EFFECT OF PARTICLE SIZE ON THE KINETICS OF MICROBIOLOGICAL LEACHING OF CHALCOPYRITE

By

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ABSTRACT

An experimental investigation was undertaken to study the microbiological leaching of chalcopyrite by Thiobacillus ferrooxidans. Leach tests were conducted on a small scale using shake flasks.

Tests were done which showed that the optimal time for transfer of inocula was between 6 and 8 days.

Attempts were made to clarify the complex media-mineral-bacteria interactions that occur in the bioleaching process relating bacterial growth with the changes in media composition as a result of the activities of the bacteria at the mineral surface. In so doing it was observed that a significant amount of copper was leached during the stationary phase of bacterial growth.

A sedimentation technique was used to separate the chalcopyrite into various size fractions which were then used to determine bacterial leaching rates in separate experiments. The particle size ranges had average diameters of 1.07, 1.78, 2.52, 3.56, 5.48 and 7.41 μm. The method used to measure particle size was based on the direct comparison of the particles with the scale of an eyepiece micrometer using a microscope.

Measurements of particle size distribution made during the course of leaching showed that as the leach proceeded, particle size decreased and the particle size distribution moved in the direction of more particles in the smaller size ranges.

An attempt was made to apply Levenspiel's shrinking core model to the data obtained for leaching of the various sized particles. Agreement was reasonable but not perfect between the predicted and measured values of % copper extraction. Better agreement was observed at lower leaching times.

Electron micrographs are presented which illustrate the attack of the chalcopyrite particles by the organisms. They also show the effects of jarosite precipitation.

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CHAPTER 1

CHAPTER I

1.1 INTRODUCTION

Biological leaching is a process in which metals are extracted from ores and minerals by enzymic transformations. The leaching of metals using Thiobacillus ferrooxidans is currently applied to the leaching of low grade, and waste sulphide ores by dump and heap leaching techniques for the recovery of copper and uranium.

Studies conducted on a variety of sulphide minerals have demonstrated that bacterial oxidation can also be used for the recovery of lead, cobalt, nickel, zinc and other base metals.

The possibility of using Thiobacillus ferrooxidans for the leaching of metals from ore concentrate is currently being considered. This type of leaching would take place in a batch or a continuous flow chemical reactor in which a controlled process could be established. The advantages of biological leaching over conventional pyrometallurgical and hydrometallurgical processes are claimed to be lower costs, the elimination of the air pollution problems associated with smelting operations, and suitability for a smaller scale of operation.

Studies have been previously carried out with the purpose of optimizing the parameters that affect the biological process such as temperature, pH, type and concentration of nutrients, aeration, etc., and to obtain increased metal yields.

It is only recently that attempts to describe the biological leaching process using mathematical models have been made.

Given that the biological leaching process involves complex interactions between the mineral, the bacteria and the aqueous phase, attempts at modelling multiparticle leaching systems have only been partially successful. Mathematical models are based on hypotheses about the mechanisms that control the process and when the results of such models are compared with experimental results, a greater understanding of the process is generated. Mathematical models are also used to predict the results of changes in the operating conditions thereby eliminating lengthy and costly experiments.

1.1.1 Objective

The objectives of this work were to obtain information about the mechanisms of leaching of chalcopyrite (copper-iron sulphide) by Thiobacillus ferrooxidans using monosize particles in batch reactors, to try to quantify the reaction kinetics and verify the applicability of the shrinking core model to the biological leaching of copper.

CHAPTER II THE BACTERIA THIOBACILLUS FERROOXIDANS

During the first half of the twentieth century large amounts of copper were recovered from chalcopyrite-pyrite heaps at the Rio Tinto operation in south-western Spain (Trussell, 1964), but it wasn't until 1947 that bacteria were recognized as an integral part of this process. Colmer and Hinkle (1947) showed that ferrous iron oxidation occurring in acid mine water was biological in origin; the isolation of the organism responsible was made by Colmer, Temple and Hinkle in 1949. Further studies were conducted by Temple and Colmer (1951) to establish that the bacterium was an autotrophic iron oxidizer; they named it Thiobacillus ferrooxidans.

Autotrophic bacteria can be divided into two groups on the basis of their source of energy: the first group is named photosynthetic and derives its energy from light; the second group is called chemosynthetic and derives its energy from the oxidation of inorganic compounds. Thiobacillus ferroxidans belongs to this second group of bacteria which also uses carbon dioxide as a carbon source for the synthesis of its organic compounds. It has been further considered as an obligate chemoautotroph given its inability to use alternate carbon sources (more complex than carbon dioxide).

2.1 MORPHOLOGY AND CHEMICAL COMPOSITION

Thiobacillus ferrooxidans is a motile, non-spore forming, gram negative, rod-shaped organism which occurs singly or occasionally in pairs. Its size is 0.6-1.0 μm width by 1.0-1.6 μm in length and like any other microorganism its basic elemental composition is C, H, O, N, S, P. All of these elements are then required for its growth and have to be supplied in forms utilizable by the bacteria.

In addition an energy source is required for transport of nutrients, synthesis, locomotion, etc.

Thiobacillus ferrooxidans can obtain energy from the oxidation of sulphide minerals such as: copper-iron sulphides, lead sulphide, nickel sulphide, zinc sulphide, etc.

CHAPTER III SUBSTRATE

3.1 DESCRIPTION

Chalcopyrite is part of a series of complex copper-iron sulphides that occur as minerals. It is a widely disseminated mineral that occurrs in metallic veins and pockets frequently associated with iron pyrites, pyrrhotite, siderite, bornite and other minerals (Mellor, 1947). The mineral sometimes contains gold and silver.

Burdick and Ellis (1917) found that the space-lattice of chalcopyrite is tetragonal with the axial ratios a:b:c = 1:1:0.985. The iron and copper atoms are located so that they together form a face-centred tetragonal lattice, the planes perpendicular to the tetragonal axis being made up alternately of copper atoms alone and iron atoms alone. The sulphur atoms are located on a similar face centred lattice with the planes of the sulphur atoms lying midway in all three of the axial directions between the planes of the iron and copper atoms (see Figure 1).

The composition of the mineral can be represented by the formula $CuFeS_2$, although it has been suggested that the atoms have no fixed valences, but fluctuate between $Cu^{+}\ Fe^{+++}\ S_2$ and $Cu^{++}\ Fe^{++}\ S_2$ (Pauling, 1932).

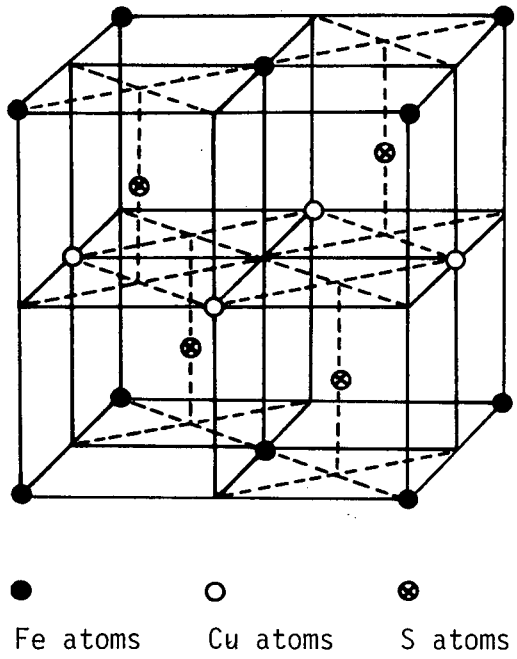


Fig. 1 Space - Lattice of Chalcopyrite

3.2 MINERAL AND MICROBE INTERACTIONS

Chemical leaching of metallic sulphides is carried out using ferric-sulphate solutions in sulphuric acid media. The main reaction can be expressed as:

$$MS + 2Fe^{3+} \longrightarrow M^{2+} + S^{\circ} + 2Fe^{++} \qquad (3.1)$$

where MS represents a metallic sulphide. The ferric iron is reduced to ferrous iron and has to be supplied constantly. Ferric sulphate also hydrolyses at low pH to ferric hydroxide according to:

$$Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^{+} \qquad (3.2)$$

It was first suggested (Silverman, 1961, 1963, Duncan, 1973, Lau, 1970) that the role of bacteria in the leaching of sulphide minerals was to oxidize the ferrous iron produced in reaction 3.1 as follows:

$$2Fe^{++} + 1/2O_2 + 2H^{+} \longrightarrow 2Fe^{3+} + H_2O \qquad (3.3)$$

This reaction would replenish the ferric iron (consumed in reaction 3.1 and 3.2). The bacteria would also produce sulphuric acid from the oxidation of sulphur in addition to the

acid generated by the hydrolysis of ferric iron according to the following reaction:

$$S^{\circ} + 3/2\ O_2 + H_2O \xrightarrow{\text{bacteria}} H_2SO_4 \qquad (3.4)$$

Subsequently Duncan (1973) provided evidence of the direct attack of Thiobacillus ferrooxidans on the mineral surfaces of chalcopyrite and pyrite.

The oxidation of insoluble ferrous iron and sulphide occurs simultaneously (Landesman, 1966) and independently (Duncan, 1967) but the relative rates depend on how the cells are grown. It has been demonstrated that the ability of Thiobacillus ferrooxidans to grow on iron is constitutive, while the use of sulphide minerals seems to be subject to specific adaptation mechanisms (Touvinen, 1972). Analysis of the base ratio of DNA obtained from cells growing on different substrates conducted by Guay (1976) led him to suggest that subculturing would cause the production of high metal concentration resistant strains or new species by selection and mutation mechanisms.

3.2.1 Mechanism of oxidation of ferrous iron

If Thiobacillus ferroxidans uses the oxidation of ions from the mineral surface of sulphides to obtain energy then the two possible energy transfer mechanisms are that either the bacteria

attach to the surface where the ions can be contacted with enzymes at the membrane level or, the bacteria use extracellular enzymes to make these ions available and subsequently transport them into the cell. Attachment of Thiobacillus ferrooxidans to mineral surfaces has been demonstrated (Razzell, 1963, McGoran, 1969) and studies of the cell envelope of Thiobacillus ferrooxidans (Berry, 1980) have provided evidence for both mechanisms. According to Lundgren (1978) the cell envelope of Thiobacillus ferrooxidans consists of three zones:

1) A cytoplasmic membrane which constitutes the inner layer of the envelope bordering on the cytoplasm.

2) A central zone comprising a rigid layer of peptidoglycan and a periplasmic space.

3) An outer layer which contains lypopolysaccharide and lipoprotein. This outer layer might act as an initial binding site for ferrous iron (Touvinen, 1972). The transfer of electrons is carried out at the outer membrane or at the peroplasmic space level ($2Fe^{++} \longrightarrow 2Fe^{++} + 2e^{-}$) while the energy associated reaction ($2e^{-} + 1/2\ O_2 + 2H^{+} \longrightarrow H_2O$) is probably located within the inner membrane (Lundgren, 1978).

An extracellular complex from the culture filtrate of Thiobacillus ferrooxidans has also been isolated (Agathe, 1968) and suggested to act as a substrate for ferrous iron oxidation (donating electrons for electron transport via a cytochrome system within the cell) or as a solvent (Touvinen, 1972). The cytochrome system role in iron oxidation was first presented by Duncan (1967) who showed that cytochrome inhibitors inhibited iron oxidation; furthermore cytochromes a and b were isolated from Thiobacillus ferrooxidans by Din (1967a) who also suggested a ping pong bi bi mechanism for iron oxidation shown in Figure 2 (Din, 1967b).

3.2.2 Mechanism of Oxidation of Sulphides

Concerning the mechanism of sulphide oxidation, Duncan (1967) found that N-ethyl maleimide (NEM), a thiol-binding inhibitor acted as an inhibitor of sulphur oxidation, showing that thiol groups participated in sulphur oxidation. A suggested mechanism is the oxidation of sulphur to sulphite and to sulphate either by a sulphite:cytochrome c oxidoreductase or with the intermediate formation of adenylyl sulphate. The mechanism of contact of Thiobacillus ferrooxidans with sulphur is not clear but Agathe (1968) suggested that the extracellular complex might act as a wetting agent for sulphur granules.

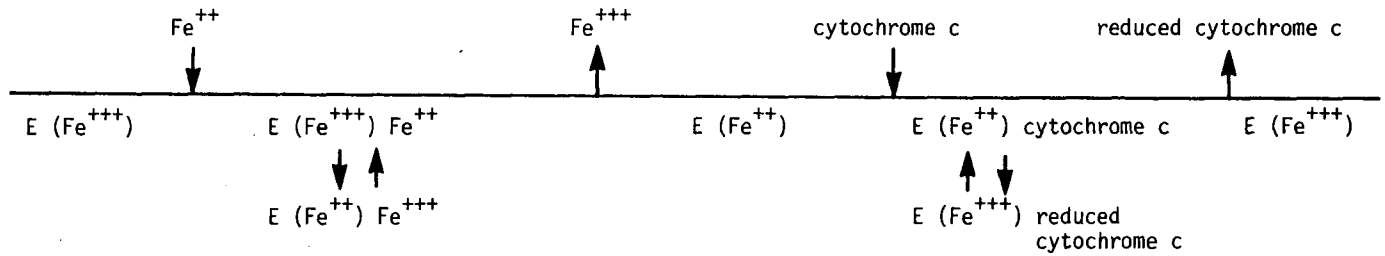


Fig. 2 Ping Pong bi bi mechanism of Fe^{++}-cytochrome c reductase of Thiobacillus ferrooxidans (Din, 1967b)

Tributsch (1981) suggested that bacterial activity on sulphides was based on the chemical reaction of protons with the metal sulphide surface which then caused a shift in the electronic states and produced surface states described as $-SH^{-\delta-}$ groups which were removed by bacterial activity.

The use of sulphide as a source of energy by Thiobacillus ferrooxidans has been considered the rate limiting step in the leaching process. It has been further suggested that the high initial leaching rates are due to oxidation of ferrous iron atoms available at the surface of the mineral (Duncan, 1967). When these atoms are exhausted, the use of sulphide controls the rate of dissolution of the mineral (Tributsch, 1981).

3.3 MINERAL-MEDIA INTERACTIONS

During the biological leaching of sulphide minerals a variety of inorganic species is present in the media at any time and secondary reactions take place between these species. McGoran (1969) found that most of the ferric sulphate hydrolyzed would precipitate as a basic ferric sulphate. At pH <3 jarosite will normally form (Duncan, 1972; Sakaguchi, 1976) according to the following reaction:

$$3Fe_2(SO_4)_3 + 14H_2O \rightarrow 2(H_3O)Fe_3(SO_4)_2(OH)_6 + 5H_2SO_4 \quad (3.5)$$

The jarosite salts of potassium, sodium, ammonium and hydronium are formed when these ions are available (Pickering, 1968).

The leaching of chalcopyrite usually yields 50-60% copper extraction (Bruynesteyn, 1970). This incomplete solubilization of copper has been attributed to the formation of an impermeable layer of sulphur around the partially leached chalcopyrite (Miller, 1979; Chakraborti, 1979) and to the accumulation of gangue and precipitation of basic ferric sulphates ($(Fe(OH)SO_4$ and $H\,[Fe\,(SO_4)_2 \cdot 2Fe(OH)_3]$) (Torma, 1973). This latter explanation is supported by the fact that increased yields can be obtained when the residues of the leaching are subject to re-grinding and re-leaching (Torma, 1973, 1977).

The overall reactions of biological leaching of chalcopyrite can be expressed as:

$$2\,CuFeS_2 + 8\,1/2\,O_2 + H_2SO_4 \xrightarrow{\text{bacteria}} 2\,CuSO_4 + Fe_2(SO_4)_3 + H_2O \quad (3.6)$$

$$3\,Fe_2(SO_4)_3 + 14\,H_2O \rightarrow 2(H_3O)Fe_3(SO_4)_2\,(OH)_6 + 5H_2SO_4 \quad (3.7)$$

$$CuFeS_2 + 2Fe_2\,(SO_4)_3 \rightarrow CuSO_4 + 5FeSO_4 + 2S^\circ \quad (3.8)$$

$$2S^\circ + 3O_2 + 2H_2O \xrightarrow{\text{bacteria}} 2H_2SO_4 \quad (3.9)$$

The biological leaching of chalcopyrite can then be considered as a series of events caused by interactions of bacteria, the mineral and the aqueous phase.

CHAPTER IV FACTORS AFFECTING BIOLOGICAL LEACHING

4.1 PARTICLE SIZE AND SURFACE AREA

The extraction rate is a function of the surface area and will have its maximum value at the start of the leach and gradually decrease when accumulation of by-products increases the mass transfer resistance. The surface area available depends on the particle size and for a fixed amount of material increases with the fineness of the material. Optimum particle sizes for biological leaching have been proposed as: <325 mesh (Duncan, 1964), 42 μm (Torma, 1977), <44 μm (Razzell, 1963). In theory, the optimum (minimum) particle size will be reached when the particle is formed by a single crystal (Touvinen, 1972).

4.2 NUTRIENTS

4.2.1 Carbon Source

Thiobacillus ferrooxidans being an autotroph uses carbon dioxide as a carbon source. The mechanisms of carbon fixation are the Calvin reductive pentose phosphate cycle and the secondary carboxylation of phosphoenolpyruvate (PEP) derived from the carbon cycle (Touvinen, 1972).

The carbon dioxide can be supplied to the liquid media through gas exchange with the atmosphere or sparged. For the first case Touvinen (1972) showed that the carbon dioxide consumption exceeds the maximum soluble amount present in the media at any time. For this reason the use of a carbon dioxide enriched atmosphere is recommended.

4.2.2 Nitrogen Source

The primary source of nitrogen for Thiobacillus ferrooxidans is ammonium ion.

Mackintosh and Herbet (Duncan, 1972) believed that the bacterium can fix nitrogen, but attempts to detect nitrogenase in Thiobacillus sp. failed (Tsuchiya, 1974).

Silverman (1959) found that the media composition of his 9K medium supplied ammonia and other nutrients (potassium, magnesium, calcium) in adequate amounts to support the growth of up to 5×10^8 cells/mL.

