

Tasmanian Geological Survey Record 1995/05

An investigation of the potential for bacterial leaching at Mt Lyell

by W. E. Baker

INTRODUCTION

The decision by Renison Goldfields Consolidated to discontinue mining at Mt Lyell by the end of 1994 led Tasmania Development and Resources to examine the likelihood of survival of this mining field. It was evident that any viable future venture would have to embrace new technologies and involve downstream processing of the remaining resource to high purity copper.

As part of this examination, the Laboratory Services Section of Industry Safety and Mines became involved in the potential for bacterial leaching of Mt Lyell ore. Copper ores have been subjected to bacterial leaching at numerous mineral fields around the world but in all cases where the process has had some measure of success, the host mineralisation has been dominated by sulphide minerals of the supergene zone (chalcocite, covellite, bornite, etc.). Chalcopyrite, which is the dominant copper mineral in the Mt Lyell ore, is a primary sulphide of high stability. Considerable research effort is currently being expended world-wide on the leaching of chalcopyrite by bacterial or other chemical procedures, as the supply of less stable copper sulphides will ultimately become exhausted. Investigation of bacterial leaching of Mt Lyell ore was undertaken in three phases:-

- (1) Bottle Roll Chemical Leaching
- (2) Stir Flask Bacterial Leaching
- (3) Column Bacterial Leaching

Minproc Engineers Ltd were retained as consultants for the period of investigation.

BOTTLE ROLL INVESTIGATIONS

The purpose of bottle roll studies of the leaching of ores is to ascertain the degree to which metals can be released from the minerals in which they occur. It is well known that solutions of ferric sulphate will leach metals from sulphides. With respect to bacterial leaching, there has long been

disagreement between on-site metallurgists, who favour the view that the bacteria simply assist in the formation of ferric sulphate, and the research bacteriologists, who suggest that the bacteria play a far more fundamental role in the release of metals.

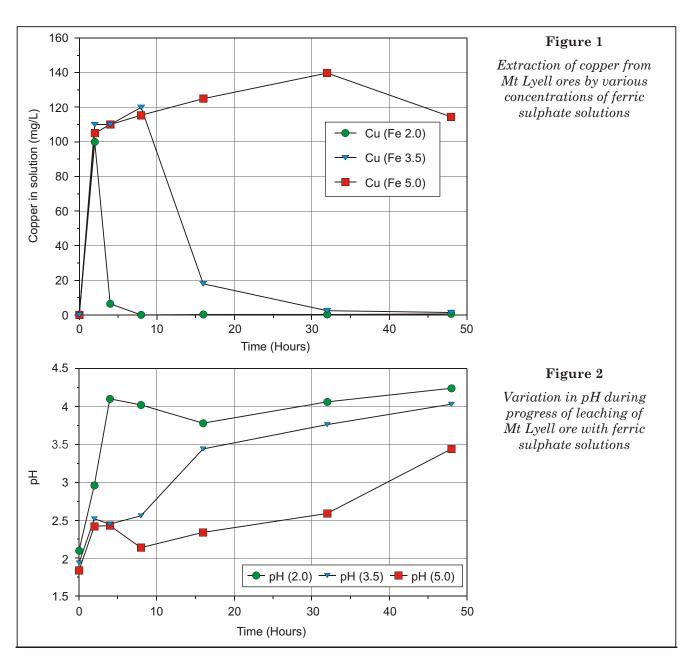
In the case of the Mt Lyell ore the dominant sulphide is pyrite (FeS^2) with copper largely being contained in chalcopyrite $(CuFeS^2)$. The leaching of these two minerals occurs as shown in the following equations:—

$$FeS_2 + Fe(SO_4)_3 + 4O_2 + 4H^+ \Longrightarrow 3FeSO_4 + 2H_2SO_4$$
(1)

$$CuFeS_2 + 2Fe(SO_4)_3 + 4O_2 + 4H^+ \Longrightarrow CuSO_4 + 5FeSO_4 + 2H_2SO_4$$
(2)

A sample of Mt Lyell ore assaying 1.9% Cu was pulverised to minus 200 mesh and 800 g quantities mixed with 1500 mL solutions of ferric sulphate containing 2.0, 3.5 and 5.0 g/L Fe3+. These three pulps were placed in 2 L plastic barrels and agitated by means of a laboratory bottle roller for 48 hours. Progress of the reaction of the ferric sulphate with the pulverised ore was monitored by sampling at time periods of 2, 4, 8, 16, 32 and 48 hours. Determinations were made of the pH and concentration of copper, total iron, ferrous iron and sulphate in solution for each period. In the discussion of the results which follows, information is presented in the form of graphs; the analytical results on which these are based are given in Appendix 1. The results for the extraction of copper from the ore by the various solutions of ferric sulphate are shown in Figure 1.

