

Bacterial leaching: an introduction to its application and theory and a study on its mechanism of operation

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SYNOPSIS

In the first section, a brief background to the practical and theoretical aspects of bacterial leaching is presented. Descriptions are given of present and potential methods for exploiting bacterial leaching in metal-winning.

In the second section, the results of recent research are presented. The aim of this work was to obtain a greater understanding of the mechanism of bacterial leaching of sulphide minerals. Bacteria were observed to catalyse leaching reactions by oxidising ferrous ions to ferric ions, by removing protective films at the mineral surface and by depolarising cathodic areas.

SINOPSISIS

Die eerste deel is 'n kort samevatting oor die agtergrond van die praktiese sowel as die teoretiese aspekte van bakteriese loging. 'n Beskrywing van huidige sowel as metodes met moontlikhede in die toekoms deur die gebruikmaking van bakteriese loging in die herwinning van metale word gegee.

Die tweede deel handel oor die resultate verkry as gevolg van onlangse navorsing op die gebied. Die doel hiervan was die verkryging van 'n beter insig tot die meganisme van bakteriese loging van sulfiedminerale.

Met die oksidering van ferro-ione na ferri-ione het dit opgeval dat bakteriële katalisatore van logingsproses optree, deurdat die beskermende laag op die mineraaloppervlak verwyder word en sodoende depolarisering van die negatiewe belaaide gedeeltes veroorsaak.

APPLICATION AND THEORY

INTRODUCTION

The element sulphur is involved in one of the great natural cycles (Fig. 1). Within this cycle there is a secondary process in which the element is cycled solely by the action of micro-organisms and it is here that biological reactions of relevance in extractive metallurgy occur, namely, the bacterial oxidation of sulphur and metal sulphides. A wide range of metals may be dissolved from the corresponding sulphides (Table I) by this latter process which has been exploited in practice as bacterial leaching¹.

The ancient Romans are reputed to have recovered green and blue vitriol (iron and copper sulphates) from areas where natural sulphide leaching was taking place. It is probable that leached copper was first recovered on any large scale at the old Rio Tinto mines in Spain. Records from the seventeenth century show that copper was then being recovered by cementation on scrap iron from ground waters which had percolated through sulphide areas².

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TABLE I

SULPHIDE MINERALS OXIDISED BY BACTERIA

| Formula | Mineral |
|---------------------------------------------------|--------------|
| FeS ₂ , FeAs ₂ | Arsenopyrite |
| Cu ₅ FeS ₄ | Bornite |
| CuFeS ₂ | Chalcopyrite |
| CuS | Covellite |
| 3Cu ₂ S,As ₂ S ₅ | Enargite |
| PbS | Galena |
| FeS | Marcasite |
| NiS | Millerite |
| MoS ₂ | Molybdenite |
| As ₂ S ₃ | Orpiment |
| FeS ₂ | Pyrite |
| Sb ₂ S ₃ | Stibnite |
| ZnS | Sphalerite |
| Cu ₈ Sb ₂ S ₇ | Tetrahedrite |

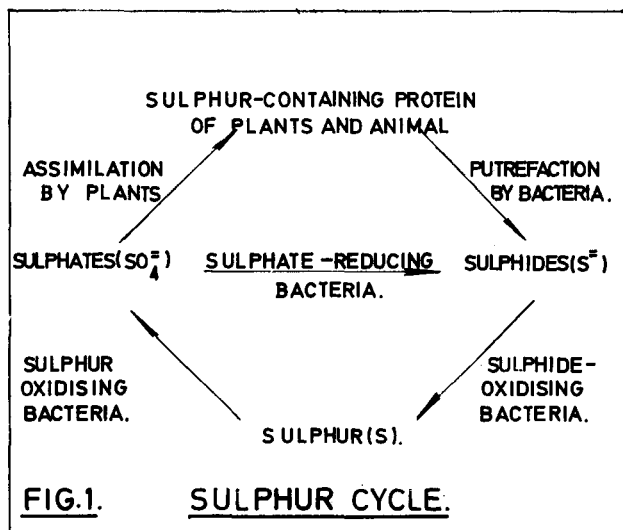


Fig. 1—Sulphur cycle

It is only during the last 30 years that it has been shown that bacteria are associated with sulphide leaching and actually play a fundamental role in the leaching process³. These bacteria are classified as members of the genus *Thiobacillus*; viz. *T. ferrooxidans* and *T. thiooxidans*. Other species of bacteria were originally thought to be involved, e.g. *T. sulphooxidans* and a separate genus *Ferrobacillus* was postulated by some workers. Recent work on the classification of these bacteria has however shown that the genus *Ferrobacillus* is invalid and that the bacteria are probably strains of the original two species of *Thiobacilli*⁴. Other species of *Thiobacilli* are known to oxidise sulphides at higher pH values but these are not discussed in this paper. Bacterial leaching is currently carried out in acid solutions (pH 2,0-3,0) where the metal cation remains in solution. At higher pH values hydrolysis will normally occur preventing the metal from being leached. A recent patent describes the leaching of sulphide minerals at higher pH values (7,0-9,0)⁵. This method may be of use in treating basic ores but at present it is still in the developmental stage.

Thiobacilli belong to a group of micro-organisms known as chemosynthetic autotrophs. (Table II). Autotrophic organisms obtain all nutrients for growth from inorganic compounds, and the chemosynthetic types secure energy by oxidation of inorganic compounds.