4.3 TEMPERATURE

The optimum temperature for Thiobacillus ferrooxidans growing on chalcopyrite was determined to be 35°C (Duncan, 1964; Landesman, 1966, Sakaguchi, 1976).

4.4 pH

The optimum pH has been determined to be 2.0 (Landesman, 1966b) although it grows well between 2.0-4.5 (Morrison, 1969).

4.5 DISSOLVED OXYGEN

The effects of the dissolved oxygen concentration on the growth of Thiobacillus ferroxidans were studied by Liu (1973) who calculated the solubility of oxygen in 9K medium at 35°C to be 6.42 mg O_2/L and found the critical oxygen concentration to be 0.29 mg O_2/L.

The maximum respiration rate for Thiobacillus ferrooxidans growing on chalcopyrite was reported to be $QO_2(N)$ = 3200 μL (STP)/mgN-h (Landesman, 1966).

During the leaching of metallic sulphides, oxygen concentrations have been found to be as low as 0.2-0.55 ppm (Torma, 1973), which suggest a possible oxygen limitation when oxygen is provided only by surface exchange.

4.6 AGE OF CELLS

There is no agreement on the literature as to the best inoculum age. Some of the reported values are: 3 days (Landesman, 1966), 4 days (Landesman, 1966b), late lag phase (Torma, 1977) and stationary phase (Sakaguchi, 1976).

CHAPTER V MODELLING BIOLOGICAL SYSTEMS

5.1 BACTERIAL KINETICS AND MODELLING

In order to use mathematical models to describe microbiological processes, it is necessary to establish relationships between the physically important variables which will best describe the phenomena.

Microbiological processes for the most part are described by making use of the relationships between biomass production, substrate utilization and product yield kinetics.

The knowledge of these relationships is then used to set the process operating conditions in which maximum yield of the product of interest would be obtained.

Most of the models used for biological systems have been derived for homogeneous systems in which all the reacting materials are found within a liquid phase.

In the case of heterogeneous systems, where the reacting materials are found in more than one phase, kinetic analyses have been made to quantify reaction rates in microbial films (Atkinson, B. and Fowler, H.W. 1974), liquid hydrocarbon fermentations (Moo-Young, M. 1975) and for immobilized enzymes

(Bailey, J.E. and Ollis, O.F., 1977). These analyses are based on mathematical models previously developed for non-biological reactions.

5.2 MODELLING BIOLOGICAL LEACHING

Earlier kinetic studies of biological leaching processes were conducted to investigate the relationships between either product formation and cell growth (Landesman, 1966a, 1966b; McGoran, 1969) or substrate utilization and product yield (Torma, 1973; Bruynesteyn, 1974). The results of these investigations provided a limited understanding of the interactions between the bacteria, the mineral and the liquid phase in a biological leaching process. The importance of those aspects relating to the role of bacteria on the leaching process has been underestimated for the most part.

It has been proposed (Bailey and Ollis, 1977) that for bacteria growing at interfaces, two different growth rates would be present depending on the ratio between cell size and substrate size.

One growth rate would be evident for the case when the cell diameter was less than the substrate diameter, and another growth rate when the substrate size was less than the cell size and the substrate would be absorbed onto the cell surface.

Based on surface area the kinetic analysis would show two different growth stages. The first after introduction of the inoculum when the bacteria would grow at its maximum growth rate; and the second stage in which growth would occur at expense of substrate present at the interface between phases, when the surfaces were totally covered by bacteria. These two stages combined produce a growth curve which is linear after the surface is saturated. Gormely (1973) found that when the substrate surface was completely covered by bacteria, the leaching rate of zinc from a zinc sulphide concentrate was a function of the substrate area. He tried to model this using the Shrinking Core Model of Levenspiel (1972) for the case when chemical reaction controls.

Based on a constant leaching rate per unit surface area, he calculated the leaching rates of particles of different sizes. Estimates of product formation using these values gave percentage extractions of zinc which were low by a factor of ten compared with the experimental values. He also found that the rate of leaching reached a maximum soon after initiation of the metal release, then the leach curve became linear until close to the completion of the leach, but he did not provide an explanation for this phenomena.

Sanmugasunderam (1981) also conducted studies on zinc sulphide leaching. He determined experimentally the leaching rates for different particle sizes and used them to predict extraction of

zinc using the Shrinking Core Model. His predictions of percentage extraction of zinc were equal or less than the experimental values with a maximum difference of 25 percent. The difference was attributed to the methods used to estimate the surface area of the particles and its sizes.

5.3 THE SHRINKING CORE MODEL

For non-catalytic reactions of particles with surrounding fluid there are two simple idealized models according to Levenspiel (1972):

1) The progressive conversion model in which the solid reactant is converted continuously and progressively through the particle.

2) The unreacted-core model in which the reaction zone moves into the particle and the unreacted core shrinks in size with time.

Given that the bacterial activity on solid substrates is limited to the surface since the bacteria cannot penetrate the interior of the particle until the outer layer is dissolved, the unreacted core model suggests itself for application to the modelling of biological leaching systems.

There are several conversion-time expressions for particles of different size and shapes, and for reactions in which the rate controlling step is either diffusion controlled or chemical reaction controlled.

For the case of spherical particles when chemical reaction controls, the intrinsic reaction kinetic data (or the time needed for complete reaction of a particle) can be obtained for monosized particles. At any time the extent of conversion of the substrate can be calculated from the particle size distribution data and the overall fraction reacted for any given size. The shrinking core model was used successfully for modelling the chemical leaching of chalcopyrite (Sepulveda, 1978) where the mechanism was suggested to be an electrochemical reaction in which the conduction of electrons through the sulphur layer was the rate limiting step.

Levenspiel's shrinking core model predicts that with mixed flow of single size solids, the fraction of the solid that is converted to product in a certain time is given by:

$$Z = 1 - \int_{o}^{T} (1-Xa)\, \frac{e^{-t/\bar{t}}}{\bar{t}}\, dt \qquad Xa \leq 1 \qquad (1)$$

where: Z is the average fractional conversion of the solid, T the time required for complete conversion of a single particle, Xa the fractional conversion for particles in time t + dt, t the mean residence time of particles in the reactor and t time.

If chemical reaction is the rate controlling step, then:

$$\frac{t}{\bar{T}} = (1-Xa)^{1/3} \qquad (2)$$

Substituting and integrating we get:

$$Z = 3\left(\frac{\bar{t}}{\bar{T}}\right) - 6\left(\frac{\bar{t}}{\bar{T}}\right)^2 + 6\left(\frac{\bar{t}}{\bar{T}}\right)^3 \left[1 - \exp\left(-T/\bar{t}\right)\right] \qquad (3)$$

where T for microbiological leaching is given by:

$$T = \frac{pdo}{2\bar{r}_{z/s}} \qquad (4)$$

where: p is the density of the concentrate, do is the diameter of the feed solid particles, and $r_{z/s}$ is the metal extraction per unit solid surface area.

Thus, if the metal extraction rate for particles in each step is known and the particle size distribution of the concentrate is also known, Equation 3 can be used to calculate the overall extraction at any given time.

CHAPTER VI MATERIALS AND METHODS

6.1 BIOLOGICAL LEACHING TECHNIQUES

The bacteria used for the experiments was a strain of Thiobacillus ferrooxidans originally isolated from the Britannia Mine near Vancouver (Razzell and Trussell, 1963), and routinely maintained on copper concentrate at B.C. Research.

The liquid medium used was the medium 9K described by Silverman (1959) in which the copper concentrate replaced $FeSO_4$ as the energy source. The medium had the following composition (Table 1).

Table 1

Culture Media Composition

Component	Concentration (g/L)
$(NH_4)_2SO_4$	3.0
KCl	0.1
K_2HPO_4	0.5
$MgSO_4 \cdot 7H_2O$	0.5
$Ca(NO_3)_2$	0.01

The chalcopyrite concentrate used in this study was a commercial flotation concentrate supplied by Newmont Mines Limited, Similkameen Division, Princeton, B.C.

All leaching experiments were carried out on concentrate from a 2 kg grab sample drawn from a barrel containing approximately 120 kg of thoroughly mixed concentrate which had previously been ballmilled at 55 percent solids for 1 h to 91.8 percent -400 Tyler mesh, filtered and dried at 60°C. The analysis of the concentrate is tabulated in Table 2.

Table 2

Elemental Analysis of the Copper Concentrate
(B.C. Research Data)

Element	Percentage by Weight
Copper	27.8
Iron	28.0
Sulphur	31.1
Insol.	5.5

This study was carried out using the shake flask leach technique where 7.5 g of concentrate were placed in bottom-baffled, 250 mL, Erlenmeyer flasks; 70 mL of iron-free 9K medium solution were added and the pH of the suspension was adjusted to 2.0. The flasks were loosely stoppered with a cotton plug, and incubated on a gyratory shaker (Model 591-70, New Brunswick Scientific, N.J.).

The shaker was located in a dark room with a carbon dioxide enriched atmosphere provided by bubbling carbon dioxide through water in a container open to the atmosphere (dry carbon dioxide, Canadian Liquid Air Ltd.).

The temperature of the room was controlled at 35°C by means of a temperature controller (Honeywell type RP 908). Before inoculation the flasks were incubated for 24 h to allow for acid consumption caused by alkaline gangue present in the concentrate; after this period the pH was adjusted back to 2.0 using sulphuric acid and the flasks were stored in a refrigerator at 4°C until they were used.

6.1.1 Sampling Techniques

Different sampling techniques were used depending on the type of analysis to be carried out. The soluble metal content was determined in 1 mL of supernatant drawn from the flask after 10-15 min settling time. For the analysis of cells and particle size, a sample of slurry was used; the sample was obtained using a pipette to draw the required amount of slurry from the flask, after its contents were thoroughly mixed by shaking.

6.2 Analyses

6.2.1 Metal Leach Rates

The copper and iron contents of the medium were determined by atomic absorption spectrophotometry (Atomic Absorption Spectrophotometer, Perkin Elmer 306).

1 mL samples, after the necessary dilutions, were analysed following the standard practices recommended in Perkin-Elmer's manual (1973).

The copper extraction rate was calculated as the slope of the linear portion of the copper concentration vs. time curve using a least squares curve fitting method.

6.2.2 Hydrogen Ion Activity

Measurements of hydrogen ion activity (pH) were made by introducing a pH electrode into the slurry. This was connected to a pH meter (Fisher Accumet model 610A).

6.2.3 Oxidation-Reduction Potential

Measurements of the Eh potential were made directly in the flask using a platinum electrode connected to a pH meter (model 28 Radiometer, Copenhagen).

6.2.4 Bacterial Growth

In order to obtain information on the role of Thiobacillus ferrooxidans in the leaching of metallic sulphides and of the relationship between bacterial growth and substrate utilization, a method of estimation of cell numbers or biomass is necessary. A literature search showed that measurements of leaching

kinetics related to bacterial growth have been neither consistent nor systematic. This arises from the fact that no single proven method of estimating bacterial numbers has been established.

When Thiobacillus ferrooxidans is cultured on solid substrates, it attaches to the solid surface (Gormely and Duncan, 1974). Because of this attachment the conventional methods of estimating cell numbers or cell mass (turbidity, dry weight, direct count) cannot be used.

Measurements of $^{14}CO_2$ fixation, oxygen utilization, ATP and DNA levels have been used as estimators of biomass, but require the use of complex instruments and techniques.

A simple and widely used method for estimating biomass is the measurement of organic nitrogen or protein content; this latter method usually involves a colorimetric determination and cannot be used when colored substances are present. Organic nitrogen is normally measured using the total Kjeldahl nitrogen analysis (AOAC, 1965), but Gormely and Duncan (1974) found that the ammoniojarosite precipitate, produced during the leaching of metallic sulphides, would be included as bacterial nitrogen. They suggested that a method based on the difference between the organic and inorganic nitrogen contents of the media would eliminate this problem.

Bacterial nitrogen is then calculated as the difference between Kjeldahl nitrogen (organic and inorganic nitrogen) and the distillable ammonium ion concentration (inorganic nitrogen). Samples of 1 mL of slurry were used to measure the Kjeldahl nitrogen (Micro-Kjeldahl technique (AOAC, 1965)) and the distillable ammonium ion concentration was measured by the acidimetric method using a preliminary distillation step (APHA, 1973). Using L-Alanine (15.69%N) a standard curve for the test was obtained. Samples containing 0.6, 0.8, 1.0, 1.2, 1.4, 1.6 and 1.8 mL of a solution of L-Alanine (1 mgN/mL) were analysed for nitrogen content. The standard curve is shown in Figure 3.

Twenty identical samples of slurry were used to measure the accuracy of the test. The probable errors were calculated to be 2.01% for the Kjeldahl test and 3.98% for the distillable ammonia test.

6.3 FRACTIONATION OF CONCENTRATE

Methods for separation by size of particles in the subsieve range are based on differences in the terminal settling velocities of the particles. Centrifugation, elutriation and sedimentation methods are all based on the principle of gravity sedimentation.

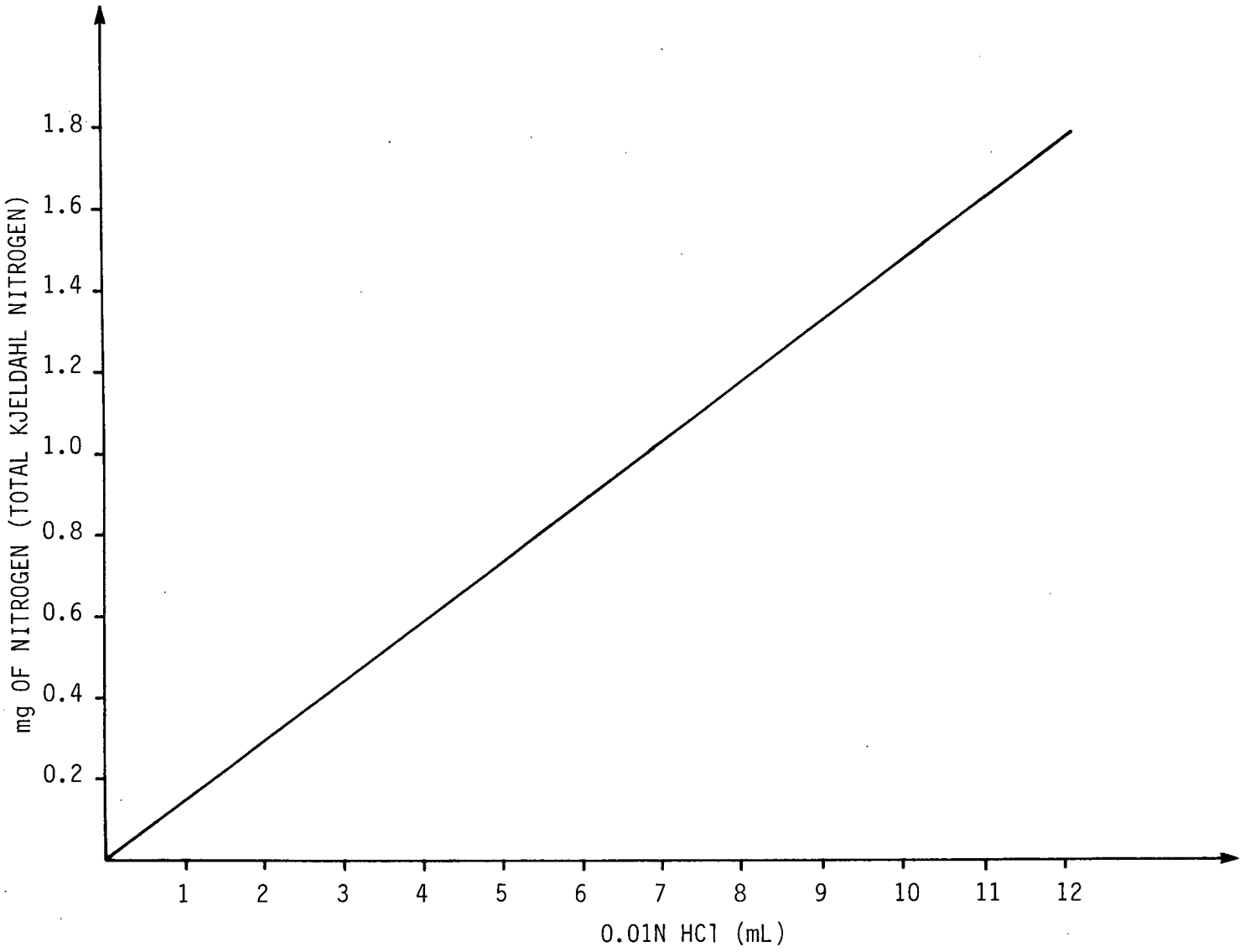


Fig. 3 Standard curve for nitrogen determination.

Elutriation grades particles by means of an upward current of fluid, usually water or air. The process is the reverse of gravity sedimentation (Allen, 1968). Centrifugal methods speed up the gravitational settling and are useful for sizes <5μm where the settling times are long. A number of apparatus for particle size separation has been designed based on these principles such as the Cyclosizer (hydraulic cyclone elutriator), and the Bahco microparticle classifier (air elutriator combined with a centrifuge). These apparatus are normally used for determination of particle size distribution in finely divided materials and are not suitable for the recovery of large amounts of material.

Beaker decantation (Pryor, 1965) is a simple sedimentation method which does not require any special equipment.

The parameter by which particles are classified is their falling speed which is not uniquely related to their size (Allen, 1968), but beaker decantation can be used to obtain the fractions and subsequently their size could be measured by some other means.

The beaker decantation method is based on the difference in the free terminal velocities of spherical particles of different sizes falling through a fluid at such rates that the Reynolds' number is less than 0.2.

Theoretical size ranges were initially arbitrarily defined and the free falling velocities (V) of the smallest defined particles in each fraction were calculated on the basis of the overall density of the concentrate according to Stokes' Law:

$$V = \frac{d^2 g\ (\sigma - P)}{18\eta}$$

where:

V = free falling velocity cm/sec

σ = density of the particle g/cm^3

P = density of the fluid g/cm^3

g = gravitational acceleration cm/sec^2

η = absolute viscosity g/cm·sec

d = Stokes diameter of the particle cm

Theoretical settling times for 6 fractions of diameters <40µm were then calculated for a liquid height of 13.5 cm employed in the beaker decantation method.