The highest extraction value was a disappointing $140\,\mathrm{mg/L}$ copper with the $5.0\,\mathrm{g/L}$ ferric iron solution. The copper values for the other solutions are lower and the copper extracted begins to be removed from the $2.0\,\mathrm{g/L}$, $3.5\,\mathrm{g/L}$ and $5.0\,\mathrm{g/L}$ ferric iron solutions at about 2, 8 and 32 hours respectively from the commencement of leaching. Figure 2 gives the variation in pH throughout the leaching. This graph shows that copper removal occurs as the acidity decreases in the range of pH = 2.7 to pH = 3.0.



The results of monitoring the changes occurring with iron in solution for the three leaching studies are shown in Figures 3 to 5. For the reaction between the Mt Lyell ore and the 2.0 g/L solution of ferric sulphate, the total iron concentration in solution plunges before the increasing ferrous iron content causes some recovery. The initial loss of ferric iron is most likely due to the adsorption of this trivalent ion on the surfaces of the finely pulverised silicates present in the ore sample. The effect is less obvious with the 3.5 g/L ferric sulphate solution and is absent from that with a strength of 5.0 g/L. As reaction between the ferric sulphate solutions and the ore proceeds, ferrous iron becomes the only species present in solution. Within experimental error the values for total iron and ferrous iron are near identical for a large part of the reaction history in the case of the 2.0 g/L and 3.5 g/L ferric sulphate solutions, and some of the data points have been separated to allow clear graphical presentation. This outcome shows that whilst the ferric sulphate solutions had little effect on chalcopyrite as given in equation (2) above, they were very effective in the destruction of pyrite as predicted by equation (1). For the reaction involving the 2.0 g/L ferric sulphate (fig. 3) it can be seen that the activity of this solution ceases about eight hours from the commencement of leaching. From this point on there is a gradual decrease in the iron present in solution.

A similar pattern occurs for the 3.5 g/L ferric sulphate (fig. 4), with the higher concentration of this solution allowing destruction of the pyrite to proceed for 16 hours.

In the case of the 5.0 g/L ferric sulphate solution (fig. 5), the concentration was high enough to allow reaction to proceed for the 48 hours that the leaching was continued.

Figures 3 to 5 show that the reaction between pyrite and solutions of ferric sulphate has been accompanied by an overall loss of iron from the system. The behaviour of sulphate during reaction is shown in Figure 6, which indicates little change in

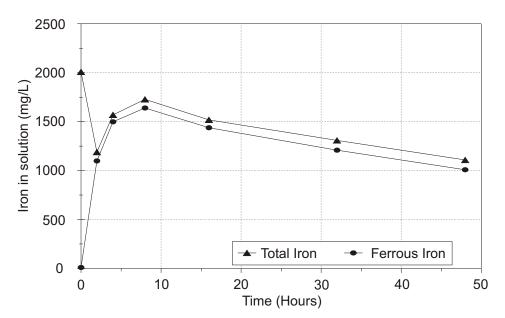


Figure 3

Behaviour of iron in solution during reaction between Mt Lyell ore and 2.0 g/L ferric iron solution

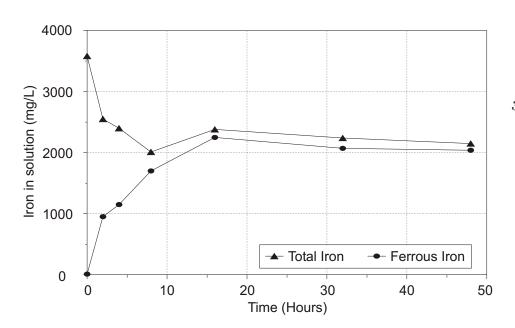


Figure 4

Behaviour of iron in solution during reaction between Mt Lyell ore and 3.5 g/L ferric iron solution

