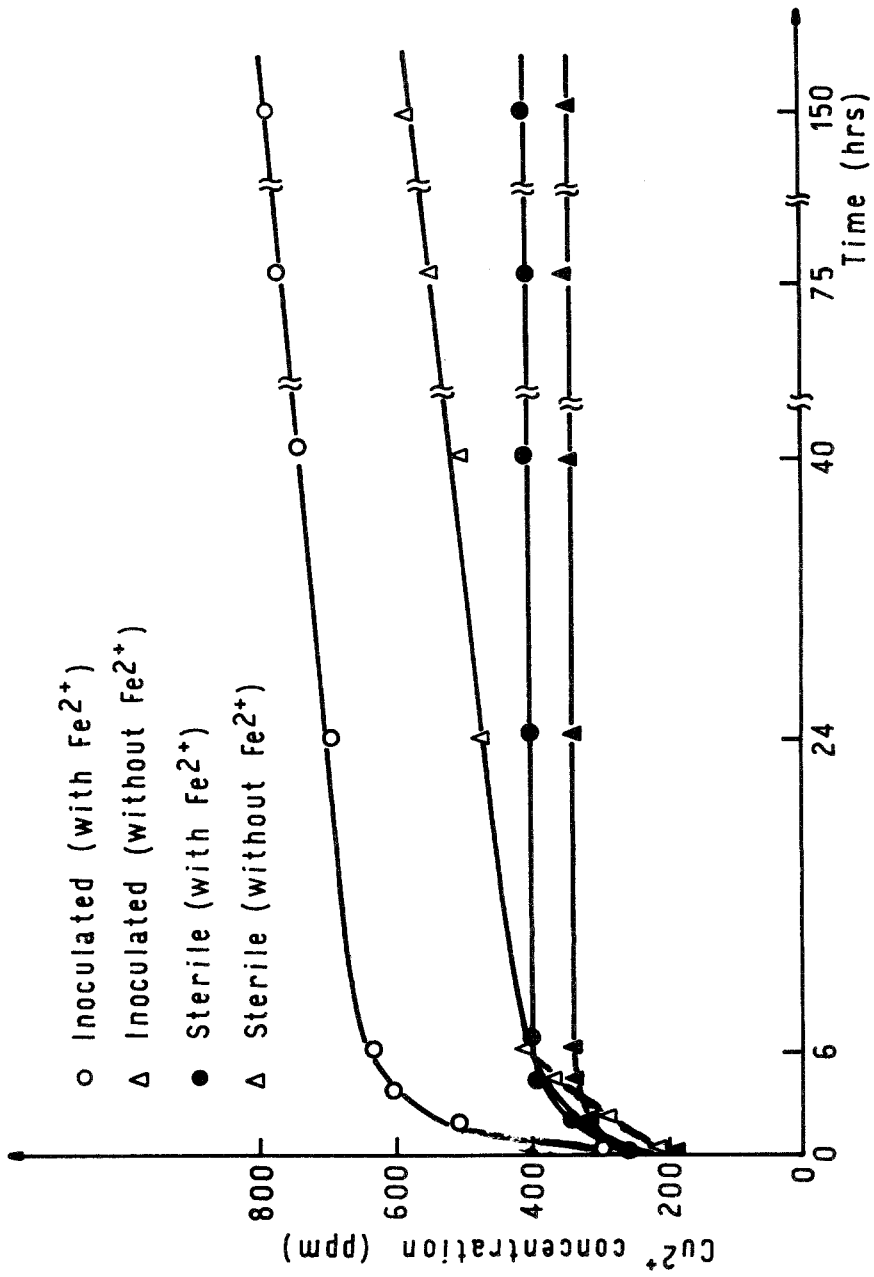
Figure 1 : Bioleaching of CuS

- ○ Inoculated (with Fe^{2+})
- △ Inoculated (without Fe^{2+})
- ● Sterile (with Fe^{2+})
- ▲ Sterile (without Fe^{2+})

Cu^{2+} concentration (ppm)

Time (hrs)

2)both processes occurs principally near the surface but the need of surface
  is more important for the bacterial action than for the chemical action of
  the Fe^{3+};so the surface is not the limiting factor for the indirect rate.

In any case,if it is accepted that the bacteria and the Fe^{3+} are
fundamentally electron acceptors,the higher rate in presence of Fe^{3+}
(observed for all pulp densities at two temperatures)can be explained
considering that the number of acceptors(Fe^{3+} and bacteria)is higher than in
absence of Fe^{3+} (only bacteria).

Moreover ferric ion appears very quickly in the leaching medium because
bacteria are able to act much more quickly on soluble substrate(Torma,1977).
According to this,it is reasonable to consider the first period of leaching
as due almost exclusively to the Fe^{3+} action because the bacterial action on
the sulphide will be more retarded than in absence of Fe^{3+}.

Whether this lower rate for the attack of an insoluble substrate is
conected with the bacterial sorption on the surface it is not yet known.

It has to be stated again that the assumption according to which the
indirect rate can be calculated as the difference between the total and the
direct rate is no more than a rough approach,because it implies that the
direct mechanism occurs in the same quantitative way with and without Fe^{3+},
which is very unlikely.Nevertheless,if that approach is correct it would
explain the strange relationship between indirect rate and surface,according
to which an increase of surface produces a decrease of rate.

Another interesting fact is that after a variable period of leaching
(depending on the pulp density)the direct and total rates tend to the same
value,as can be observed in figure 1(same slopes).This suggest a similar
action in both cases,possibly the direct mechanism,which is the only one
that occurs both with and without Fe^{3+}.