Using a mechanical stirrer 100 g of the concentrate were dispersed in a litre of water with the aid of a deflocculant. When the suspension was uniform the outside of the beaker was sharply tapped with a glass rod covered with rubber tubing, and the suspended particles allowed to settle for the calculated time, after which the supernatant pulp was poured quickly into a second beaker. The settled particles remained as a compact cake

which was again dispersed in water and the procedure repeated five more times to eliminate the material of smaller sizes that was entrapped during settling. The recovered material was then dried and weighed.

The calculated velocities and theoretical settling times for the different fractions obtained are shown in Table 3.

The particle size distribution for the ballmilled concentrate was obtained from the weight of the different fractions and is shown in Table 4. The weight percentage of fraction seven was calculated by difference since this, the finest fraction, forms a very stable suspension.

The beaker decantation method requires the use of a deflocculant in order to obtain a uniform suspension. A variety of dispersing agents are suggested in the literature: Aerosol O.T., sodium linoleate, sodium arsenite, sodium pyrophosphate, sodium silicate, potassium citrate, sodium oxalate (Skinner et al, 1965), aerosol N.Y. (Pryor, 1965) and sodium hexametaphosphate (Pinches, 1972).

The criteria used to select the deflocculant were as follows:

1) Solubility of the dispersant in water.
2) Amount of fines obtained during the fractionation (the amount of fines indicates the effectiveness of the dispersant).

Table 3

Fractions of Ballmilled Concentrate: Theoretical Size Ranges, Free Falling Velocities and Settling Times

Fraction No.	Stokes Diameter for Assumed Particle Density (4.3 g/cm^3) (μm)	Calculated Velocity (cm/sec)	Theoretical Settling Time (sec) For Liquid Height=13.5 cm
1	>40	0.992	13.60
2	>32 <40	0.635	21.26
3	>24 <32	0.357	37.81
4	>16 <24	0.159	84.90
5	>8 <16	0.0396	340.90
6	>4 <8	0.009	1500
7	<4	-	-

Table 4

Fractions of Ballmilled Concentrate: Weight Percentages Collected

Fraction No.	Weight Percentage
1	11.55
2	2.33
3	3.86
4	11.95
5	32.62
6	18.33
7	19.36

3) Possible effects of residual dispersant on the growth of the leaching bacteria.

Based on these criteria, sodium arsenite was ruled out for possible toxicity. Trivalent arsenic (arsenites) are reported to be toxic for bacteria (Porter, 1946).

Razzell's (1963) and Landesman's (1966) studies have shown that carboxylic acids and fatty acids are inhibitors of iron oxidation by Thiobacillus ferrooxidans; based on these studies sodium linoleate, potassium citrate and sodium oxalate were also ruled out. The use of sodium silicate was not considered due to the difficulty of its removal by simple washing after the fractionation.

6.3.1 Deflocculant Selection Tests

The first dispersing agent used was aerosol G.P.G. (sodium dioctyl sulfosuccinate in ethanol and water. Cyanamid Canada Inc.).

A 0.1% solution of this dispersant was prepared and added to a leach test to detect any effects on the ability of the bacteria to extract copper from chalcopyrite. The result of this test is shown in Figure 4 compared with a similar test in which no dispersant was added.

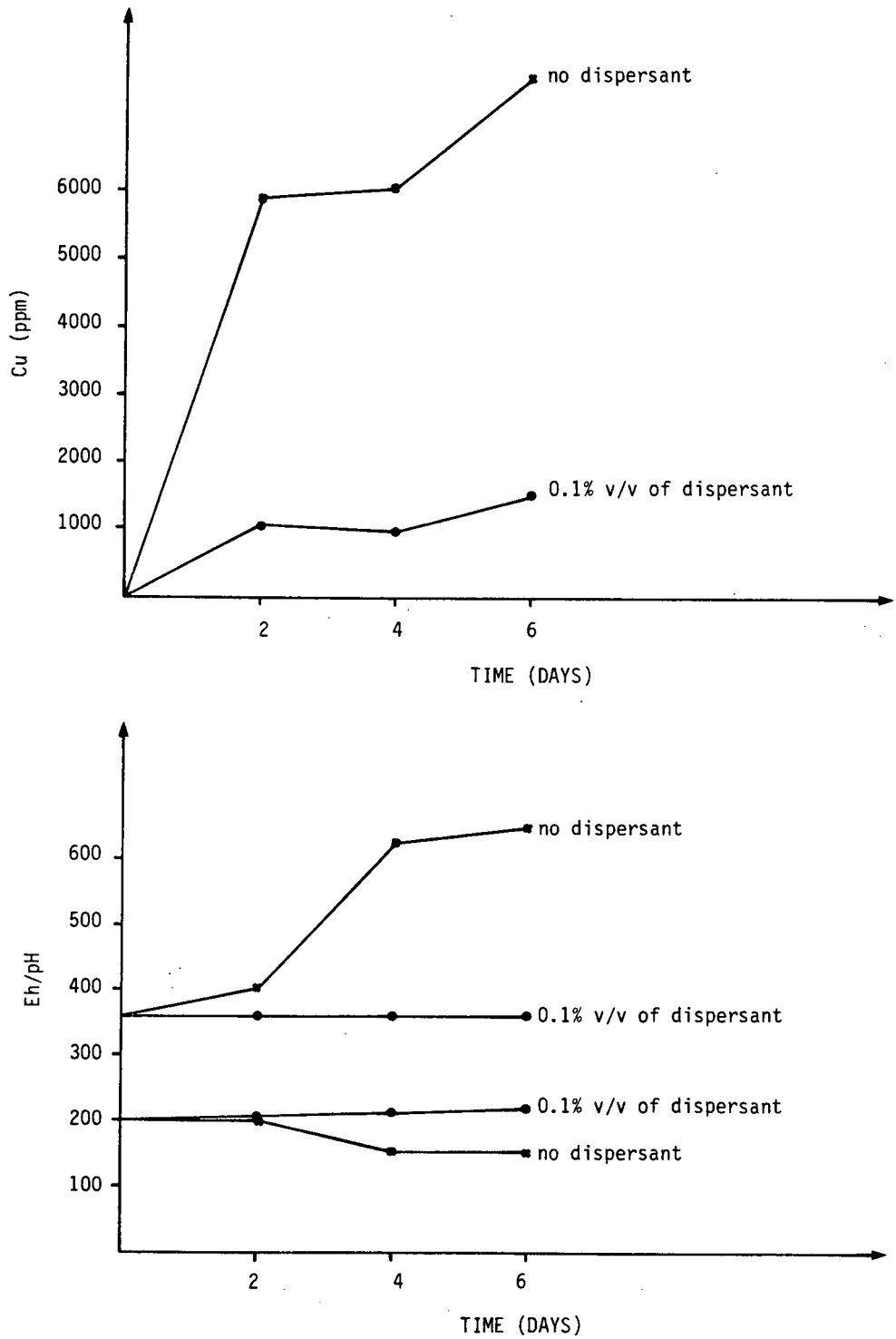


Fig. 4 Effect of aerosol in the growth of T. ferrooxidans

The results indicate that the copper extraction over a six day period was only 20% of the extraction in the blank; this difference was attributed to the presence of the dispersant aerosol G.P.G.

Considering that the aerosol's chemical structure has two large hydrocarbon chains with hydrophobic properties, the molecule then has an affinity for organic solvents. Acetone, chloroform and isopropanol were used to remove the residues of the aerosol from the fractionated concentrate. 10 g of concentrate were placed in a separatory funnel and 50 mL of the solvent added. The funnel was vigorously shaken for 10 minutes, and the phases allowed to separate; then a small portion of concentrate was withdrawn and tested for MBAS (Methylene Blue Active Substances) (APHA, 1973). The MBAS test indicated that the following amounts of dispersant had been extracted by the various solvents used: acetone-96%, chloroform-95% and isopropanol-98%. Isopropanol was the most effective.

Concentrate treated with isopropanol was then washed with distilled water and dried at 50°C for 24 h, then the biological leach test was repeated. This time the copper extraction was 33% of that of the blank, showing that the aerosol maintained its inhibitory effect even at very low concentrations.

At this point two other dispersing agents were considered; sodium hexametaphosphate and Tween 40 (polyoxyethylene (20) sorbitan monopalmitate) both from J.T. Baker Chemical Co., N.J. Biological leaching inhibition tests using 0.1% v/v media of dispersant showed no effects on the copper extraction rate by Tween 40; hence this dispersing agent was used in the fractionation procedures. Subsequent tests with fractions of concentrate obtained by fractionation showed an unexpected retardation in the copper extraction rate, suggesting that binding of the dispersing agent to the surface of the mineral during fractionation had taken place and affected its leaching properties. This apparently did not occur during the earlier inhibition test.

A more drastic treatment to remove residual Tween 40 was then implemented based on the OECD method (1976). This method is used for the extraction of surfactants from detergents, and involves a binary extraction with isopropanol in the presence of K_2CO_3. Using this method, 99% extractions of the dispersant were obtained. To remove K_2CO_3, a series of washing steps followed by centrifugation were used until the liquid medium showed no signs of carbonates; no inhibition occurred when the material obtained by this procedure was subjected to leaching.

6.4 PARTICLE SIZE MEASUREMENT

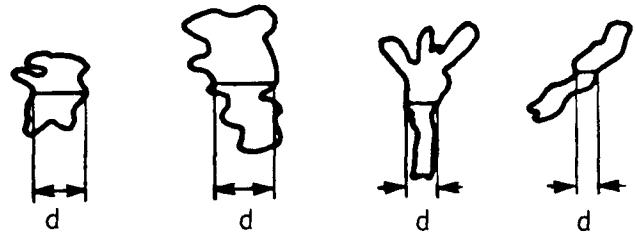
The measurement of particle size in the subsieve range has been analyzed extensively in the literature (Schweyer and Work, 1941; Loveland, 1958; Chamot and Mason, 1938; Allen, 1968). The most widely used methods are based on measurements of physical properties of the material previously correlated with the size, such as: light scattering, absorption of light, filtration by media of known pore size, sedimentation, centrifuging, etc. The size that is measured will then depend on the method employed.

The use of the microscope is the only method in which the individual particles are measured and it is often used as a standard for comparison with other methods. Direct observation and measurement can be made down to less than one micron (Pryor, 1965).

The measured particle size depends on the particle shape. The diameter of an equidimensional particle (sphere or cube) has a single value but for irregular particles the size may be expressed by any one of several dimensions (Pryor, 1965) such as the length of the circumscribing rectangle, when the particle is in its most stable position; by the diameter of a sphere having the same terminal velocity; by the diameter of a sphere having the same volume; and so forth.

Martin's diameter is the simplest expression of the diameter of irregular particles and is sufficiently accurate when averaged for a large number of measurements. It is the horizontal dimension bisecting the projected area of the particle as shown in Figure 5 (Welcher, 1963). Experimental comparison of various proposed diameters are reported (Chamot and Mason, (1938) to have shown satisfactory agreement between Martin's diameter and the three actual dimensions of the individual particles (length, breadth and thickness).

Fig. 5
MARTIN'S DIAMETER



In this study, a microscope eyepiece micrometer calibrated for the objective in use against a stage micrometer (Ann Arbor, U.S.A.), was used to measure Martin's diameter in a Leitz-Wetzlar microscope (HM-Lux, Germany).

6.4.1 Preparation of Concentrate for Size Measurement

A small sample of concentrate was placed on a microscope slide and a few drops of water were added. The powder was worked into the fluid using a small glass rod and a cover slip was put

carefully in place so as to exclude air bubbles. Two slides were prepared for each sample and observed under the microscope.

The number of particles counted was 100 considering the standard practice of a model class containing at least 25 particles. For the narrow range of sizes examined the count will give a standard error 10 in the mean size (Allen, 1968; ASTM, 1974).

The average particle diameter was then calculated by the Sauter mean (mean diameter based on surface) using the following expression (Coulson and Richardson, 1976).

$$ds = \frac{\Sigma \; d_1 S_1}{\Sigma \; S_1} = \frac{\Sigma \; n_1 d_1^3}{\Sigma \; n_1 d_1^2}$$

where:

n = number of particles

d = measured Martin's diameter

S = total surface of unit mass material

The computed particles sizes for the different fractions of concentrate are shown in Table 5.

Table 5

Average Particle Size in Fractionated Concentrate

Size Class Limits Based on Stokes diameter		Particle Size μm
>32	<40	7.41
>24	<32	5.48
>16	<24	3.56
>8	<16	2.52
>4	<8	1.78
<4		1.07

The values of particle sizes were also used to calculate the specific surface area of the particles with the following expression assuming spherical particles:

$$ssa = \frac{6}{dsp}$$

6.4.2 Scanning Electron Microscope Techniques

For pre-leaching observations samples of chalcopyrite were obtained from several fractions of the dry-concentrate. Samples for post-leaching observations were obtained as follows: At the end of the leach the contents of the flasks were filtered through Whatman filter paper #1 and dried in air in a covered container for 48 h at 35°C. The specimens to be examined in the scanning electron microscope were drawn from the surface of the filter using a metallic spatula.

All specimens were then mounted on aluminium stubs (14 mm x 14 mm) over a thin layer of graphite in ethanol (20% graphite (Dag 154) Acheson Colloids Canada Limited) and coated with gold using a Hummer gold spotter coater for 4 minutes at 170 millitorr vacuum and 9 milliampers D.C.

The mounted specimens were examined in a scanning electron microscope (Autoscan number 26, Etec Corporation) operated at 20 kV in the secondary electron emission mode.

CHAPTER VII EXPERIMENTAL RESULTS AND DISCUSSION

7.1 SELECTION OF THE INOCULUM AGE

When fresh medium in a closed system is inoculated with cells a number of changes take place. After a lag phase where no increase in cell numbers occurs, the culture enters a phase of exponential growth until some nutrient is exhausted or some by-products reach toxic levels. At this point the rates of death and growth are in equilibrium and the culture is in the stationary phase. What follows is a decline phase when the death rate exceeds the growth rate.

The length of the lag phase is related to the age and size of the inoculum. What is meant by age is the time between the start of growth of the parent culture and the transfer of the inoculum to the subculture (Dean and Hinshelwood, 1966). Bailey and Ollis (1977) found that when young cells are transferred, short lag phases are obtained and when older populations are transferred long lag phases result, because older populations have a slower growth rate due to nutrient depletion in the media and/or the accumulation of toxic products.

It is clear then, that the introduction of an active culture growing in the exponential phase will reduce the lag phase. For this study the selection of the inoculum age was based on the

results of a series of batch leaches carried out using inocula of various ages between 1-10 days. The copper concentration was monitored during the leaches and the results used as a measure of inoculum performance. The results are shown in Figure 6a, b.

Figure 6a shows the time elapsed between inoculation and the maximum copper concentration found in solution for the different inoculum ages. The gradual decrease in the number of days needed to reach the maximum copper concentration indicated a shortening of the lag phase (assuming a direct relationship between copper extraction and cell growth), and hence a minimum of 6 days between transfers would ensure short lag times. Figure 6b shows the copper extraction rate as a function of the inoculum age. The curve shows that the highest rates were obtained for between 6 and 8 day old inocula. Based on these results a serial subculture was started, and routinely performed throughout the experimental study, making transfers every 8 days to provide inocula for all the experiments.

7.2 BACTERIAL GROWTH KINETICS

7.2.1 Bacterial Growth

In this section the relationship between bacterial growth and copper extraction is explored. It is shown that bacterial growth was limited to the early stages of leaching.

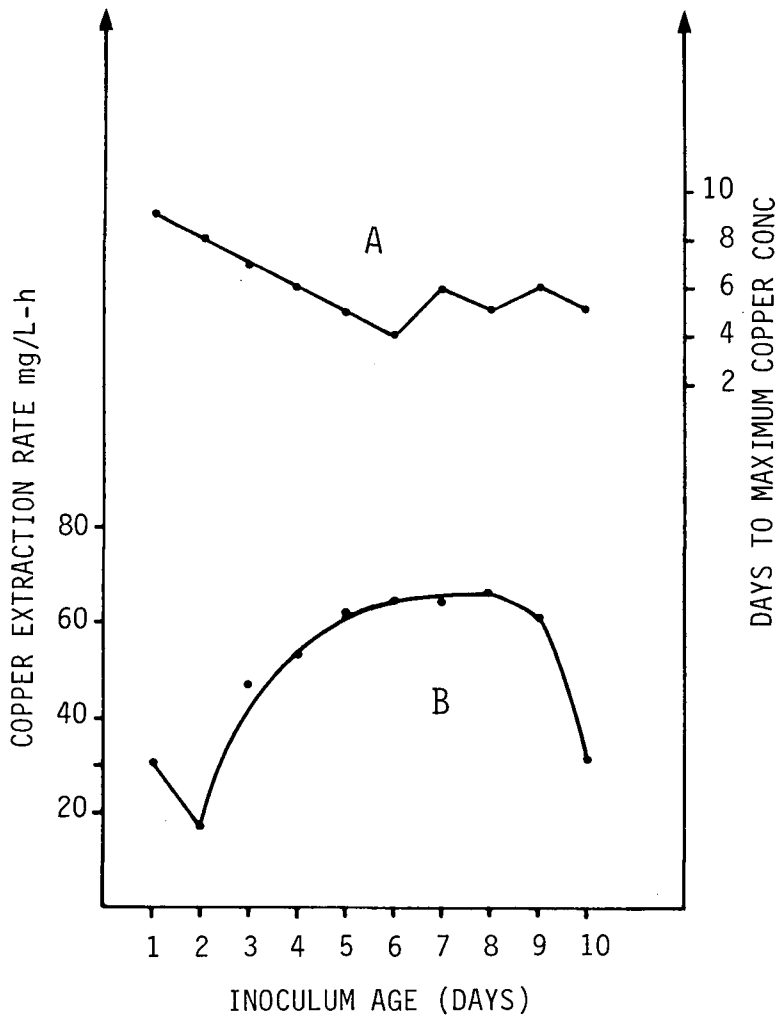


Fig. 6 Effect of the inoculum age on copper extraction

An estimate of the mineral surface area calculated from the mean diameter of the particles and their size distribution in the concentrate was used to calculate the fraction of the total surface area available for bacterial coverage.