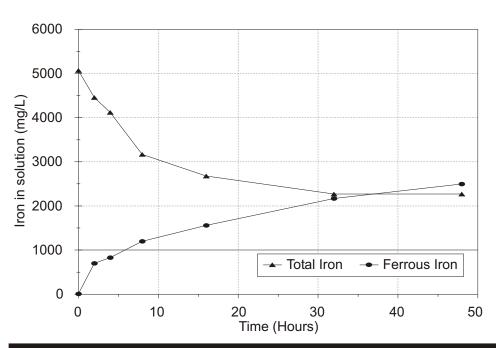


Figure 5

Behaviour of iron in solution during reaction between Mt Lyell ore and 5.0 g/L ferric iron solution

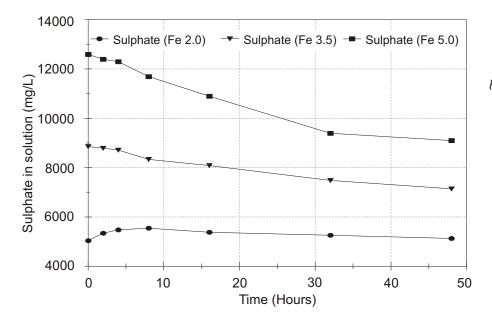


Figure 6

Behaviour of sulphate in solution during reaction between Mt Lyell ore and ferric sulphate solution

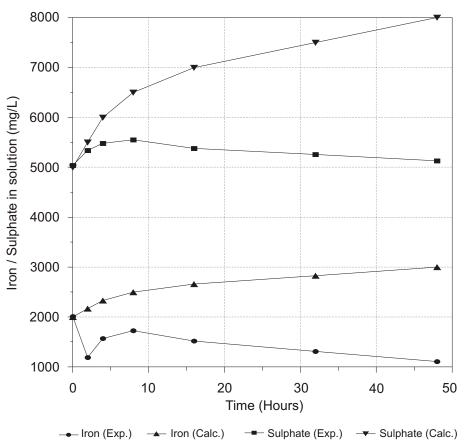


Figure 7

Comparison between the experimental and theoretical behaviour of iron and sulphate during leaching

the case of the $2.0\,\mathrm{g/L}$ ferric sulphate leach but a loss of sulphate for reactions with the more concentrated solutions. From a theoretical approach based on Equation (1) above, there should be a substantial increase in both iron and sulphate as a result of reaction, as is shown in Figure 7.

The evidence presented for the behaviour of iron and sulphate (fig. 3 to 7) clearly indicates that the reactions occurring during the leaching of the Mt Lyell ore resulted in the removal of these ions from

solution. This result is most likely explained by the production of jarosite $[(K,Na)Fe_3(SO_4)_2(OH)_6]$ through reaction of the iron and sulphate with potassium and sodium from the destruction of silicate minerals present in the ore. It was noted earlier that the small amount of copper leached from chalcopyrite was lost to the solution as the acidity decreased in the pH range of 2.7 to 3.0. The loss of copper is probably due to the inclusion of this ion in the structure of the precipitating jarosite.

STIR FLASK BACTERIAL LEACHING

Ore dressing metallurgists and many of their associates in the mining industry, tend to be very conservative in the interpretation of the chemistry of the bacterial leaching process and as a result it is held to be largely due to the action of ferric sulphate which is a product of bacterial metabolism. From this point of view, and given the very low yields of copper from the chemical leaching investigations, there was little to encourage a continuation of the study of the Mt Lyell ore. Fortunately, research over recent years has indicated that far more complicated biochemical activity is involved in leaching and this being the case further study of Mt Lyell ore was warranted.