A better understanding of these facts would require an analysis of the
causes of the decrease of rates through the processes.The most important
reason in the presence of iron is the precipitation of basic iron salts on
the surface.Others reasons-perhaps the only causes in the absence of iron-
are:

1)the rather abundant precipitation of sulphur.
2)a progressive sorption of bacteria on the surface,which would delay the
  dissolution of sulphide and,as a consequence,its oxidation.
3)a decrease of bacterial action with time,if they act directly on the
  surface.

If this can be proved it would clarify this point.

In tables 3 and 4 it is possible to observe that the influence of
temperature is higher at higher pulp density,probably due to the strong
dependency of the action associated to the surface with the temperature,
although the indirect mechanism is the more affected by temperature changes.

We think that is necessary to solve some other points,like the magnitude
of the indirect mechanism in absence of the direct one,because it has been
only proved so far with the action of increasing amounts of Fe^{3+} but without
possibility of its constant regeneration.This is important to a better
understanding of bacterial leaching of metallic sulphides or natural ores.

REFERENCES

Brierley,C.L.(1978) CRC.Crit.Rev.Microbiol.,6,207.
Bruynesteyn,A.(1980) presented at the Conference"Use of microorganism in
    Hidrometallurgy".Pecs,Hungary.
Colmer,A.R.,Hinkle,M.E.(1947) Science,106,253.
Duncan,D.W.,Trussell,P.C.,Walden,C.C.(1964) Appl.Microbiol.,12,122.
Holt,S.C.,Shiveley,J.M.,Greenawalt,J.W.(1974) Can.J.Microbiol.,20,1347
Kelly,D.P.(1976) in Microbial Energy Conversion,Schlegal,H.G. and Barnea,J.
    Eds.(F.Cotze KG,Gottinger).
Lundgren,D.G.,Silver,M.(1980) Ann.Rev.Microbiol.,34,263.

Sakaguchi,H.,Silver,M.(1978) Biotechnol.Bioeng.,18,1091.
Silverman,M.P.,Lundgren,D.G.(1959) J.Bacteriol.,77,642.
Silverman,M.P.,Ehrlich,H.L.(1964) Adv.Appl.Microbiol.,6,153.
Torma,A.E.,Walden,C.C.,Branion,R.M.R.(1970) Biotechnol.Bioeng.,12,501.
Torma,A.E.(1977) Advances in Biochemical Engineering,6,16.
Torma,A.E.,Sakaguchi,H.(1978) J.Ferm.Technol.,56,173.
Torma,A.E.,Rozgonyi,T.(1980) in Biogeochemistry of Ancient and Modern
    Environments,Trudinger,P.A.,Walter,M.R. and Ralph,J.Eds. Springer-
    Verlag,Berlin.
Torma,A.E.(1982) Progress in Industrial Microbiology,16,77.
Torma,A.E.,Banhegyi,I.G.(1984) Trends Biotechnol.,2(1),13.
Tributsch,H.,Bennett,J.(1981) J.Chem.Tech.Biotechnol.,31,565.
Tributsch,H.,Bennett,J.(1981) J.Chem.Tech.Biotechnol.,31,627.
Tuovinen,O.H.,Kelly,O.P.(1972) Z.Allg.Mikrobiol.,12,311.

Table 1:Rates of Cu^{2+} dissolution(in % w/v $.h^{-1}$).Direct and Indirect mechanism.

Pulp Density(% w/v)	Temperature(C)	Total Rate $.10^4$	Direct Rate $.10^4$
0.5	31	125	80
1.0	31	150	123
1.5	31	180	160
2.0	31	190	176
2.5	31	205	200
0.5	35	130	85
1.0	35	186	144
1.5	35	240	200
2.0	35	260	236
2.5	35	300	277

Table 2:Order of reaction and rates constants for the total,direct and indirect processes.

Temp.	K tot.10^4	n tot.	K dir.10^4	n dir	K indir.10^4	n indir.
31 C	149	0.32	123	0.54	24.5	−0.74
35 C	186	0.48	143	0.72	41.6	−0.26

Table 3:Influence of the temperature on each mechanism.

$$r_c = V_c^a / V_c^b \quad , \quad a = 35\ C \quad , \quad b = 31\ C$$

r_1= ratio of total rates.

r_2= ratio of direct rates.

r_3= ratio of indirect rates.

Pulp Densities(% w/v)	r_1	r_2	r_3
0.5	1.11	1.03	1.22
1.0	1.24	1.16	1.70
1.5	1.33	1.25	2.06
2.0	1.36	1.34	2.40
2.5	1.46	1.39	2.63

Table 4: Ratio of rates of the different processes

$$r_{1/2}^a = V_1^a / V_2^a \quad , \quad r_{2/3}^a = V_2^a / V_3^a \quad , \quad a = 35\ C$$
$$r_{1/2}^b = V_1^b / V_2^b \quad , \quad r_{2/3}^b = V_2^b / V_3^b \quad , \quad b = 31\ C$$

V_1 = total rate

V_2 = direct rate

V_3 = indirect rate

Pulp Density(% w/v)	$r_{1/2}^a$	$r_{1/2}^b$	$r_{2/3}^a$	$r_{2/3}^b$
0.5	1.42	1.54	2.07	1.74
1.0	1.21	1.30	5.02	3.44
1.5	1.11	1.18	8.43	5.11
2.0	1.08	1.10	12.10	6.80
2.5	1.02	1.08	16.10	8.50

Table 5:Activation energies for the total,direct and indirect mechanisms.

Act.Energy Total	Act.Energy Direct	Act.Energy Indirect
42.6 KJ/mol	29.3 KJ/mol	103.0 KJ/mol