In order to calculate the number of bacteria present at any given time during the leach, the non-distillable nitrogen (n.d.n.) concentration was measured during fermentation in duplicate experiments.

The n.d.n. measurements were correlated to bacterial numbers using the values derived by Gormely and Duncan (1974). These workers calculated that 10^{10} cells are equivalent to 0.191 mg cell nitrogen. This gives a lower estimate of bacterial numbers compared to those calculated using Beck's yield (Touvinen, 1972) who reported a nitrogen content of only 0.033 mgN/10^{10} cells.

A typical growth curve for Thiobacillus ferrooxidans growing on chalcopyrite is shown in Figure 7 with the data tabulated in Table I (Appendix I). The curve shows a lag phase of 20 h followed by an exponential increase in cell numbers for 30 h and a stationary phase up to 200 h.

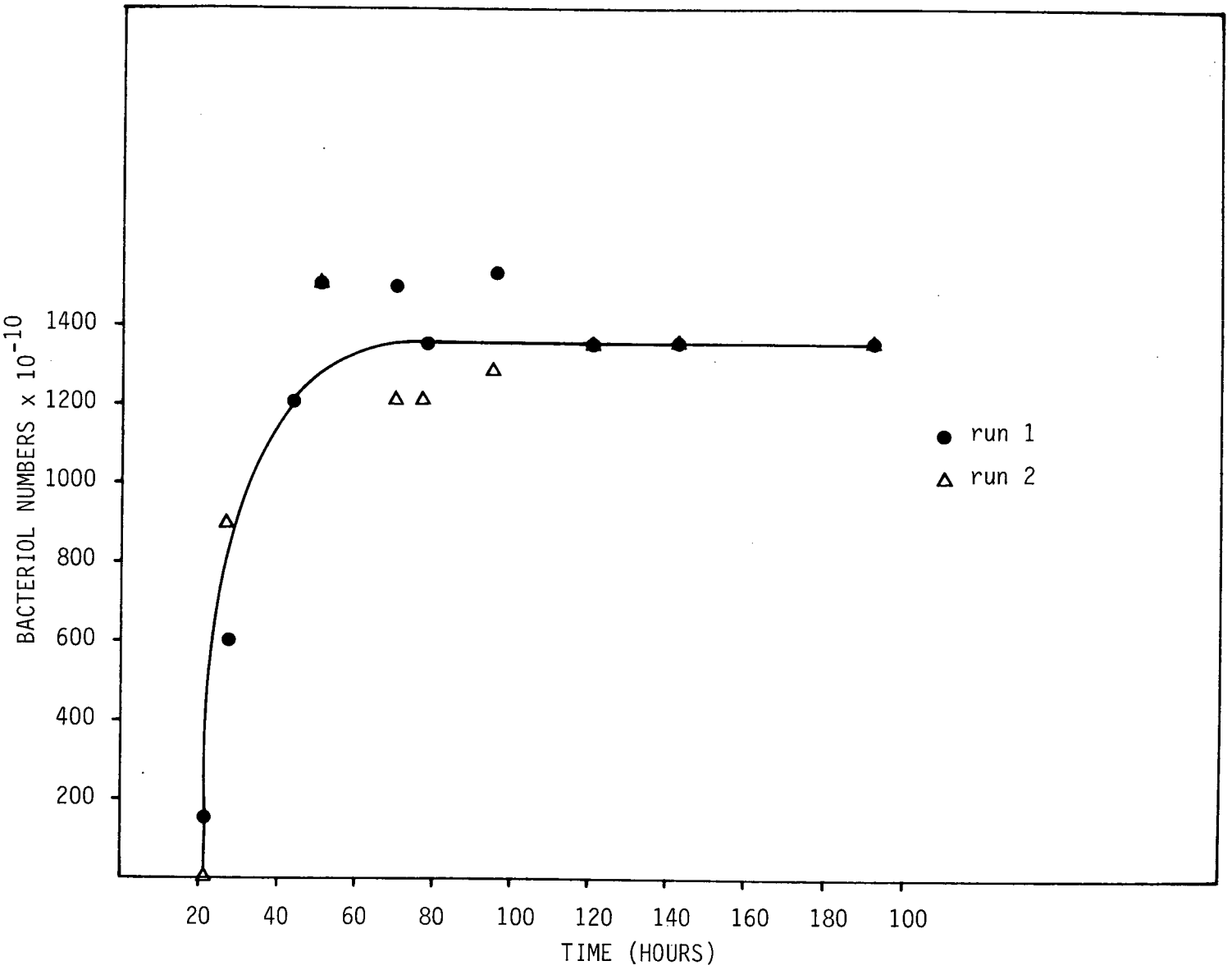


Fig. 7 Bacterial Growth of T. ferrooxidans in copper concentrate. Bacterial numbers vs time.

7.2.2 Copper Extraction

A series of experiments were conducted to investigate the relationship between bacterial growth and copper extraction. Cell numbers, copper concentration, iron concentration, Eh, and pH were carefully monitored in biological leaches. Figure 8 shows the average values determined in three of such experiments. The data are presented in Table II (Appendix I).

Analysis of Figure 8 shows that the exponential growth was again limited to the early stages of the leach.

During this period a close correlation between growth and copper and iron extractions was found. McGoran (1969) conducted similar experiments and found that the logarithmic rates of copper release and cell multiplication were identical, but he further stated that copper extraction could be used as an indicator of growth rate. Figure 8 indicates that the bulk of the copper extraction occurs during the late lag phase and stationary phase. This difference in the growth patterns of Thiobacillus ferrooxidans arises from the fact that McGoran estimated his bacterial concentrations using a Kjeldahl analysis which probably included the nitrogen content of jarosite precipitate formed during the leach.

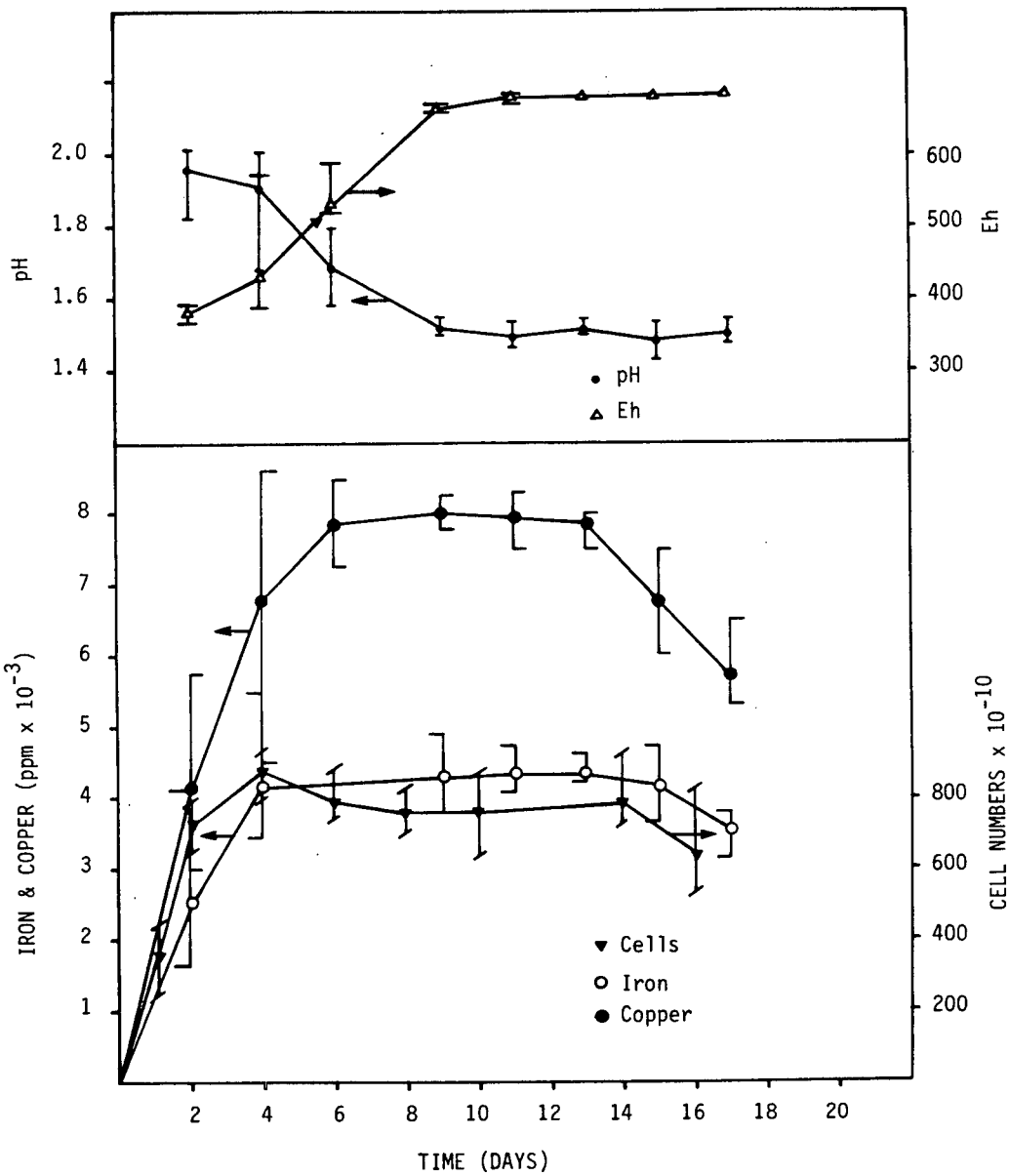


Fig. 8 Bioleaching data average for three experiments
Soluble copper and iron concentrations
Cell numbers, pH, Eh

During the leach the pH gradually decreased, indicating bacterial activity. Acid production stops (minimum pH is reached) at the same time that the maximum copper concentration is reached.

The Eh increase is also an indicator of bacterial activity. It is caused by the oxidation of ferrous iron. This rise in potential has been previously related to logarithmic growth (Touvinen, 1972).

The transition from the logarithmic growth phase to the stationary phase shown in Figures 7 and 8 could be caused by a number of environmental factors. Nutrient exhaustion and accumulation of by-products are known to cause the change from logarithmic growth to stationary phase in microbial cultures.

For the bioleaching of chalcopyrite, the by-products are sulphuric acid and jarosites. The pH values indicate that the production of sulphuric acid had lowered the pH but it was still within the normal range of growth of Thiobacillus ferrooxidans.

Jarosite precipitation becomes significant above Eh values of 500 mv (Torma, 1977), where most of the iron present is in the ferric form from which hydroxides and jarosites are formed. This change of growth phase from logarithmic to stationary occurred when the Eh values were below 500 mV and so cannot be attributed to this phenomena.

It is assumed then, that nutrient limitations caused the change of growth phase, in this case the availability of an energy source which for the bioleaching of chalcopyrite is provided by the concentrate surface.

Above 500 mV of Eh the precipitation of jarosites becomes significant and may explain the decrease in the copper extraction rate between days 4-6 and ultimately the termination of copper extraction. This may be because the ammonium and potassium ions are stripped out of solution when the jarosites are formed. The jarosite that precipitates over the mineral surface (see photographs of leached particles, section 7.5), will cause mass transfer limitations of carbon dioxide, oxygen and nutrients from the bulk of the solution to the bacteria attached to the surface.

An estimate of the magnitude of precipitates of basic ferric sulphates and jarosite can be obtained when the iron and copper concentrations in solution are compared.

The chemical composition of the chalcopyrite $CuFeS_2$ indicates that equal amounts of copper and iron are produced when the mineral dissolves. Figure 9 shows the copper/iron ratio (average values for 3 leaches) and indicates that hydrolysis and precipitation reactions are taking place because the ratio is always >1.

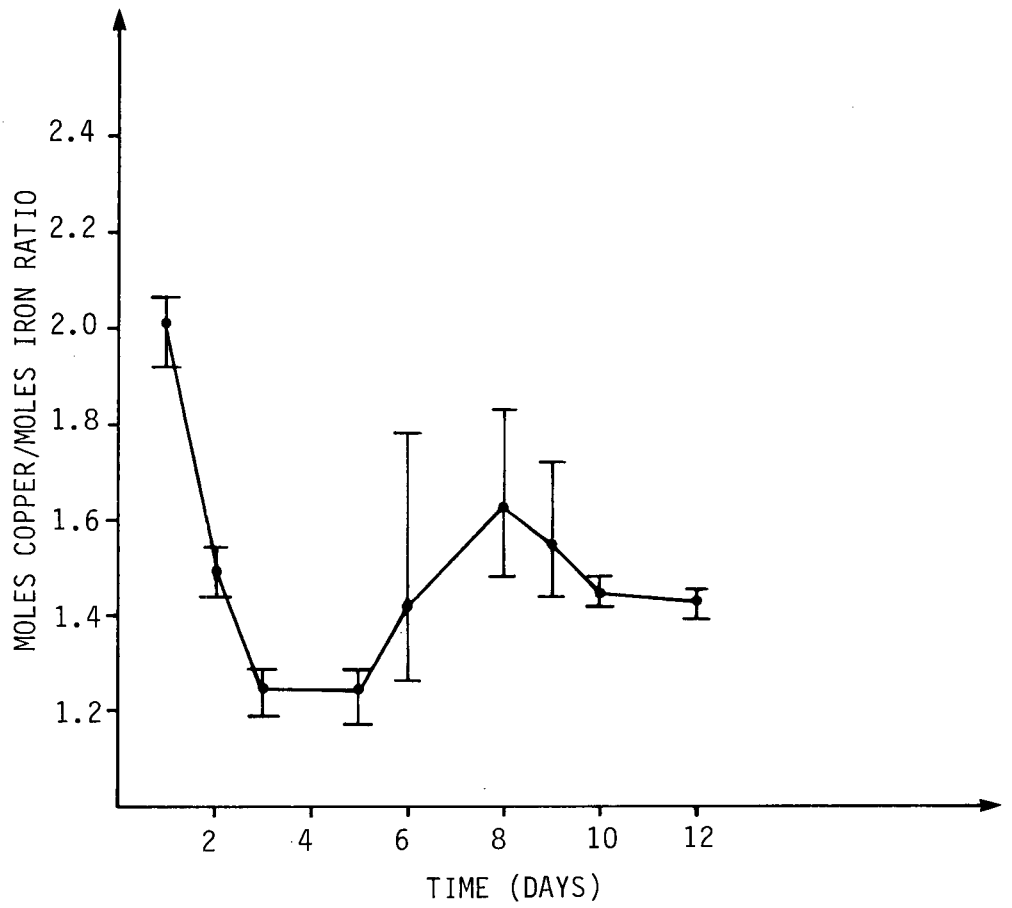


Fig. 9 Average Values of Copper/Iron Ratios for 3 Leaches

7.2.3 Surface Area Utilization

The total surface area for the 7.5 g of concentrate used in each of the biological leaches was calculated from the mean diameters of the particles and the size distribution of the concentrate, and has a value of 4.96 m^2 (Table III, Appendix I). The average dimensions of one bacterium (length 1.0 μm and breadth 0.6 μm) can be used to calculate the surface area covered by a single bacterium, assuming an elliptical form for its projected area. Thus, the surface area covered by a single bacterium would be approximately 0.5 μm^2. The number of bacteria times the surface area used by one bacteria would then give an estimate of the surface covered by bacteria at any given time. It is assumed that all bacteria are found associated with the mineral and none can be found in the liquid phase. Pinches (1972) has shown this to be true up to the end of the exponential phase.

Figure 10 shows the percentage of the total surface covered by bacteria against time for the average values of cell numbers obtained in three leaches. The data are presented in Table IV (Appendix I).

The curve in Figure 10 shows a maximum coverage after 4 days when 88% of the surface is covered by bacteria. The chemical

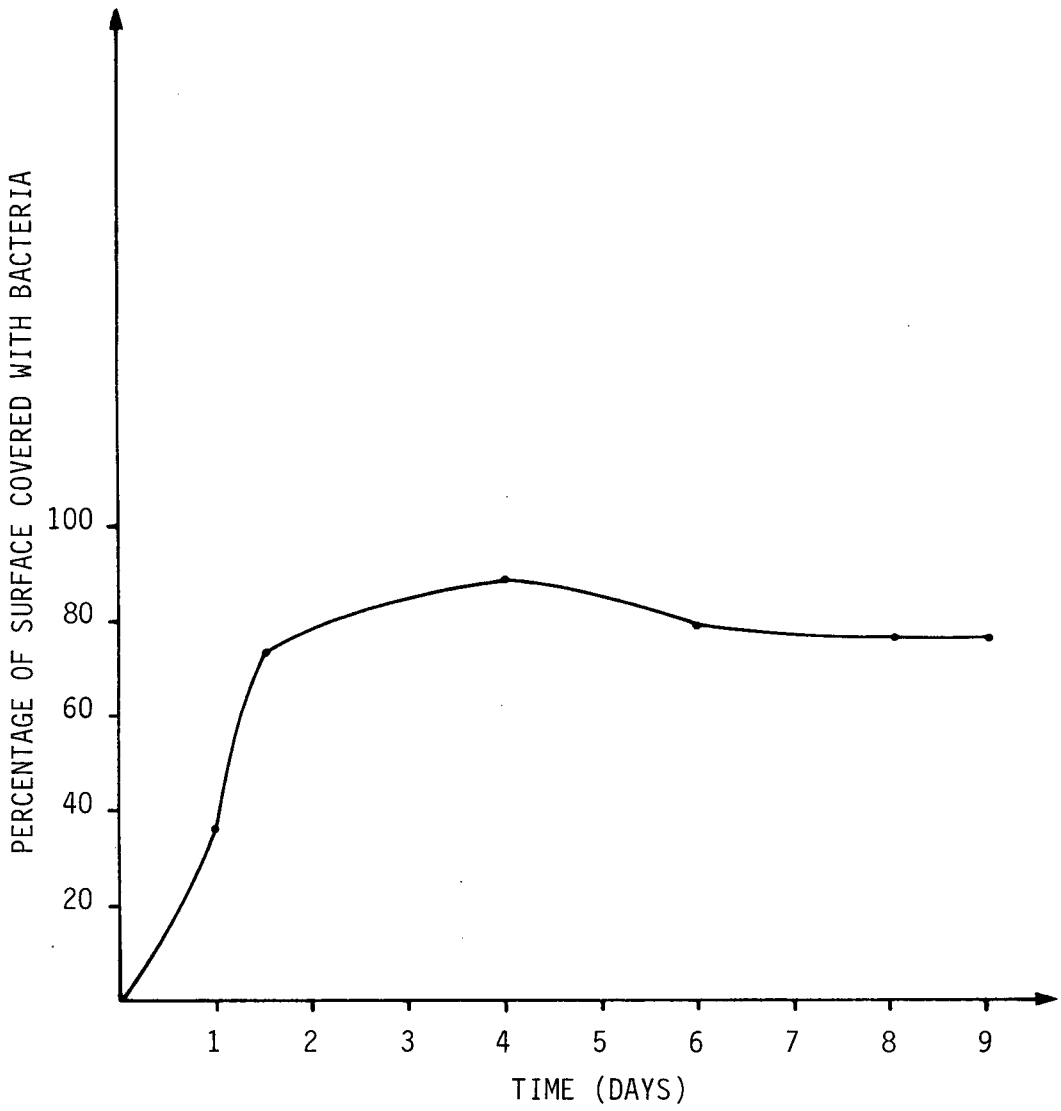


Fig. 10 Bacterial coverage of the mineral surface

analysis data of this concentrate showed that 86.9% of the material is sulphide, which suggests that the bacteria attach selectively to the sulphide phase over gangue materials present in the concentrate.