The literature on bacterial leaching of ore is becoming vast and some 800 references have appeared during the last 15 years with much of the pioneering work being carried out by A. E. Torma (e.g. 1972) and C. L. Brierley (e.g. 1973). The main bacterial species involved is Thiobacillus ferrooxidans which has a dependence on ferrous iron for its metabolism. Other species, such as Thiobacillus thiooxidans and Leptospirillum ferrooxidans also play an important role in the leaching process. Overall equations for the leaching of pyrite and chalcopyrite by ferric sulphate were given in (1) and (2) above. The types of reaction occurring in the presence of bacteria can be more completely represented as is shown in following equations:-

C = chemical leaching B = bacterial leaching

It can be seen from Equation (3) that both chemical and bacterial oxidation can produce ferrous sulphate, which is essential for the metabolism of Thiobacillus ferrooxidans, from a sulphide. In utilising ferrous sulphate, Thiobacillus ferrooxidans produces ferric sulphate (Equation 4) which reacts with iron and copper iron sulphides to yield further ferrous sulphate, copper sulphate and elemental sulphur (Equations 5 and 6). The appearance of elemental sulphur as a product of reactions shown in Equations (5), (6) and (7) provides the essential nutrient for the growth of Thiobacillus thiooxidans which is also capable of utilising this element directly from sulphides. The bacterial attack on sulphides is thus seen to result from two species of Thiobacillus, one releasing the metal whilst the other utilises sulphur or sulphide with the production of sulphuric acid. Until recently it was believed that bacterial leaching was produced by the

activity of the various species in the aqueous solutions that percolated through the sulphide bearing material (mining residue dumps, secondary and primary ores). It has become apparent that for effective leaching, the bacteria must be directly attached to the sulphide surface (Shrihari *et al.*,1991). It is now generally believed that the species *Leptospirillum ferrooxidans* plays an important role in bacterial attachment to minerals by forming a biofilm on the surfaces and thus providing a substrate on which the other species develop (Sand *et al.*, 1993).

The preceding discussion demonstrates that the natural leaching of sulphide ores involves more than purely inorganic reactions. A series of bacterial leaching tests were undertaken to assess the potential for this process in the recovery of copper from Mt Lyell ore. Bacteria for the investigation were collected in underground drainage at Mt Lyell and encouraged to develop in 500 mL of an aerated solution of Modified Kelly's Medium (Brierley, 1993) which consisted of:—

Ammonium sulphate	$0.40~\mathrm{g/L}$
Magnesium sulphate	$0.40~\mathrm{g/L}$
Potassium dihydrogen phosphate	$0.04~\mathrm{g/L}$

The medium would normally include 33 g/L of ferrous sulphate to support the metabolism of $Thiobacillus\ ferrooxidans$ but for these investigations it was replaced by 50 grams of pulverised (minus 200 mesh) Mt Lyell ore to ensure that the bacteria remained adapted to this ore type. The acidity was adjusted to pH = 1.8 with sulphuric acid and the temperature was maintained at 30°C. A similar setup was used to produce a supply of $Thiobacillus\ thiooxidans$ by substituting elemental sulphur for the Mt Lyell ore. The bacteria were allowed to develop in these flasks for ten days.

Leaching of the ore was carried out in two litre three-neck flasks which were immersed in a water bath at 30°C. Three flasks were set up with 75 g of minus 200 mesh ore and 1500 mL of solution adjusted to pH = 1.8 with sulphuric acid. Flasks 1 to 3 contained respectively, distilled water; 1400 mL of MKM with 100 mL of Thiobacillus ferrooxidans inoculum; and 1400 ml of MKM with 50 ml of Thiobacillus ferrooxidans plus 50 ml of Thiobacillus thiooxidans inoculum. A stirrer shaft was located in the centre hole of each flask, with the other holes containing a water-cooled condenser to reduce evaporative loss and a compressor serviced aeration jet. Samples were taken at two day intervals over a period of twenty days, with the solutions being maintained at pH = 1.8 and 1500 mL volume.

All graphs of the bacterial leaching have been adjusted to take account of initial copper present and they reflect accurately the amount of copper extracted from the ore. Figure 8 shows the results of the leaching of the ore by the solutions detailed

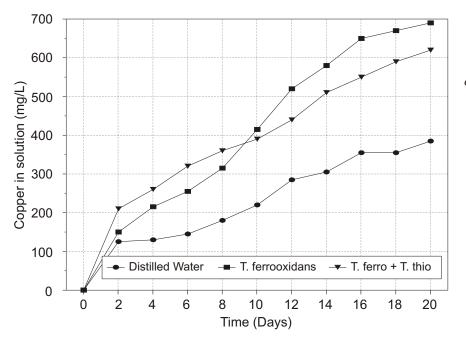


Figure 8

Comparison of the leaching of Mt Lyell ore at pH = 1.8 in the absence and presence of bacteria