Biological catalysts called enzymes are synthesised by the bacteria and accelerate the rates of the oxidation reactions. The oxidation of sulphide minerals can be expressed by equations of the form:

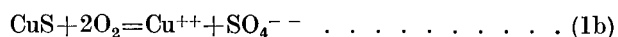
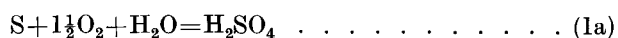


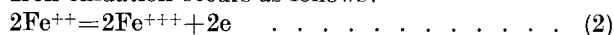
TABLE II

PRINCIPAL CHARACTERISTICS OF SOME MINE WATER BACTERIA

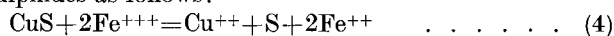
| Bacteria | Nitrogen source | Oxidation of | | |
|-----------------|------------------------------|--------------|---------------|-------------|
| | | Sulphur | Thio-sulphate | Ferrous ion |
| T. Thiooxidans | NH ₄ ⁺ | yes | yes | no |
| T. Ferrooxidans | NH ₄ ⁺ | yes | variable | yes |

The direct oxidation of reduced sulphur species by bacteria is accompanied by the formation of acid soluble cations. This has been referred to as the *direct mechanism* of leaching.

Iron oxidation occurs as follows:



Ferric iron itself is a good oxidant and can attack sulphides as follows:



One function performed by the bacteria is the rapid re-oxidation of ferrous iron to the ferric state. This process has been referred to as the *indirect mechanism* of leaching.

Iron is always found in leach solutions so that in practice both mechanisms probably operate. The relative importance of each is largely dependent on the type of mineral being leached. Large gaps exist in our knowledge of the biochemistry of these micro-organisms, especially regarding the mechanism of attack on a solid mineral surface⁶. Optimum conditions^{7, 8} for growth correspond with optimum leaching conditions and are generally in the range pH 2-4, temperature 25°-35°C, and Eh 300-500 mV. A supply of dissolved oxygen is also essential.

The heap leaching operations in the western U.S.A. are the largest exploiting bacterial leaching as a means of metal-winning. There are also other techniques of bacterial leaching which are less widely employed, or which show promise as future methods for extracting metals. These are discussed below.

HEAP LEACHING

The large tonnages of waste rock and tailings which accumulate near mining operations (especially at open cut workings) can often be leached profitably to recover some of the residual metals. A typical heap leaching operation is shown in Fig. 2.

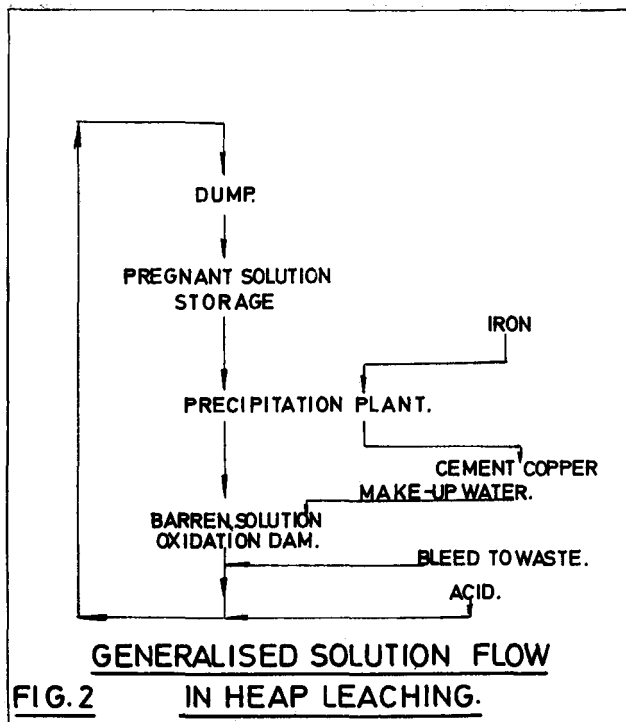


Fig. 2—Generalised solution flow in heap leaching

The low grade waste is dumped to form a heap from 10 to 20 metres high. An impermeable base is sometimes prepared before dumping commences to ensure that liquor percolating through the heap is collected and not lost by seepage. In some operations, for example Bingham Canyon in Utah, features of the natural terrain are utilised to aid drainage, by dumping rock in a steep sided valley.

Leach liquor is pumped to the top of the heap and allowed to percolate through the dumped material. The liquor may be applied at the surface by a system of small flood dams or by spraying. The latter method has the advantage that oxygenation of the liquor is achieved but has the disadvantage that excessive evaporation may occur in dry areas.

The size distribution and porosity of the rock in the heap are two of the most important factors influencing the performance of the operation. In practice there are several inter-related parameters affected by these two properties and the optimisation of leaching rate is usually achieved by empirical means. Some of these parameters are:

Rate of Percolation: A high rate of percolation results in the rapid transfer of reactants (especially oxygen) into the heap and of products (soluble metal ions) out. This situation is favoured by large particle size and high voidage in the heap.

Exposed Surface Area: A large exposed surface area of the material increases the amount of mineral in direct contact with the leaching solution, i.e. the available surface area for reaction is increased. This situation is favoured by a high percentage of fines in the dump, although this may decrease permeability.

Porosity of the rock: Most of the valuable mineral

usually occurs within the rocks and for leaching to occur it is necessary that the material be sufficiently porous to allow transport of reactants and products through the micropores.

An even distribution of rock size from about 0,5 metre down to 0,5 cm and a voidage of between 20 per cent and 40 per cent usually satisfies both conditions 1 and 2 above. Porosity is often checked before leaching is started⁹.

Bacteria will grow spontaneously in the heap if sulphide mineral surfaces and sufficient dissolved oxygen are available to them. Nutrients such as nitrogen and phosphorus are usually available in sufficient quantities from the gangue material of the rock.