Berry (1978) showed that the attachment of Thiobacillus ferrooxidans to low-grade waste-rock surfaces was specific to exposed FeS_2 and $CuFeS_2$ regions. Myerson and Kline (1983), arrived at the same conclusion after calculating a surface utilization value of 122 μm^2/cell for coal with a sulphide content of 1.66% when they compared this value with the sulphide utilization value per bacterium (0.5 μm^2).

Our experiments then indicate that most of the available surface is covered by bacteria 4 days after inoculation and further supports the hypothesis of a change in growth phase due to surface area limitations.

7.2.4 Leaching in the Absence of Bacteria

To evaluate the contribution of chemical leaching to the copper extraction obtained in the biological leaching experiments, a sterile leach was set up.

No bacteria were introduced and sterile conditions were provided by adding phenol which is a known germicide. Porter (1946) reported that a ratio of 1:70 v/v phenol:media was effective in 10 minutes for Staphylococcus aureus, the most resistant of the four species he examined. This same ratio was used in the sterile control; microscopic examination failed to detect any microorganism in the media containing phenol. The results for the analysis of samples for the sterile run are tabulated in Table V in Appendix I and shown in Figure 11.

During the sterile run the Eh values remained constant, an indication of the low levels of oxidation of ferrous iron. Duncan (1972) indicated that there is seldom any ferrous iron present when the bacteria are alive.

The hydrolysis of ferric iron which generates acid was therefore almost nil and no acid was formed. The pH curve indicates consumption of acid, probably due to alkaline gangue and to chemical extraction of copper and iron. Given the low values of copper extraction (2.95%) obtained during the sterile experiment, no account for chemical leaching was introduced in the calculations of copper extraction in the biological leaching experiments.

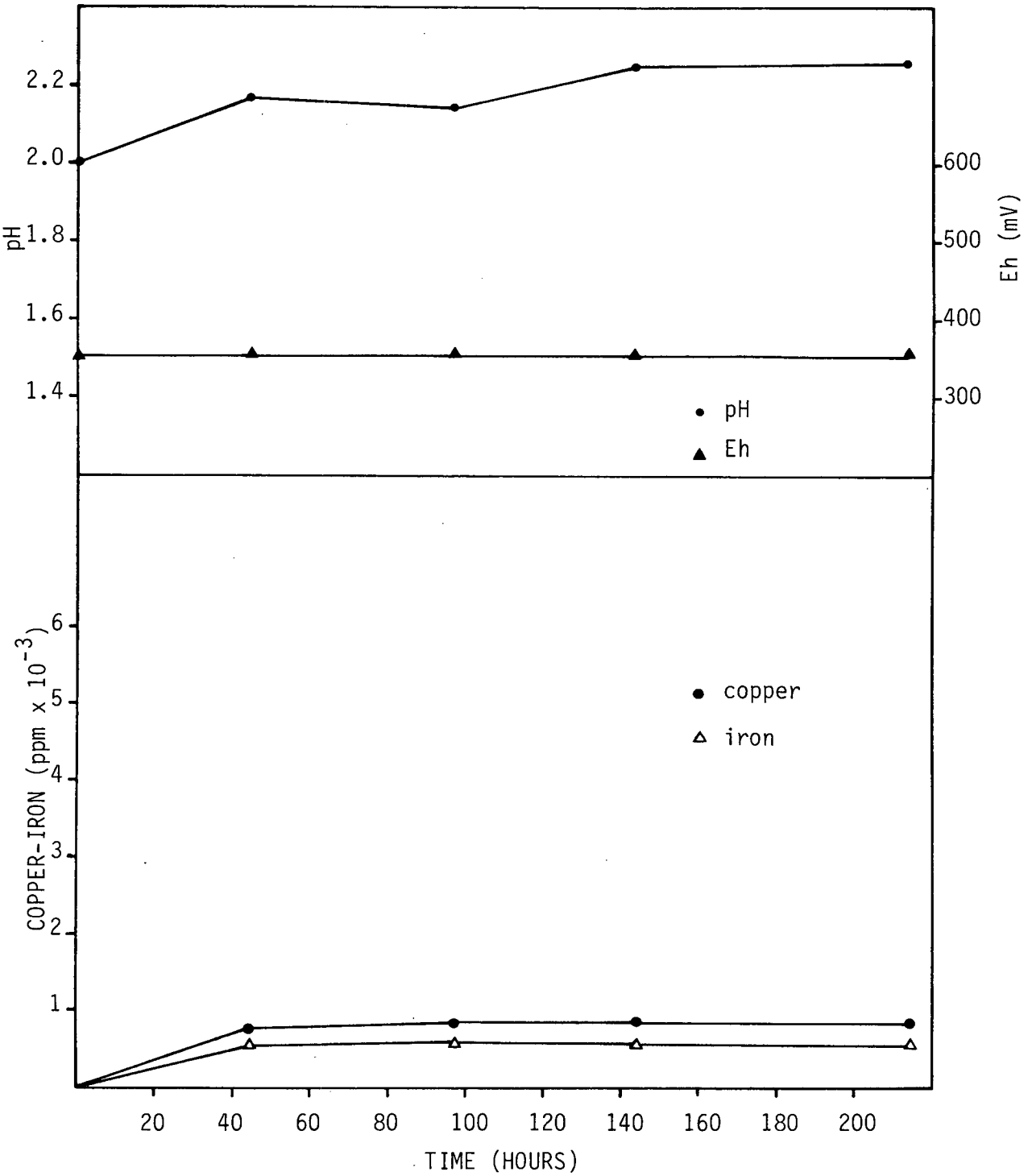


Fig. 11 Chemical Leaching of Chalcopyrite

7.3 EFFECTS OF PARTICLE SIZE ON THE LEACHING OF COPPER

A series of experiments using monosized fractions of copper concentrate was conducted. Results of these experiments are tabulated in Tables VI-XI (Appendix I), and the equations for copper concentration as a function of time, fitted by the method of least squares are given. Figure 12 presents the results for the leaching of copper using chalcopyrite concentrates having the following mean particle sizes: 1.07, 1.78, 2.52, 3.56, 5.48 and 7.41 μm.

Experiments using the 3.56 μm fraction were conducted in triplicate to verify the accuracy of the measurements, and the results are plotted together in Figure 12. The series of curves obtained indicates that the amount of copper extracted increased when the particle size decreased from 5.48 μm to 1.07 μm, with the maximum being obtained for the 1.07 μm fraction. The extent of the copper extraction was maximum for the 1.07 μm fraction and could not be reached with any other particle size. This suggests that for the case when the ore particles have sizes smaller or equal to the bacterium size the attachment of particles to the cell surface increases the leaching rate. Microscopic examination of the culture showed a tangled mass of bacteria and particles in the fermentation broth which was not found for any other particle size.

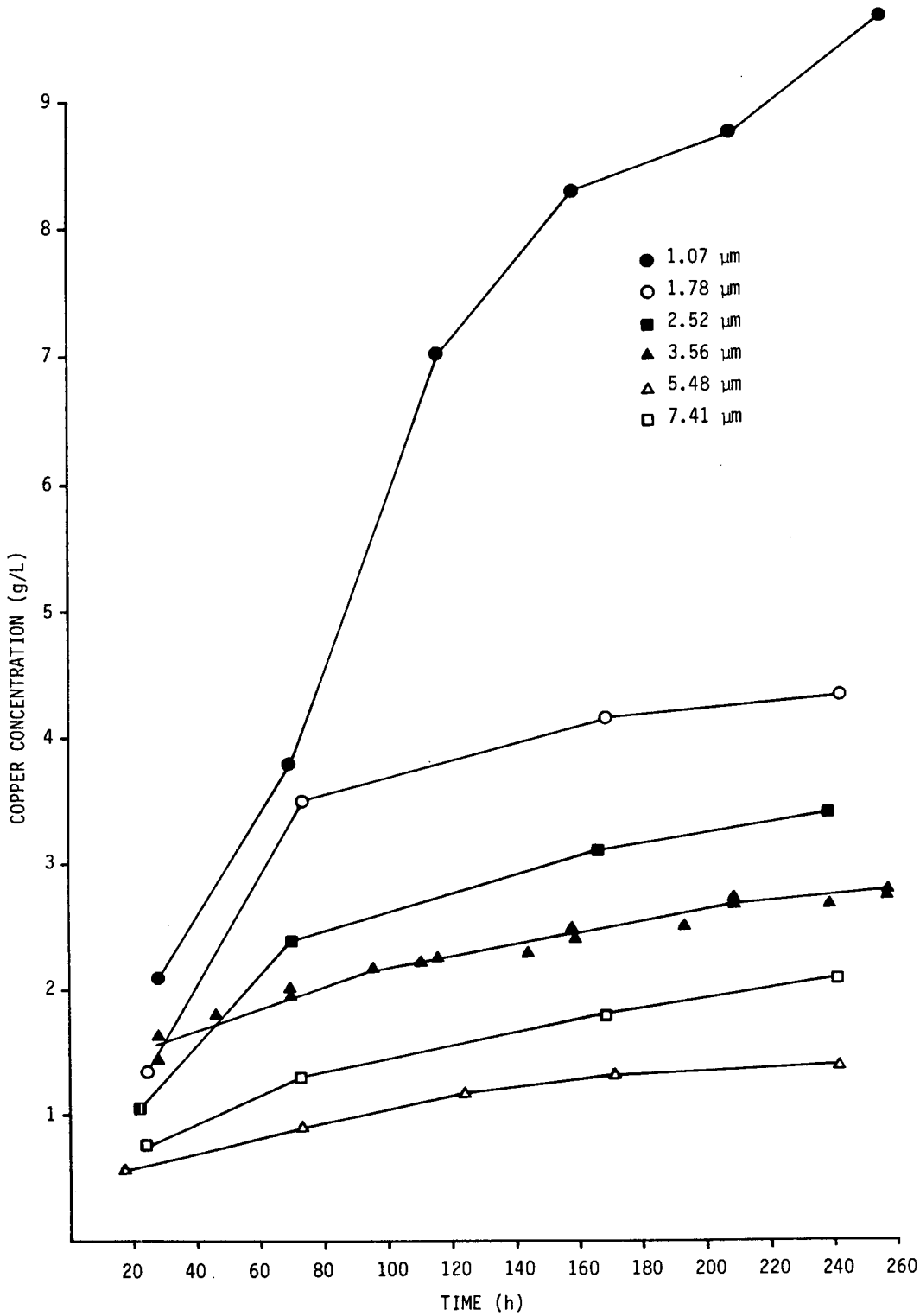


Fig. 12 Effect of particle size on the copper extraction

The extraction rate was approximately constant during the leach for the larger sizes (7.41, 5.48 and 3.56 μm), while a two rate curve was obtained for the smaller sizes (2.52, 1.78 and 1.07 μm).

Two rate copper extraction curves would result from the two phases of growth of the bacteria. The first rate would occur when the cells are growing logarithmically and surface is available. The second lower rate would occur for the stationary phase when the surface becomes limiting.

For the particles in the larger sizes (>3.56 μm) the surface was rapidly covered with bacteria during the first few hours of the leach and surface limitation occurred earlier in the leach; consequently the curves showed a trend towards a single copper extraction rate.

Copper extraction rates as a function of the particle diameter are shown in Figure 13. The copper extraction rate increases as the particle size decreases.

The upper part of Figure 13 shows how the surface increases with reduction of the particle diameter. If the extraction rate was a unique function of the surface area available, then the extraction rate would increase in a similar fashion. A plot of copper extraction versus specific surface would produce a straight line. Figure 14 shows such a plot for the experimental data.

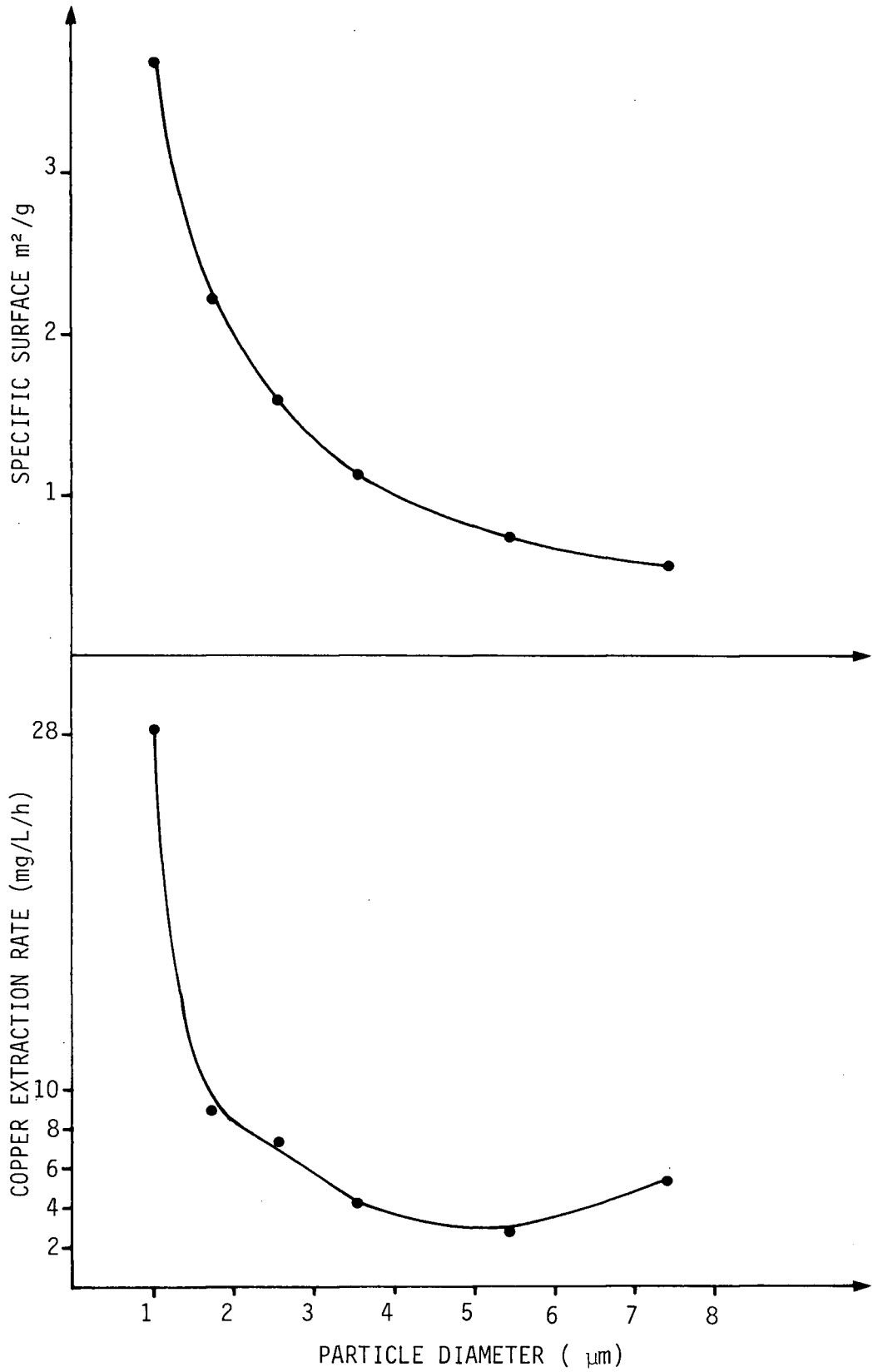


Fig. 13 Copper extraction rates as a function of the particle diameter

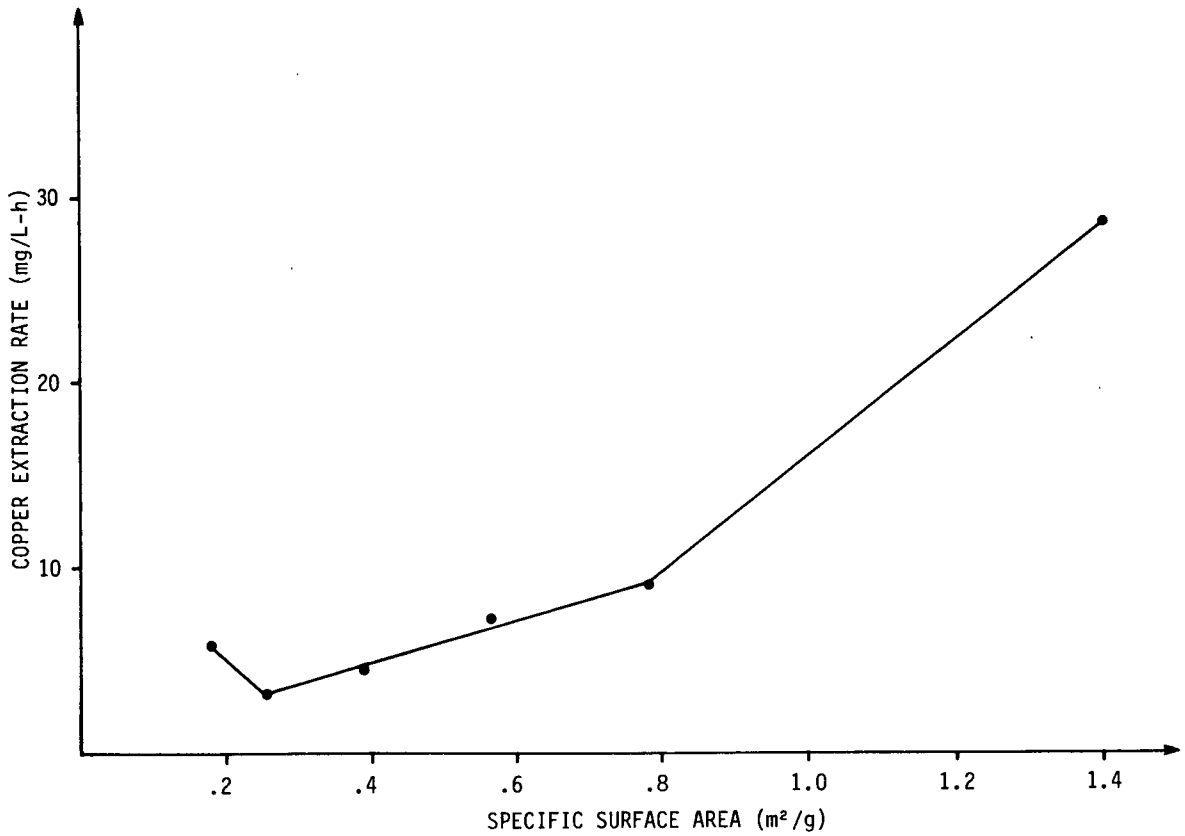


Fig. 14 Extraction rate as a function of the surface area.