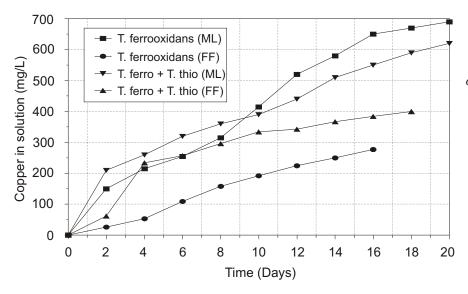


Figure 9

Results of bacterial leaching of chalcopyrite ore from Mt Lyell and Flin Flon mine, Canada, as mg/L copper in solution

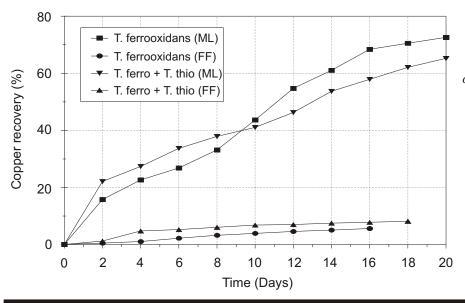


Figure 10

Results of bacterial leaching of chalcopyrite ore from Mt Lyell and Flin Flon mine, Canada, as % recovery of available copper

above. This figure shows that the bacterially-assisted leaching is far more effective than that with acidic water lacking the initial bacterial population boost by inoculation.

The mixed inoculate of *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* produces the most effective leaching early in the process but becomes inferior to the *Thiobacillus ferrooxidans* "monoculture" inoculate with time. After 20 days the copper in solution was 620 mg/L and 690 mg/L respectively. Lizama and Suzuki (1988) made a similar and more exhaustive study of the bacterial leaching of ore containing 14% chalcopyrite (4.9% Cu) from the Flin Flon mine, Manitoba, Canada. Examples of some of their results are compared with those from Mt Lyell in Figure 9.

Leaching of copper from the Mt Lyell ore is far greater than that from the Flin Flon. The Mt Lyell study has some advantage in that conditions were designed to promote bacterial development at a near ideal acidity of pH = 1.8 and a temperature of 30° C, whereas the Canadian study was carried out at pH = 2.3 and 25°C. The Flin Flon ore however contains 4.9% copper compared with 1.9% for Mt Lyell. The relative effectiveness of the Mt Lyell leach is shown more clearly in Figure 10 where the overall recoveries of copper from the ore at 20 days were 73% from the Thiobacillus ferrooxidans leach and 65% from the Thiobacillus ferrooxidans plus Thiobacillus thiooxidans leach. The Canadian study was terminated at 18 days with a copper recovery high of 8% compared with 70% for the Mt Lyell ore at the same time. In the Canadian study the mixed culture produced the best results whereas for Mt Lyell the "monoculture" was the more effective. Numerous strains of the sulphide leaching bacteria, with variable leaching characteristics that are not always predictable, have been developed by researchers world-wide and an explanation of the differing behaviour of Mt Lyell and Flin Flon bacteria cannot be offered. Clearly, the bacteria appear to be extremely active in the oxidation of Mt Lyell ore to the extent that there is a possibility they may offer an alternative process for the recovery of pure copper either by leaching of the ore or of a flotation concentrate.

At the completion of the stir flask leaching experiments a yellow crust was found to be strongly attached to the glass surface above the level of the reacting solutions. X-ray diffraction analysis of this material proved it to be a jarosite with the composition $(K,NH_4,H)Fe_3(SO_4)_2$ $(OH)_6$, which is compatible with the chemistry of the leaching system.

COLUMN BACTERIAL LEACHING

The success of the stir flask investigation of the bacterial leaching of Mt Lyell ore encouraged further studies. In order to simulate more closely the

"on site" conditions for bacterial leaching, a set of three acrylic columns measuring 100 20 cm was constructed. Each column was necked to a funnel at the base for ease of directing outflow to a reservoir and had an internal lip to support a 10 mm stainless steel grid. A quantity of crushed Mt Lyell ore was sieved to yield a plus 20 mm/minus 35 mm product that was washed clean of fines. Forty kilograms of this ore was placed in each column where it was retained by the grid.