Acid consumption of the gangue material is an important economic consideration. Under ideal conditions a pH of 2-3 should be maintained in the leach solution solely by the autogenous production of sulphuric acid from sulphides. In practice however it is normal to add acid and the amount required is important to the economics of the operation.

In a typical operation a section of the heap is irrigated for about 20 per cent of the time during which metal ions are washed out. During the remaining 80 per cent of the time the solution retained by the heap penetrates the pores of the rock and reacts with the sulphide minerals. In the later stages of this period evaporation helps to transport products back to the surface of the rocks ready to be washed out at the next percolation cycle. The heap is usually divided into sufficient irrigation areas to allow continuous operation of the recovery plant.

Harris¹⁰ and others^{2, 11} have shown that mass transport of dissolved oxygen is the rate limiting step in heap leaching. Harris bases his opinion on the observation that a substantial rise in the temperature of the heap at Rum Jungle, Australia, caused no increase in leaching rate. This author has developed a useful chemical engineering approach to the leaching behaviour of a heap by treating it as a pseudo-particle.

Pregnant solution leaving the heap is treated to recover its soluble metal value. In the case of copper leach solutions the metal is usually recovered by cementation on scrap iron although solvent extraction will be more widely used in future. At present, the precipitated copper from the cementation plant is treated together with copper concentrates by pyrometallurgical processes. However, by using solvent extraction, solutions sufficiently concentrated for direct electro-winning can be produced.

After metal recovery, the solution is held in an oxidation pond where bacteria oxidise ferrous to ferric ions. Hydrated ferric oxide is precipitated, reducing the level of iron in solution and stabilising the pH. Bleeding to remove further iron, and acid make-up to adjust pH, are then carried out and the solution is pumped back to the top of the heap.

A list of some bacterial leaching operations is given in Table III.

Heap leaching usually involves low capital expenditure. Accurate test work is necessary to predict and maintain a successful operation. Many operating prob-

TABLE III
DATA FOR SOME HEAP LEACHING OPERATIONS

| Name of locality | Product | Product (tonnes p.a.) | Grade of raw material (%) | Year |
|-----------------------|-------------------------------|-----------------------|---------------------------|------|
| Bagdad Copper Co. | Cu | 7 800 | 0,5 | 1965 |
| Cia Minera de Cananea | Cu | 3 300 | 0,3 | 1965 |
| Chino (Kennecott) | Cu | 27 000 | 0,25 | 1965 |
| Copper Queen | Cu | 5 400 | 0,3 | 1965 |
| Esperanza | Cu | 2 000 | 0,3 | 1965 |
| Inspiration Co. | Cu | 3 800 | | 1965 |
| Miami Co. | Cu | 13 000 | | 1965 |
| Ray (Kennecott) | Cu | 9 000 | 0,24 | 1965 |
| Silver Bell | Cu | 2 400 | | 1965 |
| Utah (Kennecott) | Cu | 70 000 | | 1965 |
| Rio Tinto | Cu | 18 000 | | 1945 |
| Rum Jungle | Cu | 375 | | 1967 |
| Mt. Lyell | Cu | 100 | | 1970 |
| Western Nuclear | U ₃ O ₈ | 200 | 0,1 | 1964 |

lems may be encountered. For example, it was found at Rum Jungle that the dump trucks used to construct the heap broke up the friable rock leaving an impenetrable surface layer which had to be ripped up before irrigation for leaching commenced. Fines are often produced during leaching causing clogging inside the heap. Precipitation of iron compounds (e.g. jarosite) in the heap often causes blockage of rock micropores. For this reason, iron concentration in the leaching liquors must be carefully controlled. Heap leaching appears superficially to be a simple process, but insufficient initial test work has led to extreme problems and resulted in shut downs in several areas. No doubt a lot of development and operational know-how is involved in the large and successful operations in the U.S.A.

It is impossible to do more than briefly scan the published information on heap leaching technology in this paper. More detailed information is available^{13, 14, 15}.

RECOVERY FROM GROUND WATERS

Abandoned mines often accumulate water in which the concentration of dissolved metals can reach appreciable levels. An abandoned open cut pit at Rum Jungle, Australia, contains millions of gallons of water. The pH of this water has dropped to 2,5 and the copper concentration has reached 50 ppm. The economic recovery of the copper should be possible, by solvent extraction, when metal concentration reaches 100 parts per million.

At the Mt. Morgan Mine in Queensland drainage water contains up to 200 ppm copper. Previous attempts to recover this metal by solvent extraction were unsuccessful because the high concentration of iron interfered with the process, but recent developments in the

production of selective solvent extractants could eliminate this problem.

A further example occurs at the Mt. Lyell Mine (Tasmania) which is situated in a high rainfall area (250 cm pa.). Constant run off from the mining area into a creek, results in a build-up of copper concentration to 150 ppm. A simple cementation on scrap iron yields about 100 tonnes copper per year.

UNDERGROUND LEACHING

The operation at Stanrock Uranium Mines in Canada is one of the best known examples of underground leaching¹. The mine began operating in 1958 and by 1960 the underground water had become so acid due to bacterial oxidation of pyrite that severe corrosion problems had arisen. The acidic ferric mine water also leached out uranium compounds and the uranium oxide content rose to about 0,03 kg per tonne. 13 000 kg of oxide were recovered in 1962 from this source. In 1963 high pressure hosing of the stopes with barren liquor was commenced and this operation was so successful that conventional mining was terminated in 1964 and all 1 200 stopes were hosed down on three monthly cycles. By 1966, the change in methods had cut the cost of production by 25 per cent.

Other mines in Canada are reported to be using a similar method for extracting uranium¹⁶.