Using fractions of different sizes of zinc sulphide concentrate in similar experiments Sanmugasunderam (1981) found a proportional increase between zinc extraction rate and specific surface area up to specific surface area values of 1.1 m^2/g and reported that beyond this value increases in specific surface area had almost no effect on zinc extraction rate. The results of this study show that the maximum increase in the copper extraction rate of chalcopyrite occurred when the specific surface area increased from 0.78 to 1.3 m^2/g.

7.3.1 Changes in the Particle Size Distribution During Leaching

The particle size used to characterize each fraction of the concentrate, was in fact the average size of a group of particles within a small range of sizes.

The distribution of sizes is likely to change as the leach progresses when increasing amounts of material are dissolved and oxidized.

In order to determine these changes a series of measurements of particle size distributions in different leaches was made. Samples of concentrate were withdrawn from the flasks using a Pasteur pipette and their size distribution was determined using the technique described in materials and methods.

Figures 15, 16 and 17 show the particle size distribution for the 1.78, 2.52 and 5.48 μm leaches. A gradual shift towards the smaller sizes is evident (see Figure 18). It was not possible to quantify the amount of particles of size below 0.5 μm which appear to increase rapidly during the fermentation. As a result the average particle diameter calculated from the size distribution did not appear to change very much during the leach (see Figure 18). The changes in size could only be exactly quantified if the total contents of the flask were analyzed, or a mass-based distribution determined and some correction factor introduced to account for the increase in mass due to the oxidation and jarosite precipitation processes.

7.4 APPLICATION OF THE SHRINKING CORE MODEL OF LEVENSPIEL

The results of the tests to determine the copper extraction rate obtained in leaches of six monosize fractions presented in section 7.3, and the particle diameter and surface area data for the same leaches were used to calculate the overall extraction against time curve for the biological leaching of a copper concentrate of known particle size distribution by using the Levenspiel model. Data for this calculation are presented in Table II.1 (Appendix II).

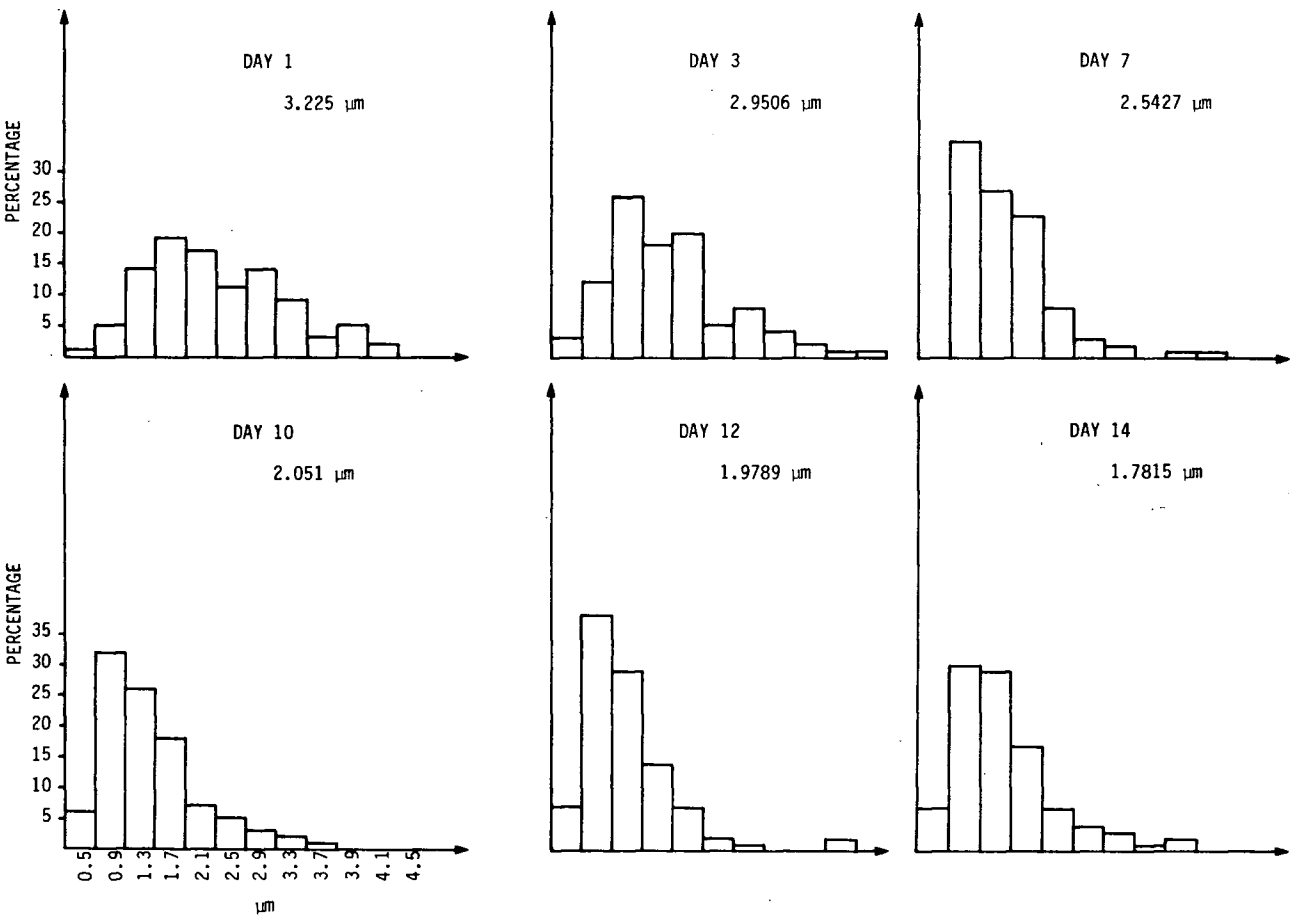


Fig. 15 Changes in the particle size distribution for the 1.78 μm Leach (Percentage vs particle size)

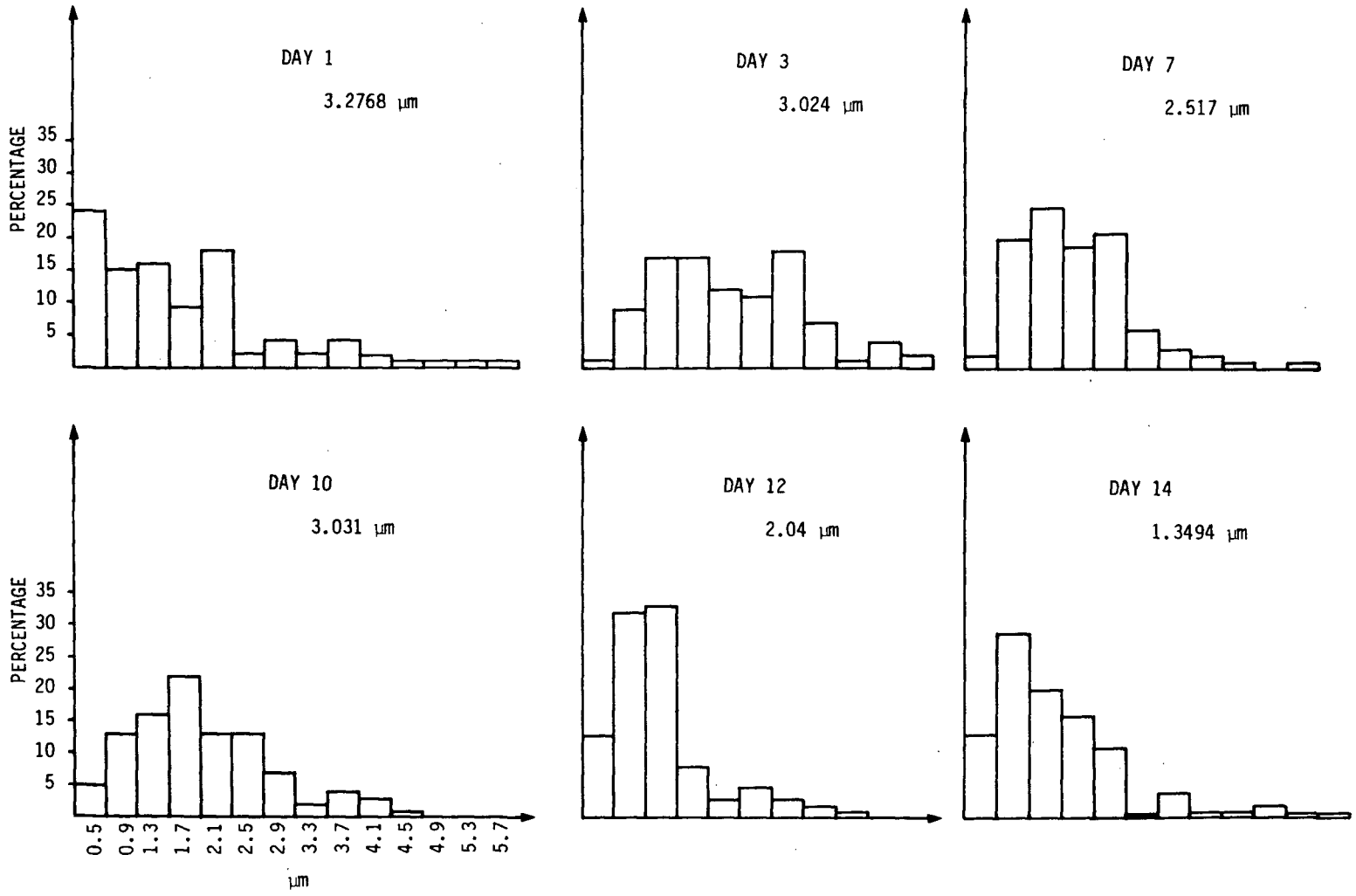


Fig. 16 Changes in the particle size distribution for the 2.52 µm leach.
(Percentage vs. particle size)

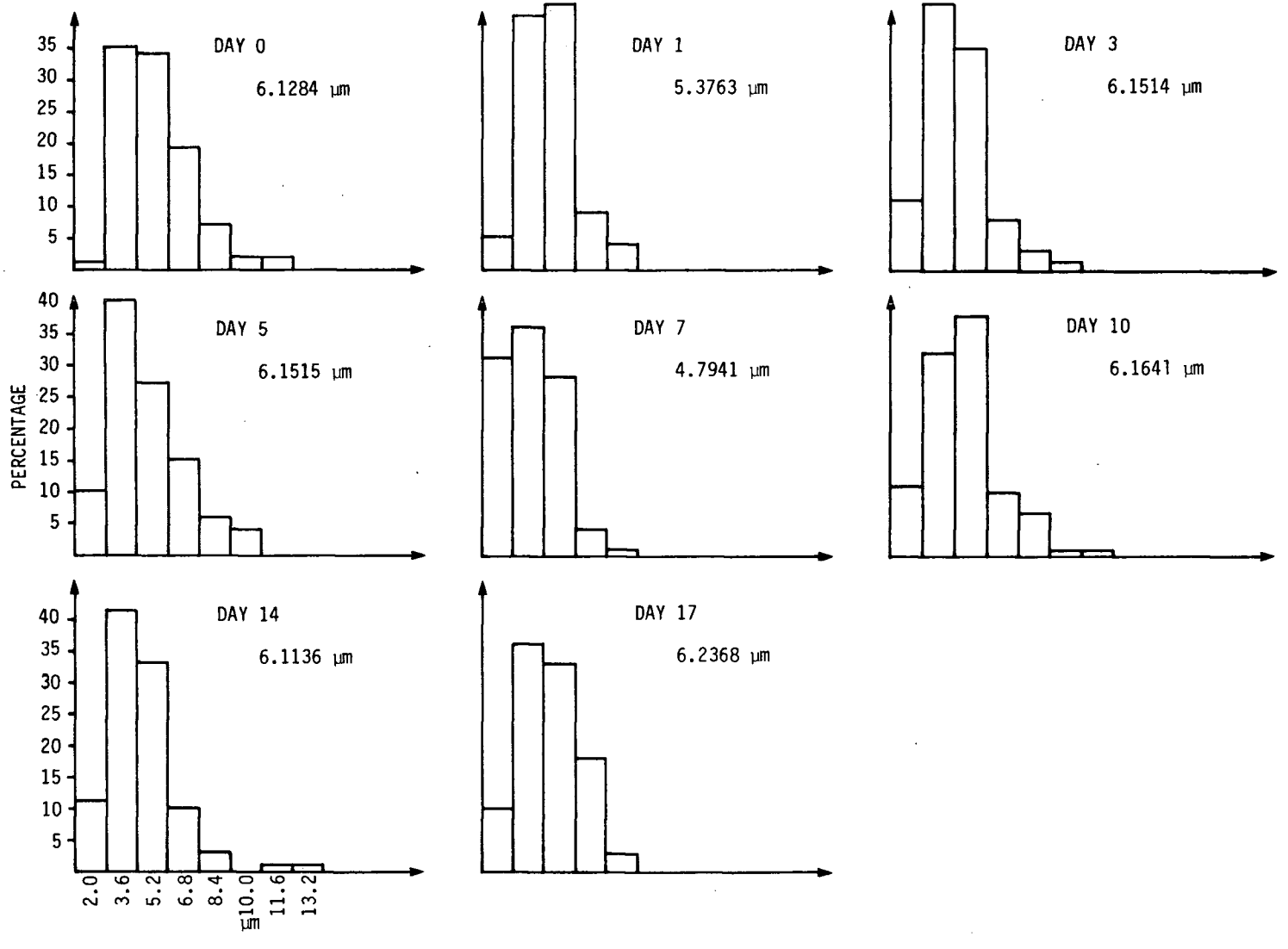


Fig. 17 Changes in the particle size distribution for the 5.48 µm leach.
(Percentage vs particle size)

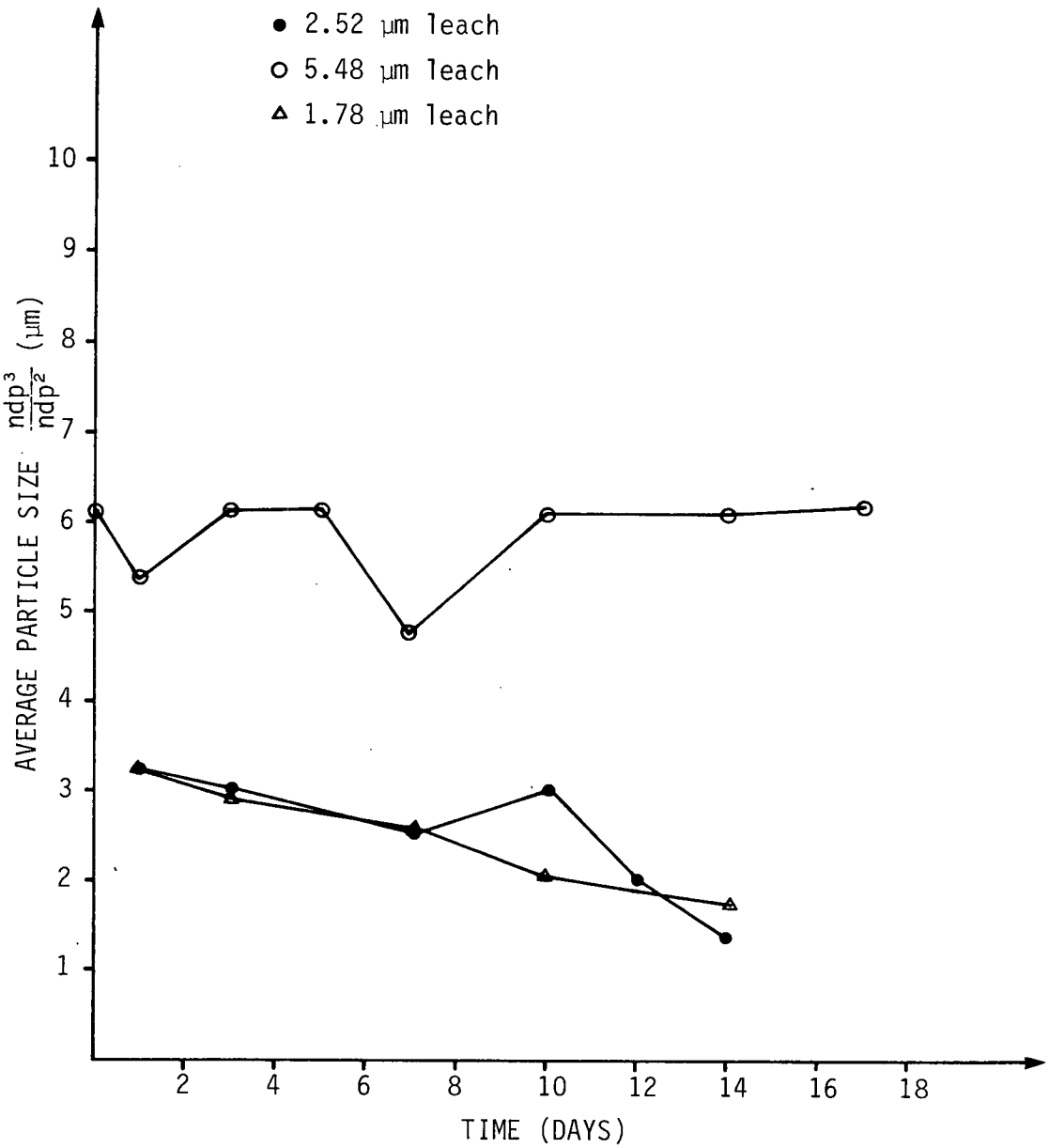


Fig. 18 Average particle size for 3 different leaches vs time.