Bacteria were prepared for these investigations in a manner similar to that used for the stir flask study but in larger volume. Five litres of mine water were left in contact with pulverised ore and nutrients at 30°C for ten days with continuous aeration. One litre samples of this bacterial supply were used to inoculate the solutions for two of the columns.

The columns were set up over 12 L plastic buckets in which were placed fish tank aerators and heaters. Solutions in the buckets were pumped to the top of the columns and allowed to trickle down to the reservoirs. Column 1 was the non-bacterial control and the reservoir contained 10 L of distilled water adjusted to pH = 2.0 with sulphuric acid. Mine water with nutrients added to make up for a low nitrogen and phosphate content was circulated through Column 2. The nutrient composition of Modified Kelly's Medium was circulated through Column 3. In each of these latter two columns one litre of bacterial inoculate was included in the 10 L total volume. The reservoir solutions were maintained at pH = 2.0 and a temperature of 30°C. At the beginning of the study circulation of the solutions was achieved by use of a multi-tube peristaltic pump but this unit was extremely troublesome, with the life of the silicone rubber tubes being totally unpredictable and often very short. This pumping arrangement was replaced by separate centrifugal pumps on each column and whilst this maintained circulation it proved difficult to keep the flow rate slow. The aerators also had a tendency to block frequently with consequent reduction of oxygen available for reaction.

The solutions were monitored on a 3-day basis for the purpose of maintaining the acidity at pH=2.0 and distilled water was added to make for evaporative loss at the same time. Sampling for copper analysis was undertaken every ten days and nutrient concentrations adjusted at these intervals when necessary. The results of the column leaching are shown in Figure 11.

Whilst some leaching of copper has taken place the level is not as high as could be expected from the stir flask study. Of more concern is the fact that the control solution has leached the ore as effectively as the inoculated solutions. It was thought that this circumstance could have arisen by contamination of the control from the other columns during the many

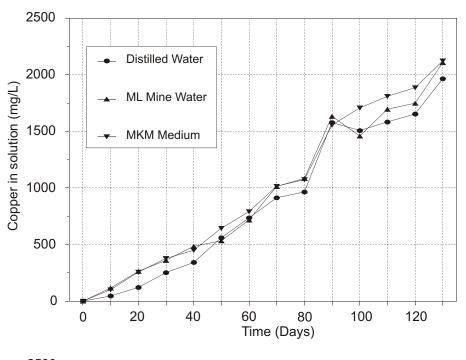


Figure 11
Copper released from Mt Lyell
ore during column leaching

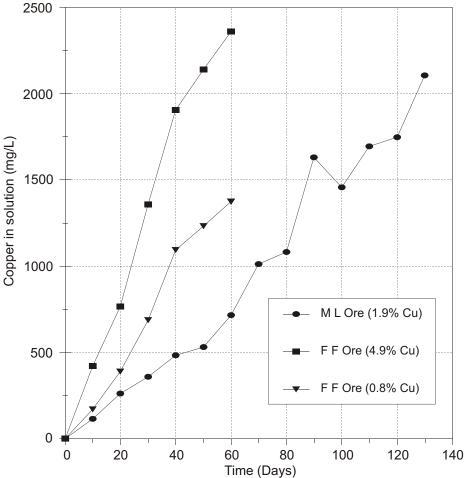


Figure 12
Column leaching of Mt Lyell
and Flin Flon ores

pumping crises that occurred whilst the peristaltic pump was in use.

A comparison of the Mt Lyell results with those obtained by Lizama and Suzuki (1989) for column leaching of the Flin Flon ore is shown in Figure 12. It is clear from this that the Flin Flon results are far better than those for Mt Lyell, which is at variance with the stir flask study. Some of the difference

could be due to varying experimental arrangement such as ore preparation, which in the Flin Flon case yielded a product that was minus 20 mm and included fines but it is very apparent that the Mt Lyell column leaching study failed to measure up to expectations.