IN SITU LEACHING

This technique has great potential for the treatment of low grade orebodies for which the costs of orthodox mining would be prohibitive. The orebody is leached in situ by providing some means of applying the leach liquor and recovering the pregnant solution. Liquor may be allowed to percolate from the surface or may be pumped under pressure into drill holes (Fig. 3). Pregnant

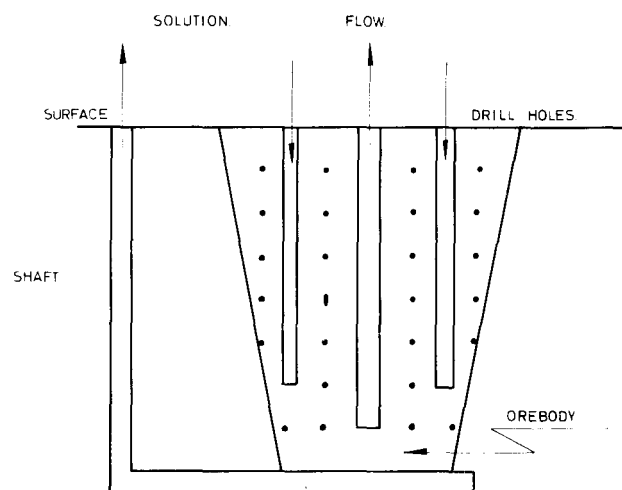


Fig 3 In Situ Leaching

solution may be recovered from adjacent holes or from horizontal drives underlying the orebody.

The crucial factor influencing the application of this technique is the permeability of the orebody itself. In a project now under way in the U.S.A., the feasibility of fracturing low grade orebodies with nuclear explosives¹⁷ is being investigated. It has been shown that an orebody containing 0,5 per cent copper could be economically treated by fracturing with a 50 kilotonne explosion, followed by leaching over a ten year period to recover 75 per cent of the copper, i.e. 30 million kg copper. The total capital of such an operation is estimated cost to be 25 million U.S.A. dollars.

STIRRED TANK LEACHING

Leaching rates in heaps are extremely low due to mass transport limitations, usually the diffusion of oxygen through the heap being the principal factor. It has been shown that under ideal conditions, rates several hundred thousands of times faster than those operative in heap leaching operations may be obtained¹⁸. These high rates are obtained when finely ground concentrates are leached with bacteria under optimal conditions in a stirred reactor.

An economically feasible process for the bacterial leaching of a 30 per cent chalcopyrite concentrate has been demonstrated by Bruynesteyn and Duncan of the British Columbia Research Council¹⁸. A continuous stirred tank reactor using conventional aeration equipment, operating at 3,56 per cent pulp density and at 35°C was used. Excessively large capacity was not needed since retention time was of the order of one day. The leach solution was recycled to allow the concentration of copper to build up to a level suitable for direct electro-winning. It should be noted that the bacteria involved can operate in solutions containing up to 25 000 ppm copper. A similar system has been shown to be economically feasible for zinc sulphide concentrate leaching.

The advantages and disadvantages claimed for reactor leaching by the British Columbia Research Council workers are:

Advantages

1. The ore can be upgraded to the metal at the mine site.
2. The capital costs are low compared to those for a smelter.
3. The equipment may be designed and installed in modules.
4. It may be applied to small and large operations.
5. The process is simple and no sophisticated operator training is needed.
6. Air pollution by sulphur dioxide is eliminated.
7. Certain mineral assemblages not amenable to treatment by conventional processes may be treated successfully.

Disadvantages

1. Sulphur by-products are not recovered.
2. The excess acid generated must be neutralised.

MATERIALS AND METHODS

It has been conclusively established by a number of workers that certain bacteria can, under appropriate conditions, greatly increase the rates of leaching of sulphide minerals. In order to obtain more detailed information on the precise mechanisms which operate in the bacterial leaching of sulphides, it was considered necessary to define the parameters more precisely than has been done in the majority of previous studies.

A pure strain of *Thiobacillus ferrooxidans* with marked abilities to oxidise ferrous iron and elemental sulphur, was employed, and synthetic copper sulphides, of known stoichiometry, provided a strictly defined and reproducible mineral substrate. Considerable attention was paid to the control of environmental factors, such as pH and soluble iron concentration, and a variety of techniques were used to assess the extent of the degradation of the mineral substrates.

The *Thiobacillus ferrooxidans* was isolated from a marine sulphide mud, and this was effected by using a dilution/enrichment technique in ferrous sulphate medium followed by single colony isolation on silica gel solid medium. The 9K medium having the following composition was used in this investigation⁷:

| | |
|-------------------------------------------------|---------|
| (NH ₄) ₂ SO ₄ | 3,0 g |
| KCl | 0,10 g |
| K ₂ HPO ₄ | 0,50 g |
| MgSO ₄ , 7H ₂ O | 0,50 g |
| Ca(NO ₃) ₂ | 0,01 g |
| Tap water | 1 litre |
| Adjust pH with H ₂ SO ₄ | |
| Energy source. (Fe ⁺⁺ or S). | |

The batch growth characteristics of this organism were determined with elemental sulphur and ferrous sulphate as energy sources (Fig. 4).

Cell concentrates for use in the subsequent leaching studies were taken in late logarithmic phase from sulphur-grown batch cultures, using a centrifugation technique⁷. Cell concentrates were used to reduce the lag phase normally associated with bacterial growth and also to ensure a greater uniformity in the inoculum. Sulphur was chosen in preference to iron as a growth substrate because cells of *T. ferrooxidans* grown on ferrous ion take some time to adapt to growth on sulphur (or sulphide) whereas cells grown on sulphur can immediately oxidise both ferrous ion and sulphur²⁰. In these sulphide leaching studies it was considered desirable to use bacteria capable of and adapted to the oxidation of reduced sulphur and iron species.