A sample calculation of the copper extraction after 48 h of biological leaching predicted by the shrinking core model is shown in Appendix II.

The predicted values of copper extraction versus time are shown in Figure 19. Experimental results from a series of leaches using copper concentrate of known particle size distribution are also shown in Figure 19 for comparison purposes with data shown in Table II.3 (Appendix II).

Previous attempts to use the shrinking core model can be summarized as follows:

1) Gormely (1973) working with zinc sulphide concentrates, predicted values of zinc extraction using the shrinking core model that were below the experimental extractions by a factor of ten. He estimated the leaching rates for different particle sizes based on a constant leaching rate per unit surface area. This study has shown that the leaching rates need to be determined experimentally.

2) Samugasunderam (1981) obtained zinc extractions within 10% of the predicted values (with a maximum difference of 25%). He attributed this difference to the method he used to estimate surface area and particle diameter. Although the method used for surface area and particle diameter determination in this

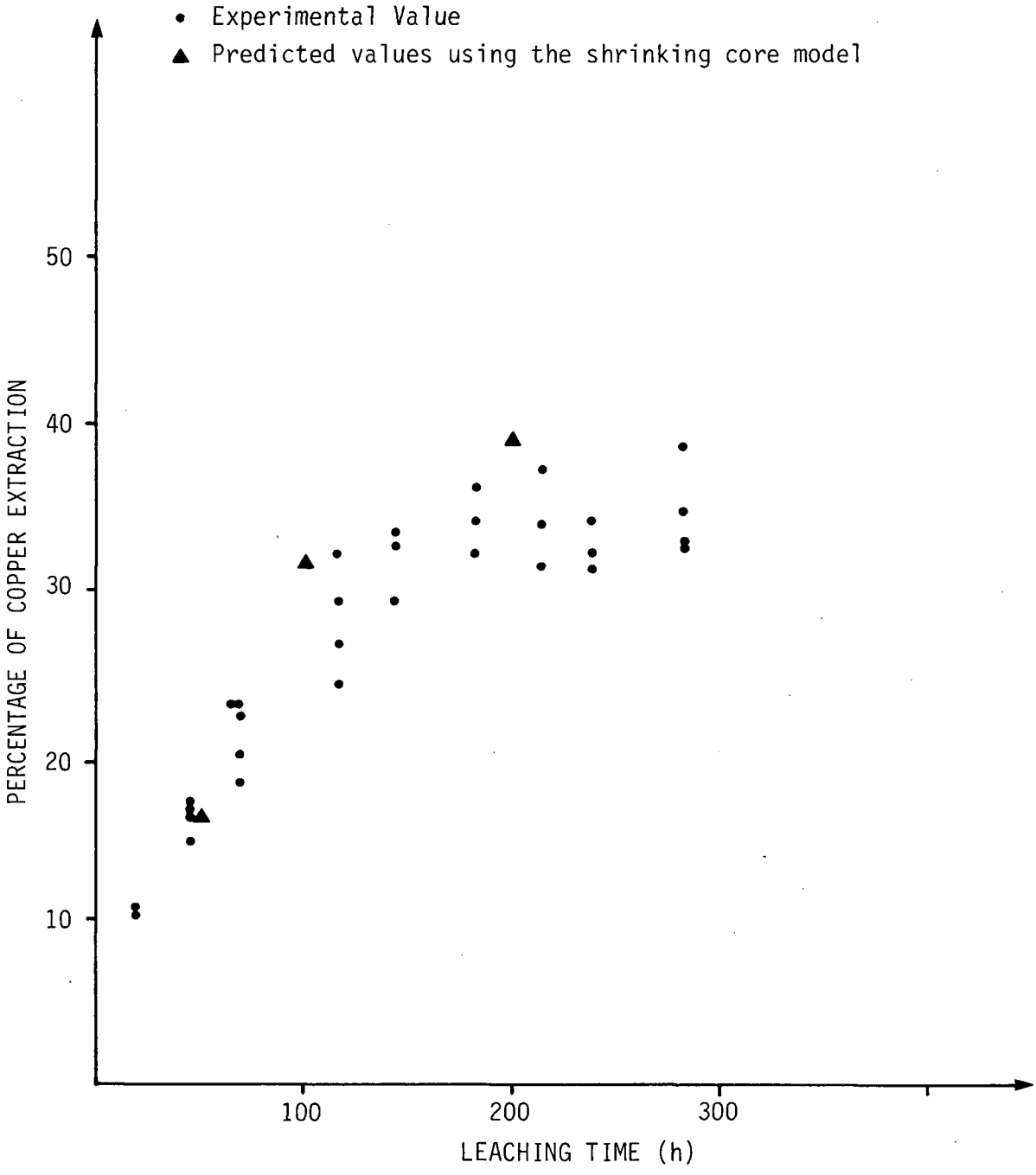


Fig. 19 Experimental and theoretical copper extraction values for the leaching of chalcopyrite.

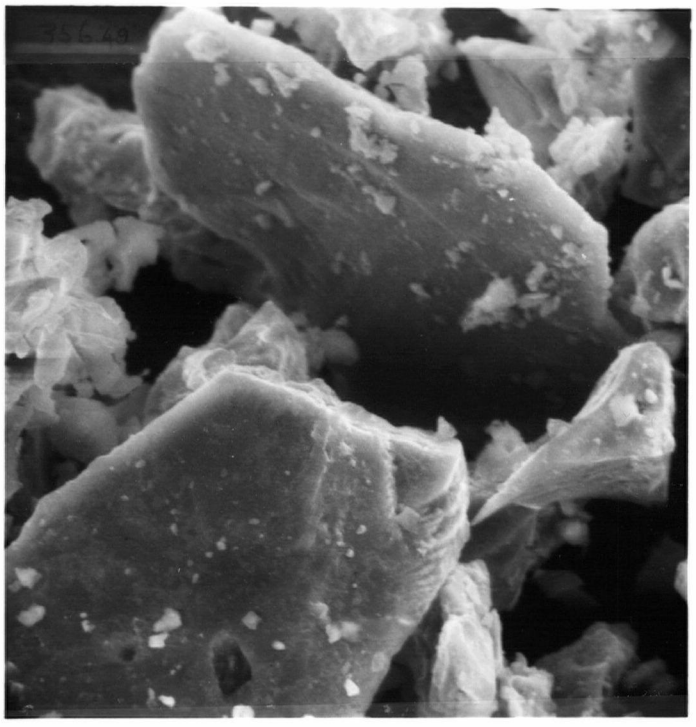
study was different, the model predictions fell in the same range, which suggests the existence of a factor related to microbial physiology that has not been incorporated in the model and causes these deviations.

7.5 POST LEACHING OBSERVATIONS

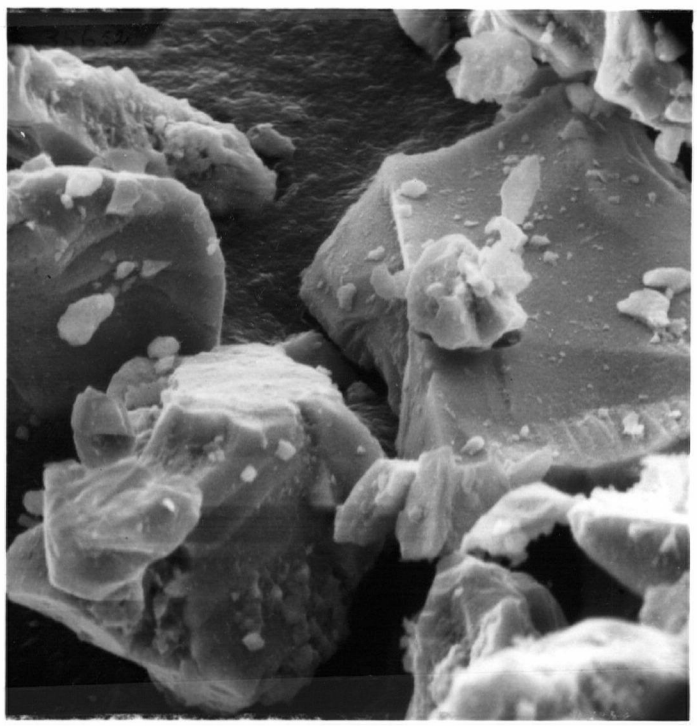
A series of scanning electron photographs were taken of several fractions of the concentrate prior to and after leaching. The objective was to obtain information on the nature of the attack by Thiobacillus ferrooxidans on the surface of the mineral.

Figure 20 shows particles of chalcopyrite before leaching. In general, the faces of the particles are smooth surfaces, while the edges are highly irregular.

Figure 21 shows chalcopyrite particles after 200 h of leaching. A cavity with dimensions similar to the dimensions of one bacterium is present in the centre of the particle shown in Figure 21a. A series of cavities covering surface areas approximately equal to the areas covered by one bacterium are present in Figure 21b. The bacteria seem to attach only to the central portion of the particles far from the edges. This same phenomena was previously attributed to surface tension effects (Berry, 1978). It is clear that the edges of the particles will



10 µm



10 µm

Fig. 20 Chalcopyrite particles before leaching

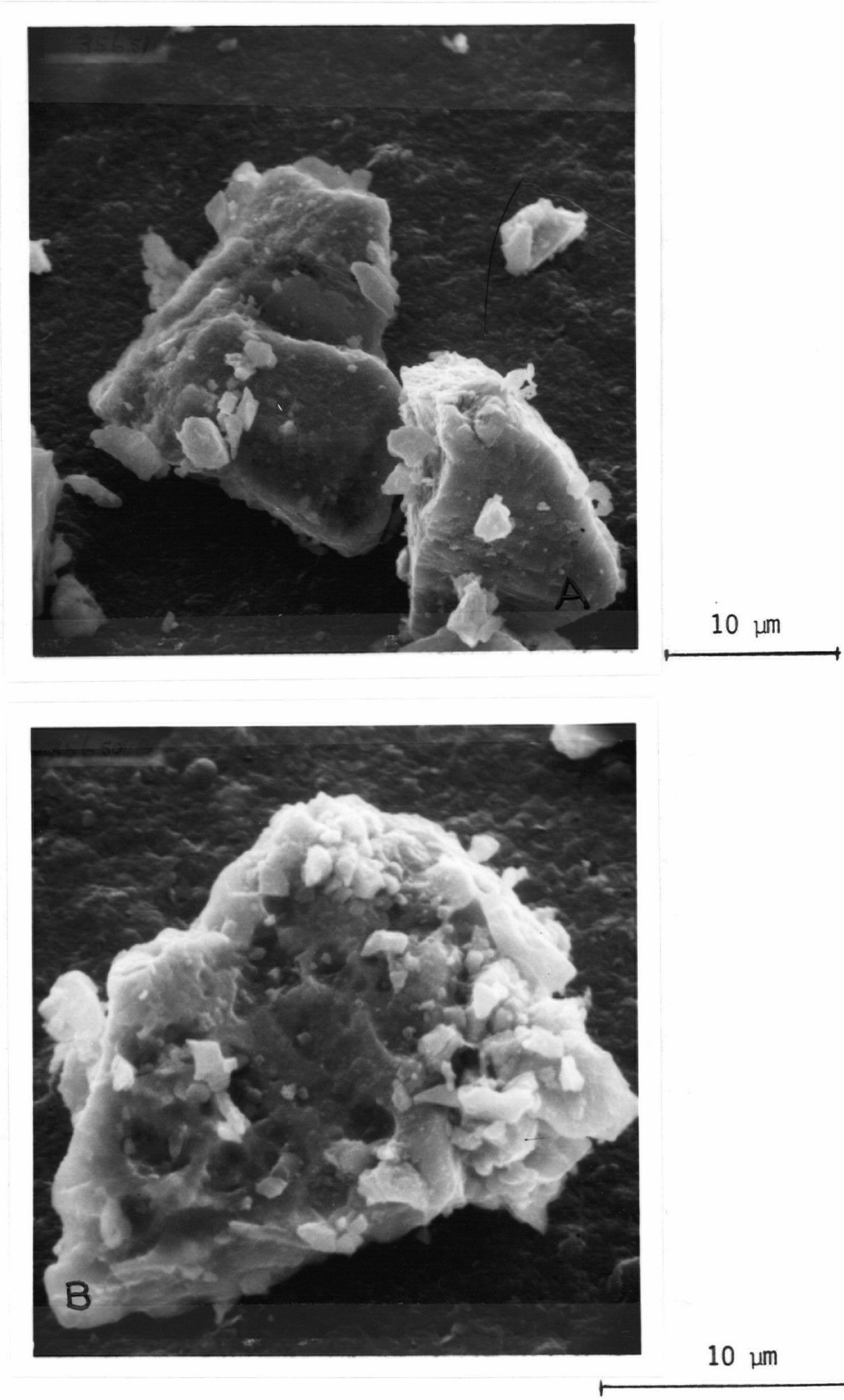


Fig. 21 Chalcopyrite particles after 200 h of leaching

be subject to friction against other particles when the suspension of particles is agitated. The shear forces generated during agitation will make it difficult for the bacteria to attach to the edges of the particles.

Small deposits of hexagonal crystals similar to jarosite crystals appear as small granules at the surfaces of the particles. The amount of these deposits increases with time. Particles of chalcopyrite after 300 h of leaching are almost covered by these deposits (Figure 22).

The presence of jarosite deposits on top of the chalcopyrite particles prevents the contact between the bacteria and the nutrients found in the liquid phase. When material subjected to 300 h of leaching was recovered and nutrient solution and inoculum added, no further extraction could be obtained. See results in Figure 23.

If jarosite precipitation was avoided or the precipitate removed by re-grinding the material, then the copper yield of the process would increase.