Samples of the reservoir solutions were sent to Bactech (Australia) Pty Ltd for bacterial

assessment. The results of this indicated that the bacterial count in the control was no greater than expected of solutions in contact with sulphide ore. For the columns that had been inoculated, the result was similar and the bacteria had completely failed to multiply. Bactech suggested that this may have been due to the flow rate of solutions being too high and thus preventing bacterial attachment to the ore surfaces and this could well have been the case. It was noted above that the aerators were not reliable and needed frequent cleaning to keep air bubbling through the reservoirs. As can be seen from Equation (7) above, large volumes of air are required to provide the necessary oxygen for reaction and it is unlikely that this was available within the columns where the bacterial activity should have developed.

ACKNOWLEDGEMENTS

Throughout the leaching investigations Les Hay assisted with the numerous analyses required. Peter Sheridan prepared the ore samples and Richie Woolley carried out the X-ray diffraction analysis of the jarosite. John Canterford of Minproc Engineers Ltd and Julia Budden of Bactech (Australia) Pty Ltd provided helpful comment on the investigations as they proceeded.

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[22 June 1995]

APPENDIX 1

Analytical Results

Table 1

Bottle roll leaching of Mt Lyell ore
(All analytical results in mg/L)

A. $Fe_2(SO_4)_3$ containing 2.0 g/L Fe^{3+}

Hours	pH	Copper	Ferrous Iron	Total Iron	Sulphate
0	2.10	0.2	10	2010	5040
2	2.96	100	1180	1190	5340
4	4.10	6.4	1570	1570	5480
8	4.02	0.1	1730	1730	5550
16	3.78	0.2	1480	1480	5380
32	4.06	0.3	1250	1250	5260
48	4.24	0.6	1050	1050	5130

B. $Fe_2(SO_4)_3$ containing 3.5 g/L Fe^{3+}

Hours	pН	Copper	Ferrous Iron	Total Iron	Sulphate
0	1.94	0.1	3580	10	8860
2	2.52	110	2550	950	8790
4	2.45	110	2400	1150	8720
8	2.56	120	2010	1700	8340
16	3.44	18	2370	2350	8090
32	3.76	2.5	2240	2280	7480
48	4.03	1.4	2140	2070	7140

C. $Fe_2(SO_4)_3$ containing 5.0 g/L Fe^{3+}

\overline{Hours}	pH	Copper	Ferrous Iron	Total Iron	Sulphate
0	1.84	0.1	5080	10	12600
2	2.42	105	4460	700	12400
4	2.43	110	4120	830	12300
8	2.14	115	3170	1200	11700
16	2.34	125	2680	1560	10900
32	2.59	140	2270	2170	9400
48	3.44	115	2270	2500	9100

 $\begin{table} {\bf Table~2}\\ Stir~flask~bacterial~leaching~of~Mt~Lyell~ore~and~comparative~data~for~Flin~Flon~ore\\ All~analytical~results~in~mg/L. \end{table}$

Time	Control	Mt Lyell	Mt Lyell	Flin Flon	Flin Flon
(Days)		T.f.	T.f. + T.t.	T.f.	T.f. + T.t.
0	105	220	190	80	100
2	230	370	400	106	162
4	235	435	450	133	334
6	250	475	510	189	357
8	285	535	550	238	396
10	325	635	580	272	434
12	390	740	630	305	443
14	410	800	700	330	467
16	460	870	740	357	484
18	460	890	780	***	500
20	490	910	810	***	***

 $\begin{table} {\bf Table~3}\\ {\it Column~leaching~results~for~Mt~Lyell~and~Flin~Flon~ore}\\ {\it All~analytical~results~in~mg/L} \end{table}$

Time	Control	$Mt\ Lyell$	$Mt\ Lyell$	$Flin\ Flon$	$Flin\ Flon$
	water	mine	MK	HG	LG
	(pH = 2)	water	medium	ore	ore
0	13	183	53	40	25
10	59	298	153	460	200
20	133	446	309	810	420
30	265	543	429	1400	715
40	355	667	501	1940	1120
50	573	715	696	2180	1260
60	748	899	843	2400	1400
70	926	1196	1068	***	***
80	977	1267	1126	***	***
90	1590	1815	16	***	***
100	1520	1641	1759	***	***
110	1595	1878	1862	***	***
120	1666	1931	1939	***	***
130	1977	2290	2175	***	***