Copper is toxic to most organisms, but *T. ferrooxidans* appears to be able to grow in fairly high concentrations of copper and other cations²¹. It has been observed that a period of adaptation is often necessary before the organism will grow under such conditions. In the case of the organism used in these investigations, the addition of 2 000 ppm copper ions to a batch culture grown on sulphur caused the lag phase to be extended to four weeks instead of the usual 1-2 days. Subsequent

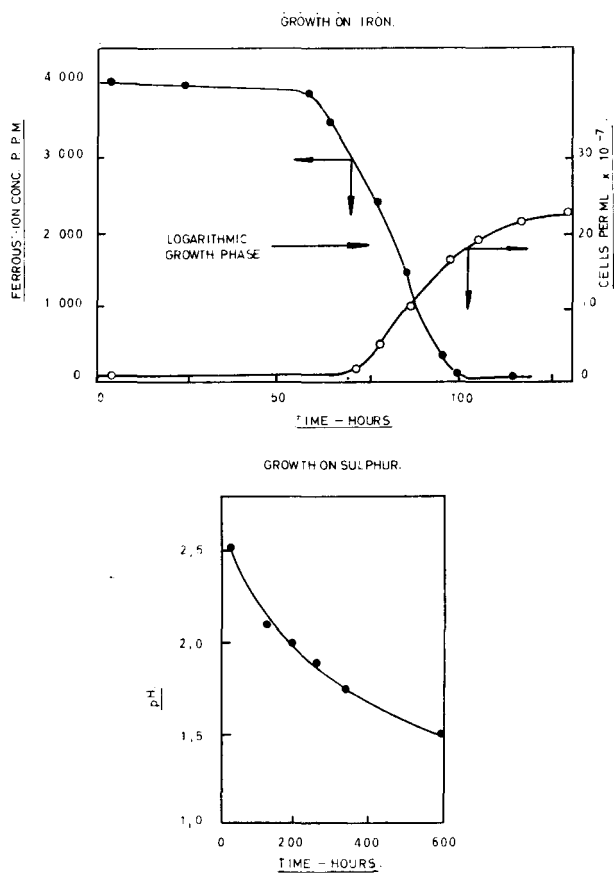


Fig 4 Growth rate of *T. ferrooxidans*

re-inoculation of this culture into similar copper-containing medium reduced the lag phase to the normal period. The growth rate of the organism appeared to be unaffected by the presence of copper. Thereafter, all batch cultures used for the preparation of cell concentrates contained 2 000 ppm copper (as CuSO_4).

Natural minerals, even of the highest museum grade, contain some contaminating mineral species or have some degree of lattice substitution by trace elements. These impurities are known to have an effect on the leaching behaviour. In order to overcome, as far as possible, the effects of these variables, it is desirable to use high purity synthetic minerals, since the properties of these materials are defined and reproducible and, in addition, iron-free conditions may readily be obtained. Because natural minerals always contain some iron it is difficult to distinguish between indirect ferric leaching and direct microbial attack on the mineral.

Covellite (CuS) and chalcocite (Cu_2S) were prepared by diffusing stoichiometric amounts of sulphur vapour into copper at elevated temperatures in vacuo²². High purity materials were used and the structure of the mineral product was checked by X-ray diffraction. The powdered minerals were washed (just prior to use) in dilute acid to remove oxide and with carbon disulphide to remove any free sulphur. The particle size was $-200 +400$ mesh in the leaching experiments.

Precise leaching studies involving the system bacteria-mineral-water demand the control and/or monitoring of the physico-chemical parameters of temperature,

pH, Eh, oxygen tension and iron concentration. Ideally, a fully instrumented reactor is desirable for such studies, but when a large number of tests are involved, the shake flask technique offers a compromise between ideal control and the rate at which results can be obtained. Several concurrent shake flask test series were used to study the mechanisms rather than the kinetics of the leaching. The various environmental parameters were controlled at or near the values known to give optimum leaching rates.

The established techniques used in the study of metallic corrosion were applied in this investigation. Polished sections of the minerals were prepared and examined before and after leaching using optical and scanning electron microscopy as well as electron probe analysis. The minerals were also used as electrodes and their potentials were measured during the leaching process. The rate of leaching was followed by determining dissolved copper at fixed time intervals.

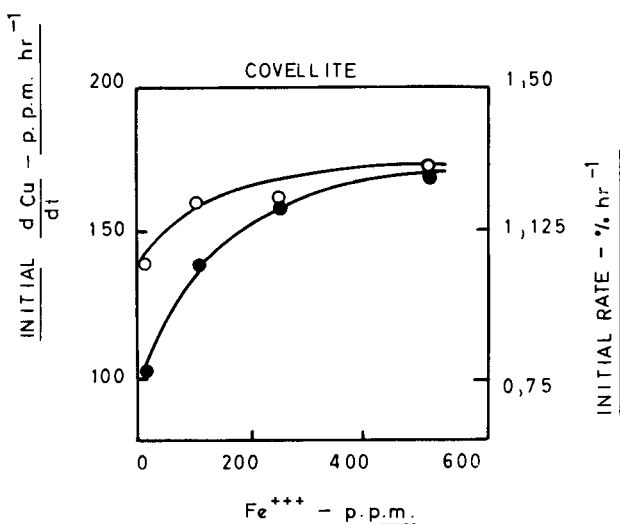
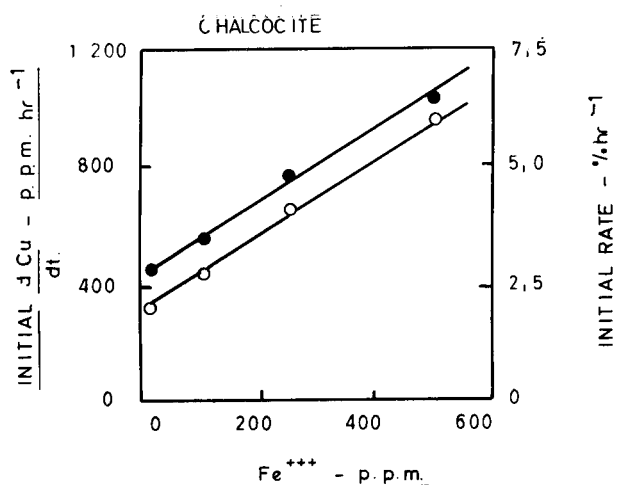
RESULTS