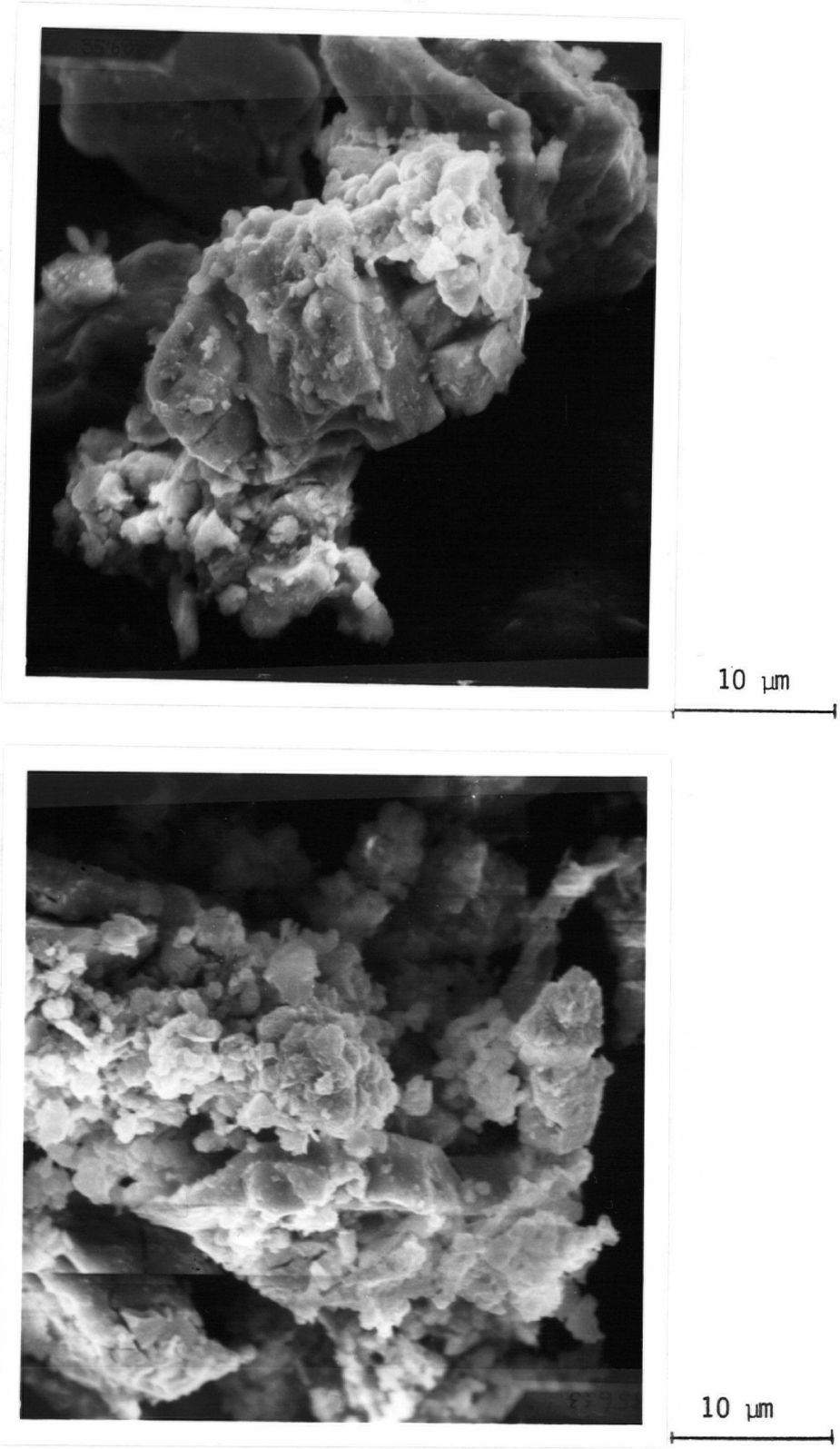


Fig. 22 Chalcopyrite particles after 300 h of leaching

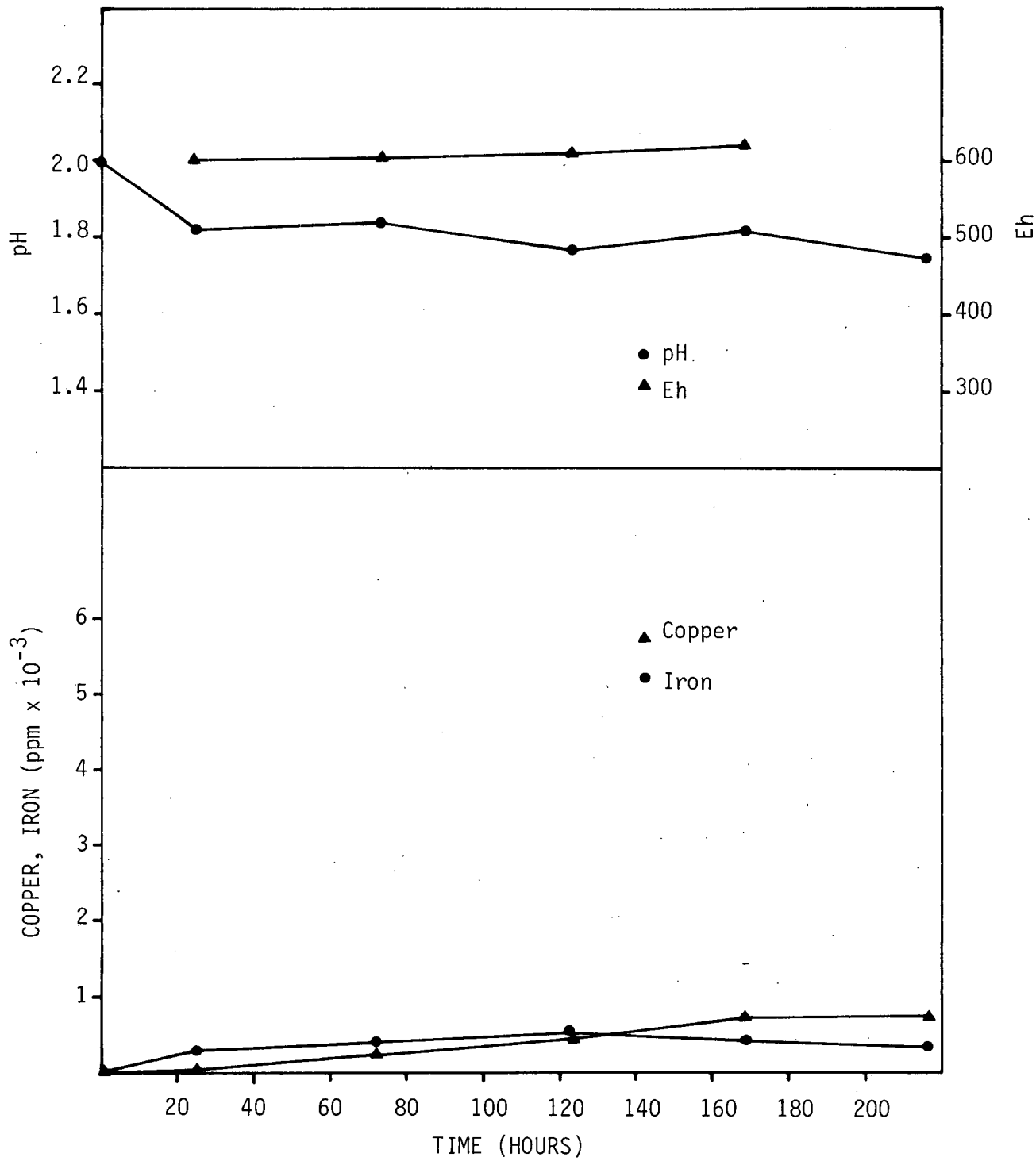


Fig. 23 Second - Pass Leaching of Chalcopyrite

CHAPTER VIII SUMMARY AND CONCLUSIONS

1. An experimental investigation was undertaken to study the application of the shrinking core model of Levenspiel to the modelling of copper extraction from chalcopyrite by Thiobacillus ferrooxidans.

2. Microscopical examination of the particles subject to leaching supported the idea of a shrinking core type of reaction.

3. The predicted extractions using the shrinking core model fit the experimental results and are useful to predict the copper extraction up to 30-35% extraction levels.

   Since no account for the physiological state of the bacterium is included in the model, it tends to overestimate the copper extraction which levels off after 120 h of leaching.

   The deposit of a solid layer of oxidation products which limited the rate of diffusion of nutrients and metabolic products to and from the cells at the reacting surface, was found to be responsible for the incomplete extraction.

4. Using electron microphotographs the solid reaction product deposits were identified as jarosites and their appearance on the mineral surface was found to be directly related to the end of the copper extraction.

5. In order to determine the effects of the particle size on the leaching of copper, the <400 mesh concentrate was fractionated into 7 particle sizes and each fraction was leached separately. The mineral particles of various sizes were oxidized simultaneously and independently with varying leaching rates dependent on their surface area. The highest rate was obtained for particles of 1 μm size and had a value of 28.3 mg Cu/l.h.

   These results indicate that the optimum particle size was reached when the particles of chalcopyrite had a size comparable to the bacterial size and that the extent of the extraction obtained at this size (97%) could not be reached with any other particle size.

6. To understand the role of the bacteria in the leaching process, the growth patterns of Thiobacillus ferrooxidans were determined. Using organic and inorganic nitrogen determinations to measure bacterial growth, the lag time was shortened to <1 day when inoculum from a 6-8 days old culture was used to seed the new flasks. This study provided evidence that the bulk of the copper extraction (62% of the total extraction) occurred once the culture had entered the stationary phase and that no direct relationship existed between metal extraction rates and bacterial growth.

8.1 RECOMMENDATIONS FOR FUTURE STUDIES

Studying the kinetic properties of individual mineral particles provides an insight to the level of mineral-bacteria interactions, which in turn serves to clarify the mechanism of leaching. In addition to what was done in this work, further studies are required regarding the effects of the changes in pH and redox potential produced by the bacterial metabolism and the leached products because the direction and intensity of bacterial synthesis is known to depend on these parameters.

The dissolved oxygen concentration should also be studied since it plays a very important role given the oxidative characteristics of this process. High oxygen demands would likely result in oxygen depletion given the limited oxygen solubility of the medium.

Studies are also required to investigate the chemical reactions resulting in the precipitation of jarosite type materials and its effects on bacterial metabolism. The use of a continuous culture could prove valuable in studying the effects of these and other parameters and in so doing would increase the control over the process and select the optimum operating conditions for the leaching of copper from chalcopyrite.

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APPENDIX I

TABLE I.1

BACTERIAL GROWTH DATA

Time (hours)	Ammonia Nitrogen (ppm)		Kjeldahl Nitrogen (ppm)		Cell Nitrogen (ppm)		Cell Numbers x 10^{-10}	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
21	1886.26	1862.56	1886.26	1886.26	0	23.7	0	151
27	1672.89	1672.89	1815.14	1767.72	142.25	94.83	906	604
44.5	1578/05	1554.34	1767.72	1744.01	189.67	189.67	1208	1208
50.5	1554.34	1530.64	1791.43	1767.72	237.09	237.09	1208	1510
71.0	1435.80	1412.09	1625.47	1649.18	189.67	213.38	1208	1359
97.0	1269.84	1317.26	1471.36	1542.49	201.52	225.23	1283	1434
121.0	1103.88	1222.42	1317.26	1459.51	213.88	237.09		1510
145.0	1151.3	1198.72	-	1412.09	-	213.37	-	1359
193.5	1103.88	1103.88	1317.26	1317.26	213.88	213.88	1359	1359

TABLE I.2

AVERAGE RESULTS FOR THREE BIOLOGICAL LEACHING EXPERIMENTS

Time (days)	pH	Eh	Cu (ppm)	Fe (ppm)	Time (days)	Cells x 10^{-10}
2	1.96	386	4033	2533	1	360
4	1.91	460	6750	4150	2	730
6	1.69	567	7875	3537	4	880
9	1.52	665	8000	4350	6	790
11	1.50	676	7933	4375	8	760
13	1.52	676	7833	4366	10	760
15	1.48	680	6750	4158	14	790
17	1.50	683	5766	3550	16	630

TABLE I.3

CHALCOPYRITE CONCENTRATE SURFACE AREA

Fraction No.	Surface Area (m^2)	Fraction Percentage	Area m^2
1	9.78045	0.1936	1.8934
2	5.87925	0.1833	1.07766
3	4.15275	0.3262	0.35124
4	2.93925	0.1195	0.35124
5	1.90950	0.0742	0.14168
6	1.37475	0.1032	0.14187

Total area in 7.5 g of concentrate = 4.96047 m^2

TABLE I.4

BACTERIAL COVERAGE OF THE SURFACE AREA DATA

Time (days)	Area Occupied By Bacteria $\times 10^{-10}$ μm^2	Percentage of Total Surface Covered By Bacteria	Cell Numbers $\times 10^{-10}$
1	180	36.29	360
2	365	73.58	730
4	440	88.70	880
6	395	79.63	790
8	380	76.61	760
10	380	76.61	760

TABLE I.5

STERILE RUN DATA

Time (h)	pH	Eh	Copper Conc. (ppm)	Iron Conc. (ppm)
0	2.0	355	0	0
44.5	2.17	355	795	532
97.5	2.17	355	820	525
143.75	2.25	355	880	550
215.25	2.26	355	880	520

TABLE I.6

LEACH DATA USING MONOSIZED MATERIAL OF 1.07 μm

Time (h)	pH	Eh	Cu (ppm)	Fe (ppm)
28	2.03	385	2125	540
69.5	1.81	415	3825	1650
115	1.63	575	7000	3850
158.5	1.49	610	8300	5550
208	1.49	650	8750	6350
256.5	1.58	660	9700	6500
305	1.46	660	10000	6450
	1.57	660		

$$[Cu] = 0.02833\ t + 2.4834$$

TABLE I.7

LEACH DATA USING MONOSIZED MATERIAL OF 1.78 μm

Time (h)	pH	Eh	Cu (ppm)	Fe (ppm)	Cells x 10^{-10}
24	2.06	345	1357	785	178
72.25	1.89	540	3532	1750	446
168	1.52	560	4157	3900	446
240.5	1.47	560	4357	4225	535
286	1.53	550	4507	4225	446
337	1.52	570	4807	4325	535

[Cu] = 0.00894 + 2.1053

TABLE I.8

LEACH DATA USING MONOSIZED MATERIAL OF 2.52 μm

Time (h)	pH	Eh	Cu (ppm)	Fe (ppm)	Cells x 10^{-10}
22	2.19	355	1057	785	446
70.25	1.93	530	2407	1650	713
166	1.49	560	3107	3325	446
238.5	1.47	545	3408	3500	535
284	1.52	550	3508	3500	535
335	1.47	575	3807	3550	535

$[Cu] = .00766\ t + 1.4576$

TABLE I.9

LEACH DATA USING MONOSIZED MATERIAL OF 3.56 μm

Time (h)	pH	Eh	Cu (ppm)	Fe (ppm)
28	2.05	505	1450	830
69.5	1.74	560	1950	1950
115	1.51	620	2250	2450
158.5	1.43	625	2400	2350
208	1.39	640	2700	2900
256.5	1.47	640	2800	2875
305	1.40	660	2900	3050

$$[Cu] = 0.004971\ t + 1.5399$$

TABLE I.10

LEACH DATA USING MONOSIZED MATERIAL OF 5.48 μm

Time (h)	pH	Eh	Cu (ppm)	Fe (ppm)
18	1.98	525	572	532
73	1.83	565	922	1025
124.4	1.73	565	1172	1900
171.65	1.60	560	1321	1900
241.9	1.56	560	1421	2000
337.65	1.46	555	1771	2300
409.15	1.42	550	1872	2350

$$[Cu] = .00315\ t + 0.6730$$

TABLE I.11

LEACH DATA USING MONOSIZED MATERIAL OF 7.41 μm

Time (h)	pH	Eh	Cu (ppm)	Fe (ppm)
24	1.95	395	782	717
72.25	1.88	535	1307	1050
160	1.57	550	1807	1300
240.5	1.47	545	2108	1400

$$[Cu] = .00315\ t + 0.6730$$

APPENDIX II

APPENDIX II

Sample Calculation for The Copper Extraction Using The Shrinking Core Model of Levenspiel

Calculations for the percentage copper extraction are done for 50 h of leaching time. The size distribution of the concentrate is given in Table 4.

Percentage Copper Extraction

For the first fraction with mean diameter 1.07 μm

ssa = specific surface area of the particles = 1.30 m^2/g

r_z = copper extraction rate = 28.33 mg/l.h.

w = weight fraction = 0.1936.

then

S = surface area concentration of the particles

S = feed pulp density x weight fraction x ssa

$$S = \frac{7.5\ g}{70\ mL} \times \frac{1000\ mL}{L} \times 0.1936 \times 1.30406\ \frac{m^2}{g} = 27.049\ m^2/L$$

$r_{z/s}$ = copper extraction rate per unit solid surface area

$= r_{z/s}$

$r_{z/s} = .001047\ g/h.m^2$

with the density of the chalcopyrite concentrate being 4.3×10^6 g/m^3.

The time for complete reaction of one particle is given by:

$$T = \frac{pdo}{2rz/s} = 2196.47 \text{ h}$$

The fractional extraction will then be calculated using equation 3, page 24:

$$z = 3 \left(\frac{\bar{t}}{T}\right) - 6 \left(\frac{\bar{t}}{T}\right)^2 + 6 \left(\frac{\bar{t}}{T}\right)^3 \left[1 - \exp\left(-T/t\right)\right]$$

$$z = 3 \left(\frac{50}{2196.47}\right) - 6 \left(\frac{50}{2196.47}\right)^2 + 6 \left(\frac{50}{2196.47}\right)^3 \left[1 - \exp\left(-\frac{2196.47}{50}\right)\right]$$

$$z = 0.065$$

The fractional extraction of the rest of the 6 fractions of the copper concentrate are similarly calculated and tabulated in Table II.2.

The total copper extraction after 50 h of leaching is found to be 16.15%.

TABLE II.1

KINETIC DATA FOR THE SHRINKING CORE MODEL

Particle Size (μm)	Specific Surface Area (m^2/g)	Surface Area Concentration (m^2/L)	Release Rate of Copper (mg/Lh)
1.07	1.30406	27.049	28.33
1.78	0.7839	15.395	8.94
2.52	0.5537	19.352	7.66
3.56	0.3919	5.0176	4.31
5.48	0.2546	2.024	3.15
7.41	0.1883	2.026	5.89

TABLE II.2

CALCULATED PERCENTAGE EXTRACTION AFTER 50 h OF LEACHING

Fraction	Diameter μm	ssa m^2/g	$r_{z/s}$ $mg/h.m^2$	Weight Fraction	T (h)	Contribution
1	1.07	1.3040	1.047	0.1936	2196.47	0.06525
2	1.78	0.7839	0.580	0.1833	6590.23	0.02241
3	2.52	0.5537	0.645	0.3262	8387.9	0.01767
4	3.56	0.3919	0.859	0.1195	8900.28	0.01666
5	5.48	0.2546	1.550	0.0742	7570.4	0.01954
6	7.41	0.1883	2.907	0.1032	5480.0	0.02686

Calculated Total Extraction = 16.15%

TABLE II.3

COPPER CONCENTRATION DATA
FOR BIOLOGICAL LEACHING OF CHALCOPYRITE

Time (h)	ppm of copper			
	1	2	3	4
24	3199	3059	3259	3079
47.8	5120	4460	5040	4860
69.25	6921	5460	6661	5981
116.8	9581	7179	8780	9781
144	9781	9981	8780	9781
183	9581	10781	9581	10181
214.5	10181	11182	9380	11182
239.25	9581	9380	9581	10181
284.8	9781	11582	9781	10381

PERCENTAGES OF COPPER EXTRACTION
FOR BIOLOGICAL LEACHING OF CHALCOPYRITE

Time (h)	ppm of copper			
	1	2	3	4
24	10.74	10.27	10.94	10.33
47.8	17.18	14.97	16.92	16.31
69.25	23.23	18.33	22.36	20.08
116.8	32.16	24.10	29.47	26.79
144	32.83	33.50	29.47	32.83
183	32.16	36.19	32.16	34.18
214.5	34.18	37.54	31.49	37.54
239.25	32.16	31.49	32.16	34.18
284.8	32.83	38.88	32.83	34.85