Rate Studies

These experiments were designed to test whether or not the presence of whole cells of iron/sulphur oxidising bacteria affect the initial rates of leaching of synthetic covellite and chalcocite in acidic ferric sulphate solutions. Fifty ml of ferric ammonium sulphate solution adjusted to various concentrations of ferric ion were added to 500 ml conical flasks. To one set of flasks, bacterial concentrate was added to give an initial cell count of 10^8 cells per ml. One gram of mineral was placed in a special receptacle in the rubber stopper. The flasks were flushed with dry nitrogen to eliminate the effect of direct oxidation of the mineral with oxygen. They were attemperated for 30 min at 30°C and then tilted to allow the minerals to fall into the ferric solution. The flasks were immediately placed on a reciprocating shaker at 30°C and the time of mineral contact recorded. Samples of supernatant solution (0.5 ml) were taken at measured time intervals and analysed for copper content. The rate curve was extrapolated to zero time and the initial leaching rates plotted against ferric concentration (Fig. 5).

In the case of chalcocite, both with and without bacteria present, the kinetics were first order with respect to ferric ion concentration although the presence of bacteria reduced the magnitude of the rate slightly. These linear kinetics are in accordance with the work of Thomas et al²³ on the ferric leaching of synthetic chalcocite.

In the case of covellite, the order of the kinetics varied over the range of concentration of ferric iron used, in the absence of bacteria. The shape of the curve indicates that the order approaches zero, i.e. it is independent of ferric iron concentration at high concentrations. At ferric iron concentrations below 500 ppm the order of the reaction increases (i.e. it becomes increasingly dependent on ferric iron concentration.) In the presence of bacteria the shape of the curve is similar but the rates are higher over the range 0-250 ppm ferric ion and are less dependent on ferric concentration. It



- WITH BACTERIA.
- WITHOUT BACTERIA.

Fig 5 Rate Data

appears that sulphur oxidising bacteria have some catalytic effect on the initial reaction between ferric iron and this mineral.

Thomas and Ingraham²⁴ have shown that chemical leaching rates for synthetic covellite are directly proportional to the ferric iron concentration up to about 280 ppm while at higher concentrations the order tends to zero. The present results are in accordance with these findings.

Short term leaching under non-growth conditions

The leaching characteristics of the two synthetic sulphides over a relatively short period of time using cell concentrates under non-growth conditions was examined. Each mineral was leached under conditions in which the presence or absence of ferric ions and of bacteria were the variables. Initial conditions used are shown in Table IV.

TABLE IV

| DETAILS OF SHORT TERM LEACHING TESTS | | | | |
|--------------------------------------|-----------------|--------------------------------------|----------------------|-------------------|
| Test No. | Mineral % by wt | pH in H ₂ SO ₄ | Fe ⁺⁺ ppm | Bacteria cells/ml |
| 1 | 2 | 2,5 | 500 | 10 ⁸ |
| 2 | 2 | 2,5 | 0 | 10 ⁸ |
| 3 | 2 | 2,5 | 500 | 0 |
| 4 | 2 | 2,5 | 0 | 0 |

The flasks were agitated on a gyratory shaker at 30°C. Samples of supernatant solutions (0,5 ml) were withdrawn every second day and the pH and the concentrations of copper, ferrous and ferric ions measured.

In the test containing both bacteria and ferrous ion, a high rate of leaching (3 per cent copper in 1 day) was observed with chalcocite. This was due to the high rate of oxidation of ferrous ion to ferric ion by bacterial catalysis, followed by an indirect ferric leach of the mineral.

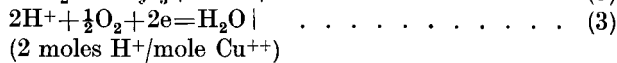
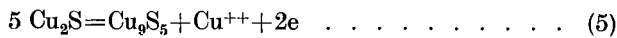
In the other three tests with chalcocite, there was an initial release of copper (1 per cent in 4 days) and an increase of the pH to 4,0. After this no further leaching was observed.

In the case of covellite, the presence of bacteria and ferrous ion resulted in the leaching of 30 per cent copper in 25 days, while in the test with bacteria only, 23 per cent copper was leached in the same time. This difference was not as significant as in the case of chalcocite, and it is considered that direct bacterial oxidation of covellite under iron-free conditions had taken place. The pH rose to 3,0 in 4 days and then remained constant. Sterile controls showed virtually zero leaching rates.

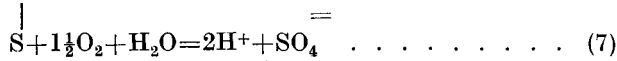
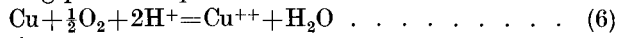
Long term leaching under growth conditions

The long term (2 months) leaching characteristics of the synthetic sulphides were tested in a growth medium inoculated with cell concentrates. One hundred ml of mineral salts medium at pH 2,5 was added to flasks containing 2 g of mineral. No iron was added and the initial cell count was 10⁷ bacterial cells per ml. The flasks were agitated on a reciprocating shaker at 30°C. Samples of supernatant solution (0,5 ml) were withdrawn at 14 day intervals and analysed for copper. The pH of the solution in each test was measured and adjusted to pH 2,5 every 48 hours and the acid consumption was recorded. These results are shown in Fig. 6.

In the case of chalcocite, leaching with bacteria present gave a similar rate of extraction to that in the sterile control. During this period the acid consumption in the test with bacteria present was lower than that in the sterile control, showing that acid was being produced by bacterial oxidation of reduced sulphur. The acid consumption in the control experiment (1,9 moles hydrogen ions per mole soluble copper) closely agrees with the value predicted from the first steps in the oxidation of chalcocite²³, if chemical and electro-chemical mechanisms are assumed.



A large difference¹ was observed in leaching rates of covellite in the presence and absence of bacteria. After a lag phase of about 100 hours, a high rate of bacterial leaching under iron-free conditions was observed and continued until 20 per cent of the copper was extracted. During this period (60 days) the acid consumption was zero. This suggests that the following reactions were taking place at equal rates.



Reaction 7 is catalysed by the bacteria.

The sterile control leached at a very low rate with negligible acid consumption.

Rest potential measurements

Electrodes consisting of polished sections of the synthetic minerals were suspended in growth medium at a pH of 2,5 and containing 10⁷ bacterial cells per ml.

Sterile controls were also set up. The rest potentials of these electrodes were measured against a saturated calomel electrode at 30°C and the measured value converted to the hydrogen scale. The potential measured in this manner is the corrosion potential, i.e. a mixed potential attributable to two or more electrochemical reactions taking place at the mineral surface. Copper sulphides behave as semiconductors²⁵ and exhibit electrode potentials. In these experiments, an attempt was made to interpret differences and changes in potential arising from bacterial action at the mineral surface.

The growth medium contained initially copper ions at a concentration of 10⁻⁴M and this did not increase by more than 10 per cent during the course of the experiment because of the relatively small area of exposed mineral. An agitation test indicated that mass transport was not rate limiting. For these reasons, it is assumed that changes in electrode potential were not caused by mass transfer effects or changes in copper concentration. These results are shown in Fig. 7.

The measured potential of the chalcocite electrode was generally slightly higher in the presence of bacteria.

The potential of the covellite electrode was substantially higher in the presence of bacteria, and this effect was observed immediately on initiation of the experiment. This observation supports the previous results obtained in the long term leaching tests where direct bacterial oxidation of covellite under iron-free conditions was observed.

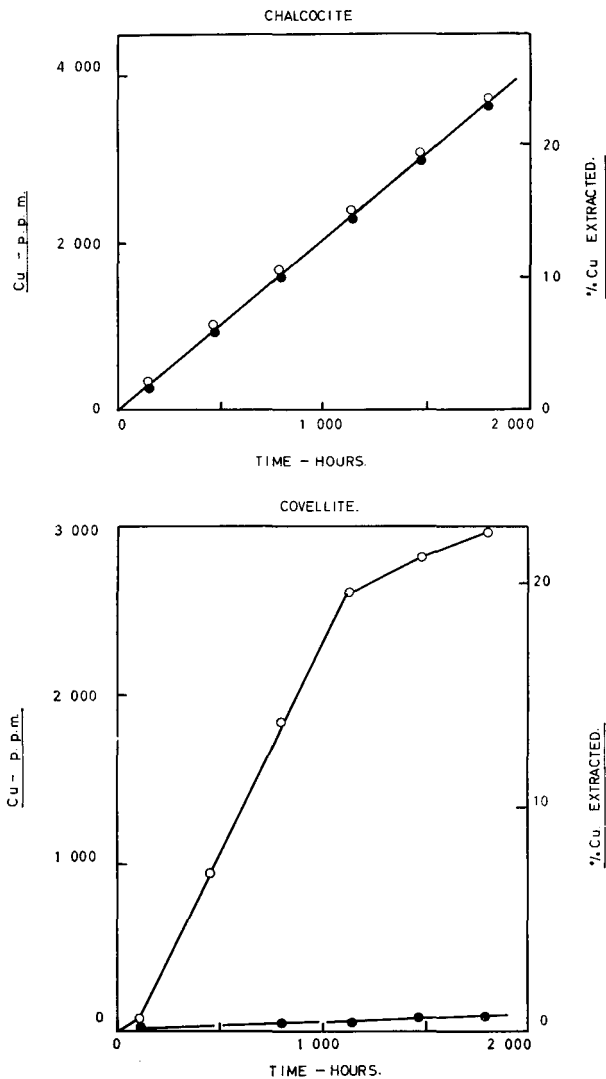


Fig 6 Long term leaching data

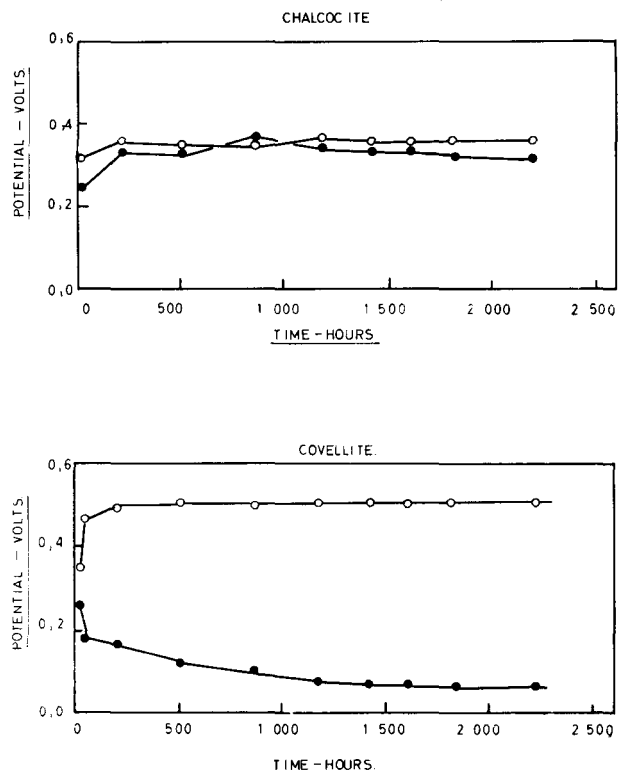


Fig 7 Rest potential measurements

Microscopy and Electron Probe Analyses

Polished sections of the minerals, mounted so as to expose only a small area of polished surface, were included in the long term leaching experiments. These surfaces were examined, after leaching, by optical and scanning electron microscopy. The specimens were then cut at right angles to the original exposed surfaces and the elemental composition gradients measured using an electron probe analyser.

The chalcocite surface had the same appearance after leaching whether bacteria were present or not. The surface was deeply cracked and shrunken and leaching had occurred evenly over the whole area. No pitting was observed. The sulphur concentration was found to increase towards the exposed surface but it did not exceed that corresponding to the sulphur content of CuS. Possibly because of the development of cracks, sharp bordering between the various copper sulphide phases were not detected.

The original polished surface of the synthetic covellite was highly optically-active under polarised light: this is a normal property of covellite.

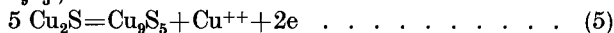
The surface of the specimen leached in the absence of bacteria displayed only slight optical activity and was pitted and slightly cracked at grain boundaries. Certain regions showed no effects of corrosion, but sulphur-rich areas were observed in the surface pits and cracks. The rest of the surface differed little from that of the unleached specimen.

The specimen leached in the presence of bacteria had a dull, non-optically-active surface, and corrosion had taken place evenly over the area. The surface was granular with little pitting. The stoichiometry of the mineral remained unchanged up to the surface. This observation supports the earlier interpretation of the results obtained in the long term leaching experiments, namely, that copper and sulphur are leached at equimolar rates in the presence of bacteria.

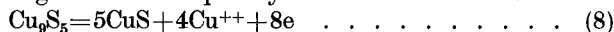
DISCUSSION

It has been shown that the leaching of metal sulphides is an electrochemical oxidation process^{26, 27, 28} and the following mechanisms have been postulated for the leaching of chalcocite and covellite in acidic ferric sulphate solutions.

The initial oxidation product of chalcocite is digenite (Cu₉S₅)



Digenite is subsequently oxidised to covellite.



These steps are relatively rapid. Covellite leaches more slowly to yield elemental sulphur or sulphur rich covellite.



The rate of this reaction gradually decreases due to the formation of a reaction layer of sulphur.

The electron probe analyses indicate that the bacteria effectively oxidise the reaction sulphur layer to soluble sulphate, thus maintaining the high initial reaction rates. Further, it is observed that the bacteria increase the initial leaching rate and it is likely that a mechanism

other than the removal of sulphur may be attributed to bacterial action.

The main cathodic reaction in the absence of iron under the physico-chemical conditions of these experiments is:



This reaction is considered to be rate limiting because the addition of ferric iron as an alternate electron acceptor increases the leaching rate. If bacterial action is to increase leaching rates by a direct mechanism (i.e. by a mechanism other than the increase of ferric ion concentration) it must stimulate this rate-limiting cathodic reaction.

The higher electrode potentials measured in the presence of bacteria are considered to indicate cathodic depolarisation. The cathodic reduction of oxygen by reaction (3) has a potential of about 1 100 mV while anodic oxidation reactions for the sulphide minerals by reactions of the form,



have potentials between 100 and 350 mV at pH 3,5²⁶. (These potentials depend on the activities of reacting species and the values given apply for the conditions of these experiments). During corrosion, when electrons flow from anodic to cathodic areas, the anodic potential rises and the cathodic potential drops because of polarisation. The measured potential (a mixed potential) will thus lie between 100 and 1 100 mV depending on the extent of polarisation at the different areas. The potentials measured for the minerals in these experiments lie closer to the anodic values indicating a greater degree of cathodic polarisation. The increase of potential observed, especially for covellite, in the presence of bacteria is considered to be due to the ability of the bacteria to depolarise the cathodic areas. Exactly how this is achieved cannot be stated with certainty. Insufficient knowledge is available about oxidation-reduction phenomena at mineral surfaces and of bacterial sulphur metabolism to be able to postulate a scheme for the ion and electron pathways at the bacteria-mineral interface. It is possible that oxidase-type enzymes play a role in catalysing cathodic reactions at the mineral surface or that the bacteria might be directly oxidising the sulphur of the mineral lattice together with a concurrent stimulation of cathodic reactions.

CONCLUSION

Bacterial leaching currently provides a means for the treatment of low grade ores or tailings, and this usage could well be of increasing importance as the grade of available ore bodies declines. Recent developments, however, suggest that microbial processes may have application by the use of slurry reactors rather than heap leaching techniques, in the treatment of high grade ores or concentrates. A considerable amount of developmental work is required on existing processes, particularly in respect of general problems such as the physical design of heaps and the improvement of oxygen availability.

However, current biological leaching technology is probably on a development plateau. Further progress may well be contingent on the securing of much more